IAEA-TECDOC-1472

Naturally occurring radioactive materials (NORM IV)

Proceedings of an international conference held in Szczyrk, Poland, 17–21 May 2004

IAEA
International Atomic Energy Agency

October 2005

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The originating Section of this publication in the IAEA was:

Policy and Programme Support Section
Division of Radiation, Transport and Waste Safety
International Atomic Energy Agency
Wagramer Strasse 5
P.O. Box 100
A-1400 Vienna, Austria

NATURALLY OCCURRING RADIOACTIVE MATERIALS (NORM IV)
IAEA, VIENNA, 2005
IAEA-TECDOC-1472
ISBN 92–0–110305–0
ISSN 1011–4289

Printed by the IAEA in Austria
October 2005

FOREWORD

Radionuclides of natural origin are ubiquitous in both working and public environments, although their activity concentrations vary considerably. Exposures to natural sources are in most cases not a matter for regulatory concern. However, there are situations where exposures to natural sources may warrant consideration as to whether controls should be applied. One such situation is where the conditions are conducive to the buildup of elevated concentrations of radon in air. Another situation is the mining and/or processing of material where the activity concentrations of radionuclides of natural origin in the material itself, or in any material arising from the process, are significantly elevated — such material has come to be referred to as **N**aturally **O**ccurring **R**adioactive **M**aterial (NORM).

In the past, regulatory attention has been focused mostly on exposures arising from the mining and processing of uranium ores because such activities are part of the nuclear fuel cycle. More recently, attention has been broadened to include exposures from other industrial activities involving NORM, in recognition of the potential for such activities to also give rise to significant exposures of workers and members of the public if not adequately controlled. More and more countries are now including provisions in their national legislation and regulations for the control of exposures to natural sources, and the body of radiological data on such exposures is growing rapidly.

This international conference, NORM IV, follows three previous conferences dealing with radon and NORM. The first was held in Amsterdam in 1997, the second in Krefeld, Germany in 1998 (NORM II), and the third in Brussels in 2001 (NORM III). In addition, an International Symposium on Technologically Enhanced Natural Radiation was held in Rio de Janeiro in 1999 — the IAEA was involved in the organization of that symposium, and published the proceedings as IAEA-TECDOC-1271.

The main topic addressed at NORM IV was exposure to radionuclides of natural origin in mining and other industrial operations involving NORM, including impacts associated with NORM residues and discharges. Other important topics addressed included legal aspects (standards and regulation) and measurement techniques, including measurement of radon.

NORM IV was organized by the Central Mining Institute, Poland with the assistance of an international scientific committee. The IAEA served on this committee and played an active role in the technical aspects of the organization and running of the conference. In line with the IAEA's safety-related programme objective to foster information exchange, it is intended that, through the publication of these proceedings, valuable new information on exposure to natural sources presented at this conference will be disseminated to a wide spectrum of technical and regulatory personnel working in this area.

This publication was compiled with the assistance of S. Chałupnik, Central Mining Institute, Poland. The IAEA officer responsible for this publication was D.G. Wymer of the Division of Radiation, Transport and Waste Safety.

EDITORIAL NOTE

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INTRODUCTION

The aim of the NORM IV Conference was to bring together technical experts and scientists working in all areas related to Naturally Occurring Radioactive Material (NORM). This is a multidisciplinary subject, related to nuclear physics, environmental studies, chemistry, hydrogeology and health physics. The main objective of the Conference was to enable and promote the exchange of information among scientists and develop future directions in this field. The environmental impacts of mining received considerable emphasis. An additional goal was to consolidate and strengthen knowledge and competence in radiation protection, which was seen as being very important in the evaluation and management of enhanced exposures to radiation from natural sources.

The conference attracted 74 participants from 25 countries. There were some 60 technical contributions in all. Most of the papers were presented orally under the following session topics: NORM in mining, environmental pollution, NORM in industry, water contamination, measurement techniques, NORM legal aspects, and radon and air pollution. In addition, there were a small number of poster presentations. The conference concluded with a round table discussion.

INDUSTRIAL PROCESSES INVOLVING NORM

Several technical contributions to the conference presented important new radiological data for activities associated with the mining and processing of raw materials for which there was a potential for exposures of regulatory significance. The presence of NORM with elevated radionuclide concentrations could be an issue at any stage of an operation, i.e. ores, mineral feedstocks, intermediate products, final products and/or wastes. A wide range of industrial activities was reported on, including oil and gas extraction, coal and peat fired power generation, the phosphate industry, the zircon/zirconia industry, the production of titanium dioxide pigments, the mining and production of metals (e.g. copper, lead/zinc, aluminium, ferro-niobium, and iron and steel), industrial uses of thorium, water treatment, and the incorporation of NORM into building materials.

The information presented included data on activity concentrations in various process materials and assessments of doses received by workers and members of the public. In the past, much of the information on doses received by workers had been derived from assessments based on modelling of exposures using standardized exposure scenarios and parameters based heavily on generalized assumptions. The information presented at this conference demonstrated that substantial progress had been made towards the more reliable assessment of worker doses by making greater use of on-site measurements and facility-specific exposure scenarios, particularly among Member States of the European Union (EU) as part of moves to comply with the Council Directive 96/29/Euratom of 13 May 1996.

Much of this new information had been gathered as part of the EU 'TENORMHARM' project. A comparison of the TENORMHARM results with those from a previous study based on generalized assumptions showed that the effective doses reported in the previous study were in some cases overestimated by as much as one or two orders of magnitude. While there were also some instances where the doses had been underestimated previously, these were generally below levels of regulatory significance. It was concluded that in most of the investigated cases occupational exposure could not be reliably assessed by automatically applying standardized factors, and that assessments should rather be based on the direct measurement of facility-specific risk factors so that the important influencing features (particular work conditions, geometry, attenuation, respiratory protection, etc.) could be properly taken into account.

Activity concentrations of radionuclides of natural origin

Newly reported data on activity concentrations, as well as data reported from the literature, continued to demonstrate that most of the process materials encountered in current operations exhibited radionuclide concentrations below 1 Bq/g (i.e. within the normal range of concentrations in soil), which in terms of international standards[1] implied that there would usually be no need to regulate such materials.

Where this level was exceeded, it was generally exceeded by only a moderate amount (up to a few times) — materials falling into this category included certain feedstocks (zircon sand and phosphate rock), water treatment sludges, ‘red mud’ from bauxite processing, solids in sludge from titanium dioxide pigment production, slag from thermal phosphorus production and from past tin smelting operations, and certain end-products (phosphate fertilizer, zircon refractories, and bricks made from NORM residues). In terms of international standards, such materials would need to be considered for regulation but, depending on exposure conditions, the optimum regulatory option might be not to apply regulatory requirements.

Only a few materials were reported as having highly elevated radionuclide activity concentrations, and thus the potential for significant individual doses:

- *Feedstocks:* One feedstock material was reported in this category — the mineral pyrochlore (for ferro-niobium production), with a ^{232}Th activity concentration of 7–80 Bq/g.
- *Wastes:* The highest activity concentrations were found in wastes, especially in scales from wet chemical processes and in precipitator dust from high temperature processes. The ^{226}Ra concentration in scales from the processing of phosphate rock, although often of the order of 10 Bq/g, could be as high as 1500 Bq/g, while in pipe scales in the oil and gas industry it could range from very low to as high as 15 000 Bq/g. In the coal mining industry, where radionuclide concentrations were usually below levels of concern, it was reported that the ^{226}Ra concentration in scales and pond sediments in Polish coal mines could reach about 200 Bq/g as a result of the inflow of radium-rich water into the mine. The concentration of ^{210}Pb in precipitator dust from thermal phosphorus production could reach 1000 Bq/g, while in dust from other high temperature processes (iron smelting and zircon refractories production) the concentration of ^{210}Pb and/or ^{210}Po was much lower (50 Bq/g or less).
- *Products:* Products in the form of tungsten filaments and welding rods were reported as having a high ^{232}Th content. A report from Germany described the recycling of these products by melting. The ^{232}Th content in the scrap fed to the furnace was up to 65 Bq/g, while the high value alloy product of the melting operation was essentially free of radioactivity.

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[1] Standards of safety for the protection of health and minimization of danger to life established by the IAEA, as specifically authorized under the terms of its Statute, in consultation with the United Nations and the specialized agencies concerned.

Effective doses

As mentioned above, new information on activity concentrations in materials in mining and minerals processing reported at this conference provided further evidence of elevated radionuclide concentrations, occasionally exceeding the maximum levels in soil by as much as one or two orders of magnitude. Despite this, there was very little evidence of the industrial processes involved giving rise to effective doses of significant regulatory concern.

New results from the assessment, by modelling, of effective doses received by members of the public were presented for the phosphate and zircon industries, for peat-fired and coal-fired power generation, for oil and gas production and for iron smelting. These results showed no evidence of members of the public receiving doses of regulatory concern, even where conservative assumptions had been made.

In the case of doses received by workers, assessments covering an even wider range of industrial process showed only isolated instances of effective doses exceeding 1–2 mSv/a. As has been reported previously in the literature, Polish underground coal mines with large inflows of radium-rich water, leading to the generation of high activity radium scales and sediments, can give rise to worker doses reaching a significant fraction of the dose limit, with the main contributions coming from radon and dust inhalation. Significant doses arising from radon inhalation were also reported for Polish underground metal mines, with maximum values again reaching a sizeable fraction of the dose limit. Apart from these cases from Poland, only one other instance of significant worker exposure emerged from the technical presentations — in a titanium dioxide plant using the sulphuric acid digestion process. The accumulation of ^{226}Ra in the cloth filters used in the first stage of the vacuum filtration process (a phenomenon reported already in the literature) was found to give rise to significant gamma dose rates close to the equipment. Although an individual working at this location could potentially receive a dose of up to 14 mSv/a, it was reported that this could be avoided by low cost measures in the form of modified working procedures.

NORM discharges

Within the EU, the identification of industrial processes giving rise to potentially significant NORM discharges has begun and some preliminary, indicative, data were reported for the amounts of activity discharged from coal-fired power stations and from facilities for the production of oil and gas, titanium dioxide pigment, bricks and roofing tiles, and cement. A proposed screening methodology was presented that could serve to identify discharges giving rise to public exposure of potential regulatory concern. Screening levels for gaseous discharges from stacks and liquid discharges into rivers and marine environments were derived by modelling the relationship between the annual activity discharged and the effective dose received by an individual for various stack heights and sizes of river. A preliminary assessment against the derived screening levels, based on typical discharges from relevant NORM industries in Europe, suggested that most discharges were below the screening levels, except possibly in the case of some liquid discharges should they occur into small rivers.

NORM residues from past practices

Several submissions to the conference dealt with residues from past practices involving NORM. One paper reported on the process of natural restoration of the Huelva estuary in Spain, following its contamination in the past by NORM residues from the phosphate industry — it was shown that, although radionuclide levels were still elevated, there was a steady downward trend towards normal background levels.

An account was given of the extent of contamination caused by uncontrolled past practices in oil and gas production in Azerbaijan. The problems highlighted were the public use of contaminated scrap and the pollution of land (as evidenced by elevated gamma radiation levels) due to the deposition of pipe scales and formation water and the dispersion of radium-rich residues from the extraction of iodine and bromine from formation water.

Past practices in Brazil involving monazite processing and extraction of rare earth elements generated wastes with ^{232}Th activities measured in thousands of becquerels per gram. These wastes had given rise to site remediation issues that now needed to be addressed, including soil and groundwater contamination, the lack of a suitable disposal site for the material, and the need for specific regulations and guidance to be developed.

Issues associated with residues from former uranium mining sites in Eastern Europe were also highlighted. At one site, an assessment was carried out to determine the feasibility of using radium-contaminated residue for road construction. The ^{226}Ra concentration in the material was very variable, with an average value of 2.2 Bq/g. It was determined that, in terms of local regulations, all but the most active material could be used after dilution with low activity material. At another former uranium mining site, investigations were conducted to identify an appropriate design of cover for the mine residue deposit, to minimize radon exhalation and water ingress. A simple, two-layer design using locally available natural materials was found to perform well.

With regard to the potential for groundwater contamination, the process of deciding whether the level of NORM contamination of a site is sufficiently low to allow exemption from further investigations and from any intervention measures or land use restrictions was the subject of a theoretical study. A stepwise methodology was proposed, and radionuclide-specific test thresholds for soil and leachate contaminant levels were developed. This could facilitate decision-making by relevant authorities.

The radiological situation with regard to Polish coal mines

Holding this conference in Poland created the opportunity for an in-depth focus on the Polish coal mining industry, which, as mentioned above, had its own particular radiological situation as a result of the inflow of large quantities of radium-rich water. A series of presentations described the results of the most recent investigations on this topic, starting from the mechanism of radium buildup in the incoming water and progressing in turn to the processes for its removal underground, the behaviour of radium during desalination, the radium balance in discharge water systems, leaching of radium from sediments in surface settling ponds, and the environmental impact of abandoned surface settling ponds. Two main types of radium-bearing water have been identified, and have been classified as types A and B. In type A water, radium isotopes are present together with barium, while sulphate concentrations are low. Because of the presence of barium, radium can be easily co-precipitated as barium–radium scales, which are high in radium activity and are formed in underground galleries and surface settling ponds and rivers. Type B water contains radium and sulphate ions, but the absence of barium means that no carrier for radium exists, and the main processes for attenuation of the radium content are adsorption on bottom sediments and dilution.

In order to better understand the radium buildup in mineralized mine water, various models and possible mechanisms for the transfer of radium from the host rocks to the formation water were investigated. It was found that these models and mechanisms did not satisfactorily explain what was observed in practice, and it was concluded that further research was needed.

The underground purification of type A water was found to be relatively simple and was implemented some years ago. The purification of type B water was the subject of a subsequent investigation, and a presentation was given of the results of the successful practical implementation of an underground purification system using a technique based on the addition of barium chloride to co-precipitate radium. An improvement in the surface environment due to the significant reduction in the amount of radium discharged was clearly evident from the results of the trial.

The results of a study of the behaviour of radium during underground desalination of mine water showed that most of the radium ended up in the gypsum produced by the process, and that prior removal of radium allowed this gypsum to be reused in the construction industry rather than having to dispose of it as a radioactive waste. Prior removal of radium also permitted the removal of restrictions on the reuse of other process output materials (sodium, potassium and calcium chlorides).

An investigation to determine the radium balance in discharge water systems revealed that approximately 60% of the radium remains underground as deposits. In surface water bodies, it was demonstrated that elevated concentrations of radium could be found many kilometres downstream from the discharge point. Purification of mine water underground, as well as measures to reduce inflows, had resulted in a noticeable decrease in the amount of radium discharged. The radium concentrations in surface water bodies affected by the discharge of type A water (from which radium tended to co-precipitate with barium) were much lower than in those affected by the discharge of type B water. Elevated radium concentrations in some rivers were found to exceed permissible levels, indicating the need for further countermeasures.

Results were reported of a study on radium leaching from bottom sediments in settling ponds. It was shown that sediments associated with type A water often had high radium concentrations but low leaching potential, whereas sediments associated with type B water had only moderately elevated radium concentrations but higher leaching potential. A comparison was made with the results of investigations carried out in Spain on leaching of radium from phosphogypsum deposits. Leaching from phosphogypsum was lower, due to the higher solubility of phosphogypsum and the effect that this had on the role played by barium in the leaching process.

Measurements conducted at three abandoned settling ponds indicated a very wide variability of radium concentrations in the sediment, ranging from 3 to 100 times the maximum values in soil. Radon exhalation was also found to be highly variable (up to four times the normal maximum from soil), but quite independent of the radium concentration. Gamma dose rates ranged from normal levels up to 2 orders of magnitude higher. It was concluded from these measurements that future disturbance of abandoned mine settling ponds could have a significant, although very localized, impact on the surrounding environment, and that remediation operations should therefore be conducted with care, particularly with regard to measures to control the entry of radon into buildings constructed in the area.

STANDARDS AND REGULATION

International standards

In a presentation on the application of international standards to exposures to radon and NORM, the relevant standards and supporting safety-related publications were described. Particular attention was focused on how the scope of regulation was defined with regard to exposures to radionuclides of natural origin.

For exposure to radon, the situation had been addressed internationally some years ago with the establishment, in the standards, of radon action levels defined in terms of activity concentration in air. In the case of exposure to NORM, however, international consensus on radionuclide activity concentrations below which it would be usually unnecessary to regulate was only now emerging. The activity concentrations concerned were 1 Bq/g for uranium and thorium series radionuclides and 10 Bq/g for ^{40}K (other than ^{40}K in the body, which was already excluded from the standards), these levels being representative of the maximum values found in soils worldwide[2].

Data presented for specific NORM industries illustrated that materials with activity concentrations of uranium or thorium series radionuclides exceeding 1 Bq/g did not necessarily give rise to effective doses of regulatory concern, and operations involving such materials therefore needed to be considered on a case by case basis. In terms of the so-called 'graded approach to regulation', the optimum regulatory option might be not to apply regulatory requirements, especially if the effective dose was only a small fraction of the relevant dose limit — such a decision would in many cases take the form of an exemption. Existing guidance contained in the international standards, as well as recent views expressed and practices adopted internationally, all pointed to a dose criterion for exemption of about 1 mSv/a, perhaps rather more for occupational exposure and a little less for public exposure.

Where exemption was not the optimum regulatory option, the stringency of the regulatory measures applied should, in terms of the graded approach to regulation, be commensurate with the level of risk associated with the material. The various levels of stringency reflected in the standards (i.e. notification, registration and licensing) and their applicability to activities involving NORM were described.

Standards and regulation within EU Member States

Within the EU, the Council Directive 96/29/Euratom of 13 May 1996 laid down special provisions concerning exposure to natural sources of radiation. An update of regulatory developments and guidance with respect to the implementation of these provisions was given, and the results of a limited review of the impact on EU Member States were presented.

In many countries, priority had been given to establishing the impact on workers. Most countries had already identified the industries that might be affected, and some were already conducting detailed studies into some industries to establish particular processes that required regulation. Most countries had also introduced regulations relating to NORM and had used the concept of exemption within their legislation to enable regulatory resources to be focused by restricting regulatory control to those industries where, for example, effective doses could exceed 1 mSv/a.

EU Member States were reported to be still at an early stage in identifying those situations where members of the public could be significantly exposed to discharges and solid wastes. Most countries did not yet have specific controls or specific assessment procedures in place. It was noted, however, that existing environmental protection measures to control particulate emissions, heavy metal releases, etc. could have a beneficial effect on limiting radiological impacts. Some information was presented on NORM discharges to the marine environment as part of the MARINA II study, the aim of which was to provide input to work conducted in terms of the Convention for the Protection of the Marine Environment of the

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[2] The international endorsement process for these activity concentration levels was completed shortly after the NORM IV conference and the levels were formally incorporated into international standards in August 2004 with the publication of IAEA Safety Guide No. RS-G-1.7.

North-East Atlantic (the OSPAR Convention). The oil and gas industry and the phosphate industry were the two main sources of NORM discharges, although discharges from the latter had been reduced in the 1990s, particularly by the United Kingdom.

It was also mentioned that the European Commission intended to create a NORM Network to enable EU Member States to share expertise; to gather, document, exchange, and summarize information; to identify and promote good practice; and to provide a basis for recommendations for further action.

A detailed presentation was given on the establishment of new legislation in Poland with implications for NORM regulation and, in particular, on the establishment of two new Acts concerning nuclear law and geological and mining law. New legislation had become necessary in order to achieve compliance with the above-mentioned European Council Directive. It was reported that the amended legislation still lacked some clarity, for instance on the issue of whether to include doses from the natural background when assessing a hazard, and it was concluded furthermore that additional legislation was required in order to adequately provide for the regulation of NORM waste.

It was reported from Sweden that a government committee on the management of non-nuclear radioactive waste (IKA) had proposed new regulations regarding waste, including NORM waste, to be included in Swedish law. The committee had proposed a mechanism by which each waste generator would have full responsibility for the future disposal of its waste, including the payment of a fee into a government fund (the IKA Fund) to cover the costs of management and future storage. A portion of such payments would be used to cover, at least in part, waste management costs where there was no present owner or where the disposal costs were unreasonably high for a private person — thus, such costs would in effect be subsidized by waste generators through their payments to the Fund. It was pointed out that 'industrial' NORM waste (e.g. mining slag, water filtration solids) was generally to be handled according to the existing Swedish Environmental Code, but it was proposed that any financial security payments required in terms of the Code should be paid into the IKA Fund. It was expected that new regulations and agreements to implement these proposals would be in force by late 2005.

MEASUREMENT TECHNIQUES

Radon in air

Measurement of radon in air continues to attract considerable attention. An intercomparison of 10 radon monitors and 6 radon progeny monitors in Poland was reported to have given generally good agreement between measurement results, especially for the radon monitors, but some important exceptions were highlighted.

The measurement of radon exhalation rate was also a topic of some interest. One presentation demonstrated the successful use of 'Picorad' passive detectors on a coal waste pile. A laboratory investigation into the measurement of radon exhalation rate from soil samples using an emanation chamber and a Lucas cell revealed that the measured exhalation rate was significantly influenced by the sample mass as well as the grain size and moisture content, and an explanation for these findings was advanced.

The use of on-filter concentrating, alpha-spectrometric instruments for high sensitivity measurement of radon progeny in air was shown to have potential for determining the contribution of ^{222}Rn from current or past mining sites to the total geogenic radon level by distinguishing, during periods of calm weather (i.e. minimal vertical air mixing), the presence of higher radon concentrations close to the ground as a result of enhanced radon exhalation.

The development of radon progeny monitors for Polish coal mines was described, in which radon progeny monitoring was combined with respirable dust activity monitoring in the same active monitoring device. Radon progeny measurement was carried out using thermoluminescent detectors mounted within the sampling probe. It was shown that the dust monitoring performance was not adversely affected by the inclusion of the radon progeny monitor.

In another Polish investigation, detailed measurements were made using a radon progeny particle size spectrometer at three indoor locations and in a coal mine, in both normal and 'enhanced' (cigarette smoking) aerosol conditions. Information on the potential alpha energy concentration for different aerosol size fractions, the unattached fraction, the aerosol size distribution and the equilibrium factor was used to determine the effective doses arising from radon progeny inhalation using a dosimetric approach based on the respiratory tract model of the International Commission on Radiological Protection (ICRP). The effective doses calculated in this manner were compared with those determined according to the ICRP's recommended epidemiological approach for radon, i.e. using the ICRP dose conversion convention. The doses calculated using the dosimetric approach ranged from 59% to 200% of the corresponding doses determined using the dose conversion convention.

Airborne dust monitoring

The use of aerosol sampling to determine intakes by inhalation is of particular importance in workplaces involving NORM, because individual in vivo and/or bioassay methods tend to be either not possible or give insufficiently reliable results. The European Commission recently supported a research project on '**S**trategies and **M**ethods for **O**ptimization of **I**nternal **E**xposures of workers from industrial natural sources' (SMOPIE). A presentation was given of a theoretical study on aerosol sampling that formed an important part of this project. A generic method was developed to facilitate the selection of the best type of aerosol sampler (i.e. inhalable, thoracic or respirable) for minimizing the respective biases between the true and estimated exposure and the true and estimated effective dose associated with the inhalation exposure to any radioactive compound. The work focused in particular on how to minimize the bias when the sampling efficiency of the device was known and corrected for, but the particle size (activity median aerodynamic diameter and/or geometric standard deviation) was not perfectly known. The results of the study concluded among other things that:

- For exposure estimates, an inhalable sampler should be selected;
- For effective dose estimates, a thoracic sampler should be chosen when the lung absorption type of the element was S or M, and an inhalable sampler should be chosen when the lung absorption type was F.

Measurement of radionuclides in water

The measurement of radon in water was the subject of a series of intercomparison exercises reported from Poland using samples of mineral spring water and water prepared in the laboratory. Six different measurement methods were compared: liquid scintillation counting (LSC), an ionization chamber, a Lucas cell coupled to a photomultiplier detector, an electrometer, a scintillation chamber with photomultiplier detectors, and a sodium iodide scintillation detector. The LSC and ionization chamber techniques were found to perform particularly well, and the general level of agreement improved as the series of intercomparisons progressed. However, there were some unacceptable results.

LSC was also the subject of a presentation in which the optimization of this technique was described for the measurement of gross alpha and beta activity, radon and radium in Portuguese drinking water.

The measurement, for dose assessment purposes, of uranium and thorium series radionuclides in surface water bodies in areas of mining activity was the subject of a presentation from South Africa. In order to measure a reasonably comprehensive range of radionuclides with acceptable lower limits of detection, various radiochemical methods, as well as inductively coupled plasma mass spectrometry (ICP-MS), needed to be used. The use of such an approach on a wide scale routine basis could impose a heavy burden on analytical facilities and, of course, was very costly. In a case study on one particular water catchment system, it was found that a good correlation was obtained between the ingestion dose determined from the full radionuclide analysis and the uranium concentration in the water, allowing the uranium concentration to be used as a single determinant of dose. It was concluded that this correlation, once determined for a specific water catchment area, could allow ongoing wide scale monitoring to be conducted using only measurements of uranium and, in some cases, radium.

Measurement of radionuclides in solid materials

Gamma ray spectrometry is a widely used technique for radionuclide analysis. An example was given of its use for the in situ measurement of radionuclides in rocks using a portable workstation. In another presentation, technical and procedural improvements in low background gamma-spectroscopic analysis of NORM over the past 25 years were reviewed, together with a discussion on methods for improving the sampling accuracy.

In addressing the question of what grain size to use when measuring gross alpha and beta activities in clay and sand samples, it was pointed out that, while radionuclides of natural origin could be distributed homogeneously throughout the sample by forming part of the crystal structure, they could also be preferentially sorbed onto grain surfaces. To avoid grain size effects when measuring activity concentration, it was concluded that the whole bulk of the sample should be reduced to the monocrystal state rather than to a fixed grain size.

THE USE OF NATURAL SOURCES OF RADIATION IN GEOPHYSICAL INVESTIGATIONS

Earthquakes are associated with increased indoor radon emanation and, on the strength of measurements made in a seismically active area of Armenia, it was proposed that this phenomenon could be used for earthquake prediction. It was reported that radiometric methods are already used in Azerbaijan to locate areas of high seismic risk. Here, the focus was on the detection of fluctuations in the gamma field to locate tectonic disturbances. A study conducted in Luxembourg demonstrated that measurements of radon in soil could be used to locate underground voids caused by old mine workings and thus identify areas with an increased risk of subsidence.

RADIONUCLIDES OF NATURAL ORIGIN IN THE ENVIRONMENT

Various investigations to quantify radionuclide concentrations in the natural environment were described. A study in Poland compared activity concentrations in cultivated soil with those in uncultivated soil. No clear differences were found, apart from an increased concentration of ^{210}Pb in the surface layer of uncultivated soils due to the deposition of this radionuclide from the air — in cultivated soils, this increased concentration was not observed because of soil mixing. No clear effect of fertilizer use was observed. The study also generated data on transfer factors for beetroot and potatoes. Other Polish studies were concerned with the measurement of uranium levels in drinking water derived from both groundwater and surface water sources, and radon in groundwater. A study conducted in Brazil looked at the high levels of radium in groundwater near a coastal lagoon. The most likely source of the elevated levels was identified as a combination of high salinity and low pH, causing leaching from natural monazite formations — the groundwater chemistry was thought to be influenced by marine aerosols, resulting in high concentrations of Na and Cl in the water.

DISCUSSION AND CONCLUSIONS

The conference concluded with a round table discussion led by three panelists comprising the conference chairman and two members of the scientific committee.

One of the topics raised was the question of terminology — in particular, the proliferation of acronyms that had occurred over the last few years (NORM, TENORM, ENOR, NOR, etc.), and which had been reflected in the various presentations to the conference. It was concluded that a single term for referring to material containing elevated concentrations of radionuclides of natural origin was preferable, and that NORM was the most general and commonly used term in this regard. It was pointed out that reference to whether or not NORM had been ‘technologically enhanced’ by processing was not always a meaningful distinction, because this did not necessarily correlate with the level of hazard. Some types of technologically enhanced material could actually be less hazardous than some unprocessed material.

Another topic of discussion was the measurement of radionuclides in various materials, including the different purposes of measurements, the costs involved, and the lower limits of detection needed. The need for simple and inexpensive measurement techniques for monitoring purposes was highlighted, and also the fact that there were various objectives in making measurements, each with its own requirements regarding sensitivity, cost, etc. All agreed that proper quality management was essential.

It was noted that many of the contributions to the conference reflected a move towards the use of facility-specific measurements, especially for dose assessment purposes, instead of relying on modelling using standardized scenarios and generalized assumptions. Modelling was still the approach chosen in many of the studies presented, however, and remained the only practical option where direct measurements were not feasible. It was concluded that each approach had its own particular merits and deficiencies. For instance, maximizing the use of measurements at a facility was the better approach when the reliability of the result was important, such as in dose assessment. On the other hand, modelling offered greater flexibility for the rapid examination of options, such as in a sensitivity analysis.

The conference concluded on a positive and enthusiastic note, with a feeling that much had been achieved but much remained to be done. It was agreed that the NORM conferences should be continued, and that the next conference in the series, NORM V, should be held in 2007. Planning for this event would start with the establishment of a steering committee.

NORM IN MINING

NORM IN MINING INDUSTRY IN POLAND

J. Skowronek[1], B. Michalik[1], J. Dulewski[2]

[1]Central Mining Institute, Katowice, Poland
[2]State Mining Authority, Katowice, Poland

Abstract

The main branches of the Polish minerals extraction industry are the coal, copper, zinc, lead, and salt mines, and oil and gas wells. In many of these branches of industry, the problem of naturally occurring radioactive materials is present. The main source of risk for workers is the short-lived radon daughter products present in air. This source of risk is present in all Polish underground mines. In coal and copper mines and in oil and gas wells, radium-bearing waters are present. This is a potential risk not only for the workers but for the environment too, because all mine water is pumped out to the rivers. In coal and copper mines, radium precipitates from the water creating risks not only of internal contamination but of external gamma radiation too. The Polish Geological and Mining Law requires the monitoring of all sources of natural radiation at the workplace and the introduction of preventive measures if necessary. In this paper the results of the monitoring and prevention measures are described.

1. INTRODUCTION

Exposure to ionizing radiation is usually treated by members of the general public in Poland as a phenomenon related to nuclear power plants and/or disasters in nuclear installations. The best example was the Polish Atomic Law [1], focused until the early 1990s exclusively on nuclear safety, application of artificial sources of radiation, and nuclear accidents. Lately more and more attention is paid to radiation exposure caused by natural radioisotopes. In the last several years, broad investigations in this field are connected not only with radon exposure in dwellings but also with the radiation hazard at workplaces and contamination of the natural environment caused by non-nuclear industries. It has been reflected in the new Atomic Law [2], prepared by the Polish Parliament to harmonize Polish regulations with European Union standards [3].

Until now, specific information on levels of natural radioactivity in waste materials and by-products created by different branches of Polish industry was scarce. Therefore it is very difficult to assess the influence of natural radionuclides on exposures at workplaces and pollution of the environment. Only in the hard coal mining has the situation been more clearly and better recognized. In this paper we would like to describe the state of the knowledge concerning this problem in Poland. Results of investigations in the exploitation industry will be shown (hard coal mines, copper ore mines, lead and zinc mines and salt mines) as well as data from processing industries (dealing with fertilizers, power generation and production of construction materials).

In the first part of the paper, results of measurements of the most important natural radionuclides (^{226}Ra, ^{228}Ra and ^{40}K) in different materials are presented — raw materials, waste and by-products produced or dumped into the natural environment. In the second part, the assessment of the doses for workers exposed to sources of natural radiation in different branches of industry will be done.

2. NATURAL RADIOACTIVITY OF RAW MATERIALS AND INDUSTRIAL SPOILS

In Table I, the main branches of the minerals exploitation industry in Poland are shown. The annual production of raw materials is about 219 million t [4]. Moreover, roughly 82 million t of solid spoils are dumped onto the surface per year. Additionally, about 2.9 million m^3 of wastewater is pumped out daily [5].

The production of phosphate fertilizers is based on imported phosphates (slightly more than 0.5 million t/a). Waste materials generated in the power industry must be also taken into account — about 13 million t/a.

There are no complete data on natural radioactivity of raw and waste materials in the above-mentioned branches of industry. The most reliable results come from the mining industry, because investigations in that field have been performed in hard coal mines, metal ore mines and other underground mines for 30 years. At the end of the 1980s, the system of radiological protection against natural radionuclides had been implemented in the whole of underground mining. At the beginning of the 1990s, requirements for radiological protection in mines were issued as a Decree of the Polish Parliament [6].

TABLE. I. PRODUCTION OF RAW AND WASTE MATERIALS IN POLAND

Branch of industry	Production (Mt/a)	Solid waste (Mt/a)	Liquid waste (million m^3/d)
Coal mining	112	40	0.58
Copper ore mining	28.4	25	0.06
Lead and zinc mining	5	4	0.44
Limestone quarries	8	3	0.50
Salt mines	4.2		0.16
Lignite open pit mines	60.8	10	1.26
Oil	0.4		0.0004

Systematic obligatory measurements enabled the gathering of a broad database of results of concentrations of natural radionuclides in air, water and solid materials, not only in underground galleries but also in the natural environment in the vicinity of mines. The most complete database exists for the hard coal mining industry [7, 8]. Fewer data have been gathered for copper ore mines and lead and zinc mines. The data are shown in Table II, together with results from salt mines and data for waste materials from the oil and gas industry.

According to the presented data, in almost all raw materials produced by the Polish mining industry (like metal ores and hard coal), typical concentrations of natural radionuclides are low. Nonetheless, in some cases we observe radium concentrations above 50 Bq/kg, quoted in UNSCEAR reports as the upper limit for the earth's crust.

Quite opposite is the situation of waste products, especially from the mining industry. The Upper Silesian Coal Basin has rather specific geological and mining conditions; therefore inflows of brines with high radium content into underground galleries are numerous. Dewatering of mines (removal of these brines from mines onto the surface and further to rivers) causes contamination of the natural environment in the vicinity of coal mines. Sometimes in these brines not only radium but barium ions are present and then radium co-precipitates with barium in the form of highly radioactive scales. Such processes can be observed not only in the underground workings, but also sometimes on the surface, in settling ponds or rivers, mainly in cases when waste waters have been not treated before dumping into rivers. Such contamination of the environment is a potential source of radiation hazard not only for miners but also for the inhabitants of adjacent lands. Similar problems have been found in copper mines and in their vicinity.

TABLE II. MAXIMUM CONCENTRATIONS OF RADIONUCLIDES IN DIFFERENT PRODUCTS OF POLISH MINING AND MINERALS EXTRACTION INDUSTRIES

Product	^{226}Ra	^{228}Ra	^{40}K
Hard coal mining [9–12]			
Hard coal (Bq/kg)	159	123	785
Waste rock (Bq/kg)	122	106	1797
Underground scales, precipitated out from waste water (Bq/kg)	204 127	83 785 (215 486)	14 815
Brines (kBq/m^3)	391	99	—
Scales precipitated out on surface (Bq/kg)	156 942	83 785	15 243
Settling ponds — water (kBq/m^3)	7.6	4.4	—
Settling ponds — sediments (Bq/kg)	104 067	83 785	—
Copper mining [10, 12–15]			
Copper ore (Bq/kg)	75	20	466
Concentrated ore after flotation (Bq/kg)	145	20	688
Waste rock (Bq/kg)	53	43	676
Waste products from flotation processes (Bq/kg)	98	39	1243
Scales, precipitated out from waste water (Bq/kg)	1340	68	1108
Copper slag (Bq/kg)	530	183	1459
Brines (kBq/m^3)	95	12	—
Zinc and lead mining [10, 16]			
Zinc ore (Bq/kg)	21	17	65
Waste rock (Bq/kg)	40	17	194
Waste products from flotation processes (Bq/kg)	26	16	80
Scales, precipitated out from waste water (Bq/kg)	76	61	—
Brines (kBq/m^3)	0.5	0.1	—
Salt mining — brines (kBq/m^3) [10]	0.3	0.5	—
Oil and gas extraction — brines (kBq/m^3)	258.1	22.8	—

3. RADIATION HAZARD AT WORKPLACES

The occurrence of natural radionuclides at workplaces is a source of radiation hazard for workers. The most important natural radionuclides are obviously radon and radon progeny, while other sources are external gamma irradiation and accidental ingestion and inhalation of long-lived radionuclides. In the Polish mining industry, monitoring of all possible sources of exposure at workplaces in underground galleries is obligatory, but in other branches such measurements have been done only occasionally.

In Table III, the results of the assessment of effective dose in different branches of industry are presented — for coal mining, copper ore mining, lead and zinc mining and in the phosphate fertilizer industry. The assessment is done for exposure arising from radon progeny, gamma rays and internal contamination.

TABLE III MAXIMUM EFFECTIVE DOSES IN POLISH MINING AND MINERALS PROCESSING INDUSTRIES

Source of hazard	Effective dose (mSv/a)		
	Rn progeny	Gamma	Internal, Ra isotopes
Coal mines, 1995–2003 [8]	7.2	1.8	4.2
Metal mines [8, 17]	9.6	0.08	—
Phosphate industry [18]	0.18	0.35	—

4. SUMMARY

Worldwide the exposure to radon progeny is usually treated as the only source of radiation hazard at workplaces. The same situation can be observed in the Polish minerals exploitation and power generation industries, except for underground mining. Due to high concentrations of radium isotopes in brines and co-precipitation of radium and barium as highly radioactive scales, gamma radiation and internal contamination could be important sources of hazard. Additionally, the release of radium-bearing waters and deposits also leads to the contamination of the natural environment in the vicinity of mines. The pollution may cause an increase in exposure for the inhabitants of adjacent lands. The maximum effective dose for the members of the Upper Silesian population has been calculated at the level of a few millisieverts per year.

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MEASUREMENT OF SHORT LIVED RADON DAUGHTERS IN POLISH MINES

K. Skubacz[*], **A. Mielnikow**

Laboratory of Radiometry, Central Mining Institute,
Katowice, Poland

Abstract

Obligatory measurements of the potential alpha energy concentration of short-lived radon daughters have been performed in the Polish underground mines since 1989. In consideration of economical aspects, it is attempted from the very beginning to combine it with measurements of the dust concentration. Therefore the developed measuring units were an integral part of the dust samplers complying with the requirements of the State Mining Authority for application in underground mines. This way the developed devices could fulfil two measurement tasks simultaneously: measurement of the dust concentration and potential alpha energy concentration of short-lived radon daughters. The new device based on the thermoluminescent detector is able to operate with the SKC universal pumps equipped with a cyclone, making it possible to operate constantly for one working day. The lower limit of detection was about 0.04 $\mu J/m^3$ at a 95% confidence level and 1 h pumping time.

1. INTRODUCTION

According to the Polish Regulations related to naturally occurring radiation hazards in underground mines, systematic monitoring of all recognized radiation sources has to be performed. Here, measurements of the potential alpha energy concentration (PAEC) of short-lived radon daughters are required [1]. These obligatory measurements have been performed in the Polish underground mines since 1989. The most suitable methods are the so-called active methods when air is pumped through a filter that intercepts radioactive aerosols. Furthermore, the measurement of the activity of these collected ‘hot’ particles makes it possible to evaluate the concentration of short-lived radon progeny in air. Depending on a chosen detection method one can measure the concentration of each short-lived radon daughter or only the PAEC.

In consideration of economical aspects, an attempt was made from the very beginning to combine it with measurements of the dust concentration. Therefore the developed measuring units were an integral part of the dust samplers complying with the requirements of the State Mining Authority for application in underground mines. This way, the developed devices could fulfil two measurement tasks simultaneously: measurement of the dust concentration and potential alpha energy concentration of short-lived radon daughters. The new device based on the thermoluminescent (TL) detector is able to operate with the dust samplers made by the Two-Met company and equipped with a cyclone making it possible to operate them constantly for one working day.

The location of this additional part inside the cyclone does not disturb the intrinsic safety of the whole construction and such a modified dust sampler can be used in the Polish underground mines while still preserving the common safety rules. Tests done with this unit showed that the lower limit of detection (LLD) at a 5% significance level, using a membrane

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[*] E-mail: k.skubaczk@gig.katowice.pl

filter and a pump flow rate of 1.9 L/min, was around 0.1 μJ/m^3 for 1 h pump operation and 0.01μJ/m^3 for 8 h pump operation.

2. OPERATION DESCRIPTION

The Two-Met dust sampler configured to measure the concentration of respirable dust consists of a universal constant flow pump and a cyclone (Fig. 1). The pump draws air through a filter with an adjusted flow rate of 0.6–2.2 L/min. The device is supplied by a battery set and can operate continuously for at least 8 h. The measurement run is supervised by a microprocessor. In the cyclone, the respirable dust is separated out and subsequently reaches a filter. The weight of this device is 550 g.

FIG. 1. Aspirator AP-2000EX.

The air flow rate through the cyclone influences the class of dust that is separated out. This way a class of particles reaching the filter contained in the cyclone cassette (Fig. 1) can be chosen. According to criteria of the International Organization for Standardization (ISO) and the European Committee for Standardization (CEN) concerning the sampling convention for aerosols, three fundamental classes of airborne dust can be specified (Fig. 2). One of these is the above-mentioned respirable class that includes particles able to reach the non-ciliary respiratory tract. The second, a so-called thoracic class, is composed of particles penetrating beyond the larynx. The broadest class of particles that includes the two above-mentioned classes is the inhalable class. All airborne particles that can be inhaled through the nose and mouth belong here. In the case of the Two-Met aspirator with the cyclone, at a flow rate of 1.9 L/min, particles with a median aerodynamic diameter (MAD) of up to 8.5 μm reach the filter inside the cyclone — these correspond with the definition of respirable dust. Very fine particles with a diameter of the order of nanometres (unattached fraction and clusters) are intercepted at the cyclone inlet.

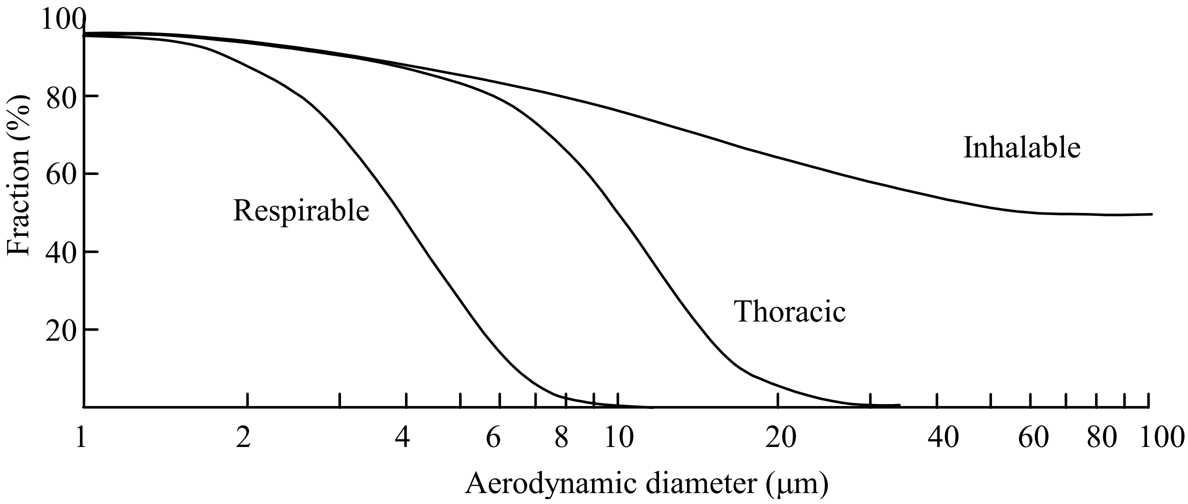

FIG. 2. Fraction of the inhalable, thoracic and respirable particles in relation to all airborne particles according to ISO/CEN criteria.

When the dust sampling is in progress, the resistance to air flow increases, especially if the dust concentration is high. If the increase of the pressure drop becomes excessive, the aspirator will be automatically switched off.

The measuring device (Fig. 3) is placed inside the cyclone cassette above the filter that intercepts the respirable dust. TL detectors are placed in three sockets and record radiation emitted by short-lived radon progeny bound up with the respirable dust. Each socket contains two DA-2 TL detectors. The first one, placed just above the filter, records the alpha, beta and gamma radiation, whereas the second one, separated with a spacer, can register only the beta and gamma radiation. The outcomes received as a result of readouts of these TL detectors make it possible to evaluate the PAEC of short-lived radon progeny averaged over quite a long time. The location of the unit inside the cyclone does not disturb the measurement of the respirable dust concentration in air.

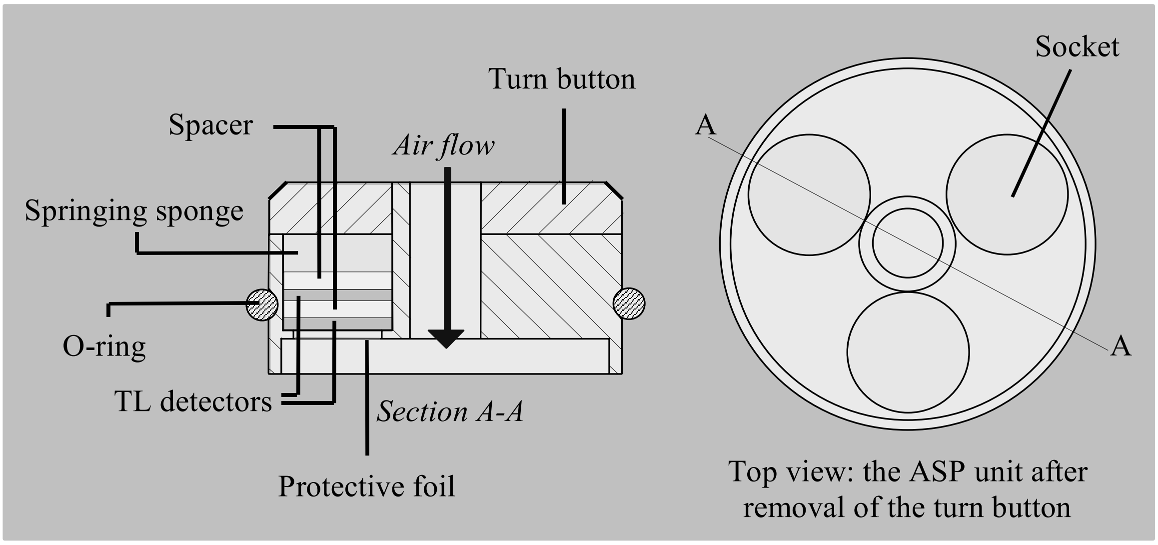

FIG. 3. Sampling probe with the DA-2 TL detectors.

The Polish Institute of Nuclear Physics in Krakow produces DA-2 TL detectors with a diameter of 6mm and $CaSO_4$:Dy luminophore. The luminophore layer is 0.1 mm thick. This layer is stuck on an aluminium base and so only one side of the TL detector remains active in relation to alpha radiation. The luminophore has good efficiency, ten times higher than LiF:Mg,Ti, a linear response up to 30 Gy and low fading: 1–2% within one month and 5–8% within one year [2]. Readouts of these TL detectors were performed at a temperature of 265°C and annealing at a temperature of 320^{o}C over 15 min. Temperature conditions during the annealing process do not have to fulfil such rigorous requirements as those of the TL detectors with LiF:Mg,Cu,P luminophore. The Da-2 TL detectors however have some shortcomings also. The most troublesome drawback is the progressive change of their sensitivity as a result of the luminophore crystals falling from the aluminium base. However, this effect becomes distinct only after the TL detectors have been used more than 10–15-times and then the device can be recalibrated.

3. TESTING OF THE SAMPLING PROBE

The sensitivity of the measuring unit was determined in a radon chamber of 7.5 m^3. Water aerosols with an activity median aerodynamic diameter of 3 μm were injected into the chamber during the tests. The PAEC in the radon chamber was evaluated with the help of the method described in Ref. [3]. According to this method, air is drawn through a filter. Afterwards the filter is immersed in a liquid scintillator to measure its activity according to the Thomas method [4]. On the basis of the results one can evaluate the PAEC in the radon chamber and determine the calibration coefficient of the unit. The results are given in the next section.

The influence of the measuring unit on the measurement of the dust concentration was determined also. These tests were done in a dust chamber of 2 m^3. During these tests a comparison between two sets of results was done. The first set of results was related to the dust concentration measurements performed by the aspirator equipped with the cyclone and measuring unit and the second related to the aspirator of the same type and configuration but without the additional measuring unit. The assessment of results was done on the base of EN Standard No 13205:2001. According to this, two dust samplers are accepted as having the same characteristics if the geometric standard deviation, calculated for two sets of results related to the compared aspirators, is below 1.3. The obtained value was around 1.03, so the differences can be regarded as statistically insignificant.

The cyclone inlet intercepts most of the very fine particles (unattached fraction and clusters) before they reach the filter. This was tested in the 12.35 m^3 radon chamber of the Central Laboratory of Radioprotection (Warsaw, Poland). To fulfil this task, impactors and diffusion battery screens were used. The results show that this kind of inlet intercepts around 80% of particles characterized by the lognormal distribution with parameters: activity median diameter (AMD) = 0.8 nm and geometric standard deviation σ_g=1.3.

The airflow is directed to a small area at the centre of the filter and the uniform dust distribution on the filter can be disturbed especially for the heavier particles (Fig. 4). However, the geometry enables the small area to be ‘observed’ by the TL detectors too. The unit was additionally tested under field conditions. Such measurements were done in an underground mine both in the dusty areas near longwalls in operation and in the regions with relatively low dust concentration like water galleries and crosscuts. No statistically significant differences were observed among the results obtained from the developed measuring unit and any other devices where the impaction effect is not present.

FIG. 4. The measuring unit Alfa-2000-Two-Met and dust distribution on the filter.

4. LLD AND MEASUREMENT UNCERTAINTY

In Table I, values of the LLD are presented at a 5% significance level. In an ideal situation, readout of TL detectors should be done 3 h after air pumping is finished, at the time when practically all short-lived radon daughters intercepted in the filter have decayed. However during routine measurements when the devices are used in underground mines, the period between the preparation of TL detectors in a laboratory and readouts after the measurements are performed can reach 4 weeks. During this period, the signal related to gamma radiation increases, meaning that detection conditions are getting worse. Such cases are also taken into consideration, by assuming the TL detectors were in a gamma radiation field of 0.07 μGy/h, an average outdoor value in the Silesia district of Poland.

TABLE I. LLD (5% SIGNIFICANCE LEVEL) AND MEASUREMENT UNCERTAINTY (95% CONFIDENCE LEVEL)

Device: Alfa-2000-Two-Met. Flow rate: 1.9 L/min. Kerma rate in free air: 0.07 μGy/h

Pumping time	Pragopor 4 filter		Fipro-37 filter		FP/B-3 filter	
	LLD ($\mu J/m^3$)	Uncertainty ($\mu J/m^3$)	LLD ($\mu J/m^3$)	Uncertainty ($\mu J/m^3$)	LLD ($\mu J/m^3$)	Uncertainty ($\mu J/m^3$)
1 h	0.105	0.1 ± 0.119	0.154	0.1 ± 0.172	0.161	0.1 ± 0.175
8 h	0.014	0.1 ± 0.025	0.021	0.1 ± 0.032	0.021	0.1 ± 0.032
1 month	<0.004	0.1 ± 0.014	<0.004	0.1 ± 0.014	<0.004	0.1 ± 0.014

The uncertainties were calculated assuming a PAEC of 0.1 $\mu J/m^3$. For values higher than 0.5–1.0 $\mu J/m^3$ the increase of the pumping time does not significantly lower the measurement uncertainty. Quite a different situation can be observed for low values of the order of 0.1 $\mu J/m^3$. In this case, the increase of the pumping time from 1 to 8 h will improve the measurement precision by about 5 times.

In the experiments described above, membrane filters (Pragopor-4) with a pore size of 0.8 μm and fibre filters of type Fipro-37 and FP/B3 were used. The sockets containing the TL detectors were protected with a polyethylene foil covered by a thin aluminium layer. The protective foil, placed from the side of the filter, has a surface density of 475 $\mu g/cm^2$.

The calculation of LLD and measurement uncertainty is described in more detail in Ref. [4].

5. CONCLUSIONS

The combination of the advantages of the TL detector with the measurement abilities of the Two-Met aspirators has brought good results. The additional measuring device does not disturb the measurement of the dust concentration and enriches its measurement abilities. The measurement of the PAEC is not burdened with an unduly large uncertainty. For a PAEC of 1 μJ/m^3, the uncertainty at a 95% confidence level should not be worse than 10% for a 1 h pumping time. The LLD at a 5% significance level for a 1 h pumping time and routine measurements should not be worse than 0.2 μJ/m^3, or 0.02 μJ/m^3 for an 8 h pumping time. Such a sampling probe can be used for monitoring the naturally occurring radiation related to the short-lived radon daughters in Polish underground mines.

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STATUS OF RADON DOSIMETRY IN ZAMBIAN UNDERGROUND MINES

P. Hayumbu[1], S. Mulenga[2], M. Nomai[1], P. Mulenga[1], R. Katebe[1], P. Shaba[1], T. Chunga[3], D. Inambao[3], F. Mangala[2], P. Tembo[2], Y. Malama[2]

[1]National Institute for Scientific and Industrial Research (NISIR), Lusaka, Zambia
[2]Konkola Copper Mines plc (KCM), Chingola, Zambia
[3]Radiation Protection Service (RPS), Lusaka, Zambia

Abstract

The Zambian economy has significantly relied on copper and cobalt mining in the relatively uraniferous Katanga Basin with a potential hazard of radon for over 50 years now. A radon preliminary survey in 1998 showed that at least 30% of the 42 randomly sampled sites in 8 underground mines had radon levels over 1000 Bq/m^3. This paper outlines ongoing radon dosimetry activities in Zambian underground mines and presents radon grab sampling and personal measurements at one of the mines identified to have high radon concentrations during the preliminary survey.

1. INTRODUCTION

Mining is a global industry undertaken for its economic benefits of wealth creation and employment [1, 2]. In Africa, commercial scale mining provides important benefits in terms of exports/foreign exchange earnings and tax receipts to nineteen African countries. One of these countries is Zambia where the sector contributes 80% of the exports, 10% of the GDP and 15% of total formal employment [3–5].

The above-mentioned social-economic benefits of the mining industry notwithstanding, in developing countries, the industry is likely to be associated with three potential negative effects. The first one is the social-economic dislocation an ill-prepared mining community goes through at mine closure, which arises from exploitation of a non-regenerative resource. The second and third undesirable aspects arise when non-optimal management of mining operations results in environmental degradation and/or negative health impacts on miners and surrounding communities. Principal health problems among miners from various countries that have been cited by the literature include respiratory diseases, neoplasms/cancers, injuries, HIV/AIDS (important studies in South Africa), chronic hypertension, mental health (often related to mine closure) and genetic impact (in the case of uranium) [1, 2, 6, 7].

Although silica has recently been identified as a carcinogen [8], the historical neoplasm/cancer hazard among miners is exposure to radon [9]. The suspicion that working in underground mines is associated with cancer goes as far back as the mid 1500s when Georgius Agricola wrote about the high mortality of miners in the Carpathian Mountains of Eastern Europe. Later autopsy studies of miners in the 1800s in that region demonstrated that chest tumours, later demonstrated to be primary lung cancer, were a common cause of death [10].

In the early 20th century, mines in the present Czech Republic were found to have high radon levels and researchers suspected that this exposure was the cause of the miners' lung cancer. In the 1950s, radiation scientists recognized that particulate radon progeny and not radon gas delivered the radiation dose ultimately responsible for causing cancer. Several epidemiological cohort studies of radon-exposed underground miners with relatively high exposures during the 1950s and 1960s confirmed the association between radon exposure and lung cancer. The main cohorts that have been studied include uranium miners in Czechoslovakia, France, Canada, Australia and the US, fluorspar miners in Canada, iron miners in Sweden and tin miners in China. In Africa, radon measurements have not been as extensive as in developed countries. Measurements have been performed by countries such as South Africa, Namibia, Niger and Morocco, which are well known for mining uranium or uranium-rich phosphate ores.

This paper is on the status evaluation of the radon hazard in Zambian copper and cobalt underground mines in the relatively uraniferous Katanga Basin with a potential hazard of radon. A radon preliminary survey [11] showed that at least 30% of the 42 randomly sampled sites in 8 underground mines had radon levels over 1000 Bq/m^3 [12]. Work to map radon in Zambian underground mines following the preliminary survey started in mines with the largest number of sites with concentrations above 1000 Bq/m^3. Thus far, radon mapping has been performed at two mines. At the first mine, only radon area measurements have been done, while at the second one, both area and personal measurements have been performed. This paper is on measurements at the second mine.

2. EXPERIMENTAL

Radon area levels were measured using two methods. In the first method, field measurements of potential alpha energy concentrations (PAECs) of radon daughters (μJ/m^3) and equilibrium factors of radon and its daughters were made using a Pylon Working Level (WLx) Meter. PAECs were directly converted to radon dose (mSv/a) for each site. In the second method, triplicate grab samples collected in Lucas Cells at field measurement sites were counted on a Pylon AB-5 Radiation Monitor to obtain radon concentrations (Bq/m^3) that were converted to mean site radon dose levels using the equilibrium factor. These area radon measurements formed a cluster of sites in one section of the mine in which personal radon dose of seven job categories were also assessed. Seven representative workers for each work category were given dosimeters using LR-115 integrating nuclear track detectors for a month. At the end of the month, detectors were sent to ALGADE in France for dose evaluation.

3. RESULTS AND DISCUSSION

Results obtained for the two methods of area radon doses using grab sample and field measurements were comparable (R^2=0.9995). Fig. 1 shows a sample of area dose measurements in one section of the mine. These results show that all radon dose levels in this section of the mine are above the action level for individual dosimetry (5 mSv/a) and some measurements are above the occupational exposure limit of 20 mSv/a.

In exposure assessment, one flaw of area measurements is the use of the assumption that a worker spends the whole year working at the site that has a radon dose level comparable to those at sampling sites of radon throughout the year. Correcting this flaw in our study entails taking measurements using personal samplers that provide radon levels integrated over a month. Fig. 2 shows personal radon dose measurements for workers operating in the work area previously characterized for area radon doses shown in Fig. 1. It is apparent that personal doses are on average four times lower than area doses and no workers in this section of the mine have radon exposures that exceed the occupational exposure limit of 20 mSv/a.

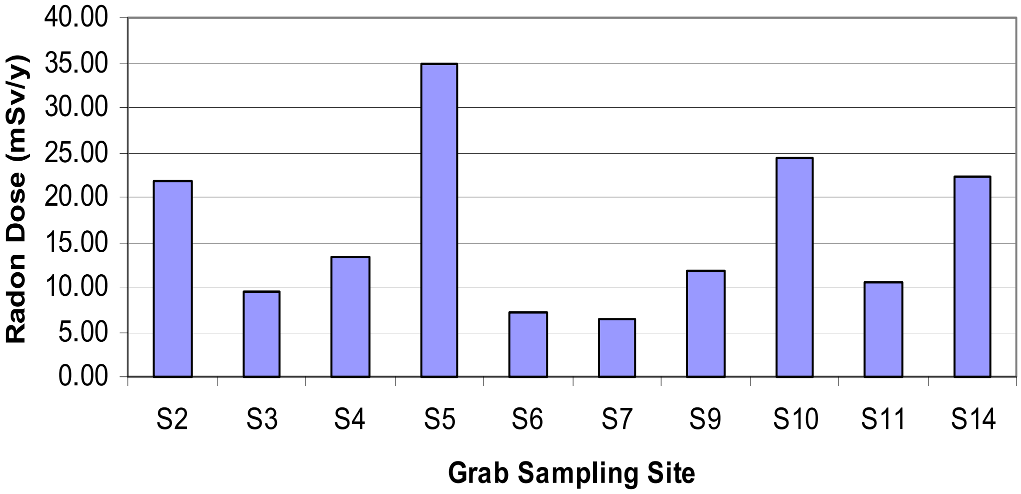

FIG. 1. Radon grab sample measurements September 2002.

4. CONCLUSION

Limited personal radon measurements performed so far in Nchanga underground mine are a factor of four lower than area measurements and indicate that during this study no worker has received personal doses above the occupational exposure limit. Further, for this mine, processing of track detectors deployed to measure area doses is underway [13] so that the mine's radon map of area doses can be prepared. Mine-wide grab sample and field radon dose area measurements performed during deployment of track detectors show a trend in radon exposure doses similar to that shown in Fig. 1. The map, when it is ready, will guide personal radon exposure assessment for the rest of the mine.

ACKNOWLEDGEMENTS

The authors thank the International Atomic Energy Agency (Project ZAM/9/006), Konkola Copper Mines plc, the Ministry of Health and National Institute of Scientific and Industrial Research for supporting this work.

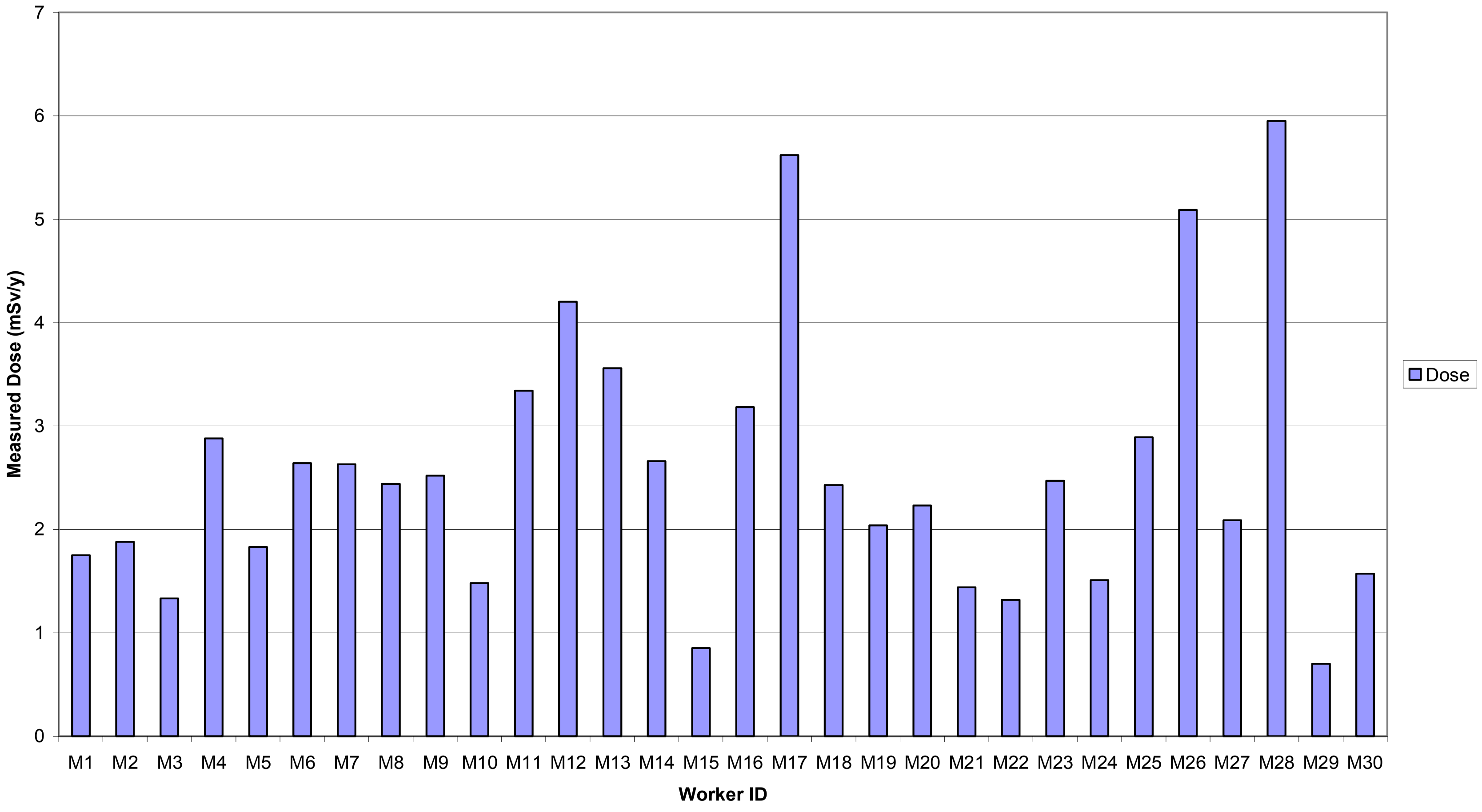

FIG. 2. Radon personal measurements September 2002–June 2003.

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RADIUM REMOVAL FROM MINE WATER — 5 YEARS OF UNDERGROUND TREATMENT INSTALLATION

M. Wysocka, E. Molenda, S. Chałupnik*

Laboratory of Radiometry, Central Mining Institute,
Poland

Abstract

In underground coal mines in the Upper Silesian Coal Basin there are inflows of highly mineralized water containing radium isotopes. This water causes radioactive pollution of the natural environment in mining areas. Therefore removal of radium from saline water is very important. Two types of radium-bearing water were distinguished — one type containing radium and barium ions, but no sulphates (type A) and another one in which radium and sulphate ions are present but no barium (type B). A very efficient and inexpensive method of purification of saline water of Ba^{2+} and Ra^{2+} ions was developed and implemented in two coal mines. As a result of the technology used, based on the application of phosphogypsum as a purification agent, a significant decrease in radium discharge was achieved — daily about 120 MBq of ^{226}Ra and 80 MBq of ^{228}Ra. The other type of radium water does not contain barium ions, but contains sulphate ions SO_4^{2-}. There is no carrier for co-precipitation of radium, so radium is transported with the discharged water to the main rivers. A different method of radium removal must be applied for such water. Laboratory and field experiments were performed, and a purification method was chosen. For purification of saline water, waste products from other industrial processes were applied. The method of purification has been applied on a full technical scale in a coal mine with very good results — approximately 6 m^3/min of radium-bearing water are treated there. The purification takes place in old underground workings without any contact between the mine workers and the radioactive deposits that are produced during the process. As a result, the amount of radium released to the natural environment is significantly lower; more than 100 MBq of ^{226}Ra and ^{228}Ra remain underground each day. Purification was started in May 1999; therefore a lot of experience has been gathered during this period.

1. INTRODUCTION

In the coal mines of Upper Silesia, inflows of brines with enhanced natural radioactivity occur. In some cases, the total dissolved solids concentration (TDS) exceeds 200 kg/m^3, while the radium concentration may reach 400 kBq/m^3. Analysis of the radium isotopes in inflows showed that the input of ^{226}Ra was about 725 MBq/d, while the corresponding value for ^{228}Ra was roughly 700 MBq/d [1]. Only 40% of the radium remained in the underground galleries and gautons, while 60% was transported in pumped water to the settling ponds on the surface and later to rivers [2, 3]. It was an important source of contamination of the natural environment.

The phenomenon of radioactivity in saline water from coal mines in Poland was discovered in the 1960s [4]. Later, investigations showed that the radium concentration in water was correlated with the salinity [5]. Moreover, two types of brine were distinguished in

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* E-mail: s.chalupnik@gig.katowice.pl

coal mines. In type A water, ions of barium and radium are present, while in type B water only radium ions and sulphate occur, but no barium [6]. From type A water, radium is very easily precipitated out with a barium carrier as sulphates after mixing with water rich in sulphate ions. In type B water there is no convenient carrier for radium, therefore no precipitation of radium scale occurs. Further investigations showed that the discharge of radium-bearing water from coal mines caused many cases of contamination of the natural environment, especially small brooks and rivers in the vicinity of these mines. The highest levels of contamination were always connected with release of type A water and precipitation of insoluble deposits with enhanced radium content. Such a process sometimes occurred in underground galleries but sometimes on the surface in settling ponds and small rivers, leading to the radioactive contamination of river beds. The purification of type A water is based on the same chemical process. From type B water, only a slow adsorption occurs, therefore the level of contamination is much smaller in comparison with type A water.

In the past, concentrations as high as about 25 kBq/m^3 of ^{226}Ra have been measured in discharge water from coal mines in Upper Silesia, and the total discharge was approximately 900 MBq/d [7]. However, regulations demanded that water in which the content of ^{226}Ra is more than 0.7 kBq/m^3 must be treated as a waste material with enhanced radioactivity [8]. In Poland, at the beginning of the 1990s, in 10 out of 66 mines such water exceeded these limits. Type A water was discharged from seven collieries, and type B water from three. As a result of the application of purification methods, at present two of the mines are allowed to discharge type A water to the surface settling ponds. The total activity of ^{226}Ra in type A water is only 30 MBq/d (reduced from 220 MBq/d). Three mines are sources of type B water, but the amount of radium in such water is much higher — about 180 MBq/d of ^{226}Ra [9]. Additionally, the concentration of another radium isotope, ^{228}Ra, is even higher than that of ^{226}Ra; the total amount of this isotope in discharge water is slightly more than 280 MBq/d.

The more stringent environmental regulations concerning radioactive discharges forced us to investigate the possibility of decontaminating the mine water. The first task was to design the method for treatment of type A water, which was relatively simple [10]. Such a method of radium removal was implemented in two collieries in the early 1990s and resulted in a substantial reduction in the amount of radium pumped to the surface — less than 55% of the previous value during the period 1990–1995 [11].

2. OCCURRENCE OF RADIUM-BEARING WATER IN COAL MINES IN POLAND

Investigations of techniques to purify radium-bearing type B water were started in the Laboratory of Radiometry of the Central Mining Institute in the late 1980s. It was connected with important factors. On the basis of regulations, concerning the permissible level of radium isotopes in waste water [8], the local authority in Katowice issued a decision that Piast Colliery was to make every effort to reduce, to as low a level as possible, the concentrations of natural radionuclides (radium isotopes) in water before discharging it into the Gostynka river. Moreover, the long-term release of radium-bearing water that caused significant local contamination in settling ponds and small rivers required the assessment of the ecological impact of radioactive pollution. Therefore this aspect of the possibility of radium removal from mine water was also important.

Laboratory and field investigations on radium removal from mine water were supported by the Polish Committee of Scientific Research. Results obtained during tests (also in underground galleries) gave a firm basis for the design of the purification station in Piast Colliery [11]. By 1996 the construction of the station had started, partly supported by the National Fund of Environmental Protection and Water Resources. The construction of the installation was finished at the end of 1998 and testing started.

To aid the co-precipitation of radium, barium chloride was chosen as an agent. During laboratory and field testing, the capabilities of this agent were proven. The chemical reaction is as follows:

$$BaCl_2 \Rightarrow Ba^{2+} + 2\ Cl^-$$

Firstly, the barium chloride dissolves in the water. The next step of the reaction is the co-precipitation of radium and barium ions as sulphates (in the case of radium reaction it is not stoichiometric):

$$Ba^{2+} + Ra^{2+} + 2SO_4^{2-} \Rightarrow BaRa(SO_2)_4$$

Unfortunately, there are some limitations on the use of that chemical. First of all, barium chloride is poisonous and the mining crew had to be trained in relevant safety procedures. Furthermore, as well as other organizational and research activities, the background radiation level had to be checked prior to implementing the purification process both in underground galleries and on the surface.

In May 1999 an underground purification station (UPS) in Piast Colliery started operation at the 650 m level. This is unique, being the only underground installation for mine water treatment and removal of radium isotopes built in a non-uranium mine. Since July 1999, the installation has been used in a routine way to purify 6 m^3/min, i.e. 7200 m^3/d, of brine with enhanced concentrations of radium isotopes.

3. UNDERGROUND TREATMENT STATION — THE CONSTRUCTION

The whole system is located in the central part of the Piast Mine, in the vicinity of the main shafts at a depth 650 m. This area was chosen by the mine’s geological service for the following reasons. First of all, although several development headings were driven in that area, the structure of the coal seams was too complicated for exploitation. Additionally, the coal quality from those seams was poor and numerous inflows of salty water were found. Therefore the exploitation of coal in the area was stopped. Also, very conveniently, the existing galleries in the chosen area were underneath the main galleries at the horizon, so no flooding would be caused by purification.

At first, the small gallery was prepared for the purification station. It had to be located close to the shafts and transportation galleries, to enable easy transport of purification agents. Water from the eastern part of the mine (3.5 m^3/min) is pumped to the purification station through a 1500 m long pipeline, but water from the western part flows along gutters and the flow rate is smaller — 2.6 m^3/min.

In the chamber of the purification station an automatic feeder of barium chloride was installed (see Fig. 1). Water flows in the trough under the feeder, and the purification agent is fed into the water. Several baffles are built in the gauton to make the water flow more turbulent. Under such conditions, the mixing of the barium chloride with water is better and the dissolution of barium chloride is faster as is the resulting co-precipitation of radium with the barium carrier as sulphates. Water is removed from the chamber through a 600 m long pipeline (600 mm internal diameter) to a system of settling galleries. These are five parallel galleries each about 1050 m long and with a cross section of roughly 11.8 m^2. In these galleries the sedimentation of radium/barium deposits and of mechanical suspension takes place.

FIG. 1. Underground treatment station — the feeder of the purification agent.

The settling galleries are isolated from the other parts of the mine. Special water dams were built to ensure no leakage of the water to adjacent headings. Additionally, radioactive deposits in the system are confined and the radiation hazard for the miners is negligible.

Water flows from the settling galleries to the main water galleries near the upcast shaft and is pumped out to the surface, initially to Bojszowy reservoir and is finally discharged to the Gostynka River.

4. RESULTS OF PURIFICATION

The purification of mine water was started in the Piast Colliery in May 1999. As the settling galleries were full of water with enhanced radium concentration, the feed of barium chloride during the first ten days was carried out continuously at a rate of about 100 g/m^3. Since the volume in the settling galleries was assessed as 80 000 m^3 and the daily inflow was approximately 10 000 m^3, we did not expect to record any changes at the outflow until 6–8 days had passed.

The radium content in the water was monitored at several locations in the system. Water samples were taken from the inflow (before purification), and at the outflow from the system and from water pumped to the surface. The Bojszowy reservoir was sampled every three months. Concentrations of radium isotopes in the water (^{226}Ra and ^{228}Ra) were measured by liquid scintillation counting, preceded by chemical separation of radium [12].

In Fig. 2, results of purification in 1999 are shown. Curves of ^{226}Ra and ^{228}Ra concentrations in the inflowing water are plotted, as well as similar curves for concentrations of radium isotopes in the outflow from the system. One important thing must be pointed out — very good results of purification have been achieved quickly, within two weeks. The efficiency of treatment was 90% on average. It means that the amount of radium isotopes in the discharge water decreased significantly — about 40 MBq/d in the case of ^{226}Ra and 65 MBq/d for ^{228}Ra. The total activity of radium isotopes remaining daily in the settling galleries of the system exceeded 100 MBq/d. In Fig. 3, the results of purification in 2000 are shown. Very good efficiency of the purification can easily be seen.

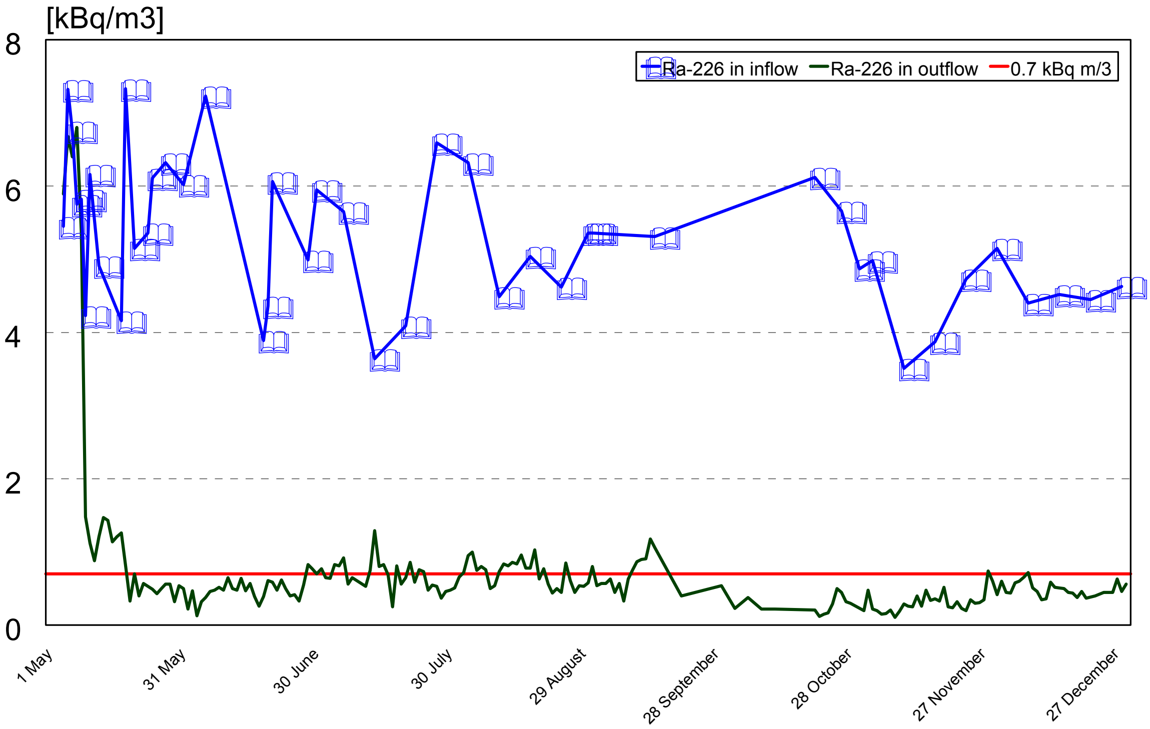

FIG. 2. Results of purification, 1999.

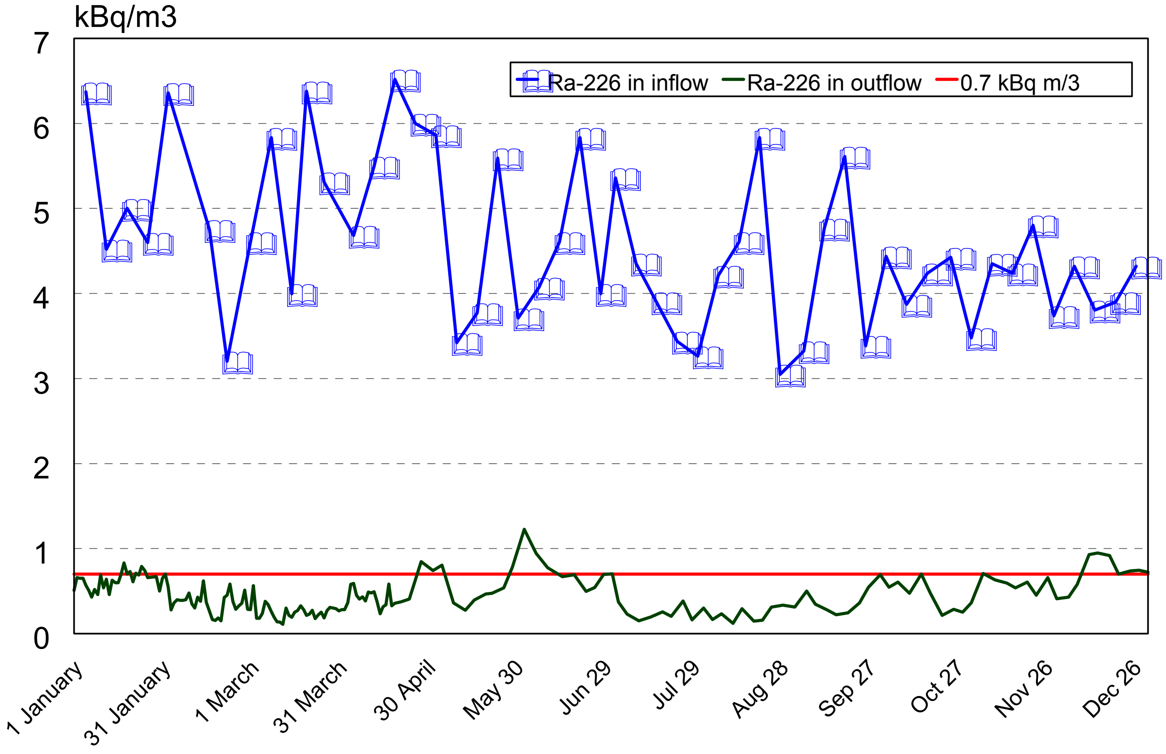

FIG. 3. Results of purification, 2000.

In Table I, the results of monitoring for the first two years are shown. In this period the average efficiency of treatment was 90%, slightly lower than that predicted during laboratory and model experiments. The most important reason for such a result was the 'human factor', i.e. the influence of miners maintaining the installation. The feeding of barium chloride must be continuous — any breaks affect the efficiency of the treatment. In the circumstances of an operating mine it is impossible to reach the same degree of purification as in the laboratory.

TABLE I. EFFICIENCY OF UNDERGROUND PURIFICATION DURING THE FIRST TWO YEARS OF OPERATION

Sampling site	^{226}Ra (kBq/m^3)				^{228}Ra (kBq/m^3)			
	Min.	Max.	Average	Median	Min.	Max.	Average	Median
Inflow into UPS	3.51	7.33	5.20±0.93	5.02	5.77	10.75	8.27±1.21	8.22
Outflow from UPS	0.05	1.47	0.55±0.24	0.53	0.05	2.29	0.86±0.37	0.80
Efficiency of purification (%)	—	—	≈ 90	—	—	—	≈ 90	—

In Fig. 4, the results of water purification for 1999–2001 are shown. At the end of June 1999, the start-up of the installation was finished formally, and the maintenance and supervision by experts probably became less careful than previously. An immediate increase of radium content at the outflow was observed. After additional training of the staff, the efficiency of purification increased. But again, at the end of the 1999, we observed worsening of the results. Therefore an increase in the amount of barium chloride fed daily into the water (from 500 to 750 kg) was ordered, with positive results. In 2001, the amount of purification agent used was only 250 kg/d within the first 3 months and 500 kg later on. The only reason was financial — problems with payment for the barium chloride caused the decrease of the efficiency of purification. Since the beginning of 2002, the financial problems were solved.

5. INFLUENCE OF THE PURIFICATION ON ENVIRONMENTAL POLLUTION

We started to measure radium concentration in water discharged from the Piast Mine into the Gostynka River several years ago [6], and the contamination in the vicinity of the Bojszowy reservoir and the river bed has been investigated more recently [13]. During this period, we gathered a lot of data on which we can assess the effects of purification. In Fig. 3, the results of measurements of radium concentration in water from different sampling points are shown. We measured the radium content in water from the main water galleries at the 650 m level, in discharge water from Piast Mine at its settling pond on the surface, as well as in water released from the settling pond into the Gostynka River, and the results are shown in Fig. 5.

During the start-up of the purification, the effect of radium removal was significant. In cumulative water from the 650 m level, the concentration of the radium isotopes ^{226}Ra and ^{228}Ra decreased from 15 to 1.5 kBq/m^3. This means that the amount of radium pumped to the surface from that horizon was reduced by a factor of ten (see Fig. 5).

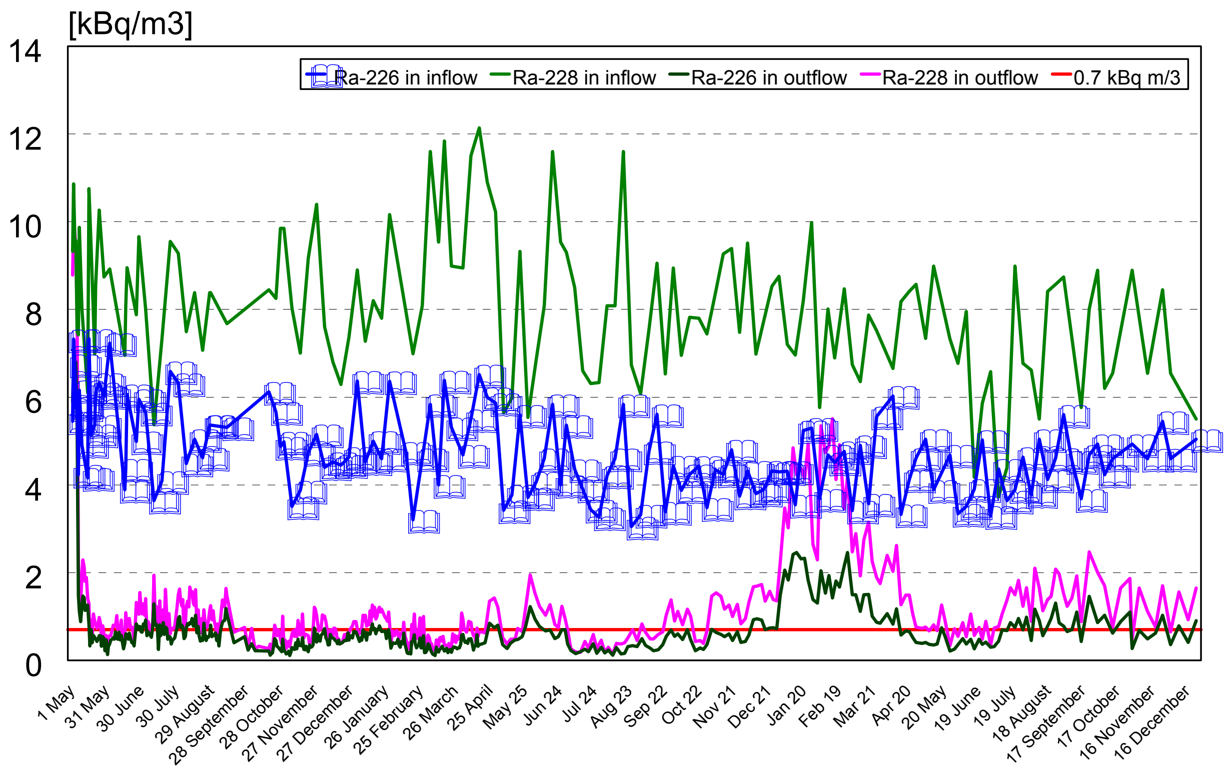

FIG. 4. Results of water treatment in the Piast Colliery, May 1999–December 2001.

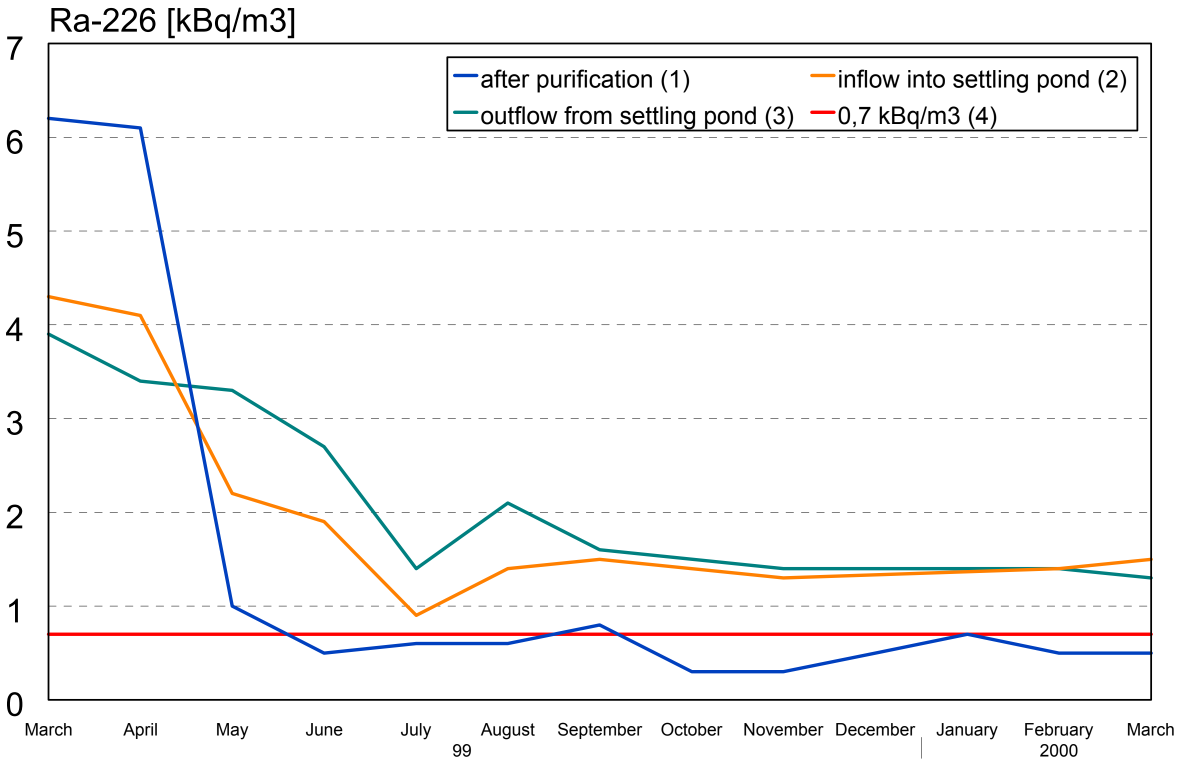

FIG. 5. Results of the purification on the surface environment, 1999–2000.

Such a major decrease of radium concentration in water from the 650 m level resulted in a decrease of concentration in the water from the settling pond on the surface. However the results are not commensurate, because water from the 500 m level water was not yet being treated. The assessment of the radium balance showed that the amount of radium released into the pond was about 65% less than previously. As expected, the same pattern was observed at the outflow from the pond, but slightly retarded due to the retention time in the pond of roughly 8–9 days.

Nonetheless, the radioactive contamination of water discharged into the Vistula River was significantly diminished as a result of the implementation of the purification method. Calculations made on the basis of actual measurements led to the conclusion that the total amount of ^{226}Ra released through the Gostynka to the Vistula river was 45 MBq/d less than before, while the corresponding reduction for ^{228}Ra was 60 MBq/d. The decrease in discharge of both radium isotopes from the Piast Colliery into the natural environment by saline water was more than 100 MBq/d.

6. POSSIBILITY OF BARIUM CHLORIDE APPLICATION IN LIQUID FORM

The idea of using barium chloride in liquid form appeared to be a solution to two main problems of brine treatment. Firstly, the feeders of the solid barium chloride were built as heavy-duty prototypes and after several years it became more and more difficult to repair mechanical damage. Secondly, the results of purification with the use of a solid cleaning agent were vulnerable to improper maintenance. Moreover, in several mines, feeders of liquids are used for coagulants and flocculants to remove mechanical suspensions from mine water. Such units are commercially available and permitted to be installed in underground galleries. Application of the feeders to the solution of cleaning agent would enable the automatic treatment of brines and would decrease the hazard of inadvertent inhalation of toxic barium chloride. Transportation of the solution from the surface to the installation should also be safer.

The first stage of the investigations was laboratory testing of the efficiency of the barium chloride solution. For the investigations, mine water from different mines with different mineralization and radium contents were used. Several series of purification tests were performed, with different contact times, loads of the cleaning solution etc. The results are shown in Fig. 6.

It can be seen that efficiency of barium chloride in solid and liquid form is similar, especially for the longer time of contact. Differences for a short time of contact were mainly due to the problem of the filtration of fine crystals of barium sulphate from the brine after treatment. For a contact time of 24 h, no differences greater than the uncertainties of the results were observed. Therefore a conclusion can be drawn that the efficiency of the liquid form of barium chloride is the same as efficiency of the solid barium chloride. Field experiments are necessary to confirm the results of the laboratory investigations.

7. SUMMARY

The purification station in Piast Colliery is unique, being the first underground installation for the removal of radium isotopes from saline water. Therefore there was no previous experience to fall back on concerning construction, application and management.

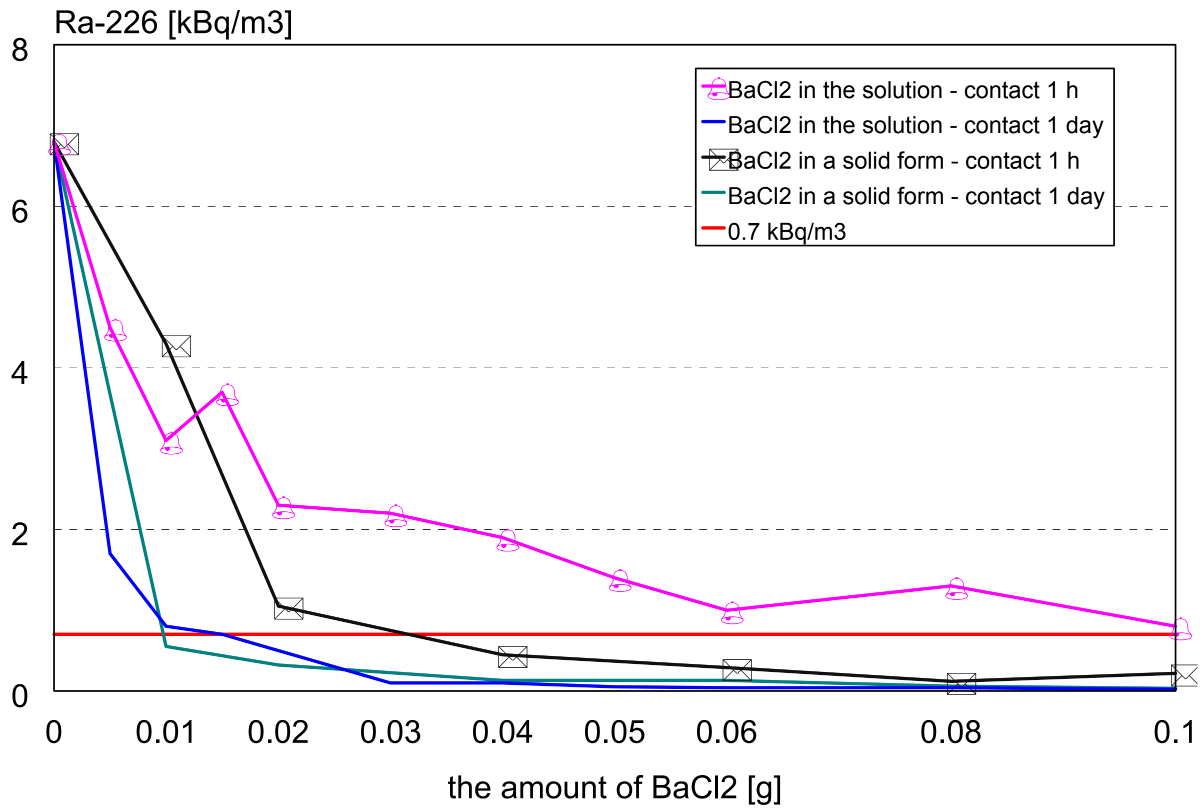

FIG. 6. Radium removal from mine water with application of barium chloride solution — results of laboratory tests.

The implementation of this method of purification of radium bearing water in a non-uranium mine was difficult. All elements of the system — sedimentation galleries, feeders, control units etc. — had to be designed without any comparison with other similar systems. In particular the proper organization of the transport of poisonous substance from the surface to the chamber within an operating coal mine was very important. On the other hand, observations and experience gathered during the implementation of the method will be advantageous in the future, and will aid in the planning and development of similar systems in other coal mines. The ecological effect of the purification is also important. On the surface, at the inflow of saline water into the settling pond, as well as at the outflow from that pond, concentrations of radium isotopes are approximately 60–65% lower than before purification. This corresponds to a decrease of about 45 MBq for ^{226}Ra and 60 MBq for ^{228}Ra in the daily release from Piast mine. It means that the total amount of radium discharged into the Gostynka and Vistula rivers is 105 MBq/d lower.

To achieve a more complete radium reduction in mine water from the Piast Colliery, the removal of radium isotopes from water at the 500 m level must be undertaken. We plan to use the existing installation for this purpose in the near future, firstly for water with the highest concentrations of radium, and later for all radium-bearing water from that horizon.

The implementation of the method and technology of mine water purification received an award in 2000 by the Ministry of the Environment for outstanding scientific achievement in the field of environmental protection. In 2001, the Central Mining Institute obtained a certificate of the President of Poland for the Best Available Technology.

A new concept for the feeding of the barium chloride as been developed to override problems with the ‘human factor’ influence on the purification results. This idea seems to be a solution to design a fully automatic feeder and to implement the treatment technique in other collieries in the Upper Silesia region. First, implementation will be on another horizon in Piast Mine (-500 m). Until now, laboratory experiments have been performed with very promising results, confirming the possibility of the application of the liquid cleaning agent with an efficiency similar to that for solid barium chloride.

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EXPOSURE FROM AN IGNEOUS PHOSPHATE MINE OPERATION

A.J. van der Westhuizen[*]

NOSA International, Pretoria, South Africa

Abstract

The International Atomic Energy Agency Safety Series 115 and European Union Council Directive 96/29/EURATOM have changed the profile of radiation protection completely, increasing the regulatory awareness of natural radiation and the industries involved. Three major industries have been identified in terms of their scope and the materials handled as industries requiring further attention. They are the oil and gas industry, the zircon industry and the phosphate and fertilizer industry. The phosphate and associated fertilizer industry has an added complication, because it has two distinct sources of raw material, i.e. being of igneous or sedimentary origin. The sedimentary material has a dominant ^{238}U series, with activities ranging from 1 Bq/g per isotope to as high as 5.7 Bq/g per isotope, but with negligible ^{232}Th content. The igneous material of the Phalaborwa Complex has fairly low levels of ^{238}U and its associated daughters, (less than 0.15 Bq/g per isotope), but with elevated levels of ^{232}Th when compared with the sedimentary material. This paper will focus on the mining operations of an igneous source located in South Africa. The mine involved received a nuclear authorization in 1993 in terms of the Nuclear Energy Act, No 131 of 1993 and in the following years completed both occupational and public risk assessments as required by the authorization. This paper places emphasis on the public risk assessment completed in 1999 and the results of the subsequent routine monitoring programme, and expands on some of the practical problems the company had to deal with. The public risk assessment was conducted in an integrated manner, assessing doses to members of the public via the atmospheric, aquatic and secondary pathways by the Nuclear Energy Corporation of South Africa and the subsequent routine monitoring programme results evaluated and reported to the regulator by the company itself. Finally, a brief description of the current monitoring programme is given, with a mention of possible future projects.

1. INTRODUCTION

The facility under discussion is a South African opencast mine that produces igneous phosphate rock, with intermediate and final products for the domestic and international markets. It provides the following strategic advantages:

- To make South Africa self-sufficient with respect to phosphate imports,
- To earn foreign currency from the export of the mineral,
- To create approximately 2000 direct job opportunities, with associated indirect job opportunities in the Greater Phalaborwa region.

Approximately 3 million t of phosphate rock are produced annually from a coarsely crystalline calcium-fluoride-phosphate compound of magmatic origin. The product is a finely ground apatite mineral. The mine is located next to the towns of Phalaborwa, Namakgale and

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[*] E-mail: riaanvdw@nosa.co.za

Lulekani, bordering on the Kruger National Park in the Limpopo Province. In 1993, the company obtained a nuclear authorization in terms of the Nuclear Energy Act, No. 131 of 1993, and has been the holder of an authorization since then. In 2002, the authorization was changed to a certificate of registration issued in terms of the National Nuclear Regulator Act, No. 47 of 1999.

2. PRODUCTION PROCESS

Fig. 1 shows a simplified diagram of the mining and beneficiation process.

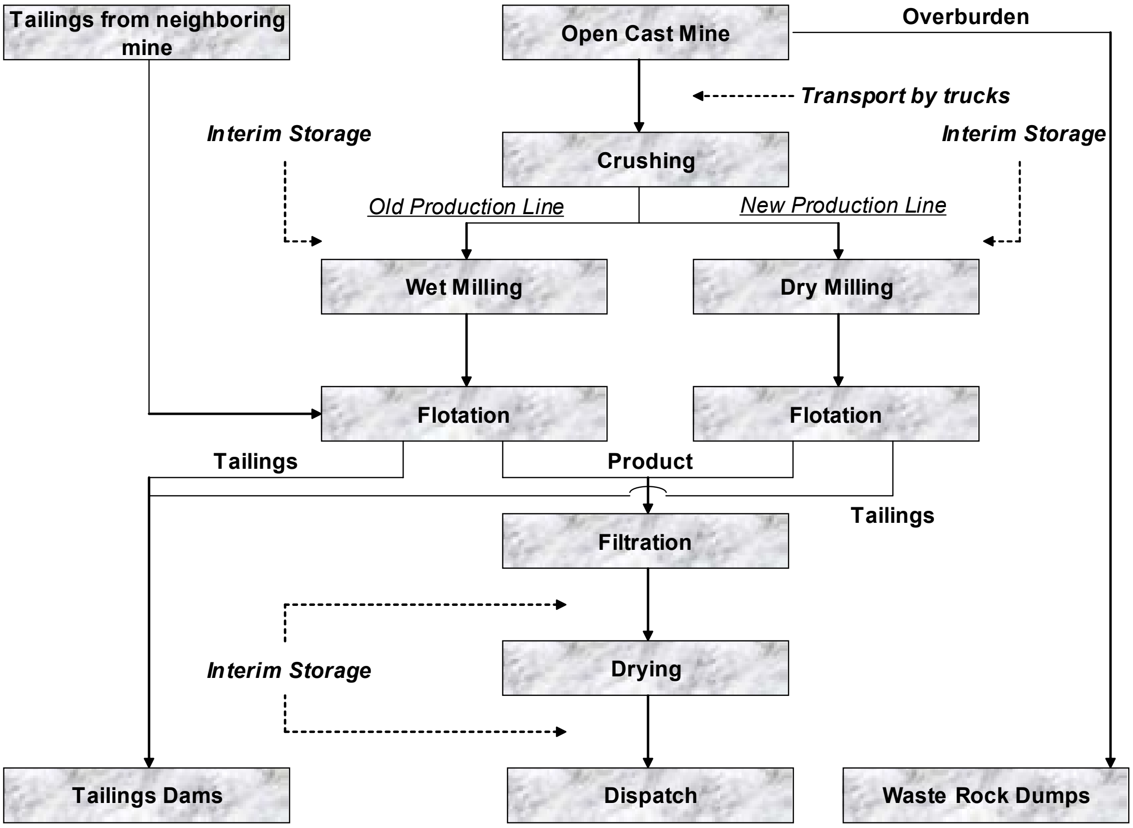

FIG. 1. Mining and beneficiation process.

3. SPECIFIC ACTIVITY

Table I summarizes the known specific activities of the major types of material involved in the process, i.e. phosphate rock and phosphate tailings.

4. ISOTOPES CONSIDERED

The following isotopes were considered in the assessment process:

- Uranium series: ^{238}U; ^{234}U; ^{230}Th; ^{226}Ra; ^{210}Pb; ^{210}Po
- Actinium series: ^{235}U; ^{231}Pa; ^{227}Ac; ^{227}Th; ^{223}Ra
- Thorium series: ^{232}Th; ^{228}Ra; ^{228}Th; ^{224}Ra; ^{212}Bi

The National Nuclear Regulator does not generally require the inclusion of ^{235}U and its daughter isotopes in the assessment process, and for the initial screening survey they were excluded. However, where the gross alpha activity was used for dose determination, it was deemed appropriate to include the actinium series when calculating the dose conversion factor as it may have a measurable effect.

TABLE I. ACTIVITY CONCENTRATIONS IN THE PROCESS MATERIAL

Radionuclide	Activity concentration (Bq/g)	
	Phosphate rock	Tailings
^{238}U	0.14	0.26
^{226}Ra	0.14	0.27
^{210}Pb	0.12	—
^{232}Th	0.47	0.31
^{228}Ra	0.55	0.33
^{228}Th	0.55	0.35

5. METHODOLOGY

5.1. Occupational exposure

For the purpose of this assessment, occupational exposure was deemed to be associated with two exposure pathways: external exposure from the gamma component, and inhalation [1, 2]. The ingestion pathway is not significant, and its inclusion was not a regulatory requirement. The external exposure was measured at various locations in a specific section, and the dose rate at 1 m was used in this assessment process.

Two methods of determining internal (dust inhalation) dose were used to calculate the occupational dose, one being more suitable for screening assessment purposes and the other being a more realistic calculation.

Method 1: The screening assessment utilized area air concentrations as determined through an occupational hygiene programme and the average radionuclide activity concentrations in the phosphate rock or tailings (See Table I). An occupancy factor of 1 was used, assuming 250 shifts per year, each lasting 9.5 h.

Method 2: The assessment was repeated but based on actual measurements in the production areas. This method used gross alpha activity measured on the area air samples collected in the plant and a calculated dose conversion factor for phosphate rock and tailings. (see comment in Section 4).

5.2. Public exposure

The radiological impact of the facility on members of the public was determined with the aid of mathematical models such as that described in IAEA Technical Reports Series No. 364 [3] and Safety Reports Series No. 19 [4]. Fig. 2 shows the generic pathways that received consideration in the public assessment process adopted by the company. The models were applied to the Phalaborwa facility to determine doses received by actual and hypothetical critical groups during the initial risk assessment [4]. Three exposure scenarios were considered, corresponding to three actual critical groups identified for the facility. The critical groups are — for scenarios 1, 2 and 3 respectively — a family living in the town of

Phalaborwa, a family living in Namakgale, (both of which were located the north and north-east), and a family living to the south-east of the facility. It was assumed that all the age groups were represented in each critical group, although for the purposes of this paper only the adult exposure is reported. The exposure pathways considered for each scenario are shown in Table II. Drinking water is generally obtained from the local Water Board, a source not affected by the facility. However, for scenario 3 it was assumed that some water for drinking purposes was extracted from the Selati River or from a borehole.

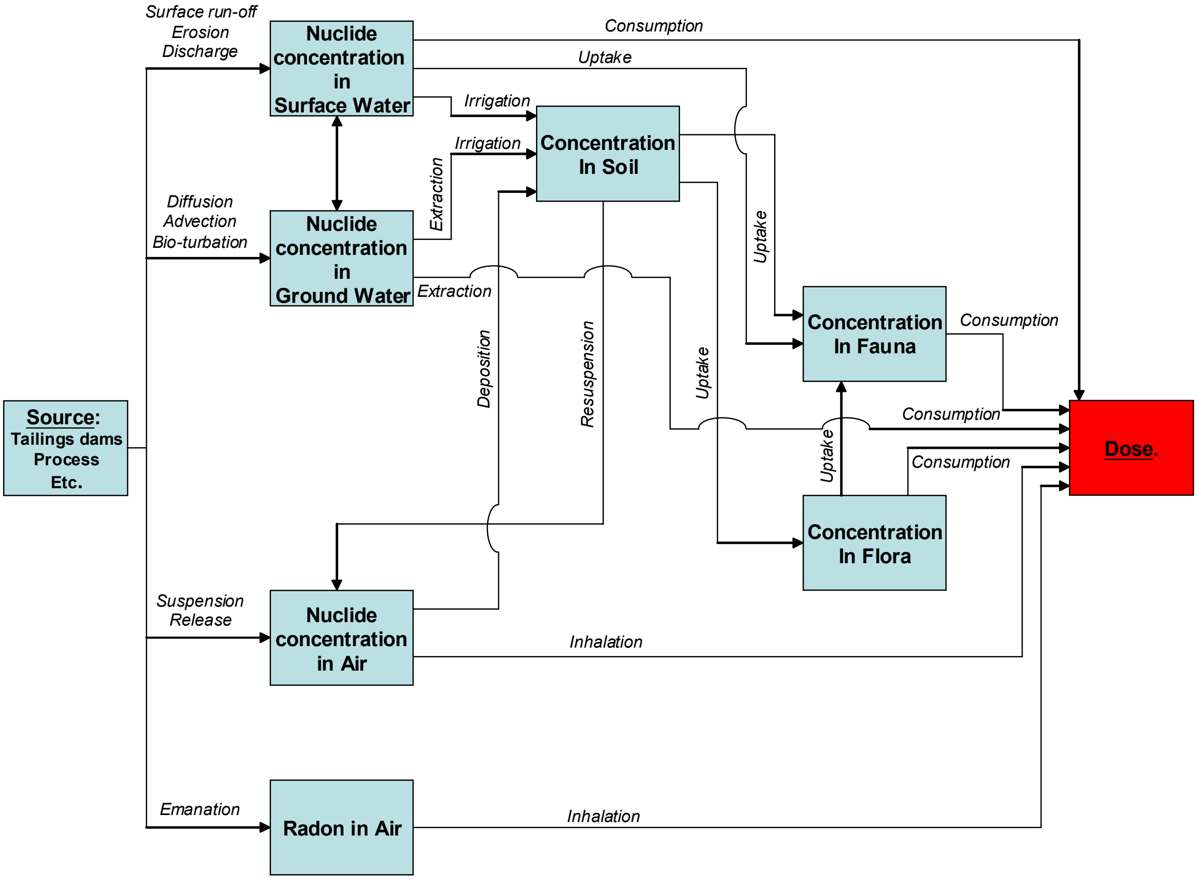

FIG. 2. Exposure pathways considered in the public dose assessment.

6. RESULTS AND DISCUSSION

6.1. Occupational exposure

For Method 2, the inhalation dose coefficients, using the average radionuclide-specific activities for phosphate rock and tailings, were calculated to be 12.3 μSv/Bq$_\alpha$ for phosphate rock and 9.63 μSv/Bq$_\alpha$ for tailings. The total dose for the various phosphate production and waste disposal areas are summarized in Table III.

The results in Table III show that occupational exposure at an igneous phosphate mine gives rise to effective doses less than 1 mSv/a and the areas are thus non-classified. Also apparent is that the dose resulting from the two assessment methods is of the same order of magnitude. The gross alpha activity determination is therefore not really necessary and can be excluded, thus saving on the cost of an initial assessment and assessment time. (Both methods require the radionuclide activity concentrations in the process material, while only Method 2 requires additional radiation measurements.)

However, it is also clear that should the dust concentration in the air or the specific activity of the material increase, some of the areas may require reclassification from non-classified to supervised.

TABLE II. PATHWAYS CONSIDERED FOR THE ASSESSMENT OF PUBLIC DOSES

Description	Scenario			Remarks
	1	2	3	
Ingestion				
Water from river or groundwater			✓	Normally obtained from local Water Board
Vegetables, fruit	✓	✓	✓	To fulfil daily needs
Fish	✓	✓	✓	In dams on mine property (actual practice)
Meat, milk, poultry, eggs, cereal		✓	✓	To fulfil daily needs
Inhalation				
Dust	✓	✓	✓	Concentration varies with source–receptor distance, climatic conditions etc.
Radon	✓	✓	✓	
External Radiation	✓	✓	✓	As a result of deposition

6.2. Occupational action level

Using Method 1, an attempt was made to establish action levels for two parameters that may change, namely activity concentration and airborne dust concentration. For the purpose of establishing the activity action levels it was assumed that all other variables remained the same, with an average annual effective dose from gamma radiation of 0.46 mSv. An upper bound on internal effective dose of 0.5 mSv/a was thus set, ensuring the total effective dose remained less than 1 mSv/a.

Fig. 3 shows the effect of an increase in radionuclide-specific activity on the inhalation dose if the airborne dust concentration remains constant.

Should the radionuclide activity concentrations remain the same but the airborne dust concentration increase (for example, due to ventilation failure), the situation shown in Fig. 4 is then applicable — an increase in airborne dust concentration rapidly leads to unacceptable doses. Should a company therefore wish to decrease its occupational exposure, the focus should be directed towards dust control, e.g. extraction, ventilation etc.

6.3. Public exposure

6.3.1. General

Table IV shows the results of the initial assessment. As stated in Section 5.2, water was included in Scenario 3 although it is highly unlikely that it is consumed or used in any manner. The groundwater is naturally very saline due to the geological formations in the area and the water is subsequently not suitable for drinking or irrigation. However, to ensure comprehensiveness, it was assumed that some water is desalinated without removing some of the activity and used for drinking purposes. Utilizing the 2001 measurement results for the applicable boreholes as well as the 2002 and 2003 river water analysis results, the incremental dose was reviewed and is presented in the Table V. Assuming the doses in Table V are typical of the current situation, the total dose for Scenario 3 will decrease by at least 250 μSv/a, even when ignoring the decreased contribution from the water through the secondary pathways, resulting in a total public dose of less than 100 μSv/a.

TABLE III. OCCUPATIONAL EXPOSURE FOR PHOSPHATE PRODUCTION AREAS

Area	Effective dose from internal exposure (mSv/a)		Dose rate from external exposure (μSv/h)	Total effective dose (mSv/a)	
	Method 1	Method 2		Method 1	Method 2
Mining					
Crushing and loading	0.25	0	0.22	0.69	0.44
Primary crushers	0.25	0.11	0.22	0.69	0.55
Secondary Crushers	0.25	0.11	0.11	0.47	0.34
Tertiary crushers	0.25	0.11	0.11	0.47	0.34
Milling					
Operations	—	0.11	0.20	—	0.51
Workshop	—	0	0.19	—	0.38
Flotation					
Copper	0.14	0	0.33	0.80	0.67
Phosphate	0.14	0	0.22	0.58	0.44
Magnetic separation	0.14	0.32	0.33	0.80	0.98
Workshop	0.14	0	0.21	0.55	0.43
Filtration					
Operations	0.31	0.24	0.21	0.72	0.65
Workshop	0.31	0	0.22	0.75	0.44
Extension 8					
Crushing	0.26	—	0.20	0.66	—
Conveyors	0.26	—	0.24	0.74	—
Milling	0.26	—	0.20	0.66	—
Flotation	0.26	—	0.19	0.64	—
Workshop	0.002	—	0.26	0.52	—
Drying and dispatch					
Operations	0.14	0.32	0.29	0.72	0.90
Workshop	0.02	0	0.24	0.50	0.49
Tailings					
Workshops	0	0.08	0.22	0.44	0.52
Research & Development					
Laboratory	—	0.11	0.31	—	0.72
Pilot Plant	—	0.22	0.21	—	0.64

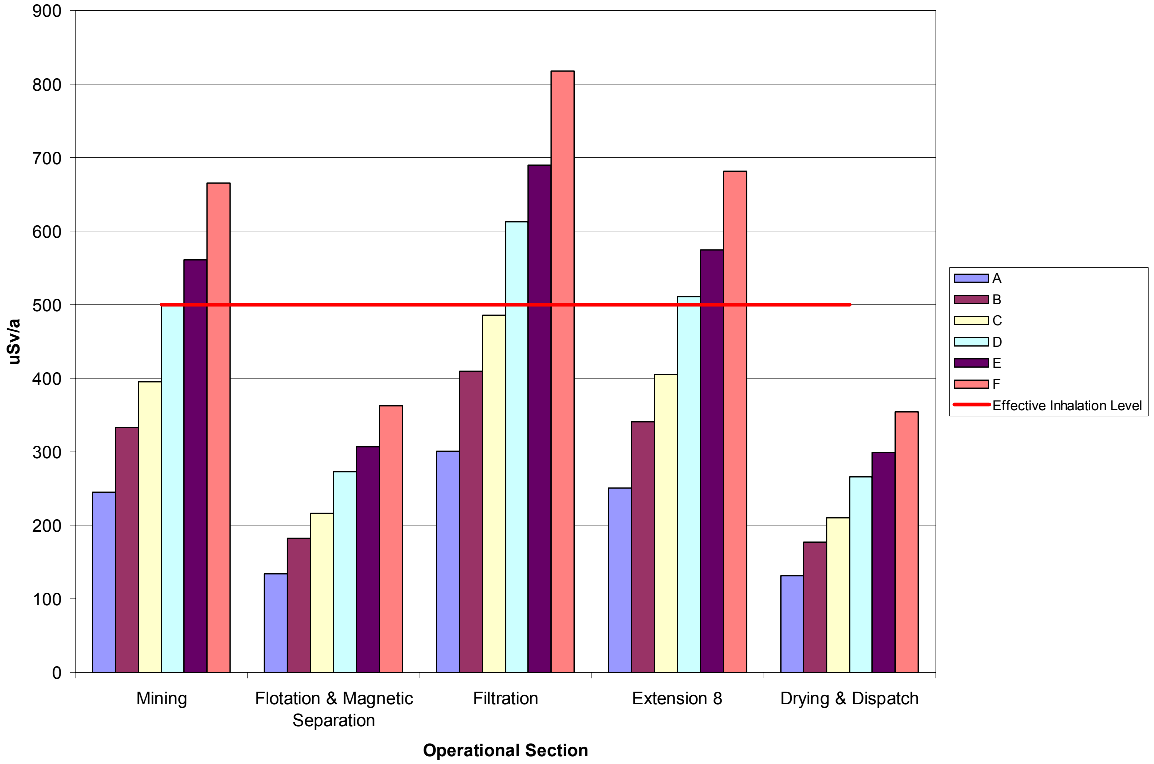

FIG. 3. The effect of radionuclide activity concentration on worker inhalation dose for a constant airborne dust concentration.

A:	^{238}U = 0.15 Bq/g;	^{232}Th = 0.5 Bq/g	B:	^{238}U = 0.5 Bq/g^{-};	^{232}Th = 0.5 Bq/g
C:	^{238}U = 0.75 Bq/g;	^{232}Th = 0.5 Bq/g	D:	^{238}U = 0.75 Bq/g;	^{232}Th = 0.75 Bq/g
E:	^{238}U = 1 Bq/g;	^{232}Th = 0.75 Bq/g	F:	^{238}U = 1 Bq/g;	^{232}Th = 1 Bq/g

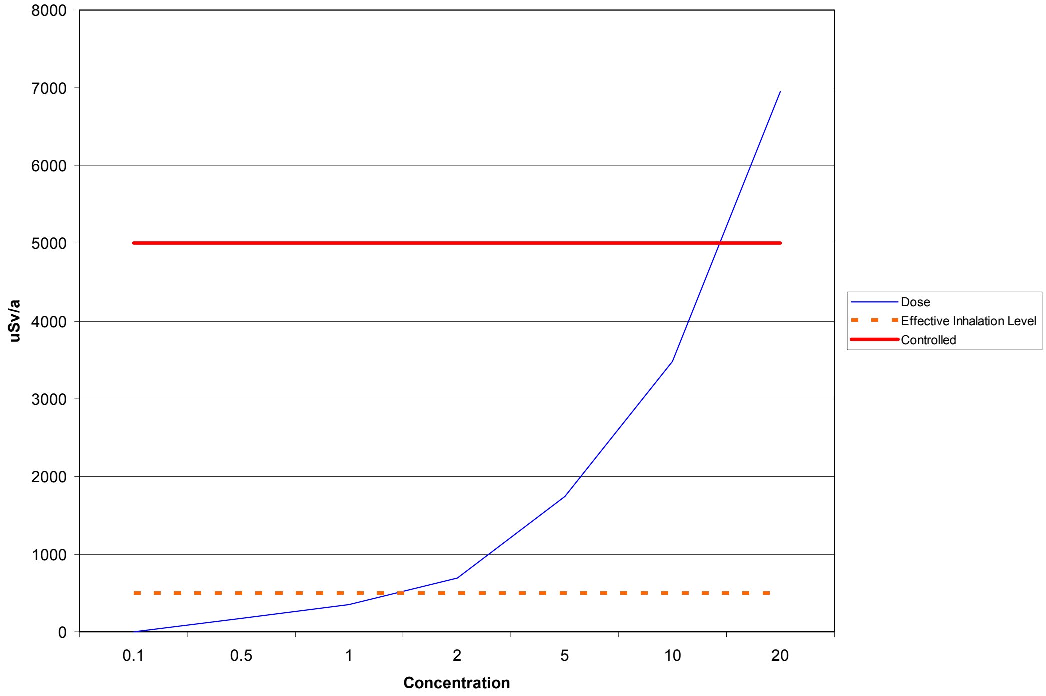

FIG. 4. The effect of airborne dust concentration on worker inhalation dose for a constant radionuclide activity concentration.

TABLE IV. EFFECTIVE DOSES RECEIVED BY MEMBERS OF THE PUBLIC

Description	Annual effective dose (μSv)		
	Scenario 1	Scenario 2	Scenario 3
Inhalation			
Dust	15.6	15.6	34.8
Radon	0.975	0.975	5.9
Ingestion			
Water (subsequently reviewed, see Table V)	—	—	273
Leafy vegetables	0.1	0.1	0.22
Root vegetables	0.272	0.272	0.599
Fruit	0.105	0.105	0.232
Meat	—	2.84	15.5
Milk	—	0.589	9.96
Cereal	—	0.146	0.323
Poultry	—	0.201	0.411
Eggs	—	0.067	0.15
External			
Air	5.19×10^{-7}	5.19×10^{-7}	1.15×10^{-6}
Soil	0.00446	0.00446	0.00982
Total (prior to review of water pathway)	17.1	20.9	341

TABLE V. BACKGROUND-CORRECTED DOSE FROM WATER CONSUMPTION (MDA taken as zero)

Season	Incremental annual effective dose (μSv)
Groundwater	
2001, wet	4.7
2001, dry	1.7
Surface water	
2002, wet	14.5
2002, dry	22.9
2003, wet	8.98
2003, dry	11.7

6.3.2. Problem encountered

Initially the South African Regulator required a company to use the minimum detectable activity (MDA) of an isotope for dose calculations if the true activity was not measurable. This, however, resulted in doses exceeding 5 mSv/a from ingestion of fish, a secondary pathway, primarily from ^{210}Pb and ^{210}Po. Refining the analysis techniques has since proven the initial methodology inappropriate as illustrated by Table VI.

TABLE VI. BACKGROUND-CORRECTED DOSE FROM FISH CONSUMPTION

Season / water source	Annual effective dose (μSv)		
	Total	Background	Incremental
2003, wet / Selati River	23.1	89.2	0
2003, wet / recreational dam	21.1	89.2	0
2003, dry / Selati River	33.2	89.2[1]	0

7. CONCLUSIONS

The occupational effective dose is less than 1 mSv/a for the production areas, resulting in such areas being non-classified. However, an increase in the ^{238}U activity concentration to 0.75 Bq/g or an increase in the airborne dust concentration to 1.5 mg/m^3 should receive attention, as the resulting dose would then probably exceed 1 mSv/a, requiring a formal radiation protection programme. The effective dose received by members of the public is less than 250 μSv/a, and is thus in compliance with South African legislation.

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[1] Background sample could not be collected due to the low level of the Selati River. The background value obtained during the wet season was used as reference.

RAIL TRANSPORT OF IGNEOUS PHOSPHATE ROCK

A.J. van der Westhuizen[*]

NOSA International, Pretoria, South Africa

Abstract

The third IAEA Research Co-ordination Meeting on *Development of a Radiological Basis for the Transport Safety Requirements for Low Specific Activity Materials and Surface Contaminated Objects (LSA/SCO)* was held in Cape Town, South Africa on 19–23 February 2001. It was attended by the Chief Scientific Investigators (CSIs) from Brazil, Canada, France, Germany, South Africa and the United Kingdom, and the IAEA Scientific Secretary. In addition to the CSIs, observers from South Africa and Japan participated. A South African phosphate rock and fertilizer producer participated in the meeting as an observer and undertook to repeat a previous zircon sand study, this time for igneous phosphate rock and phosphoric acid, in order to support the theoretical models, although the material is strictly speaking not subject to the requirements of the IAEA *Regulations for the Safe Transport of Radioactive Material*. This paper represents a partial fulfilment of the commitment, reporting on occupational exposure of loading of the phosphate rock onto the rail cars, transport and unloading in the harbour, and on public exposure during rail transport and interim storage in silos. The paper also makes some reference to undesired events such as spillage. The risk assessment is based on actual measurements where possible and only refers to modelling or theoretical calculations where no results were available.

1. SCOPE

This risk assessment evaluates the rail transport of igneous phosphate rock from the Phalaborwa Complex, South Africa, to the harbour in Richards Bay, South Africa. Marine transport and the loading and unloading of ships are not included. It reports on doses likely to be incurred during normal operations by workers as well as members of the public and makes some reference to exposures during abnormal conditions. In conclusion, the assessment identifies areas that require further assessment.

2. BACKGROUND

The third IAEA Research Co-ordination Meeting on *Development of a Radiological Basis for the Transport Safety Requirements for Low Specific Activity Materials and Surface Contaminated Objects (LSA/SCO)* was held in Cape Town, South Africa on 19–23 February 2001. It was attended by the Chief Scientific Investigators (CSIs) from Brazil, Canada, France, Germany, South Africa and the United Kingdom, with the IAEA acting as Scientific Secretary. In addition to the CSIs, observers from South Africa and Japan participated. The meeting was part of a Co-ordinated Research Project (CRP), to investigate an area of concern, specifically the radiation protection basis for the IAEA *Regulations for the Safe Transport of Radioactive Materials* [1] (the Transport Regulations). Upon completion of the CRP a TECDOC, summarizing the work of the CRP, is to be prepared.

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[*] E-mail: riaanvdw@nosa.co.za

A South African phosphate rock and fertilizer producer participated in the meeting as an observer and undertook to repeat a previous zircon sand study, this time for igneous phosphate rock and phosphoric acid, to support the theoretical models, although the material is strictly speaking not subject to the requirements of the Transport Regulations. This paper represents a partial fulfilment of the commitment, reporting on occupational exposure during the loading of phosphate rock on rail cars, transport and unloading in the harbour, and on public exposure during rail transport and interim storage in silos. The paper also makes some reference to undesired events such as spillages, as seen from a South African industry perspective. It uses, where possible, the scenarios described in the transport assessment study done for zircon sand, to allow comparison between the results.

3. PHOSPHATE INDUSTRY

3.1. Introduction

Four nutrients have been identified that are vital for healthy and rapid plant growth. They are nitrogen, phosphorus in the form of phosphate (P_2O_5), potassium (usually as K_2O) and sulphur — *“Phosphorus is primarily responsible for all processes in plant life in which energy is stored and utilized. It promotes root growth. It improves the quality of grain and accelerates its ripening”* [2]. Initially, bones were used as the prime source of phosphate, but the discovery of large deposits of phosphate rock overcame the constraints of limited supply. However, these sources contain naturally occurring radionuclides to a varying degree, with the true radiological impact of the industry yet to be fully quantified.

3.2. Activity concentrations

There are two sources of phosphate-bearing material, both containing naturally occurring isotopes, defined in terms of origin. The most common source is phosphate of sedimentary origin, accounting for approximately 86% of the world market. The second source is rock from igneous origin and represents the other 14%.

A significant difference between sedimentary phosphates and the igneous material found in the Phalaborwa Complex, South Africa lies in the difference in radionuclide activity concentrations in the natural decay chains. Sedimentary material has higher concentrations of the ^{238}U decay series and very low concentrations of ^{232}Th and its daughter isotopes. On the other hand, the Phalaborwa Complex material has much lower concentrations of the ^{238}U decay series, but with elevated concentrations of ^{232}Th and its daughters.

Almost all of the South African phosphate rock originates from the Phalaborwa Complex located in the Limpopo Province and the focus of this assessment will thus be of the effect of this material on workers and possibly members of the public.

Table I summarizes some of the known radionuclide activity concentrations as average values for the Phalaborwa material.

Para. 401(b) of the Transport Regulations refers to the activity concentration of exempt material as listed in Table I of those Regulations. The exemption level for natural uranium and thorium is 1 Bq/g. Igneous phosphate rock thus qualifies as exempt material. Nevertheless, a decision was made to conduct a detailed risk assessment to support the efforts of both the CRP and an industry risk assessment project of the Fertilizer Society of South Africa.

TABLE I. RADIONUCLIDE ACTIVITY CONCENTRATIONS IN PHOSPHATE ROCK

Radionuclide	Activity concentration (Bq/g)
^{238}U	0.14
^{226}Ra	0.14
^{210}Pb	0.12
^{232}Th	0.47
^{228}Ra	0.55
^{228}Th / ^{224}Ra	0.55

4. METHODOLOGY

This risk assessment is based on actual measurements where possible and only refers to modelling or calculated values where no actual measurements are available.

As stated in the Section 2, parameters from the zircon sand study such as distance of dwellings from the tracks and speed of the trains were used where possible to allow direct comparison between the results [3].

4.1. Scenario description

A mine in Phalaborwa is the primary supplier of phosphate rock used by the South African phosphate and fertilizer industry. The material is also exported through the port of Richards Bay, some 1000 km away.

The beneficiated rock is loaded on site and transported via rail to customers or the export harbour. Product ready for dispatch is stored in silos and from the silos loaded directly on to a rail car. Each car is covered with a tarpaulin before leaving the site. During unloading, the car is tipped over at the discharge facility, dropping the material onto a conveyor system from where it is moved to its destination. (Extraction hoses are also sometimes used.)

As a result of this process, workers and members of the public may incur a dose from the work activity during normal and possibly abnormal conditions. The basic rail transport from Phalaborwa to Richards Bay via a 1000 km railway line is thus the main focus of this assessment.

4.2. Occupational exposure

Five groups of occupationally exposed workers were identified in the assessment process for the transport portion between Phalaborwa and the harbour operations in Richards Bay. They comprise the loader, the shunter/train driver and the tarpaulin worker during loading, and the front-end loader and the discharge facility operator during the unloading process. For each of these groups, the workers were subject to full shift monitoring of inhalation and external gamma exposure. Ingestion exposure was determined by modelling.

4.3. Public exposure

The public exposure scenarios considered were the same as those considered in the previous zircon study [3]. These scenarios and the relevant exposure pathways are specified in Table II.

TABLE II. PUBLIC EXPOSURE SCENARIOS AND METHODS OF ASSESSMENT

Scenario	Method of assessment	
	External gamma	Inhalation
1. Car occupant at rail crossing	Direct measurement from stop at rail crossing as train passes	Not applicable
2. Occupant of home situated next to railway line[1]	Calculate from exposure to driver of vehicle at rail crossing	External measurement from ambient monitors on completion of dedicated discharge facility
3. Fisherman sitting against silo.	Contact dose rate measurement on exterior of silo	Not applicable

A typical train of phosphate rock is approximately 840 m long. The primary route for this material in South Africa is the one between Phalaborwa and Richards Bay and approximately 700 shipments per year travel on this route. Therefore, it was assumed that a member of the public living next to the line was exposed 700 times per year, while it was assumed to be highly unlikely that a member of the public would encounter a phosphate rock train at a crossing more than once per year. However, as in the zircon transport risk assessment, a further variation was assumed, whereby a mother takes her child to school and waits at a rail crossing at least once per day during the school year, i.e. 250 d/a.

4.4. Radionuclides considered

The following radionuclides were considered in the assessment, as they contribute almost all of the inhalation and ingested doses:

^{238}U series:	^{238}U; ^{234}U; ^{230}Th; ^{226}Ra; ^{210}Pb; ^{210}Po
^{235}U series[2]:	^{235}U; ^{231}Pa; ^{227}Ac; ^{227}Th; ^{223}Ra
^{232}Th series:	^{232}Th; ^{228}Ra; ^{228}Th; ^{224}Ra; ^{212}Bi

4.5. Background radiation

Background radiation plays a significant role in the assessment of the loading of the material as the loading site is partially situated on the igneous orebody. In addition, the loading area is surrounded by sources other than normal background. A decision was therefore made to measure the background gamma dose rate inside the Safety, Health, Environment and Quality buildings at the facility in Phalaborwa as this location is less than 100 m from the loading area, thus having similar background but with negligible contribution from the process. The background values are conservative as the shielding effect of the floors is ignored.

The background for the public dose calculations was measured in the nearby town and away from the main background source, the igneous ore body. This allowed for some conservatism when doing the public exposure assessment.

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[1] This scenario has several variations as the train travels through rural, suburban and urban areas. The most restrictive scenario was considered in the initial assessment.

[2] The South African National Nuclear Regulator does not require the inclusion of ^{235}U and daughter isotopes in the assessment process [4]. They are included in this document to ensure comprehensiveness.

4.6. Incidents

Phosphate rock is only transported by rail in South Africa and thus incidents can be divided into just two broad categories: a spillage (the worst being a derailment) and a fire involving the rail cars carrying the rock phosphate. There are thus two worker categories: a fireman and the worker responsible for the site remediation after a derailment. The pathways of interest are external exposure, inhalation and ingestion for both categories. However, there are differences in the values of parameters such as inhalation rate, concentration of respirable dust and exposure period.

An incident assessment for igneous and sedimentary phosphate rock, phosphoric acid and phosphogypsum was conducted and submitted as a dissertation to the University of the Witwatersrand, South Africa [5] and the findings of this document are reported here. (The document is under review and should be available later in 2004).

5. RESULTS

5.1. Normal operating conditions

5.1.1. Occupational exposure

(a) Dose coefficients

The inhalation and ingestion dose coefficients used in the assessment, calculated from the average radionuclide compositions reported in Section 3.2, were 1.23×10^{-5} and 2.68×10^{-7} Sv/Bq_{α} respectively.

(b) Background radiation

The mean background gamma dose, measured using electronic dosimeters over one full shift inside buildings within 100 m of the loading areas, was 2.0 μSv. The standard deviation was 0.05 μSv.

(c) Total dose

Three sets of measurements associated with the unloading/movement of the rail cars were taken, while one set of measurements was taken for workers associated with the discharge facility. The samples were collected during January and February 2002 at intervals of 1 week. Phalaborwa is a much drier area than Richards Bay, thus representing a very conservative approach when using the results to assess similar actions in Richards Bay.

A summary of the occupational exposure assessment results is given in Table III. For comparison, an assessment that formed part of Foskor's occupational risk assessment, conducted in 1995, gave an average annual effective dose of 360 μSv [6, 7].

5.1.2. Public exposure

Public exposure arises primarily from external gamma irradiation as the tarpaulin cover prevents resuspension of the material during transport, making it unavailable for inhalation. Direct measurements were carried out at a rail crossing with a train passing, but the natural background in that area was too high for a meaningful correction. (The loading area is on top of the orebody.)

TABLE III. DOSES RECEIVED BY WORKERS

Type of worker	Effective dose (μSv)			
	Inhalation, per shift	External, per shift	Ingestion, per year	Total, per year
Loader	0	0.01	47.0	49.5
	1.293	0.15	47.0	407.7
	0	0.40	47.0	147.9
				Average 201.4
Shunter	0	0	47.0	47.0
	0	0	47.0	47.0
	1.293	0.10	47.0	395.2
				Average 163.0
Tarpaulin worker	0	0.20	47.0	97.0
	0	0	47.0	47.0
	1.293	0	47.0	370.2
				Average 171.4
Front-end loader driver	0	0	47.0	47.0
Tip operator	0	0	47.0	47.0

(a) Background radiation

Background radiation was measured in a town 11 km from the facility, thus ensuring a conservative dose estimate. The dose rate measurements were integrated values, each obtained over a period of 60 s. In each instance the detector was held at a level approximately equal to that of a person sitting in a car. The mean background dose rate was 0.218 μSv/h, with a standard deviation of 0.07 μSv/h.

(b) At a rail crossing

The speed of the train, and corresponding dose, was difficult to determine, as it tends to be stop–start. A range of doses for various speeds was calculated and the results, taking cognizance of the above, are given in Table IV.

(c) House near a railway line

The results are shown in Table V.

(d) Person sitting against a silo

Seven dose rate measurements were taken on a filled silo in Phalaborwa. Silos are typically constructed from concrete. The measurements were taken on contact at various heights with the majority of the measurements taken on top of the silo where the concrete is least thick. Each measurement was integrated over a period of 1 min. The average value was 0.20 μSv/h. Since the background is 0.22 ± 0.07 μSv/h, it was concluded that public exposure from a silo is negligible.

(e) Discharge facility operations

Public exposure was calculated using generic models given as guidance by the IAEA [8]. However, these values have not been confirmed by actual measurement and the methodology is not included in this report. A summary of the calculated values is presented in the Table VI. For future assessments, attention would need to be given to the identification of a monitoring location to represent the critical group, the discharge rate (in Bq/s) of the source, and the assessment of incidents.

TABLE IV. DOSE RECEIVED BY A MEMBER OF THE PUBLIC AT A RAIL CROSSING

Train speed (km/h)	Annual effective dose (μSv)
1	0.11
5	0.02
10	0.01
20	0.006
50	0.002

TABLE V. DOSE RECEIVED BY A MEMBER OF THE PUBLIC LIVING IN A HOUSE CLOSE TO THE RAILWAY LINE

Train speed (km/h)	Annual effective dose (μSv)
1	77.6
5	15.5
10	7.8
20	3.9
50	1.6

TABLE VI. SUMMARY OF ESTIMATED ANNUAL DOSES RECEIVED BY MEMBERS OF THE PUBLIC FROM THE DISCHARGE FACILITY OPERATIONS

Age group (a)	Annual effective dose (μSv/a)
0–2	0.695
2–7	0.749
7–12	0.888
12–17	1.02
Adult	1.03

5.2. Incidents

Dose assessments of incidents involving phosphate-bearing material were calculated as part of a Masters dissertation project entitled *A Radiological Assessment of some Sectors of the Phosphate Industry* [5]. A summary of the occupational dose for a worker responsible for site remediation after a spillage or to a fireman during an emergency situation that involved phosphate-bearing material is given in Table VII.

TABLE VII. OCCUPATIONAL EXPOSURE DURING INCIDENTS

Description	Effective dose (μSv)			
	External gamma	Inhalation	Secondary ingestion	Total
Worker during site remediation without respiratory protection	0.72	1.80	0.17	2.69
Worker during site remediation with respiratory protection	0.72	0.36	0.17	1.25
Fireman during fire with respiratory protection	0.09	1.69	0.02	1.80

6. DISCUSSION

The Transport Regulations set safety standards to ensure acceptable and appropriate controls to restrict the risks associated with the transport of radioactive materials [1]. The regulations apply to radioactive materials, with provision for exclusion of certain materials, e.g. natural materials and ores. Para. 107 of the Transport Regulations states that the Regulations do not apply to:

"… natural material and ores containing naturally occurring radionuclides which are not intended to be processed for use of those radionuclides provided the activity concentration of the material does not exceed 10 times the values specified in paras 401–406"

6.1. Occupational exposure

This assessment focused on the loading, unloading and intermediate rail transport of igneous phosphate rock from the Phalaborwa Complex in South Africa. Marine and river transportation were not included. Phosphate rock is only transported in bulk; therefore, road and air transport are not applicable. Five categories of occupational exposure were identified. They are the loader, shunter/driver, tarpaulin worker, front-end loader operator, and the discharge facility operator.

The maximum occupational dose is in the range 47–360 μSv/a, and the workplaces are therefore non-classified.

6.2. Public exposure

Exposure of members of the public during transport was limited to external gamma dose in this assessment, although the loading and unloading may introduce an inhalation component.

The direct measurement of gamma dose rates in a sufficiently low background area was problematic and an off-site measurement was used for background correction. This introduced additional conservatism as the incremental gamma dose measured from a passing rail car includes the higher, on-site background. (It should be remembered that the Phalaborwa facility is built on top of the orebody.)

The distance from the source was approximately 5 m and, although representative of a person waiting at a rail crossing, is very conservative for a housing scenario. Houses are usually at a distance more than 10 m from the track and the walls allow for some shielding from the direct gamma photons. Nevertheless, in the South African environment some illegal and informal settlement may occur close to the line and such occupancy thus corresponds with a person waiting at a rail crossing.

The annual effective dose is less than 80 μSv/a for the most exposed individual, i.e. a person living in a house ~5 m from the line where a full ore train travelling at 1 km/h passes twice per day. The results reported are thus very conservative and indications are that direct gamma measurements will not be statistically detectable above normal background.

6.3. Inadvertent events

The effects of inadvertent events were modelled as part of a dissertation. The occupational dose for a person responsible for site remediation or an emergency worker during an event was found to be less than 10 μSv/a and outside the scope of regulatory control.

6.4. Hypothetical group: discharge

A hypothetical critical group was identified i.e. members of the public occupying a dwelling close to a discharge facility. The dose to the critical group, even using a pessimistic model, is less than 10 μSv/a and will probably be excluded from regulatory control. However, it must be noted that the assumptions used in this assessment were based on the area characteristics of the coastal environment of Richards Bay, South Africa and the modelled values have not been confirmed through actual monitoring. Characteristics of other facilities, for example inland facilities, may differ so significantly that a site-specific monitoring programme to accurately quantify the dose would be required.

7. CONCLUSIONS

The Transport Regulations do not apply to igneous phosphate rock, but other factors influenced the decision to proceed with the risk assessment. Occupational exposure for the most exposed individual does not exceed 360 μSv/a for normal operational conditions and is less than 10 μSv per inadvertent event. Public exposures are indistinguishable from or barely above background.

8. RECOMMENDATIONS

The transport assessment of igneous phosphate rock should be completed by including transport by sea (including loading and unloading) and public exposure from airborne contaminants released by discharge facility operations. Items requiring attention in future assessments of releases from discharge facility operations are the identification of a monitoring point to represent the critical group, the verification of the modelling results through measurement, and the discharge rate (in Bq/s) of the source. Comparison between barge and ocean transport should be made to determine if the study should be expanded to include the barge scenario. The full assessment should be repeated for the transport of sedimentary phosphate rock, as well as phosphogypsum, phosphoric acid and fertilizers of both igneous and sedimentary origin.

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INVESTIGATION OF ABANDONED SURFACE SETTLING PONDS

M. Wysocka*, **S. Chałupnik, A. Mielnikow**

Laboratory of Radiometry, Central Mining Institute, Katowice, Poland

Abstract

One of the problems that may appear during the ground reclamation of surface settling ponds of underground mines is enhanced radon exhalation from bottom sediments. This problem becomes more important when the concentration of radium isotopes in sediments is enhanced due to the discharge of radium-bearing waters into the pond. For investigations, special radon accumulation chambers have been designed and constructed. The concentration of radon in these chambers can be measured with the application of Lucas cells or activated charcoal detectors. In the latter method, radon is extracted from charcoal into a liquid scintillator and the sample is measured in a liquid scintillation spectrometer. Therefore the lower limit of detection (LLD) of the second method is as low as 0.1 $mBq \cdot m^{-2}s^{-1}$, while the LLD for Lucas cells is 1.5 $mBq \cdot m^{-2}s^{-1}$. The above-mentioned methods for the measurement of radon exhalation have been applied to investigations of a surface settling pond of one Polish coal mine, abandoned and emptied at the beginning of 2002. An agreement between the mine management and the local authority was to make the ground reclamation of the pond. A thick layer of sediments with an enhanced concentration of radium isotopes covers the bottom of the pond. The maximum concentration of radium isotopes in these sediments is as high as 2000 Bq/kg for ^{226}Ra and up to 4000 Bq/kg for ^{228}Ra. Two years after the complete release of brines from the pond, bottom sediments are still soaked with water. Therefore, measurements of radon in soil gas were not possible. On the other hand, in some parts of the pond investigations of radon exhalation coefficient were done. The preliminary results of measurements, conducted in 2002, showed that radon exhalation rates in specific parts of the pond were higher than the highest values of radon exhalation from the ground in the Upper Silesia region. Values of exhalation coefficient up to 200 $mBq \cdot m^{-2}s^{-1}$ were found. It must be pointed out that preliminary measurements were done in a period when the water had been only partly removed from the pond, and further dry-up of sediments should lead to an increase in radon exhalation. Data from 2003 confirm this assumption. During this period the water content in the bottom sediments was significantly lower than previously, and results of measurements of radon exhalation were sometimes above 300 $mBq \cdot m^{-2}s^{-1}$. Vegetation transgression into the pond occurred during 2003, mainly weeds. Samples of vegetation were collected from this area to measure the content of radium isotopes and to calculate the transfer factors for radium isotopes. Very high concentrations of radium isotopes were found at several sites. Another reason for the pollution might be the leaching of radium from sediments and contamination of groundwater. Therefore the above-mentioned sources of radiation hazard must be taken into account for planning and designing of reclamation operations for surface settling ponds of underground mines.

1. INTRODUCTION

One of the problems that may appear during ground reclamation of surface settling ponds of underground mines is enhanced radon exhalation from bottom sediments. This

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* E-mail: m.wzysocka@gig.katowice.pl

problem becomes more important when the concentrations of radium isotopes in sediments are enhanced due to the discharge of radium-bearing waters into the pond.

Measurements of radon exhalation were made at different surface settling ponds. One of them was abandoned and emptied at the beginning of 2002. An agreement between the mine management and the local authority was to make the ground reclamation of the pond. Because of elevated radium concentrations in the thick layer of sediments, measurements of different elements of radiological hazard were made, such as radon exhalation coefficient, variations of gamma background radiation and radium content in bottom sediments. Additionally radium transfer to vegetation that had transgressed into the pond has been calculated.

The results obtained showed that the above-mentioned sources of radiation hazard must be taken into account for planning and designing of reclamation operations for surface settling ponds of underground mines.

2. APPLIED INVESTIGATION METHODS AND CHARACTERIZATION OF THE TEST SITES

The principal factor, as measured to identify the state of radiological contamination in the abandoned settling ponds areas, is the radon exhalation coefficient. Radon exhalation coefficient is the quantity that defines its ability to escape from the intergranular porosity of rocks and soils and to transfer into the atmospheric air. Calculating the radon exhalation coefficient requires laboratory determination of various soil parameters. Field measurements avoid time-consuming and complicated laboratory measurements and provide a good basis for the radon potential of the study area.

The measurements were made using the field method of measuring the radon exhalation coefficient developed at the Central Mining Institute [1]. At the test sites, measurements of the variations of the natural gamma radiation background and the spectrometric analyses of the settling pond bottom sediment samples were made. In one of the ponds under study, where natural plant ingress had taken place, measurements of the radium isotope content of plant samples were taken.

3. DISCUSSION OF MEASUREMENT RESULTS

3.1. Measurements in areas not disturbed by mining operations

To determine the range of radon exhalation coefficients for the area of Upper Silesia, measurements were made at the sites not influenced by mining activity. It was found that radon exhalation depends on the geological structure of the subsurface layer. The majority of the measured values ranged from 2 to 50 $mBq \cdot m^{-2}s^{-1}$, and are considered to be average values in normal conditions [2]. The highest values were obtained from the outcrops of Triassic carbonate rocks. At those sites the radon exhalation exhibited the widest range of values, from 1 to 80 $mBq \cdot m^{-2}s^{-1}$ [1]. The values of radon exhalation coefficient over the outcrop areas of different lithostratigraphic units are summarized in Table I [3].

3.2. Measurements in surface settling ponds

The measurements were made in three surface settling ponds during closure operations. Previously, mine underground waters of different chemical compositions and different natural radionuclide concentrations had been discharged into the above-mentioned ponds.

TABLE I. RADON EXHALATION COEFFICIENTS AND RADON CONCENTRATIONS IN SOIL AT OUTCROPS OF DIFFERENT GEOLOGICAL FORMATIONS

Site of measurements / stratigraphy	^{226}Ra concentration in sediments (Bq/kg)	Radon concentration in soil gas (Bq/m^3)	Radon exhalation coefficient (mBq·m^{-2}s^{-1})	
			Range	Arithmetic mean
Triassic rock outcrops	11–51	120–66 750	1.6–80	15
Carboniferous rock outcrops	11–65	15 370–27 870	6.4–27	16
Miocene	11–43	170–7500	1.6–2.5	2
Quaternary	15–29	120–58 000	1.6–7	3.5

3.2.1. Settling pond A

Measurements in settling pond A were taken while it was being filled with waste rock. A spectrometric analysis of the bottom sediments showed that the maximum ^{226}Ra concentration was around 3000 Bq/kg. Measurements of the radon exhalation coefficient were taken both in the part of the pond where the bottom sediments had just been covered by a waste rock layer more than 10 m thick and in the part of pond where the dried bottom sediments had not been covered by any isolating layer. The radon exhalation coefficient measured over the dried bottom sediment was about 12 mBq·m^{-2}s^{-1}. This value appears to be within the range of average values [4] and within the range of values obtained from measurements taken at outcrops of carboniferous rocks within Upper Silesia [3]. The radon exhalation coefficients in the covered part of the pond were low and did not exceed 2 mBq·m^{-2}s^{-1}, compared with 3.4 mBq·m^{-2}s^{-1} measured at an old waste rock dumping ground nearby. The insignificant increase in exhalation coefficient for the waste rock from the heap compared with that of the piled-up broken waste rock material freshly drawn out from the mine can be regarded as being due to the increased sealing of the heap which reduces the radon gas seepage into the air. Thus, drying and subsequent covering of the bottom sediments by waste rocks from the adjoining heap can be a satisfactory protection measure against radon gas emission.

In the vicinity of the pond, the disturbances of the natural gamma radiation background were measured. The ambient dose equivalent rate was calculated from kerma measurements. The gamma dose rates ranged from 0.1 to 0.2 μSv/h and appeared to be higher than the corresponding average values for the area of Upper Silesia (see Fig. 3 later in this paper).

3.2.2. Settling pond B

The waters with enhanced natural radioactivity from two hard coal mines had previously been discharged into settling pond B. In this case, the possible radiological hazard caused by the enhanced exhalation of radon appeared to be more serious then in the case of pond A. That is because the settling pond area is about 16 ha and the thickness of the accumulated sediments is 1 m. The total radium radioactivity in the discharged waters was up to 120 MBq/d. Taking the statements mentioned above into the consideration, the measurements were made regularly in the settling pond area during the spring–autumn period in 2002 and 2003. The results of the spectrometric analysis showed that in the bottom sediments the maximum ^{226}Ra and ^{228}Ra concentrations were 2000 and 4000 Bq/kg respectively. In spite of nearly one year of drying of the sediments, the high ground water level made it impossible to measure the concentration of radon in the soil. In the case of wet soils, the measurements of radon exhalation coefficient have proven to be a useful tool that allows the increased radon emission to be assessed.

The measurements of radon exhalation were made under different weather conditions in 2002–2003. The first measurements were taken in July 2002 following a period of several weeks of dry weather. Certain parts of the pond were so dry that it was possible to enter them and install diffusion chambers (Fig.1(a)). The radon exhalation coefficient ranged from around 2 $mBq \cdot m^{-2}s^{-1}$ to more than 70 $mBq \cdot m^{-2}s^{-1}$. Measurements made subsequently after a week of sunny, rainless weather showed a significant increase of radon exhalation, up to more than 160 $mBq \cdot m^{-2}s^{-1}$. The measurements were repeated approximately every two weeks up to the end of October 2002. The dried area of the pond's bottom grew larger allowing us to increase the number of recording sites. The highest value of radon exhalation coefficient obtained in the first year of investigations was 202 $mBq \cdot m^{-2}s^{-1}$, being considerably above that recorded within the area of Upper Silesia [5]. It is important to note that throughout the first year of investigation, the sediments in settling pond B were wet and radon emission took place only from a subsurface layer of thickness 0.1–0.2 m.

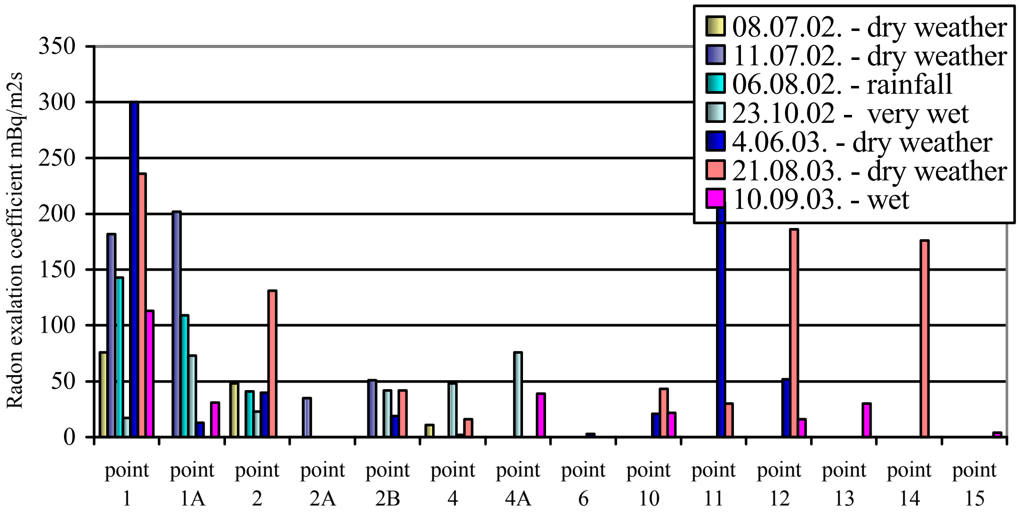
(a) First year of measurement (b) Second year of measurement

FIG. 1. Measurement of radon exhalation coefficient at the bottom of an abandoned mine water settling pond.

In the second year of measurement, the bottom of the settling pond was dry enough to allow an investigation over most of the pond area. The water level was much lower and the radon gas emanation was expected to come from a layer considerably thicker than in the previous year. The results of measurements made in June, following a longer dry period, indicated that radon gas emission measured at the most intensely dried sites of the settling pond exceeded the previous year's emission.

At recording point no. 1, the radon exhalation coefficient was around 300 $mBq \cdot m^{-2}s^{-1}$. At the sites where no measurements had been made before, high values were obtained — for instance, more than 200 $mBq \cdot m^{-2}s^{-1}$ at point no. 12 and about 50 $mBq \cdot m^{-2}s^{-1}$ at point no. 13 (Fig. 2). Subsequent measurements showed that high radon exhalation coefficients (about 100 $mBq \cdot m^{-2}s^{-1}$) persisted even after rainfall periods, exceeding the values recorded within the Upper Silesia Coal Basin area. The values of the radon exhalation coefficient measured in the vicinity of the settling pond did not exceed 3 $mBq \cdot m^{-2}s^{-1}$. Radon exhalation of the intensity found in the abandoned settling pond B has not been found at any other test site.

In order to obtain more information on radiation hazards, variations of natural gamma radiation background were measured at pond B. Values of ambient dose equivalent rate were calculated from kerma measurements. The results are shown in Fig. 3. The calculated values exceeded by many times the average value for either Upper Silesia or the whole area of Poland [6] and ranged from 0.6 to 2.6 μSv/h.



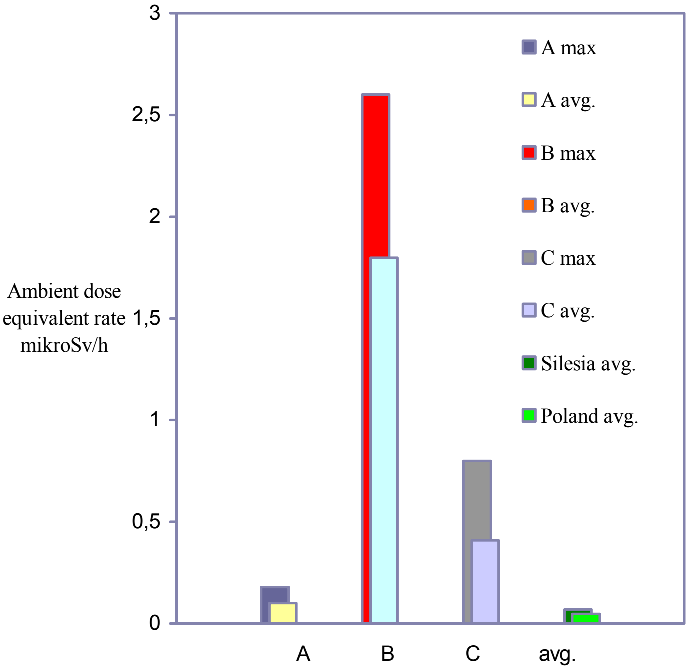


FIG. 2. Radon exhalation coefficients in settling pond B.

FIG. 3. Variations in natural background gamma radiation in areas of abandoned settling ponds.

In order to investigate the influence of the settling pond B on the ecosystem, samples of vegetation that began to overgrow the dried bottom sediments were collected. The vegetation transgression commenced in spring 2003, starting from the dried places where the salt water from the subsurface layer was either washed out or diluted by precipitation (Fig.1(b)). Samples of pigweed and reed growing on the bottom sediments at some distance from the pond bank were collected. The concentrations of ^{226}Ra and ^{228}Ra in the plants were determined and compared with data from publications (Table II). Although each cited group of results refers to a different kind of vegetation, it does give a general picture of the naturally encountered concentration ranges. According to our archive data, the radium concentrations in grass samples collected in the vicinity of settling pond B do not exceed 5 Bq/kg. However, plant samples currently collected from the bottom sediments show concentrations reaching 138 and 237 Bq/kg (dry mass) for ^{226}Ra and ^{228}Ra respectively. Far higher radium concentrations were found in grass samples collected in areas contaminated with sediments of higher radioactivity near Rybnik-Boguszowice in the 1980s [7]. The average radium content was 142 Bq/kg, with the maximum value exceeding 900 Bq/kg. According to a previous study of radium transfer from soil to plants [8], the ^{226}Ra concentrations in various plants raised in experimental plots did not exceed 3 Bq/kg. The radium ^{226}Ra concentrations used in the soil for that experiment were much lower than in the Bojszowy settling pond and did not exceed 12 Bq/kg.

TABLE II. RADIUM CONCENTRATIONS IN PLANT SAMPLES COLLECTED FROM SETTLING POND B AND CORRESPONDING DATA PRESENTED IN THE LITERATURE

Sampling site	Activity concentration (Bq/kg dry mass)		Transfer factor *TF1*	
	^{226}Ra	^{228}Ra	^{226}Ra	^{228}Ra
Settling pond B:				
1 m from bank near water inlet 1	138 ± 11	237 ± 47	0.069	0.059
2 m from bank near water inlet 2	66.3 ± 5.3	84 ± 16	0.033	0.021
Neighbourhood of settling pond	Min. 1.7 ± 0.2 Max. 4.8 ± 1.4 Mean 3.3	Min. 1.3 ± 1 Max. 4.8 ± 1.4 Mean 2.2	—	—
Rybnik-Boguszowice	Min. 6 ± 4 Max. 973 ± 97 Mean 325	Min. 3 ± 2 Max. 168 ± 33 Mean 49	—	—
Ref. [8]	Min. 0.03 ± 0.01 Max. 2.96 ± 0.11 Mean 0.75	No data	0.0054–0.51	No data
Ref. [9]	0.001 – 11	No data	-	-

The total radium transfer factors *TF1* calculated for the settling pond B plant growth are contained within the ranges given in Ref. [8] (Table II). Thus the preliminary results of the analyses of mine waste impacts on plant radiological contamination suggest a problem of some importance, which the mines and local communities will have to deal with in the future. According to research dealing with the problem of radium transfer from soil to plants, the ^{226}Ra content of plants under normal conditions is 0.001–11 Bq/kg [9]. In the light of the reported data, the measured radium content of the plants growing at the abandoned settling pond bottom exceeds by many times the radium content regarded as being the average encountered in the natural environment.

3.2.3. Settling pond C

To compare situations arising at various stages of abandonment of settling ponds, measurements were made in settling pond C. The pond was evacuated in the 1980s, the sediments were moved to an old sand pit, and water was again discharged into the repaired settling pond. The sediments from the dredging operation, showing ^{226}Ra concentrations exceeding 100 000 Bq/kg, were covered with waste rock forming, in the course of time, a heap of waste about 20 m high. Radon exhalation was measured on the waste rock pile covering the sediments and on the active settling pond bank. On the settling pond bank, the radon exhalation coefficient reached about 20 $mBq \cdot m^{-2}s^{-1}$, while on the waste rock pile it did not exceed 2 $mBq \cdot m^{-2}s^{-1}$. The perturbation of the natural background gamma radiation near the settling pond was also measured. As in the case of radon exhalation, the ambient dose equivalent rates were higher at the pond bank and lower on the waste rock pile. The values, shown in Fig. 3, were lower than those typical for settling pond B, but could still exceed the average values for Upper Silesia by many times. The sediments covered by waste rock pose no radiation hazard to the natural environment at present. However, it is important to note that if these sediments are exposed, for instance as a result of stripping of the waste rock pile to recover rock material for use in highway engineering, the radon emission will be intensified, the natural gamma radiation background will be perturbed and radium will even transfer to plants.

4. SUMMARY

Measurements of the radon exhalation coefficient and of the radium content of bottom sediments for the three settling ponds are compared in Fig. 4. The highest radon exhalation coefficients were found at the bottom of settling pond B. In the other two ponds, the radon exhalation coefficients were lower. No correlation was found between the radon exhalation coefficient and the radium (parent radionuclide) content of the bottom sediments. In settling pond B, which showed the highest value of radon emission, the radium concentration in the bottom sediments was comparable to that measured in settling pond A, where the lowest radon exhalation coefficient was found. In contrast, in the area of highly radium-rich sediment accumulation (the wastes from settling pond C), low values of radon emission were measured.

The examples of different mine water settling ponds described above show that in each case there is a different scheme of radon escaping to the atmosphere. The mere findings of high radium concentrations in bottom sediments are not grounds for assuming that the radon exhalation from these places can be high as well. On the contrary, in places where natural radioactivity of bottom sediments is far below the extreme, radon emission may be intensified. Settling pond B is an example of such a place. The ability of radon to migrate from ground and soil intergranular porosity depends on many factors associated with the physical characteristics of the material. Therefore, the radon exhalation coefficient can reach very high values even if the values of radium concentrations in the bottom sediments being investigated exhibit relatively low values.

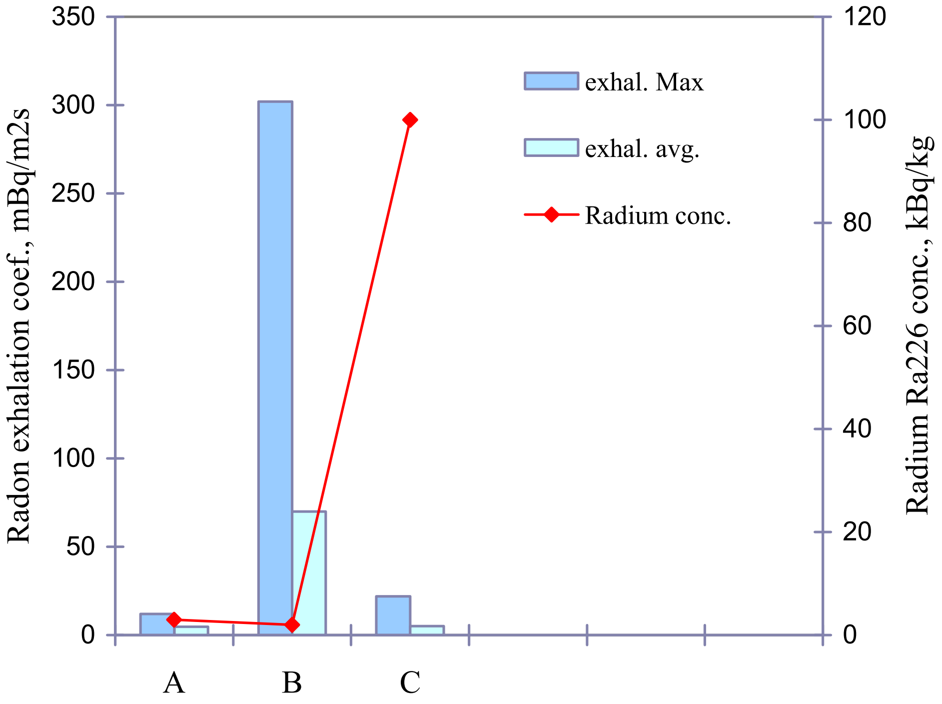


FIG. 4. Comparison of radon exhalation coefficient and radium content of bottom sediments from the abandoned mine water settling ponds.

5. CONCLUSIONS

Measurements carried out at abandoned mine water settling ponds show that measures undertaken in connection with mine closure operations may have a severe impact on the surrounding environment, as evidenced, among other things, by the following:

(i) Intensified radon emission, posing a potential radiation hazard for the residents and tenants of buildings constructed in the reclaimed settling pond areas;

(ii) Variations in natural background gamma radiation;

(iii) Contamination of plants resulting from radium transfer from sediments with elevated radium contents.

In the cases described above, the radiation hazards induced by high radon exhalation, elevated gamma radiation rates and high radium content in sediments can be confined to limited areas, situated at considerable distances from buildings. It is generally known that in Polish mines systematic measurements of all the radiological hazard-related elements have been carried out since 1986. Therefore a possibility of the formation of radiological contamination ‘hot spots’ resulting from the past uncontrolled surface disposal of bottom sediments from mine workings, as for example the sediments from pumping stations and water galleries, cannot be ruled out. Possibly, detailed future measurements carried out within both the active and closed mine areas, would show radiation hazard areas comparable to those described above.

The assessment of radon emission level from the bottom sediments is the essential information pointing to the way the post settling pond areas can be reclaimed. In the case of increased radon exhalation, the sealing of sediments should be planned so as to avoid migration and penetration of radon into future buildings that might be built in the areas of settling ponds.

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THEORETICAL STUDY OF RADIUM BEHAVIOUR IN AQUIFERS

S. Chałupnik[*]

Laboratory of Radiometry, Central Mining Institute,
Poland

Abstract

In this paper, a theoretical approach to the problem of radium in mineralized mine water is presented. Two main types of radium-bearing water have been found in Polish coal mines. In type A water, radium isotopes are present together with barium, while concentrations of sulphate ions are very low. Additionally, in these waters the ratio of ^{226}Ra to ^{228}Ra activity is usually greater than 1. In type B waters, no barium can be found, but radium is present together with sulphate ions. In such water the isotopic ratio of ^{226}Ra to ^{228}Ra is less than 1, and the activity concentrations of both isotopes of radium are lower than in type A water. No other differences in the chemical composition of mine water have been observed. Analysis shows that the activity ratio of radium isotopes is related to the dynamics of radium adsorption on the grains of the solid phase in the aquifer. During analysis, it must be taken into account that the build-up of radium in formation water due to the recoil effect is stable in time. Additionally, no correlation with elevated concentrations of uranium and thorium in rocks has been observed. Therefore the enhanced radium content in formation water must be caused by its mineralization. The relatively short half-life of ^{228}Ra (6 years) shows that the process of radium transfer from the solid to liquid phase is a short term process on a geological scale. Therefore the radium content in the mine water must be related to the concentration of natural radionuclides in the near vicinity of the aquifer or the water reservoir.

1. INTRODUCTION

Enhanced levels of gamma radiation were discovered in Polish coal mines during the early 1960s [1], and were concluded as having resulted from uranium mineralization. More detailed investigations were later initiated [2], and subsequently undertaken on a regular basis by the Laboratory of Radiometry in the Central Mining Institute, Katowice, Poland. Investigations were focused on the enhanced concentrations of radium isotopes in brines and in precipitates from radium-bearing waters. The results of the investigations showed that scales of barium and radium sulphates had been wrongly identified as being due to uranium mineralization in Ref. [1]. No elevated concentrations of uranium or thorium have been found in coal seams, in carboniferous host rocks [3, 4] or in brines [5].

Other scientists have described similar phenomena in underground non-uranium mines in other countries. For instance, enhanced radium concentrations in brines in the Ruhr Basin have been reported [6]. Other investigators, for instance in the UK [7] and Canada [8], have reported only the presence of barium in mine waters from coal mines. Reports of inflows of saline waters with elevated barium concentration have come from a diamond mine in Russia [9]. Based upon our experience as reported, for example, in Ref. [10], the presence of barium in mine water is likely to be correlated with enhanced radium concentration. High radium concentrations in formation waters from oil fields is widely reported by scientists from USA,

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[*] E-mail: s.chalupnik@gig.katowice.pl

Romania, Ukraine and Norway [11–14]. All these reports confirm the thesis that the phenomenon of radium presence in brines is rather common, especially in confined aquifers isolated from the influence of meteoric waters by impermeable layers like clays or other deposits with low porosity [2, 15] or even a thick permafrost layer.

In Polish coal mines, two types of radium-bearing brines have been distinguished. The first, called type A, contains radium and barium ions but no sulphates. Type B waters contain radium and sulphate ions but no barium. The presence of barium in brines is a very important factor controlling the behaviour of radium, because barium acts as a carrier. Therefore radium can be easily co-precipitated with barium from type A waters as scales of barium/radium sulphate. This chemical reaction leads to the formation of highly radioactive deposits in underground galleries and surface settling ponds and rivers. In type B brines, no carrier for radium exists and the main processes leading to a decrease in the concentration of radium isotopes are adsorption on bottom sediments in settling ponds and rivers, and dilution. The activity concentration in sediments in the vicinity of mines discharging B type waters into the environment is not very high but often clearly enhanced.

Typical chemical analyses of the two different radium-bearing brines are presented in Table I. The results show little difference in the dissolved solids fractions of the two brines. The major difference is the absence of sulphate ions in type A water and of barium in type B water. Another significant difference is in the isotopic ratio of radium. In type A waters, the ^{226}Ra concentration is higher than the ^{228}Ra content — typically the ratio is about 2. In type B water, the opposite can be seen — the ^{226}Ra to ^{228}Ra ratio can be as low as 1, and sometimes even 0.3.

The occurrence of radium-bearing waters in different coal mines in the Upper Silesian Coal Basin, the range of radium concentrations in brines and the influence on the natural environment have been investigated since the 1970s and are well recognized. On the other hand, the origins of and differences between the two types are still without adequate explanation.

2. RADIUM TRANSFER AND MIGRATION WITH WATER

The process of radium transfer from the solid phase into water occurs in three phases [16]:

- Transfer of radium from the crystalline lattice into capillaries or pores in the mineral or rock, caused by the alpha-recoil effect resulting from the decay of parent nuclei (^{230}Th for ^{226}Ra and ^{232}Th for ^{228}Ra);
- In the pores, an equilibrium between radium in solution and radium adsorbed onto the surface of the mineral phase is established — most of the radium seems to be adsorbed onto the surfaces;
- When mineral grains are in contact with flowing water, some of the radium may diffuse out of the pores and capillaries (if a concentration gradient exists), but simultaneously part of the radium can be desorbed from the surfaces to balance the concentration.

Aqueous radium migration studies have been carried out by numerous scientists, but mainly for groundwater aquifers [17–19]. One of the most important investigations is reported in Ref. [20], in which the adsorption/desorption ratio for radium was assessed and the retardation factors for radium migration in the ground were estimated.

TABLE I. TYPICAL CHEMICAL COMPOSITION OF BRINE TYPES A AND B

Parameter	Unit	Type A	Type B
Conductivity	µS/cm	151 000	91 000
pH		7.25	7.53
TDS at 378K	mg/L	124 300	85 300
^{226}Ra	**Bq/L**	**62.76**	**3.449**
^{228}Ra	**Bq/L**	**34.67**	**5.10**
Cations			
Ca^{2+}	mg/L	6500	1840
Mg^{2+}	mg/L	3750	1980
Na^{+}	mg/L	34 720	28 050
K^{+}	mg/L	299	268
Fe	mg/L	<0.05	<0.05
Mn^{2+}	mg/L	<0.05	<0.05
Ba^{2+}	mg/L	1480	—
Total	mg/L	46 740	32 140
Anions			
Cl^{-}	mg/L	77 350	50 830
SO_4^{2-}	mg/L	0.0	2140
CO_3^{2-}	mg/L	0.0	0.0
HCO_3^{-}	mg/L	24.4	67.1
SiO_4^{4-}	mg/L	2.00	3.45
Br^{-}	mg/L	241	155
J^{-}	mg/L	10.9	11.2
Total	mg/L	77 630	53 210

The simplified model of radium migration is based on the assumption of equilibrium between the concentration of radium in the liquid phase and that adsorbed onto the surfaces of the solid phase [21]. In this model the factor K_d describes the ratio of radium concentrations in solid and liquid phases according to:

$$K_d = \frac{C_S}{C_W} \qquad (1)$$

where: C_s is the concentration in the solid phase (Bq/kg);

C_w is the concentration in the water (Bq/L)

This factor can be used to assess the migration velocity of radium in the ground, which is defined in Ref. [22] as:

$$V_{\mathrm{Ra}} = \frac{V_{\mathrm{H_2O}}}{1+\rho K_{\mathrm{d}}/\theta} \tag{2}$$

where: V_{Ra} is the velocity of radium migration in the ground (m/a);

$V_{\mathrm{H_2O}}$ is the velocity of water movement in the aquifer (m/a);

ρ is the density of the solid phase;

θ is the moisture content of the ground.

The radium movement in the aquifer is retarded significantly in comparison with water movement, and the retardation depends strongly on the K_{d} value.

During one half-life of ^{226}Ra (1600 a) the transport distance can be estimated as a maximum of several metres only. The effect of retardation is more important for ^{228}Ra due to its relatively short half-life of 6 years. Within this period, radium might be transported only several centimetres. It seems to be a certain limitation for the possible volume of the solid phase, influencing the radium concentration in the formation water.

However, radium migration in aquifers is far more complex. Numerous data confirm that K_{d} values depend on the concentration of other ions in the liquid phase [23], and this renders the simple model of no use for the analysis of radium transport in brines.

Another method that can be considered is based on the idea of cation exchange capacity (CEC). Cations in an aquifer compete for adsorption on a limited and stable number of adsorption centres, given by the CEC. This problem is relatively simple if only two types of cations are present in the water. Otherwise, as in saline mine waters, several different cations can be found in the brine (see Table I). The analytical solution of such complex equations is very difficult, and only a numerical approach is possible [24]. The main limitation for this approach is that exchange factors are not stable, but depend on the total concentration of cations and the chemical composition of the dissolved solids.

The author would like to present a simple mathematical approach to the problem of adsorption and desorption of radium in aquifers. The results for the simulation of changes in the radium isotopic concentration in water are compared with the results of long-term monitoring of radium content in different brines. That problem is not necessarily specific to the Silesian Basin, because reports of similar brines in different underground mines (especially non-uranium mines) and also in deep aquifers are common.

One additional issue is very important. One of the most important ions in brines is barium, which has very similar geochemical properties to radium. It seems that a most important problem would be to explain the presence of barium in some brines and its absence in others. It is known that barium is relatively easily dissolved by some hydrothermal fluids. For instance, in such fluids within basalts in the Galapagos region, the ratio of ^{226}Ra to Ba was found to be similar to that in the host rocks [25]. Moreover, similar values for this ratio were discovered in other volcanic areas. Of course, the mechanism of radium transfer into the liquid phase may be different, but the idea is supported by elevated barium contents in some saline waters.

3. ION EXCHANGE KINETICS

Equations describing the balance of radium in aquifers are quoted below from Ref. [22]. Equation (3) represents the change in radium activity in the liquid phase and equation (4) on the surface of the solid phase.

$$N_{\mathrm{rec}} + k_2 N_{\mathrm{s}} = \lambda N_{\mathrm{w}} + k_1 N_{\mathrm{w}} \tag{3}$$

$$k_1 N_{\mathrm{w}} = \lambda N_{\mathrm{s}} + k_2 N_{\mathrm{s}} \tag{4}$$

where: N_{rec} is the production of radium due to the recoil effect;

k_1 is the adsorption coefficient;

k_2 is the desorption factor;

N_{w} is the radium concentration in the water;

N_{s} is the radium content in the solid phase.

The ratio of the radium atoms in the solution, N_{w}, to the transfer velocity into the water as a result of recoil, N_{rec}, can be described as:

$$\frac{N_{\mathrm{w}}}{N_{\mathrm{rec}}} = \frac{\lambda + k_2}{\lambda + k_1 + k_2} \tag{5}$$

Theoretically, the radium concentration in the water could be calculated taking measured or arbitrarily chosen adsorption and desorption coefficients into consideration — different values for types A and B brines. During in-situ measurements, the parameters k_1 and k_2 must be measured for each aquifer. Data for in-situ investigations of these parameters are scarce [26, 27]. Measured values of adsorption/desorption coefficients often were not reliable [28]. Therefore such an approach, based on the kinetics of ion exchange, may lead to wrong conclusions if the above-mentioned parameters are not known reliably.

It is proposed that a simplified, mathematical approach to this problem be used and the results compared with the actual results for Polish mines. One could consider this phenomenon as a product of the normal decay of radium in the liquid phase with additional exchange with solid surfaces (adsorption and desorption). A modified form of the Bateman equation for radium in the formation water [28] needs to be considered, because not all of the radium atoms are transferred into the water from the solid phase. The number of radium atoms recoiling into the liquid phase can be calculated as:

$$N_{\mathrm{rec}} = N\lambda\varepsilon = A\varepsilon \tag{6}$$

where: N is the number of parent isotope atoms in the volume unit;

λ is the decay constant of the parent isotope (^{230}Th);

ε is the recoil efficiency.

Consider first the case of simple decay with possible adsorption, while desorption is omitted [29]. On such an assumption, the equation describing changes in the radium content in the liquid phase is as follows:

$$\frac{\mathrm{d}N_{\mathrm{Ra}}}{\mathrm{d}t} = N_{\mathrm{rec}} - \lambda N_{\mathrm{Ra}} - k_1 N_{\mathrm{Ra}} \tag{7}$$

When desorption is also taken into account along with another assumption — that the number of atoms in the liquid phase is similar to the number adsorbed on solid surfaces — the final formula is different:

$$\frac{\mathrm{d}N_{\mathrm{Ra}}}{\mathrm{d}t} = N_{\mathrm{rec}} - \lambda N_{\mathrm{Ra}} - k_1 N_{\mathrm{Ra}} + k_2 N_{\mathrm{Ra}} \tag{7a}$$

where: λN_{Ra} is the radioactive decay of radium in the solution (λ being the decay constant of radium and N_{Ra} being the number of radium atoms in the liquid phase);

$k_1 N_{\mathrm{Ra}}$ is the adsorption on the solid phase (k_1 being the adsorption coefficient);

$k_2 N_{\mathrm{Ra}}$ is the desorption into the liquid phase (k_2 being the desorption coefficient).

The solution to equation (7a) is:

$$N_{\mathrm{Ra}}(t) = \frac{N_{\mathrm{rec}}}{\lambda + k_1}\left[1 - e^{-(\lambda + k_1)t}\right] \tag{8}$$

λ or, for the case with desorption:

$$N_{\mathrm{Ra}}(t) = \frac{N_{\mathrm{rec}}}{\lambda + k_1 - k_2}\left[1 - \mathrm{e}^{-(\lambda + k_1 - k_2)t}\right] \tag{8a}$$

Some conclusions can be drawn from these equations. Firstly, the dynamic equilibrium in the liquid phase seems to depend mainly on adsorption and desorption rates. The main reason is that the decay constants of ^{226}Ra and ^{228}Ra are much lower than the adsorption/desorption coefficients. The decay constant of ^{228}Ra is only 3.7×10^{-9} s^{-1} and for ^{226}Ra is even lower, while the estimate of the adsorption rate for groundwater gives values within the range 0.5×10^{-6} to 1×10^{-6} s^{-1} [22]. It means that the equilibrium level of radium in the liquid phase should be controlled by processes other than the decay. On the other hand, the adsorption and desorption rates of radium must depend on the solutes in the formation water and especially the presence of barium ions.

From the above equations it is clear that the adsorption and desorption processes affect the radium concentration in the liquid phase. The ratio of equilibrium concentrations for cases without and with adsorption/desorption is $\lambda/(\lambda+k_1-k_2)$. Taking into consideration the assumption that $k_1-k_2 \gg \lambda$, the activity ratio is about $\lambda/(k_1-k_2)$. This effect should be more important for ^{226}Ra, the isotope with the lower decay constant. Although the concentrations of radionuclides from the uranium and thorium series in the solid phase are usually similar, the situation in the liquid phase should be different. If adsorption and desorption rates for both isotopes are the same, than the activity ratio in the solution should be $A_{^{226}\mathrm{Ra}}/A_{^{228}\mathrm{Ra}} = 6/1600 \approx 0.004$. Such low ratios are not usually observed in aquifers, if at all. It means that another explanation is required.

4. RADIUM IN MINE WATERS

Any theory must explain the different effects observed in brines in coal mines. As mentioned earlier, the ratio of radium concentrations (^{226}Ra/^{228}Ra) in type A brines is greater than 1. It might be explained as a combination of the low adsorption rate, resulting in longer time needed to reach equilibrium in the liquid phase, and the higher concentrations of radium in type A waters. In type B waters the lack of barium leads to the higher adsorption rate and slower desorption. The main effect is that there is a shorter time required to reach equilibrium in the liquid phase. Additionally, the ratio of radium concentrations ^{226}Ra/^{228}Ra should be below 1, as observed. Assuming that recoil is the only mechanism of radium transfer into the liquid phase and that no adsorption occurs, the build-up of activity can be described as:

$$A_{\mathrm{Ra}}(t) = \frac{N_{\mathrm{rec}}}{\lambda}\left(1-e^{-\lambda t}\right) = \frac{A\varepsilon}{\lambda}\left(1-e^{-\lambda t}\right) \tag{9}$$

where N_{rec}/λ is the maximum activity of radium in the water. By considering the following parameters for the host rock in the aquifer:

- Uranium and thorium isotope concentrations each of 25 Bq/kg;
- A rock density of 2000 kg/m^3;
- A recoil coefficient of $e \gg 10\%$ [30];
- A porosity of 10%;

then the calculated maximum radium activity in the liquid phase should be 50 kBq/m^3. However in Polish coal mines, much higher values have been measured, up to 400 kBq/m^3 [31]. This is understandable, because the concentrations of radionuclides in the rock body are often higher, up to 200 Bq/kg. The fact that the ^{226}Ra concentrations are higher than those of ^{228}Ra has been explained in Ref. [22] as being the result of the above-mentioned recoil and adsorption of ^{230}Th on the surface of the solid phase. It is possible that the recoil dissolution of ^{226}Ra may be more effective than ^{228}Ra, since the parent ^{232}Th is probably entirely embedded in the lattice. It is necessary to stress again that such high radium concentrations in water are not connected with uranium or thorium mineralization.

Comparing equation (9) for the two isotopes of radium — ^{226}Ra from the uranium series and ^{228}Ra from thorium chain — and making the assumption that the recoil coefficient is similar for both radionuclides and that no adsorption occurs, the ratio of their activities in the liquid phase is as follows:

$$\frac{A_{\mathrm{Ra\text{-}226}}}{A_{\mathrm{Ra\text{-}228}}} = \frac{\lambda_{\mathrm{Ra\text{-}228}}}{\lambda_{\mathrm{Ra\text{-}226}}} \times \frac{A_{\mathrm{U}}\left(1-\mathrm{e}^{-\lambda_{\mathrm{Ra\text{-}226}}\,t}\right)}{A_{\mathrm{Th}}\left(1-\mathrm{e}^{-\lambda_{\mathrm{Ra\text{-}228}}\,t}\right)} \tag{10}$$

Taking into account the adsorption and desorption (equation (8a)), the activity ratio can be denoted as:

$$\frac{A_{\mathrm{Ra\text{-}226}}}{A_{\mathrm{Ra\text{-}228}}} = \frac{A_{\mathrm{U}}}{A_{\mathrm{Th}}} \times \frac{\lambda_{\mathrm{Ra\text{-}228}} \big/ \left(\lambda_{\mathrm{Ra\text{-}226}} + k_1 - k_2\right)}{\lambda_{\mathrm{Ra\text{-}226}} \big/ \left(\lambda_{\mathrm{Ra\text{-}228}} + k_1 - k_2\right)} \times \frac{1-\mathrm{e}^{-\left(\lambda_{\mathrm{Ra\text{-}226}}+k_1-k_2\right)t}}{1-\mathrm{e}^{-\left(\lambda_{\mathrm{Ra\text{-}228}}+k_1-k_2\right)t}} \tag{11}$$

If the adsorption coefficient is significantly higher than the decay constant of both radium isotopes, then equation (11) can be simplified further (taking into account a longer time for water contact with the solid phase):

$$\frac{A_{\mathrm{Ra\text{-}226}}}{A_{\mathrm{Ra\text{-}228}}} = \frac{A_{\mathrm{U}}}{A_{\mathrm{Th}}} \times \frac{\lambda_{\mathrm{Ra\text{-}228}} \big/ \left(\lambda_{\mathrm{Ra\text{-}226}} + k_1 - k_2\right)}{\lambda_{\mathrm{Ra\text{-}226}} \big/ \left(\lambda_{\mathrm{Ra\text{-}228}} + k_1 - k_2\right)} \tag{12}$$

If we assume a much higher value for the adsorption coefficient in comparison with desorption, a final equation is simpler:

$$\frac{A_{\text{Ra-226}}}{A_{\text{Ra-228}}} = \frac{A_{\text{U}}}{A_{\text{Th}}} \times \frac{\lambda_{\text{Ra-228}}}{\lambda_{\text{Ra-226}}} \tag{13}$$

The conclusion from the last equation is important. A large activity ratio is not observed in mine waters. It means that the adsorption and desorption coefficients in saline water aquifers are similar, rather low and comparable with the decay constants of radium isotopes. Therefore, equation (13) cannot be used for the prediction of radium concentrations in brines.

The use of the concept of an effective adsorption coefficient, k_{eff}, obtained from the subtraction of adsorption and desorption factors $(k_{\text{eff}} = k_1 - k_2)$, for the numerical simulation of the build-up of radium isotope concentrations in the liquid phase in aquifer is proposed. Such a simulation has been made for different values of effective adsorption coefficients and the results are presented in Fig. 1 and Table II. The activity concentrations of radium isotopes have been normalized and thus shown as relative values, to enable comparison of the increase of these values with time. The uranium–thorium ratio in the solid phase has been chosen as 1, which is close to reality.

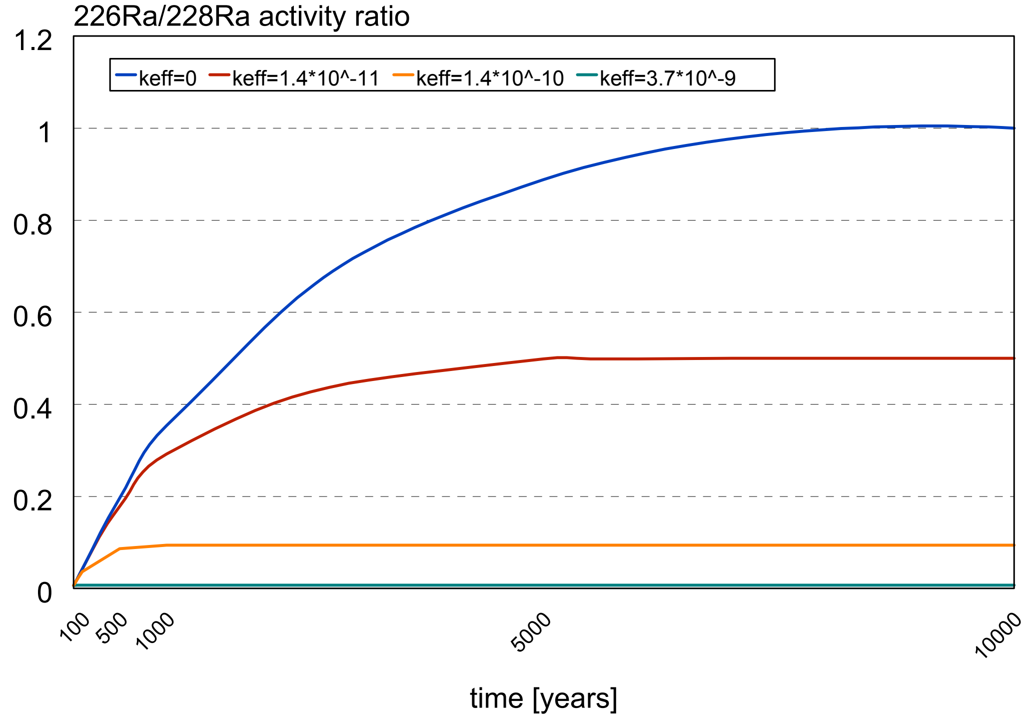

FIG. 1. Simulation of the activity ratio of radium isotopes in brines for different effective adsorption coefficients.

The results of these approximate estimations seem to be a little surprising. First of all, the effective adsorption of radium from brines is a very slow process. For type A waters, the value of k_{eff} must be close to zero and adsorption simply does not occur. The calculated ^{226}Ra/^{228}Ra activity ratio reaches about 1, close to the chosen activity ratio in the solid phase. The observed higher values — up to 2 — can be explained in accordance with Ref. [22] by the higher recoil rate for ^{226}Ra as a result of a previous recoil of the parent isotope ^{230}Th. A recoil ratio of 2 for radium isotopes has been calculated in Ref. [22], and this value is in a good agreement with experimental data.

TABLE II. RELATIVE ACTIVITY CONCENTRATIONS OF RADIUM ISOTOPES IN THE LIQUID PHASE FOR DIFFERENT VALUES OF EFFECTIVE ADSORPTION COEFFICIENT

k_{eff} (s^{-1})	Time (a)	Relative activity concentration		Activity concentration ratio, $^{226}Ra/^{228}Ra$
		^{226}Ra	^{228}Ra	
0	1	0.000437	0.110118	0.003972
	5	0.002185	0.441965	0.004944
	10	0.004365	0.688597	0.00634
	50	0.021637	0.997072	0.021701
	100	0.042807	0.999991	0.042807
	500	0.196477	1	0.196477
	1000	0.354351	1	0.354351
	5000	0.887803	1	0.887803
	10 000	0.987412	1	0.987412
1.4×10^{-11}	1	0.000437	0.110095	0.003972
	5	0.002183	0.441528	0.004944
	10	0.004356	0.687379	0.006337
	50	0.021403	0.99341	0.021545
	100	0.041891	0.996256	0.042048
	500	0.177176	0.996264	0.17784
	1000	0.291569	0.996264	0.292662
	5000	0.493706	0.996264	0.495557
	10 000	0.499921	0.996264	0.501795
1.4×10^{-10}	1	0.000436	0.109882	0.003972
	5	0.002161	0.437628	0.004939
	10	0.004271	0.676556	0.006313
	50	0.019442	0.961588	0.020219
	100	0.034726	0.96385	0.036029
	500	0.082713	0.963855	0.085815
	1000	0.09017	0.963855	0.093552
	5000	0.090909	0.963855	0.094318
	10 000	0.090909	0.963855	0.094318
3.7×10^{-9}	1	0.000413	0.104049	0.003968
	5	0.001655	0.344205	0.004809
	10	0.002576	0.451321	0.005708
	50	0.003721	0.49971	0.007447
	100	0.003732	0.499714	0.007468
	500	0.003732	0.499714	0.007468
	1000	0.003732	0.499714	0.007468
	5000	0.003732	0.499714	0.007468
	10 000	0.003732	0.499714	0.007468

For an effective adsorption coefficient equal to the decay constant of ^{226}Ra ($k_{\text{eff}} = 1.4\times10^{-11}$ s^{-1}), the calculated activity ratio reaches about 0.5, close to the activity ratio measured for type B waters. In such waters the adsorption prevails over desorption, but the process appears to be very slow. The reason is that the sodium and calcium ions in the liquid phase compete with radium ions for the CECs.

Higher values of effective adsorption coefficient seem to be too high for aquifers with saline waters. For instance, the activity ratio calculated for $k_{\text{eff}} = 1.4\times10^{-11}$ s^{-1} corresponding to a period of 160 years (one tenth of the half-life of ^{226}Ra) is 0.1. In Polish coal mines such an activity ratio has not been observed. Again, this conclusion supports strongly the thesis that the ionic exchange of radium with the solid phase is an extremely slow process.

On the other hand, we have to remember that all conclusions are related to the effective adsorption coefficient, which describes the difference between adsorption and desorption. Physically, both processes are fast and there have been numerous investigations on this subject, each giving clear evidence that desorption could take place within hours or even minutes [32]. The problem needs further analyses and in-situ measurements to investigate brines and deep aquifers. One of the best possible sites is a colliery in the southern part of the Upper Silesian Coal Basin, where both types of radium-bearing brines are present.

5. SUMMARY

An approach to the problem of radium transfer from the solid to the liquid phase in aquifers is described in this paper, with special emphasis on brines that occur in coal mines. The main process controlling the radium concentration in water is the adsorption of radium onto the surfaces of the solid phase. However, the adsorption coefficient depends strongly on the dissolved solid content of the brines, and primarily on the presence of barium in saline waters.

The migration length of radium isotopes in an aquifer is rather short — several metres for ^{226}Ra and less than 1 m for ^{228}Ra. Therefore, investigations of the stratum in the close vicinity of mine galleries should give important information on the uranium and thorium content in the solid phase as well as other parameters of the aquifer such as the porosity, Eh, pH etc. All these results will be essential for the further investigation of radium behaviour in deep aquifers.

The results of a simulation based on a mathematical approach to radium changes in the liquid phase reveal that the effective adsorption rate of radium from brines is very low, either comparable with the decay constant of ^{226}Ra or even lower. Differences of adsorption coefficient, mainly due to the presence of barium ions in type A brines, lead to significant differences in the activity ratio of radium isotopes. The reason for barium occurrence in some aquifers is therefore one of the most important features. From that point of view, changes in radium concentration are a secondary problem.

Further research is required, mainly in-situ experiments directly within aquifers. The best possible sites seem to be deep underground mines, like collieries, with easy access to different aquifers. In one of the coal mines in Poland, both types of radium-bearing waters are present (A and B); therefore we would like to use this mine during future investigations.

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RADIUM BEHAVIOUR DURING DESALINATION PROCESSES OF MINE WATERS

S. Chałupnik[*], **K. Skubacz**

Laboratory of Radiometry, Central Mining Institute,
Poland

Abstract

In the 1980s and 1990s, investigations of radium behaviour in a desalination plant were performed by the Laboratory of Radiometry of the Central Mining Institute. This plant, for the complete removal of dissolved solids from mineralized mine water, is located in Dębieńsko Mine. The installation was a unique solution, the only installation constructed for such purposes in Poland and in the world. In the plant, brine from two coal mines is treated. This saline water was, in addition, radium-bearing, containing enhanced levels of radium isotopes (^{226}Ra and ^{228}Ra). Our investigation showed enhanced concentrations of radium in different waste materials and by-products of the process. Therefore the economic use of such products was not possible. In recent years, the planning of the construction of such a desalination plant for another group of mines has been under discussion (Piast and Ziemowit Collieries). The results of investigations of contamination of the natural environment caused by radium-bearing water from these mines indicated how severe this problem was. To solve this, the removal of radium in underground galleries was applied in one of these mines. On the basis of previous investigations in the Dębieńsko desalination plant, an analysis of radium behaviour in the planned installation was conducted. It was done for two possible scenarios — with and without the prior removal of radium from the mine water. The results of the analysis are presented in this paper. This assessment gives a very good opportunity to point out the potential importance of the removal of radium from mine waters, not only to minimize environmental pollution but also to enable the utilization of certain products of the desalination process.

1. INTRODUCTION

Saline water discharged from coal mines in the Upper Silesia region often causes significant pollution of the small brooks and rivers in the vicinity. This is due to high mineralization, sometimes up to 200 g/L. Such water also contains natural radionuclides, mainly radium isotopes. It is difficult to control the negative impact of salinity on the surface water, and only a few methods are applicable. One of the possible methods is desalination.

In the 1970s, a desalination plant was built for the removal of salinity from brines of two coal mines in Poland [1]. The construction of the plant was supported by the United Nations within the UNDP programme. This plant, for the complete removal of dissolved solids from moderately mineralized mine water, is located at the Dębieńsko Mine. The installation was a very unique solution, the only one constructed for such purposes in Poland and in the world. In the plant, brines from two coal mines were treated. The saline water contained, in addition, enhanced levels of radium isotopes (^{226}Ra and ^{228}Ra). In the plant, so-called 'type B' water was treated in two separate installations. The primary installation was used to concentrate salts by evaporation. This process produced sodium chloride (with

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[*] E-mail: s.chałupnik@gig.katowice.pl

potential use for human consumption), gypsum as a waste product, deionized water and a liquid by-product. The saturated solution of different salts was transferred into a secondary installation to be utilized for the production of iodine and bromine, potassium chloride, magnesium hydroxide and deionized water. No waste was produced in this installation.

In the 1980s and 1990s, the Laboratory of Radiometry of the Central Mining Institute performed investigations of radium behaviour in the desalination plant [2, 3]. We investigated the concentration of radium isotopes in different products and by-products of the primary and secondary installations. It was found that different products of the desalination process contained enhanced concentrations of radium. Moreover, the presence of scales with a high radium content inside the primary installation was confirmed by gamma dose rate measurements. It should be pointed out that the brine demineralized in this plant was not very salty and did not contain high radium concentrations — the salinity did not exceed 30 g/L, and the concentrations of ^{226}Ra and ^{228}Ra did not exceed 1.5 and 3 kBq/m^3, respectively.

At the end of the 1990s, a feasibility study for a new desalination plant (the Central Desalination Plant, or CDP) was conducted for three collieries in the Vistula catchment area, where huge inflows of highly mineralized brine occur. This water was also a type B brine, but the concentrations of radium isotopes were significantly higher — up to 7 kBq/m^3 of ^{226}Ra and 15 kBq/m^3 of ^{228}Ra. The direct desalination of these brines could lead to the creation of products and by-products with much higher levels of radionuclides than in the existing plant. Additionally, we anticipated the deposition of scales with enhanced levels of radium in the evaporation units or reverse osmosis units, and the gamma dose rates near particular parts of the primary installation might cause workers to receive a dose exceeding 1 mSv/a. The way to avoid such a situation was to remove radium from the mine water prior to desalination. An assessment of the radium levels in different products of the desalination process was conducted for two scenarios. The first scenario involved the desalination of untreated brines and the second involved the demineralization of brine from which radium had first been removed.

2. PRIMARY DESALINATION SYSTEM

The main aim of the primary installation was to concentrate the brine in the evaporation or reverse osmosis processes (during which stage, distilled water was produced), and then to separate gypsum and sodium chloride. The concentrated brine was transferred to the secondary system. The majority of the radium activity was removed from the solution with the gypsum — about 60% of the initial activity. Small quantities of radium were found in the sodium chloride, but only in admixtures of poorly separated gypsum. Additionally, in the primary system, scales of gypsum (calcium sulphate), barium and radium sulphates were deposited in some parts of the evaporating units and the salt crystallizer. These scales contained high concentrations of radium isotopes — up to a few tens of thousands of becquerels per kilogram. The fraction of radium total activity in the scales was very low, but its deposition led to a significant increase in gamma dose rates in particular parts of the system, creating a possible hazard for workers. Also, a significant portion of the radium remained in the concentrated brine and caused contamination of the products in the secondary installation. No radium was found in the distilled water — this was very important for the possible use of such water as potable water.

2.1. Radium in the gypsum

Several samples of gypsum from the system were measured by gamma spectrometry. It was found that the average concentration of ^{226}Ra was about 60 Bq/kg, while the maximum value did not exceed 100 Bq/kg. Instruction No. 234 of the Institute of Construction Techniques [4] permits the use of materials with a ^{226}Ra concentration below 185 Bq/kg for the construction of dwellings. A secondary condition for the total activity of natural radionuclides in the material is as follows:

$$0.00027\, C_{\mathrm{K}} + 0.0027\, C_{\mathrm{Ra}} + 0.0043\, C_{\mathrm{Th}} < 1$$

where C_{K}, C_{Ra} and C_{Th} are the concentrations (in Bq/kg) of ^{40}K, ^{226}Ra and ^{228}Ra respectively. This second requirement was also satisfied for the gypsum by-product from the primary installation. The results of the assessment for the planned installation are shown in Table I. Only with prior removal of radium is it possible for the gypsum to be reused for construction purposes.

TABLE I. PREDICTED RADIUM CONCENTRATION IN THE GYPSUM

Process	Activity concentration (Bq/kg)		Possible applications for reuse
	^{226}Ra	^{228}Ra	
Without radium removal	400	800	None
With radium removal	10	20	Construction industry

2.2. Radium in the sodium chloride

The presence of radium isotopes in the sodium chloride was due to poor separation of gypsum at the first stage of the primary system. It was found that the gypsum fraction in the salt varied over a wide range, affecting the radium content in this product. The maximum ^{226}Ra concentration was 7 Bq/kg, while the ^{228}Ra concentration was slightly higher — up to 10 Bq/kg. Therefore it is difficult to predict the radium concentration in sodium chloride in the CDP installation. By assuming proportionality between the gypsum content and the radium content, a very rough assessment of the radium isotope concentrations was made, see Table II. In both cases, the sodium chloride produced in the CDP could be used for human consumption. However, in the case of no purification of the brine before desalination, an effective dose must be estimated. Assuming an annual salt consumption of 1 kg, the total ingested activity of radium isotopes would be 120 Bq and the annual dose would be close to 0.1 mSv. In terms of the European Council Directive 96/29/Euratom [5] this is a permissible level of additional dose caused by radionuclides in drinking water (10% of the 1 mSv annual dose limit). Therefore some restrictions must be applied for the use of salt from the CDP as well as the requirement for periodic monitoring of its radium content.

TABLE II. PREDICTED RADIUM CONCENTRATION IN THE SODIUM CHLORIDE

Process	Activity concentration (Bq/kg)		Possible applications for reuse
	^{226}Ra	^{228}Ra	
Without radium removal	40	80	Human consumption with restrictions
With radium removal	1	2	Human consumption

2.3. Scales in the primary installation

The presence of scale with an enhanced radium content was discovered during measurements of the gamma dose rate at the primary installation. The highest dose rate was measured in the vicinity of the heat exchangers of the evaporation units. In scales taken from these exchangers, the ^{226}Ra content was up to 10 000 Bq/kg, while the maximum values of gamma dose rate varied from 3 to 5 μGy/h on the surfaces of pipes and up to 1 μGy/h at 1 m distance.

In this case, the assessment of radium concentrations in scale is difficult. One of the reasons is that the radium content in scales is not only controlled by the radium concentration in the brine but also depends on the abundance of radium sulphate in the gypsum. The assumption can be made that the radium concentration in scales of the CDP would be similar or slightly higher than that measured in the Dębieńsko desalination plant if no purification of brines were to be applied. The values of radium content estimated on this basis are 10 000–20 000 Bq/kg for ^{226}Ra and 20 000–40 000 Bq/kg for ^{228}Ra. But the total activity of radium in the scales would be correlated with the radium concentration in the raw brine and with the total mass of scales in the installation. The gamma dose rates would depend, of course, on the total activity of radium isotopes in the scales. We should predict an increase in gamma dose rates during the operation of the CDP, but the maximum values would be similar to values measured in the Dębieńsko plant. *It must be taken into account that the concentration of radium isotopes in the scales would be higher than 10 000 Bq/kg, and that such scales must be treated as waste products with enhanced natural radioactivity* [6]. In such a case, special measures must be undertaken during any repairs at the primary installation of the CDP or scale removal from pipes. This problem may appear after a few years of CDP operation.

3. SECONDARY DESALINATION SYSTEM

In the secondary system of the Dębieńsko desalination plant, iodine, bromine, potassium chloride, magnesium hydroxide and calcium chloride were produced. Saturated brine from the primary installation was utilized in this system, and the radium concentrations in this brine were up to 10 times higher in comparison with the raw brine. In the saturated brine in the secondary system of the Dębieńsko plant, the ^{226}Ra concentration sometimes reached 15 000 Bq/m^3, while the radium content in the raw brine was on average 1500 Bq/m^3. As no waste or by-products were created in the secondary installation, 30–40% of the total radium activity from the raw brine was therefore distributed among different products of that system. A similar situation would be observed in the CDP.

3.1. Iodine and bromine solutions

The radium concentration in solutions containing iodine and bromine has been measured several times at the Dębieńsko plant. No radium (above the detection limit) has been found in these samples. We can assume the same situation at the CDP, so no contamination of these products is predicted.

3.2. Potassium chloride

In the potassium chloride, not only radium isotopes were found but mainly ^{40}K. The abundance of ^{40}K in natural potassium is a constant value. Its presence in potassium chloride is a possible source of radiation hazard for workers, as its concentration in the material is about 15 000 Bq/kg. This isotope may cause an increase in external gamma radiation dose.

Radium isotopes could appear in the potassium chloride as a result of poor separation of gypsum. The maximum ^{226}Ra concentration in the potassium chloride from the Dębieńsko plant was 300 Bq/kg, but the average concentration was much lower — 70 Bq/kg. For the CDP, the most important factor influencing the radium content in this product would be proper technology and maintenance of the system. Results of a rough assessment of the radium isotope concentrations in the potassium chloride from the CDP are shown in Table III. It can be seen that with purification of mine water before desalination, the potassium chloride can be reused in all possible applications without any restriction.

TABLE III. PREDICTED RADIUM CONCENTRATION IN THE POTASSIUM CHLORIDE

Process	Activity concentration (Bq/kg)		Possible applications for reuse
	^{226}Ra	^{228}Ra	
Without radium removal	1200	2400	Limited application as a fertilizer
With radium removal	30	60	No restriction

3.3. Magnesium hydroxide

In the Dębieńsko plant, one of the products from the secondary installation was magnesium chloride. No ^{226}Ra has been found in samples of this product, and therefore no restrictions on use were applied.

In the CDP installation, it is proposed to produce magnesium hydroxide instead of magnesium chloride. Therefore, another approach is needed for the assessment of radium content in this product. An analogy can be drawn from the results of investigations of another desalination installation, designed and built by the Silesian Technical University as a model installation at Ziemowit Mine. We found that the ^{226}Ra content in samples of magnesium hydroxide from this installation did not exceed 25 Bq/kg. The results of the assessment are shown in Table IV. Such a product can be used in any application without restriction.

TABLE IV. PREDICTED RADIUM CONCENTRATION IN THE MAGNESIUM HYDROXIDE

Process	Activity concentration (Bq/kg)		Possible applications for reuse
	^{226}Ra	^{228}Ra	
Without radium removal	25	50	No restriction
With radium removal	3	6	No restriction

Traces of gypsum from the primary system constitute an additional by-product at this stage of the process. It is difficult to assess the radium concentration in this by-product, as in the Dębieńsko desalination plant only small amounts of gypsum were obtained from the secondary system. Concentrations of up to 1000 Bq/kg of ^{226}Ra have been measured. Therefore, it would be possible to produce gypsum in the CDP with a ^{226}Ra content of up to several thousand becquerels per kilogram and up to 10 000 Bq/kg of ^{228}Ra. Such a by-product must be treated as a waste with an enhanced content of natural radionuclides, but these small amounts of gypsum could be mixed with low activity gypsum from the primary installation.

3.4. Calcium chloride

The last stage of the proposed desalination process is the separation of calcium chloride. In the Debieńsko desalination plant, as well as in the model installation at Ziemowit mine, this element of the process did not exist. The only analogous process was the production of calcium carbonate in the Ziemowit installation. This similarity is not adequate, as radium in the form of carbonate is insoluble while in the form of chloride is soluble. Therefore, the radium behaviour might be different. Taking into account a certain similarity of both processes (in the case of the Ziemowit installation, the radium concentration in the calcium carbonate was 800–2000 Bq/kg), the predicted results are shown in Table V.

TABLE V. PREDICTED RADIUM CONCENTRATION IN THE CALCIUM CHLORIDE

Process	Activity concentration (Bq/kg)		Possible applications for reuse
	^{226}Ra	^{228}Ra	
Without radium removal	2000	4000	Very limited possibilities
With radium removal	80	160	No restriction

It must be pointed out that this stage of the planned process is not very well understood and, should the technology be implemented, must be investigated very carefully.

A very important conclusion from the long term monitoring of radium isotopes in the distilled water is that the concentrations of ^{226}Ra and ^{228}Ra in the water produced in the Debieńsko desalination plant were close to zero, usually below detection limit.

4. RADIOLOGICAL HAZARD DUE TO THE DESALINATION OF MINE WATERS

The desalination plant is a possible source of radioactive contamination for the environment, but only when desalination of untreated mine waters is performed. Under such circumstances, the radium concentration could exceed permissible levels in particular products of the process. The basic product of the process — distilled water — can be used for human consumption without any restriction. A slightly more complicated problem is the use of the sodium chloride, but human consumption also seems to be possible in this case, especially when proper and careful maintenance of the plant is ensured.

The situation regarding the other products can be rather complicated due to the enhanced radium content. Gypsum, potassium chloride and calcium chloride produced from untreated brines should be treated as waste with enhanced radioactivity. The uncontrolled reuse or disposal of such materials may lead to a radiation hazard to the population, in that the annual dose limit (1 mSv) can sometimes be exceeded. Therefore, the disposal of large amounts of such materials as waste, for instance 10 t/h of calcium chloride, may be complicated.

If pretreatment of brines is applied, i.e. removal of radium, no radiation hazard exists for the local population and consumers of the desalination products. Nonetheless, monitoring of the radium content in these products would be necessary.

The problem of scales in the primary system is a little bit different. Even during the desalination of previously purified brines, the sedimentation of deposits with a radium concentration above 10 000 Bq/kg is possible. Of course, the sedimentation progression will be different, and the increase of gamma dose rate and radiation hazard for the operating staff will be much slower. The only possible hazard from the contamination arises from the repair of elements of the installation and from the uncontrolled release of scales into environment.

The assessment of the CDP impact on the environment shows that there is no possible hazard for the local population, and a very low probability of contamination of the natural environment is predicted during desalination of mine water if radium is first removed.

The analysis described in this paper shows that desalination of mine water has a multidimensional context — it is not only environmental issue. The problem of the impact of brines from the Upper Silesian mines must be solved sooner or later. From an economic aspect, desalination seems to be very expensive and not the proper choice. But radium removal from brines must be applied if this technology is to be used in the future.

5. CONCLUSIONS

(i) The problem of the discharge of saline mine water into rivers is well known in Poland, but not yet solved. One of the possible solutions is desalination of brines. Results obtained in the Dębieńsko Desalination Plant have shown that the application of evaporation technology is possible. Unfortunately, enhanced concentrations of radium isotopes in the products of desalination have been observed. Therefore, the application of similar technology in other mines may lead to the contamination of the products as well.

(ii) The underground purification of mine water prior to desalination can avoid problems with enhanced radioactivity. The products of desalination technology obtained from pretreated waters should contain low concentrations of radium isotopes and the economical use of the technology should be possible. For instance, both the sodium chloride and deionized water products would be free of radium. Additionally, the radiation hazard for the desalination plant workers would not exceed permissible levels.

(iii) The underground purification of mine water to remove radium is possible, as results from the treatment installation in Piast mine show [7]. Further implementation in other mines is predicted soon.

(iv) When underground water is pretreated, the desalination plant will cause no radiation contamination of the natural environment and no hazard for the general public is predicted.

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SOURCES OF TENORM — INVENTORY OF PHOSPHATE FERTILIZER AND ALUMINIUM INDUSTRY

D. Georgescu, F. Aurelian, M. Popescu, C. Rădulescu

Research and Development National Institute for Metals and Radioactive Resources[*],
Bucharest, Romania

Abstract

In Romania, seven fertilizer plants based on H_2SO_4 and HNO_3 attack were built and commissioned in the period 1964–1978. Phosphogypsum resulting from H_2SO_4 attack of imported phosphate rock has been deposited since 1978, close to the plant, which is located in the eastern part of Bacau city. The following composition was measured in samples from the surface of the phosphogypsum deposit and from drilling to a depth of 16 m — U: 15–21 ppm, ^{226}Ra: 0.45–0.87 Bq/g, Th: <3 ppm, K: <1%, gamma dose rate: 0.18–0.25 μSv/h. The radon and thoron concentrations at the pond surface (irregular areas) were 4860 and 496 Bq/m^3 respectively. For HNO_3 attack, the tailings pond with process water and calcium carbonate occupies a surface of about 33 ha, close to the plant, which is located in the western part of Targu-Mures city. The process water from the tailings pond had the following composition — pH: 1.45, U: 0.045 mg/L, ^{226}Ra: 1.4 Bq/L. The calcium carbonate composition was U: 23 ppm, ^{226}Ra: 0.35 Bq/g, Th: 2 ppm, K: 0.2%. In the western area of Oradea city there is a bauxite processing plant. The composition of the red coloured material in the 'red sludge' pond was U: 11 ppm, ^{226}Ra: 0.21 Bq/g, Th: 61 ppm. For the dark coloured material, the composition was U: <1 ppm, ^{226}Ra: 0.137 Bq/g, Th: 70 ppm. For the light coloured material, the composition was U: 127 ppm, ^{226}Ra: 1.675 Bq/g, Th: 11 ppm. The radon and thoron concentrations in the air at the pond surface were 21 and 1220 Bq/m^3 respectively. The composition of the water was radon: 101 Bq/m^3, thoron: 0 Bq/m^3, ^{226}Ra: 0.023 Bq/L, pH: 12.05. At an alumina plant in Tulcea, the composition of the red sludge was U: 15 ppm, ^{226}Ra: 0.212 Bq/L, Th: 62 ppm. The composition of the water from the pond was pH: 12.2, ^{226}Ra: 0.026 Bq/L, U:0.01 mg/L. The radon and thoron concentrations in the air at the surface of the red sludge pond were 248 and 6270 Bq/m^3 respectively.

1. INTRODUCTION

For activities linked to uranium ore mining and processing, due to the high content of uranium, radium and other decay products, international and national organizations have developed limits for occupational and public exposure. Less attention has been paid to occupational and public exposure as a result of the utilization of some materials with naturally occurring radionuclides, but their radioactivity may not be ignored. In these cases, the industrial processes can enhance the concentrations of some radionuclides (isotopes of uranium, radium, potassium and thorium) in the final products, in intermediate products, and in process waters or residual materials.

As there is a potential for incremental exposure resulting from the handling of such materials and also from the utilization or removal of wastes, the European Commission established a work programme in this field, orientated towards the following industrial activities:

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[*] E-mail: icpmrr@iodes.ro

- Coal-based power generation,
- Processing of phosphate ores,
- Production of aluminium,
- Production of oil and gas,
- Production of titanium oxide and titanium metal,
- Smelting of metals,
- Processing of copper,
- The ceramics and zirconium industry,
- Building materials,
- Uses of the natural radionuclides radium and thorium.

Many of the above categories have not been considered as industries with a potential radiological impact on people or the environment, and are not under radiological control because they are not systematically monitored. On that basis, studies are necessary to determine and create inventories of the additional sources of natural radiation from different geographical zones as a result of 'technological activities', in order to assess and control the required level of regulatory intervention in cases where there is a significant increase in the exposure of workers or the public from sources of natural radiation.

2. PHOSPHATE FERTILIZER INDUSTRY

In Romania, seven fertilizer plants based on sulphuric acid (H_2SO_4) and nitric acid (HNO_3) attack were built and commissioned during the period 1964–1978.

2.1. Plants based on H_2SO_4 attack

The dihydrate wet process, which forms the basis of all phosphoric acid plants in Romania, is the process most widely used around the world, due to its simplicity and especially to its compatibility with any phosphate rock with a P_2O_5 content of 29–39%. The raw materials used in phosphoric acid manufacture are:

- Phosphate rock with a P_2O_5 content of 29–39%,
- Concentrated H_2SO_4 (94-98%).

This is by far the most important process discussed here and is based on the chemical reaction:

$$Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 + 20H_2O \rightarrow 6H_3PO4 + 10CaSO_4{\cdot}2H_2O + 2HF$$

Two products result from this process:

- Phosphoric acid (liquid phase), in which more than 90% of the uranium from the rock is found.
- Gypsum (solid phase), usually called phosphogypsum, which may contain 80% of the ^{226}Ra originating from the phosphate rock. Phosphogypsum may also contain 5–20% of the uranium from the rock.

The phosphoric acid product (50–52% P_2O_5) can be combined with ammonia to produce ammonium phosphate, or can be combined with phosphate rock in a ratio of 3 to 1 to produce superphosphate. The following wastes are generated in the phosphoric acid facilities:

- Solid waste — phosphogypsum,
- Liquid waste — acidic waters,
- Gaseous waste — fluorine.

Contamination of the environment (water, air, soil, underground) by one of the above-mentioned wastes can be prevented by the use of specific technological measures.

Phosphogypsum, a solid waste arising from the filtration stage, can be removed from the plant:

- Hydraulically — it is collected together with chemically impure water from the plant in a phosphogypsum receiving vessel where it is neutralized at the same time as the water by 10% $Ca(OH)_2$ and then deposited by pumping into an impermeable settling tank, the decanted waters being recirculated in the plant;
- Mechanically — it is removed from the plant by means of a conveyor belt onto a waterproofed waste heap with drainage ditches.

The chemically impure waters are neutralized at the same time as the phosphogypsum and then removed from the neutralization vessel, decanted and disposed of in sewage.

2.1.1. Plant residues from SC Marway–Fertilchem SA, Năvodari

The neutralized phosphogypsum has been deposited in three ponds located on the west side of the processing plant:

- Tailings pond A was commissioned 1961 and decommissioned in 1975; it has a volume of 1.15 million m^3 and is partially covered by spontaneous vegetation;
- Tailings pond B was commissioned in 1975 and abandoned in 1996; it occupies an area of 21 ha and has a height of 7–11 m;
- Tailings pond C was commissioned in 1996 and occupies an area of 10 ha.

The composition of collected samples was: U: 15 ppm; ^{226}Ra: 0.48 Bq/g, Th: <3 ppm, K: 1.48%, Al_2O_3: 0.4%, V: 2 ppm, Sn: 30 ppm, P_2O_5: 0.57%, Pb: 15 ppm, Cu: 20 ppm, S: 18%, ppc: 21%. More information is given in Figs 1 and 2.

In recent years, the processed ore was phosphate rock from Syria with the following composition — P_2O_5: 30.2%, CaO: 47%, SiO_2: 3.2%, ΣTR_2O_3: 0.3%, MgO: 0.7%, Cl: 0.07%, Na_2O: 0.2%, K_2O: 0.03%, ^{226}Ra: 0.7 Bq/g, U: 0.0035%, Zn: 0.018%, Be: 0.002%, Ba: 0.03%, Pb: 0.002%, Cu: 0.003%.

In the 35 years of plant operation, raw material has been imported from Morocco, Algeria, Egypt, Indonesia, Tunisia, and Israel. This raw material has similar composition in terms of the main components P_2O_5 and CaO, but with variations concerning the minor elements and especially the radioactive ones.

The gamma dose rate across the pond surface is 0.18–0.22 μSv/h, compared with a background value of 0.08 μSv/h.

The process water from pond C has the following composition — Fe: 7 mg/L, Ca: 1000 mg/L, PS: 0.4 mg/L, Cu: 0.5 mg/L, Ra: 0.01 Bq/L, Zn: 0.7 mg/L, U: 0.027 mg/L.

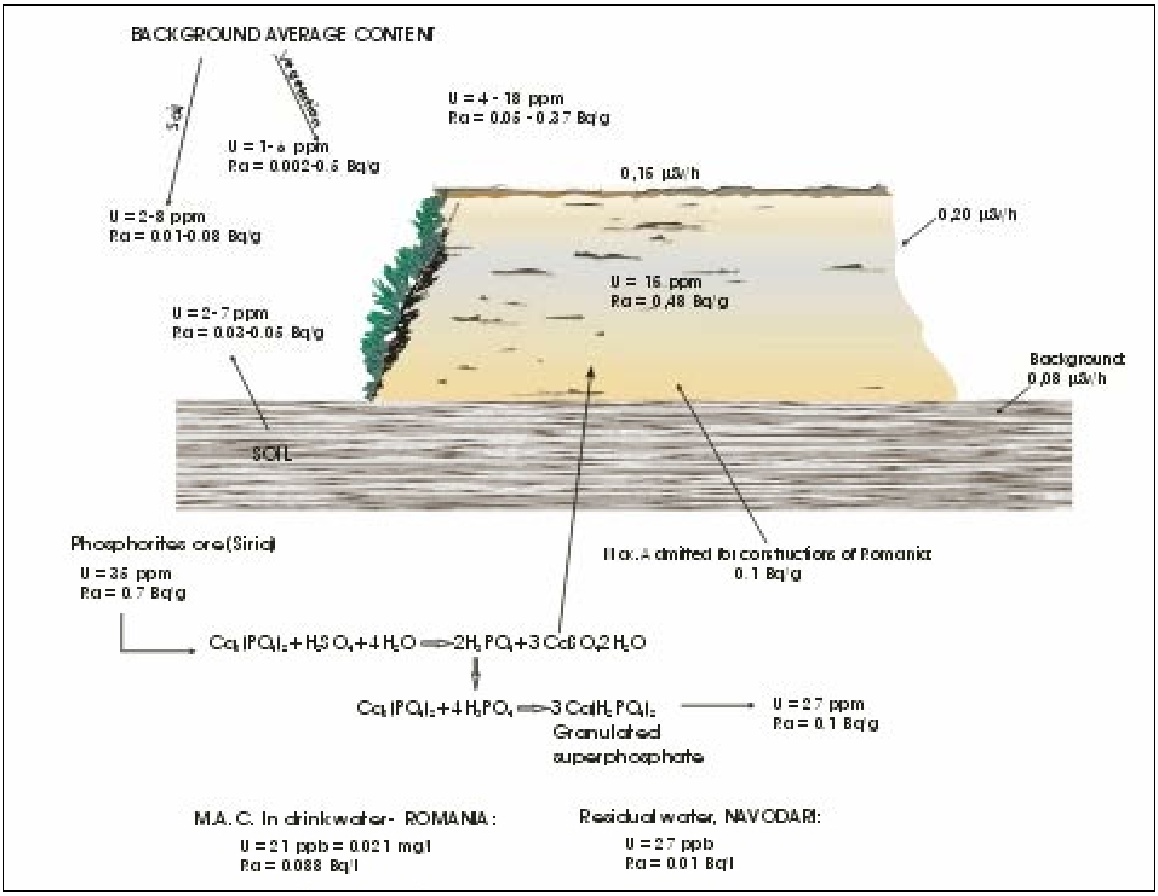

FIG. 1. Phosphogypsum dump — Năvodari.

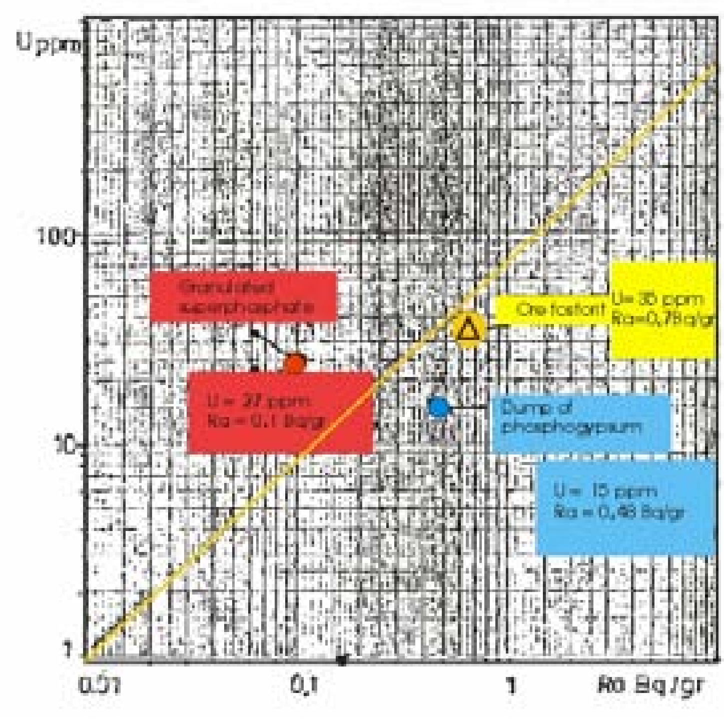

FIG. 2. Distribution of Uranium and Radium in the raw material, phosphogypsum and granulated superphosphate — Năvodari.

2.1.2. Plant residues from SC Sofret SA, Bacau

The phosphogypsum generated by H_2SO_4 attack of imported phosphate rock has been deposited since 1978, close to the plant, which is located in the eastern part of Bacău city. The phosphogypsum is removed from the plant by a conveyor belt and occupies an area of 28 ha.

Over the past year, ore for processing has been imported from Togo and has the following composition — U: 117 ppm, ^{226}Ra: 1.3 Bq/g, Th: 27 ppm, K: 1.5%. The gamma dose rate from the ore was 0.5–1.3 μSv/h and the radon and thoron concentrations were 104 and 346 Bq/m^3 respectively.

In potassium chloride ore imported from Russia, the radon and thoron concentrations were 22.2 and 0 Bq/m^3 respectively. The ore has the following composition — K: 57.08%, U: 2 ppm, ^{226}Ra: 0.015 Bq/g.

The following composition was measured in samples collected from the surface of the phosphogypsum deposit and also from drilling to a depth of 16 m — U: 15–21 ppm, ^{226}Ra: 0.45–0.87 Bq/g, Th: <3 ppm, K: <1%, gamma dose rate: 0.18–0.25 μSv/h. The radon and thoron concentrations at the pond surface (irregular areas) were 4860 and for 496 Bq/m^3 respectively.

2.2. Plants based on HNO_3 attack

The only process waste is calcium carbonate at the calcium nitrate conversion stage. The product can be easily filtered, and is very reactive when used as an agricultural additive. The particle size is 40–100 μm, the medium size fraction being 60–80 μm. The moisture content is a maximum of 15% free water when sent to the waste heap. The waste calcium carbonate quantity depends entirely on the CaO content in the phosphate rock used at the nitro-phosphate plant. At a capacity of about 300 t/day P_2O_5, 100% in complex fertilizers, for the average rock quality, about 700 t/day (231 000 t/a) of dry calcium carbonate are generated.

At the plant SC Azomures SA, located in the western part of Targu-Mures city, the tailings pond containing process water and calcium carbonate occupies an area of about 33 ha near the plant. The raw material imported from Morocco and Kola has the chemical composition shown in Table I.

- The process water from the tailings pond has the following composition — pH: 1.45, U: 0.045 mg/L, ^{226}Ra: 1.4 Bq/L;
- The calcium carbonate has the following composition — U: 23 ppm, ^{226}Ra: 0.35 Bq/g, Th: 2 ppm, K: 0.2%.

2.3. Radioactivity in fertilizers

The radioactivity in fertilizers depends on the chemical composition of the raw material used for their production, as well as on the type of attack process used. The results are shown in Table II and Fig. 3.

TABLE I. COMPOSITION OF IMPORTED PHOSPHATE ROCK

Constituent	Concentration	
	Morocco	Kola
P_2O_5	24.13%	34.23%
CaO	52.32%	45.7%
MgO	0.26%	0.5%
F	3.56%	3%
Na_2O	0.77%	0.3%
SiO_2	1.75%	10%
Al_2O_3	0.33%	4%
Fe_2O_3	0.5%	—
U	131 ppm	11 ppm
^{226}Ra	1.51 Bq/g	0.125 Bq/g
K	0.07%	0.10%
Th	3 ppm	17 ppm

TABLE II. RADIOACTIVITY IN FERTILIZERS

Type of fertilizer	Concentration of radioactive constituents								
	Bacau (H_2SO_4 attack)			Navodari (H_2SO_4 attack)			Targu-Mures (HNO_3 attack)		
	U (ppm)	^{226}Ra (Bq/g)	Th (ppm)	U (ppm)	^{226}Ra (Bq/g)	Th (ppm)	U (ppm)	^{226}Ra (Bq/g)	Th (ppm)
Ammonium nitrate	—	—	—	—	—	—	5	0.015	2
NPK	2	0.015	1	—	—	—	21	0.26	6
NP	5	0.079	38	—	—	—	29	0.36	4
Granulated superphosphate	—	—	—	27	0.1	3	—	—	—

3. ALUMINIUM INDUSTRIES

3.1. Bauxite mining and processing

Bauxite is the most important raw material for aluminium production. It is a mixture of aluminium hydroxides, with iron hydroxides and oxides (specular iron, goethite), with hydrated aluminium silicates, colloidal silica, titanium dioxide and water. The composition of bauxite varies appreciably: Al_2O_3: 40.75%, Fe_2O_4: 2–37%, SiO_2:1–25%, TiO_2: 1–5%, H_2O: 8–28%. The bauxite used in aluminium production has to contain over 45% Al_2O_3 in the ratio $Al_2O_3/SiO_2 = 3$.

In Romania, the exploitable bauxite deposits are located in the Padurea Craiului region. Their origin has been widely discussed. Until 1970, the accepted theory was that the aluminium ore represented the lateritization products of aluminium-rich clay impurities from the tithonic limestones in tropical climate conditions. These products have been concentrated in the karst relief of tithonic limestones and covered by Neocomian limestones. This concept, which was well accepted by many researchers from other countries, was gradually replaced with the concept that the initial material lateritic transformed even for bauxite located on limestones was constituted from andesite through their pyroclastic products.

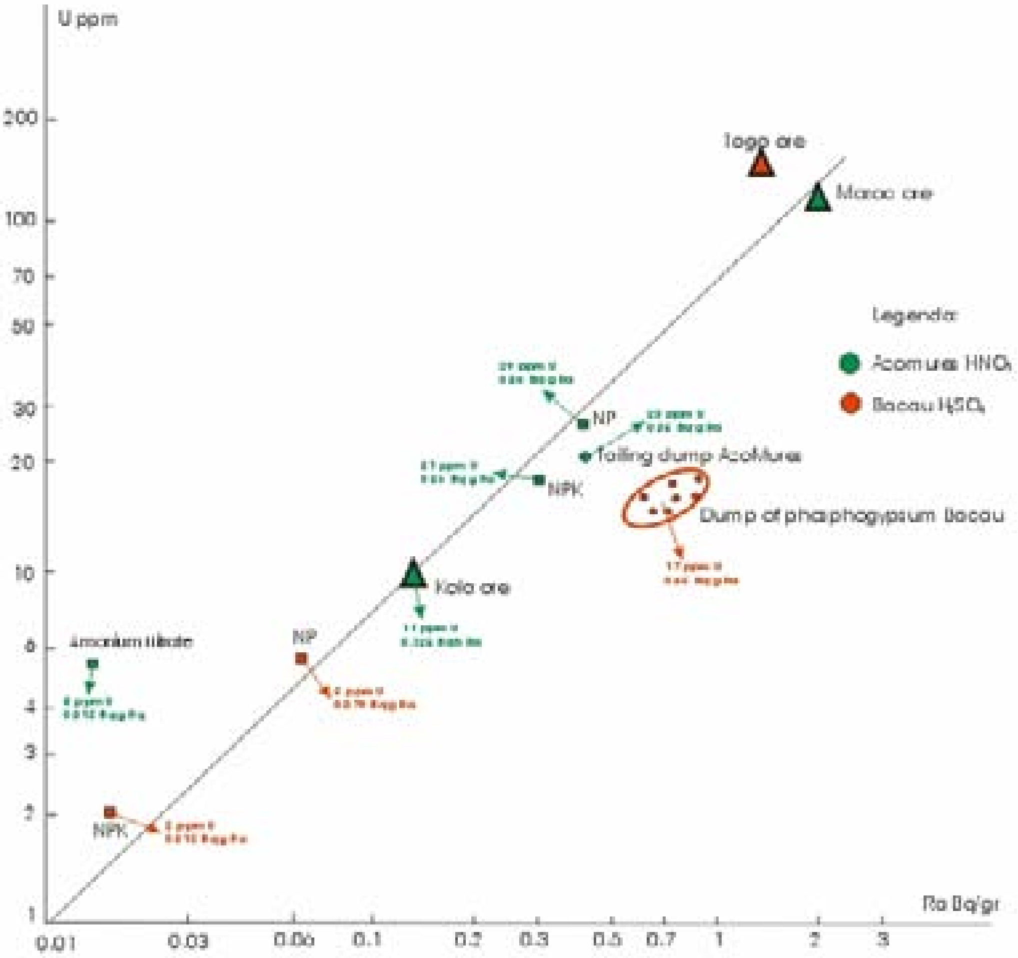

FIG. 3. The distribution of uranium and radium in raw material, phosphogypsum and phosphate fertilizers.

The chemical composition of the ore exploited from the Rosia zone, processed at that time at the Dobresti plant, was as follows — SiO_2: 4.5%, Al_2O_3: 55%, FeO: 0.5%, Fe_2O_3: 25%, TiO_2: 3%, CaO: 1%, ppc: 11%. The mineralogical components are:

• Kaolin	8%
• diaspore + boehmite	53.6%
• leptochlorite	0.63%
• hematite	24.8%

The radioactivity levels in the process materials at the Dobresti plant are presented in Table III. The radioactivity levels in the air and water at the Rozia mine and the Dobresti processing plant are presented in Table IV.

The processed ore from the Dobresti plant used to be transported to the alumina plant at Oradea. This activity has been suspended for 1 year.

Concerning the centres of alumina and aluminium manufacturing in Romania, alumina is produced in our country at Oradea (from the bauxite exploited from the Padurea Craiului Mountains) and at Tulcea (from imports).

TABLE III. RADIOACTIVITY IN PROCESS MATERIALS AT THE DOBRESTI PLANT

Process material	Concentration of radioactive constituents		
	Uranium (ppm)	^{226}Ra (Bq/g)	Thorium (ppm)
Bauxite stock before grinding	12	0.162	30
Final product after washing	<10	0.062	31
Neutralized phosphogypsum	10	0.11	22
Material from Dobresti pond	<10	0.087	28
Ore from Gallery 2, Rosia	16	0.112	41

TABLE IV. RADIOACTIVITY IN AIR AND WATER AT THE ROSIA MINE AND DOBRESTI PROCESSING PLANT

Medium	Concentration of radioactive constituents			
	Radon	Thoron	Uranium (mg/L)	^{226}Ra (Bq/L)
Rosia mine				
Air from gallery	55 Bq/m^3	208 Bq/m^3	—	—
Mine water	0.161 Bq/L	0 Bq/L	0.0044	0.018
Dobresti processing plant				
Air from bauxite deposit	0 Bq/m^3	127 Bq/m^3	—	—
Water from bauxite washing	12.9 Bq/L	—	0.010	0.04
Water from bauxite processing pond	3.96 Bq/L	0 Bq/L	0.0010	0.006

3.2 Red sludge

3.2.1. Alumina plant at Oradea

In the western area of Oradea city there is a bauxite processing plant. The red sludge pond resulting from alumina extraction is shown in Fig. 4. The radioactive constituents of the pond are shown in Table V. The radioactivity levels in the air and water at the pond are presented in Table IV.

TABLE V. RADIOACTIVITY IN THE RED SLUDGE POND AT ORADEA

Material	Concentration of radioactive constituents		
	Uranium (ppm)	^{226}Ra (Bq/g)	Thorium (ppm)
Material of red colour	11	0.21	61
Material of dark colour	<10	0.137	70
Material of light colour	127	1.675	11

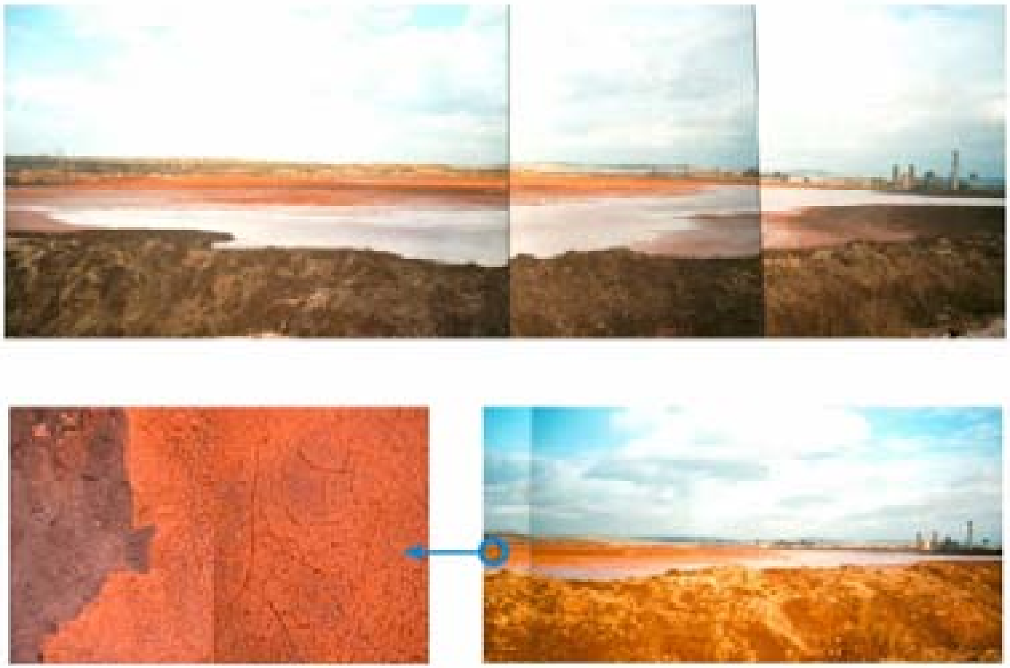

FIG. 4. *The red sludge pond from bauxite processing, Oradea.*

TABLE VI. COMPOSITION OF THE AIR AND WATER AT THE RED SLUDGE POND, ORADEA

Medium	Concentration of radioactive constituents			pH
	Radon	Thoron	^{226}Ra	
Air at the pond surface	21 Bq/m^3	1220 Bq/m^3	—	—
Water from the pond	3.74 Bq/L	0	0.023 Bq/L	12.05

3.2.2. Alumina plant at Tulcea

A map of the bauxite processing plant and the red sludge pond at Tulcea is shown in Fig. 5. The radioactive constituents of the imported raw material, red sludge, and the air and water at the red sludge pond are shown in Table VII.

TABLE VII. COMPOSITION OF PROCESS MATERIALS, AIR AND WATER AT THE TULCEA ALUMINA PLANT

Process material	Concentration of radioactive constituents					pH
	Radon (Bq/m^3)	Thoron (Bq/m^3)	Uranium (ppm)	^{226}Ra (Bq/g)	Thorium (ppm)	
Imported raw material:						
Brazil, Trombeta zone	—	—	40	1.5	21	—
Guinea Bissau, Boke zone	—	—	17	0.27	27	—
Red sludge	—	—	15	0.212	62	—
Water from pond	—	—	0.010	0.026	—	12.2
Air at pond surface	248	6270	—	—	—	—

FIG. 5. Tulcea bauxite processing plant and the red sludge pond.

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ENVIRONMENTAL POLLUTION

SOIL CONTAMINATION IN A RURAL SITE USED FOR RARE EARTH INDUSTRY BY-PRODUCT DISPOSAL

C. Briquet, M. Cipriani, A.C. Ferreira

Comissão Nacional de Energia Nuclear (CNEN),*
Rio de Janeiro, Brazil

Abstract

In the past, the chemical processing of monazite sand for production of rare earth elements was performed in São Paulo State. This industry produced large quantities of by-products and wastes: cake II (uranium and thorium hydroxides) and mesothorium cake ($Ba(Ra)SO_4$). At that time the Brazilian Nuclear Energy Commission, CNEN, did not have regulations for this kind of activity. From 1975 to 1981, 3500 t of cake II were stored in seven rectangular pools with 180 m^3 capacity each. These pools were built in a country area of the São Paulo State, a region of farms. A river flows across the property into the public water supply of a city, 12 km from the site. Activity concentrations of ^{228}Ra up to 70 000 Bq/kg were identified in the soil by a previous survey, which indicated that the site was contaminated by radionuclides of the ^{232}Th series. The inhabitants of the region are very concerned about the situation. The aim of this paper is to present the actual status of this storage site, and to discuss the preliminary results of the area radiological characterization.

1. INTRODUCTION

The chemical processing of monazite performed by a Brazilian industry has produced two radioactive residues:

- Thorium concentrate cake, a by-product named cake II with an average content of 20% thorium hydroxide and 1% uranium hydroxides, and a specific activity around 1800 Bq/g;
- Mesothorium — $Ba(Ra)SO_4$ — a waste with a specific activity around 4400 Bq/g.

Approximately 3500 t of cake II were stored on a 283 679 m^2 site located in a farm region encircling a basin, streams of other declivities, eight wells and nineteen springs that supply the local inhabitants (Fig. 1). It is crossed by a brook that flows into a river supplying a large town 12 km away. The cake was stored in seven rectangular pools 3.5 m deep with concrete walls 15 cm thick. Each pool is 1 m above the soil surface and 2.5 m underground (Fig. 2).

From 1975 to 1981, when the pools were filled, there was a lack of national regulations on this kind of industrial residue. Neither radiological environmental impact nor geological studies were considered in the choice of the storage place [1]. At the moment, CNEN is preparing regulations regarding NORM processing industries and also for intervention in these situations. In the past, the monitoring programme performed by The Institute for Radiation Protection and Dosimetry (IRD/CNEN) showed values up to 4.0 Bq/L for ^{226}Ra, with average values of 0.1 Bq/L in a site well [2]. The same programme has pointed out some

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* E-mail: cbriquet@cnen.gov.br, cipriani@cnen.gov.br, aloisio@ird.gov.br

soil contaminated areas with activity concentrations of up to 70 000 Bq/kg for ^{228}Ra, 890 Bq/kg for ^{226}Ra and 13 000 Bq/kg for ^{238}U [3]. The aim of this paper is to present the actual status of this storage site and to discuss the preliminary results of the radiological soil characterization.

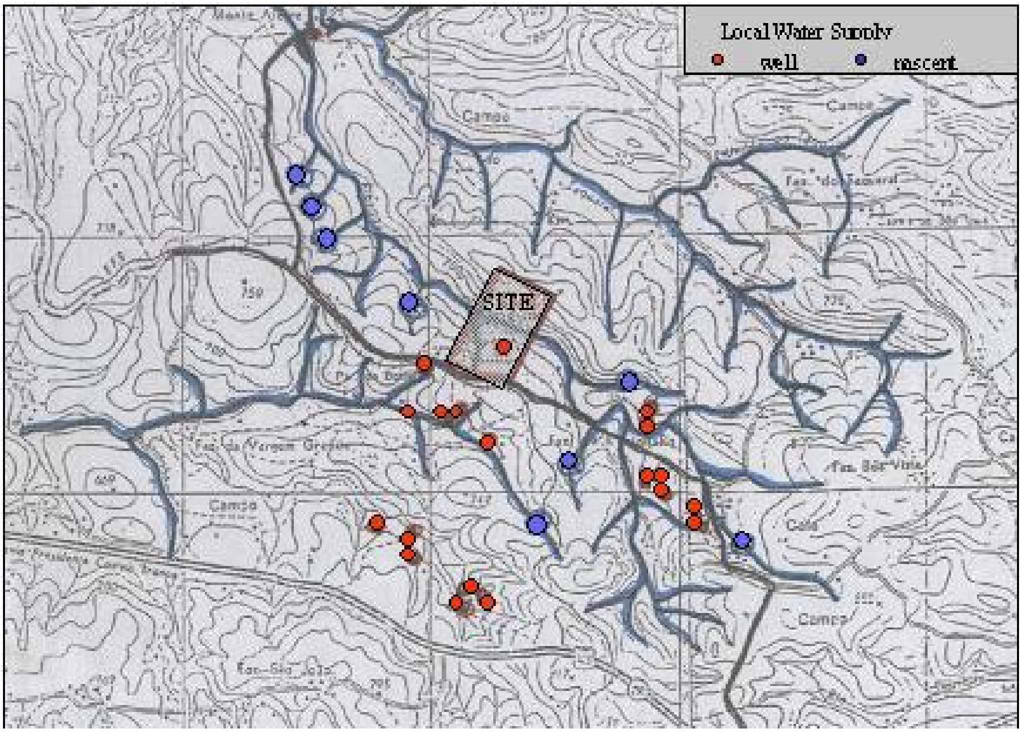

FIG. 1. Diagram of local water supply

FIG. 2.Concrete storage pools

2. METHODOLOGY

According to MARSSIM methodology [4], the site was subdivided into 6 survey units, classified as impacted or not impacted on the basis of the historical site assessment. Four survey units (Fig. 3) were defined as having higher potential for radioactive contamination: units A, B and C located around the pools, and unit D outside the storage area fence in the slope of a hill and along the preferential direction of water flow.

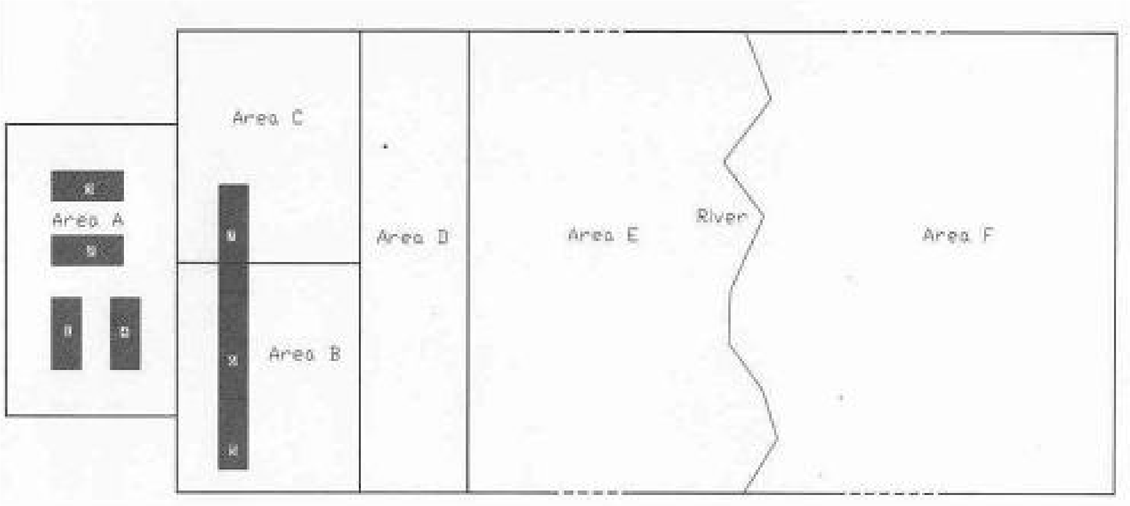

FIG. 3. Soil characterization areas

In order to optimize the screening, a triangular grid system was applied to these units, as this is more efficient for locating small contaminated areas (Fig. 4). The distance between points of the grid was 11 m and the points were located with a theodolite. The number of data points for each survey unit, calculated with the Wilcoxon Rank Sum Test [4], was 10. The same number was used for the non-impacted area (Area F), and low potential area (Area E). In these units, where no contamination was expected, the 10 soil samples were taken at random. Units A, B and C each have an area of approximately 2000 m^2. Unit D was around 800 m^2 and unit E around 60 000 m^2.

As a background reference, the region on the other side of the river was selected (Area F), clearly a non impacted area, with a forest undisturbed by human activities, and biological, chemical and physical characteristics similar to the original environment of the site.

Surface (15 cm) and subsurface (150 and 300 cm) soil samples were collected at each point; each sample consisted of 2 kg, conditioned in plastic bags.

3. RESULTS AND DISCUSSION

As the storage facility is a site established from a past practice, some of the information describing its complete history, from the start to the present time, is lacking. The authors are still collecting information to complete the site historical assessment. Older facilities such as this are far from compliance with current legislation and must be accommodated in the new safety documentation requirements. Conditions may have changed since the previous surveys — the owner of the property allegedly removed 2 m of superficial soil from the site. Thus, some ‘hot spots’ identified by the monitoring programme measurements might no longer exist in the surface soil layer, underlining the importance of this new site characterization.

The soil samples for background evaluation were analysed using a LEGe detector, Canberra model GL2020R,. The background samples showed an average value of 39.2 Bq/kg for ^{228}Ra, the highest value being 58.8 Bq/kg and the lowest 17.3 Bq/kg.

Although the site characterization is not complete, the preliminary results have identified three hot spots in area A with ^{228}Ra concentrations in the range 339–2965 Bq/kg. In area D, two hot spots were identified, showing values of 3650 and 3810 Bq/kg for ^{228}Ra, the latter being 97 times the average background. The samples from area B have not yet been analysed. In area C, two points with ^{228}Ra concentrations of 274 and 712 Bq/kg were identified.

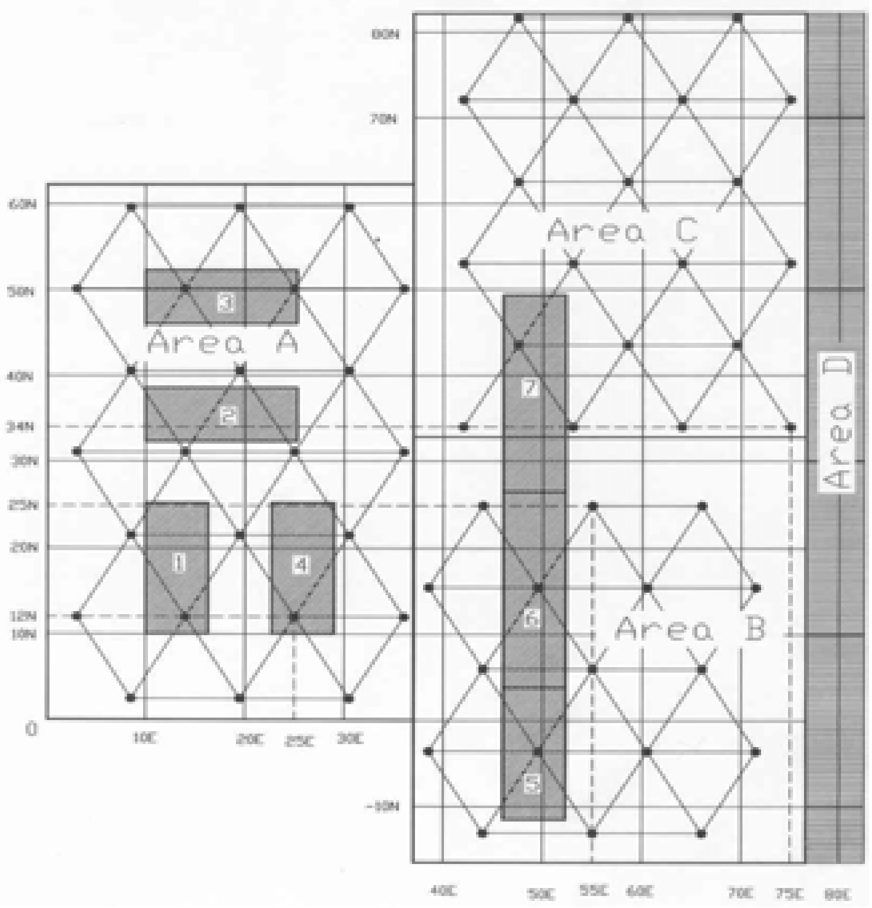

FIG. 4. Triangular grid adopted to determine soil sample locations

In the past, the radiological environmental monitoring programme performed by São Paulo State Environmental Protection Agency CETESB and CNEN showed, in a well on site, values up to 4.0 Bq/L for alpha activity and 3.6 Bq/L for beta activity [2]. Other measurements in wells off site showed values not exceeding 0.08 Bq/L for ^{226}Ra and 0.01 Bq/L for ^{228} Ra, which are considerably below the 2001 Ordinance of the Ministry of Health, which prescribes limits of 0.1 Bq/L for alpha emitters and 1 Bq/L for beta emitters.

Up to now, the origin of the contamination is still unknown, with two possibilities to be tested:

- Impact from the storage site — fracturing of the bottom of the pools due to deterioration from long term storage, causing migration of radionuclides;
- Past contamination of the surface soil due to spilling that took place during material transportation and filling of the pools, eventually causing migration of radionuclides to the water table.

Both possibilities have associated regulatory aspects — for the first possibility, a lack of regulations to guide the original construction and safety evaluation to CNEN radioprotection standards and, for the second possibility, poor training of workers. CNEN started regulating radiological occupational and environmental surveys after the site construction. Testing this hypothesis will be fundamental to support the decision-making process about the site.

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THE ASSESSMENT OF EXPOSURE TO IONIZING RADIATION AT SPOIL BANKS

B. Michalik[*]

Central Mining Institute, Laboratory of Radiometry,
Katowice, Poland

Abstract

Until 1970, Polish hard coal mining was not considered to be a source of radiation exposure arising from the presence of enhanced concentrations of natural radionuclides. After radioactive scales in pipelines for the draining of brines had been found, a need emerged for an assessment of the radiological risk. During the next few years, many different surveys were carried out, resulting in a comprehensive system of occupational radiological protection. In 1982, in accordance with the relevant national regulations, enforcement of the system was extended to the whole of Polish underground mining. The system of protection consists of systematic measurements of particular factors contributing to the miners' radiation risk, such as radioactive aerosols, sediments and waters. Unfortunately, less attention has been given to exposures that can occur as a result of the release of naturally radioactive materials to the environment. The territory around the Upper Silesian Coal Basin is densely populated. Since the phenomenon of enhanced natural radioactivity has become well known to members of the public, many social problems are emerging. The majority of them were, unexpectedly, related to waste rock piles that were deemed to be as hazardous as radioactive scales and sediments. According to the claims of local society, an assessment of the radiation exposure at waste rock piles had to be done. Concentrations of natural radionuclides in samples extracted from underground rocks slightly exceed the natural background on the earth's surface. This results in an enhanced gamma dose rate at places where this kind of waste was dumped. Additionally the structure of spoil banks creates the possibility of an increase in radon exhalation. Taking into consideration the total amount of spoil and gangue and the current international recommendations, the enhanced level of external radiation and radon exhalation seems to be significant from the point of view of radiological science. Due to the fact that the waste rock has not undergone any chemical transformation, the potential for enhanced radiological risk is directly related to the geological origin of the rock that constitutes that waste. Therefore, two different mining regions have been chosen for investigation. The coal seams exploited in those regions lie in different carboniferous systems, so the properties of the rocks occurring with the coal differ from each other. Measurements of radiation risk have been done on three waste rock piles that vary in age and state of land reclamation. For comparison, the same measurements have been done in neighbouring rural areas. The results of investigations show that the major contribution to the slightly enhanced radiation risk at these areas arises from external radiation due to the enhanced concentration of natural radioactivity in the waste material.

1. INTRODUCTION

Mining activity leads to two different scenarios in which the occurrence of diverse waste results in an enhanced radiation risk to workers and members of the public. In the first scenario, radium-bearing brines discharged from mines into surface water bodies, and the sediments precipitated from them, have to be taken into consideration. The second scenario

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[*] E-mail: b.michalik@gig.katowice.pl

includes all kinds of gangue (waste rocks) extracted with hard coal. The radionuclide concentration in this kind of waste is not found to be so high, but it is very often higher than the average concentrations in soil.

The phenomenon of radioactivity in saline water from coal mines in Poland was discovered in the 1960s [1]. Later, investigations showed that the radium concentration in water was correlated with the salinity [2]. In some cases, the concentration of total dissolved solids (TDS) exceeds 200 kg/m^3, while the radium concentration may reach 400 kBq/m^3. The analysis of radium isotopes in underground inflows showed that the total input of ^{226}Ra (in all currently working collieries) was about 725 MBq per day, while the corresponding value for ^{228}Ra was roughly 700 MBq per day [3]. In coal mines, two types of brine were distinguished. In the so-called type A brines, ions of barium and radium are present while, in type B brines, only radium ions and sulphate occur [4]. From type A brines, radium isotopes easily precipitate out as sulphates with the barium carrier after mixing with water rich in sulphate ions. In the case of type B brines, precipitation does not occur due to the lack of the barium carrier. Radium is removed from such water in a slow process of sorption on bottom sediments. These two processes are the source of sediments with enhanced radium content [5]. Due to local hydrogeological conditions, less than a half of the total yearly amount of radium remains in the underground galleries while about 60% is transported with the pumped water to settling ponds on the surface. [6]. The main task for these ponds is to remove the suspended matter from the underground water before discharging to rivers. Incidentally, depending on the dimensions of the settling ponds and their retention periods, a certain fraction of the radium carried with water is deposited together with the suspended matter on the bottom and banks. The amount of sediments deposited depends on the type of the water. In the case of type A water, it can be up to 90%, while in the case of type B water it is only about 7%. The specific activity of radium isotopes in these sediments may sometimes reach 400 kBq/kg [5], so they constitute an important source of contamination of the natural environment in the surrounding area. In spite of precipitation and sorption, the significant fraction of radium is released into rivers. The majority of Polish hard coal mines lay on river basins of the Oder and the Vistula rivers — this leads to enhanced concentrations of radium in these rivers, even several tens of kilometres from the point of mining water discharge [7].

The radiation risk to members of the public caused by these phenomena is rather low, despite a very wide range of specific activities of radium observed in the sediments. Currently, all the settling ponds are located in areas that belong to particular collieries. Access to these areas is restricted to authorized personnel — this is why the potential for exposure to external radiation is limited to exposure of the staff engaged in certain practices and ultimately controlled within the framework of occupational risk monitoring. Additionally, during normal exploitation, settling ponds are filled with water that constitutes a cover against external radiation from the bottom sediments. A serious problem will emerge in the near future when the mines are closed. So far, an inventory of all settling ponds of interest (from the radiological point of view) has been prepared [8].

The second kind of waste produced by hard coal mining differs from the first in terms of the total amount and specific activity of particular natural radionuclides. This kind of waste consists of diverse rocks that have been extracted together with hard coal. Hard coal exploitation has been carried out in the Upper Silesian Coal Basin since the 16th century, and the average yearly production of coal after World War II was about 100 million t. Thus it is not so easy to find in this area a place that has not been affected by mining activity. Up to 20% of the surface of the Upper Silesian conurbation is covered with waste material originating from collieries. The current production of hard coal (about 80 million t/a) causes the emergence of a few square kilometres of new spoil banks each year. The radionuclide concentration in this kind of waste is not found to be so high, but it is very often higher than average concentrations in soil. Although the specific activity of certain natural radionuclides in the waste rock is only a few times more than in the surrounding area, the related radiation risk can be significant when taking into account the high population density of Upper Silesia. In comparison with the risk caused by the sediments, this potential risk was considered not significant enough to warrant any assessment effort. This led to a lack of reliable data, resulting in a situation where the waste rock heaps are sometimes regarded by the local population as being as dangerous as radioactive waste.

2. SITES OF INVESTIGATION

The waste rock from the hard coal industry generally consists of two categories, created during different stages of coal exploitation. The first one, gangue, is created during the driving of shafts and underground galleries. This category contains all kinds of carboniferous rocks. The second category consists of tailings from coal cleaning sub-processes such as coal wet or dry cleaning, jigging, sink–float. This category contains mainly carboniferous argillaceous rocks originating from the floor or roof and the interlayer.

During the process of exploitation, the chemical properties of this type of waste have not changed and it was not possible for any sub-process to lead to an exchange of matter with the surrounding area. Thus, the potential for an enhanced radiation risk is related only to the primordial properties of the waste rock resulting from its geological origin. Therefore, in order to carry out the radiation risk estimation properly, two different mining regions were chosen for survey. Coal seams exploited in these regions lie on different carboniferous systems, so the properties of the rocks occurring with the coal differ from each other.

In these regions, measurements of radiation risk were carried out on three waste rock piles that varied in age and state of restoration. For comparison, the same measurements were done in neighbouring rural areas where, according to available information, no kind of waste had ever been stored. These sites were named Areas I and II respectively (Table I). In order to create an additional opportunity for comparison, one more area was chosen. This was a military training area in a neighbouring province, far from the mining areas under investigation. This region had never been subjected to any kind of mining activity. For the purpose this work, the site was termed ‘neutral territory’.

TABLE I. GEOLOGICAL CHARACTERISTICS OF MINING REGION CHOSEN FOR INVESTIGATION

Location	Chronostratigraphical classification	Beds	Petrgraphical composition	Mineralogical composition
Area I	Crakow sandstone series	Łaziska and Libiąż beds	Sandstone (variable-graded), arkose-sandstone, siltstone, shists, silstone	Quartz, kaolinite, chlorite, pyrite
Area II	Upper Silesian sandstone series	Orzesze, Załęże, Ruda beds	Siltstone, siltstone-coal shists	Calcite, siderite, dolomite

The first area of investigation was located close to the town of Bieruń, where waste rocks were used as landfill in an area of about 13 ha that had collapsed due to underground mining activity. About 1.5 million m^3 of waste rock had been used for this purpose. About two thirds originated from a coal cleaning process. The remaining third consisted of gangue. This area was earmarked as a recreation park for local residents. In this case, two series of measurements were carried out. The first was done where initial biological land reclamation had just been carried out. The second was performed in an area that was still under exploitation, on which fresh waste rocks were being dumped.

The second area of investigation was near the town of Rybnik. In this case, two completely different sites were chosen. The first one, ‘Stara Hałda’, was an old waste rock heap. Exploitation had been completed in 1950. In the course of time, the process of self-reclamation went on and now this heap is overgrown with birches a few metres high. This heap contains about 0.6 million m^3 of waste rock, mainly burned carbonaceous shale, and occupies an area of 6 ha. The second site where investigations were done was quite new in comparison with the first. It was the waste rock dump ‘Rejon D’ that had been being exploited for a few years and then was prepared for land reclamation. The area of this waste dump was about 16 ha. The altitude of all the investigated sites, including reference areas and neutral territory, was 200–300 m.

3. RISK FACTORS AND MEASUREMENT METHODS

To ensure an adequate risk assessment, the following radiation risk factors were taken into consideration:

(a) The specific activities of ^{226}Ra (from the uranium decay series), ^{228} Ra (from the thorium decay series) and ^{40}K.

All specific activities were determined by high-resolution gamma spectroscopy with germanium detectors and Genie 2000 software from Canberra. The concentration of ^{226}Ra was measured using the 186.2 keV energy peak, the concentration of ^{228}Ra through ^{228}Ac, and the concentration of ^{40}K directly from the 1461 keV energy peak. The measurement system was calibrated using a set of standard samples. The standard samples consisted of an adequate carrier with very low activity and a known amount of a reference material. All substances used for the carriers had been pre-screened for gamma-emitting radionuclides. IAEA Gamma Spectrometry Reference Materials RGU-1 for the uranium series, RGTh-1 for the thorium series and RGK-1 for potassium were used for the efficiency calibration. The calculation of the efficiency curve was based on standard samples for each detector. It was very important that as basic points for efficiency calculation were taken into account only the lines derived from radionuclides whose specific activity had been being intended to measure in waste rock and environmental samples. The total uncertainty, at one sigma level was in each case less than 10% and the minimum detectable activity for a particular determined isotope was less than 1 Bq/kg.

The measured samples were crushed and sieved to a grain size of smaller than 2 mm. In addition, grinding samples were dried at 105°C to a stable mass. Depending on the intended detector, the prepared sample was put into the relevant measurement container. Three kinds of measurement containers were used — polyethylene Marinelli containers with volumes of 1, 0.6 and 0.11 L.

(b) Air kerma free-on-air, K_a, above the ground.

This was measured by a Gamma-31 dosimeter. This dosimeter, around 30 mm in diameter, 8mm high and 7 g in weight, was equipped with 3 MCP-N thermoluminescence detectors (TLDs). These TLDs had been made as sintered discs, about 1 mm thick and 4.5 mm in diameter. They were built on the base of the LiF luminophore with dopants such as Mg,Cu,P. It was a very sensitive luminophore but required quite a precise annealing process at temperature-controlled conditions of 240^{o}C ± 2^{o}C over a period of 10 min. Its sensitivity was ten times higher than that of the popular LiF:Mg,Ti TLDs.

Every dosimeter was marked with permanent signs and could be used as a personal dosimeter or only as an environmental one. If necessary, they could be sealed with lead.

After the TLDs had been annealed according to the relevant procedure, the dosimeters were exposure at the appropriate site for one month. After exposure, the dosimeters were returned to the laboratory where the TLDs were read out and calibrated using a certified ^{137}Cs source. Afterwards, air kerma rates were evaluated. The measurement uncertainty at a 95% confidence level, a dose rate of 0.07 μGy/h and a one-month exposure time was less than 7%.

(c) Concentrations of radium isotopes in seepage from the spoil banks and surface waters in the vicinity.

The concentrations were determined by a method that enables simultaneous determination of ^{226}Ra, ^{228}Ra and ^{224}Ra [9]. In essence, radium was co-precipitated with a barium carrier and lead, and then the precipitate was dissolved in EDTA. After that, radium was separated from Pb by co-precipitation of Ra and Ba as sulphates at pH = 4.5. The barium–radium sulphate precipitate was mixed with a gelling scintillation cocktail, which ensured that the precipitation was suspended uniformly in the whole volume of the scintillation cocktail. Afterwards the sample was measured using a low-background Wallac Quantulus 1220$^{\text{TM}}$ LS spectrometer that had heavy Pb shielding, selected construction materials of low radioactivity, an anticoincidence guard, a sophisticated spectrum analyser, and a pulse-shape analyser, which enabled α and β particles to be distinguished. For a sample prepared from 1 L of water, and with two 1 h measurements, the lower limits of detection at a confidence level 0.95 were as follows:

- ^{228}Ra: 20 Bq/m^3
- ^{224}Ra: 20 Bq/m^3
- ^{226}Ra: 3 Bq/m^3

(d) Radon concentration in soil gas.

This was determined by an alpha radiometer RGR equipped with an additional photomultiplier, enabling the read-out of Lucas cells. The soil gas samples were taken using a special pipe from a depth of approximately 1 m. The radon concentration was evaluated from the counting rate obtained 3 h after sampling. The method applied enabled the radon concentration in soil gas to be assessed with quite a low level of uncertainty (less than 15 %) and a low limit of detection (about 12 Bq/m^3).

All the applied measurement methods were certified in 1993 by the Polish Centre for Accreditation [10]. Determination of the specific activities of particular radionuclides and their distribution in waste or soil enables the value of dose rate (or air kerma free on air) above the ground to be calculated. Therefore, having the results of direct measurements of this quantity it was possible to make a comparison, to distinguish and then exclude the contribution to the total value of this quantity originating from agents not related directly to the properties of the waste rock, for example ^{137}Cs fall-out or cosmic radiation. This approach permitted a clear assessment of the potential increment in risk caused by external radiation from a waste rock pile. Additional information about the remaining factors, namely the radium concentration in surface water permeating the heaps, the radon concentration in soil gas and, finally, the stone dust concentration in the ground layer of atmospheric air, will complete the estimation of the total radiation risk.

4. SAMPLING

Taking into consideration that the contribution to the gamma dose rate coming from a source of radiation more than 10 m from the detector is negligible [11], it was assumed that the distance between the sampling points should not be greater than 20 m. According to this and to local conditions, the sampling points were placed along a straight line crossing the waste dump or in a grid covering a relevant part of the investigated site. In each point, three Gamma-31 detectors were exposed at 1, 2 and 3 m above the ground. Samples of waste or soils were taken from the surface and from a depth of 50 cm. At the majority of the sampling points, the radon concentration in the soil gas was double-checked, especially at sites where the permeability of the ground was very low. Samples of water were taken twice from small streams that were fed mainly by rainwater infiltrating the spoil banks, during summer and autumn. Finally, 190 samples of waste rocks and soil were taken, 306 Gamma-31 detectors were exposed, about 500 individual measurements of radon concentration in soil gas were done and 26 samples of water were analysed.

5. SPECIFIC ACTIVITY AND DOSE FROM EXTERNAL GAMMA EXPOSURE

The results of the gamma spectroscopy analysis suggested that the concentration of natural radionuclides in the samples collected on the surface did not differ from that of samples collected from a depth of 50 cm. Application of the statistical ‘t test’ to the average values of radionuclide concentrations in particular layers verified that they were equal. The results obtained proved that, except for one small part of the first investigation site (where land reclamation had been carried out), a homogenous distribution of radionuclides in the waste and soil could be assumed. Thus, the average concentration values for radium and potassium isotopes were calculated. These are presented in Figs 1–4.

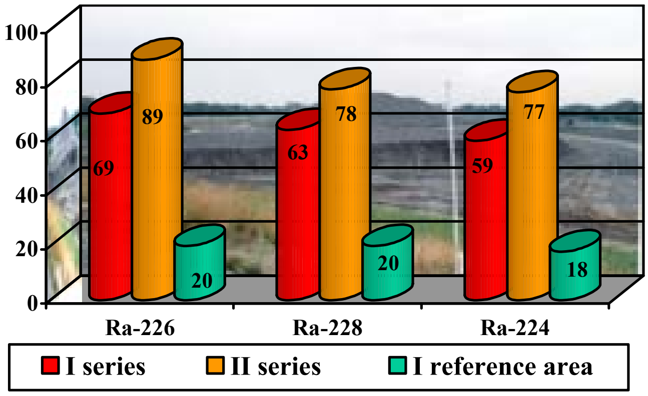

FIG. 1. Specific activity (Bq/kg) of waste rocks and soil from the first area of investigation

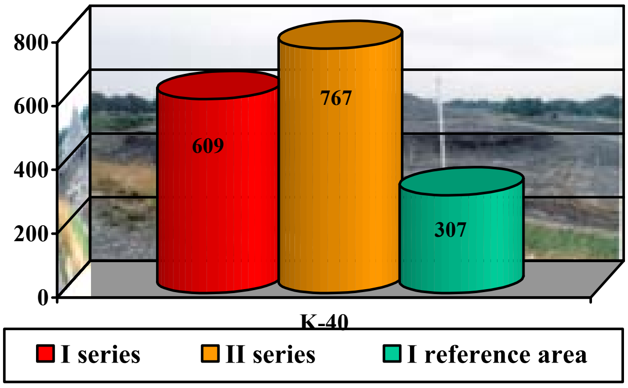

FIG. 2. Specific activity (Bq/g) of waste rocks and soil from the first area of investigation

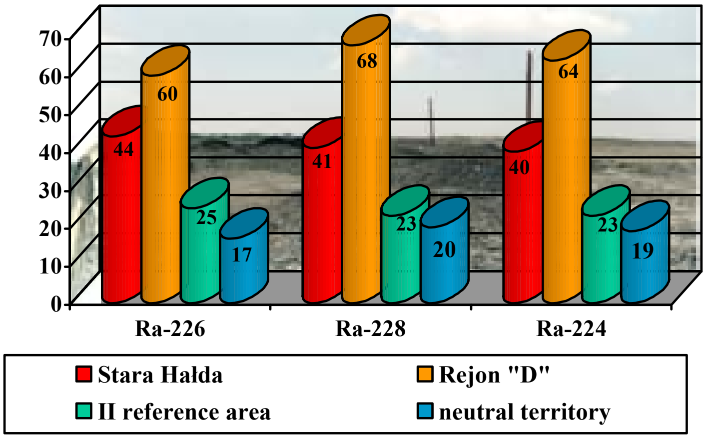

FIG. 3. Specific activity (Bq/g) of waste rocks and soil from the second area of investigation

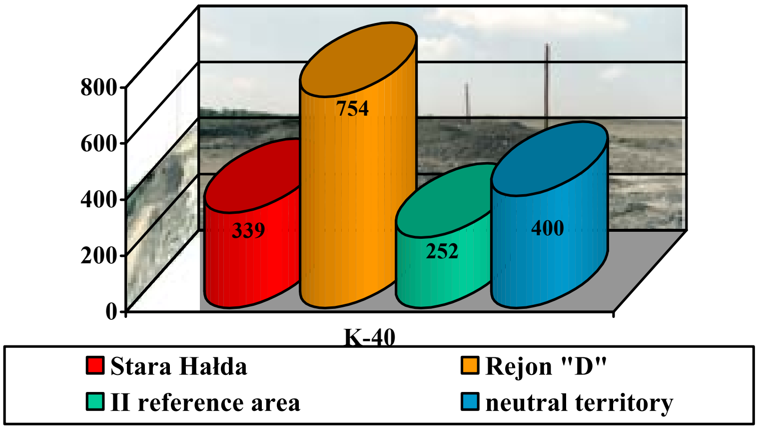

FIG. 4. Specific activity (Bq/g) of waste rocks and soil from the second area of investigation

The average activity concentration of the radium isotopes measured in the waste rock samples was a bit higher than in samples from the reference areas and the neutral territory. The biggest difference occurred in the case of the first site of investigation, where the specific activity of ^{226}Ra was four times higher than in the relevant reference area. The smallest one was observed on the Stara Hałda, where, probably due to the soil-creation process lasting for several years, the concentration of radium isotopes was diluted. Differences in ^{40}K concentration were not so high and do not exceed the upper limit of the range reported as typical for the earth's crust [12].

In the case of caesium, the situation was completely different. All waste rocks extracted from underground after the Chernobyl disaster were generally not affected by radioactive fall-out. Only a very small amount of caesium has been deposited on the surface of Stara Hałda due to precipitation or dust fall. In contrast, the concentration of caesium in samples taken from the reference areas, and especially from the neutral territory, was quite high and depended strongly on depth. The results of the ^{137}Cs specific activity measurements are presented in Fig. 5.

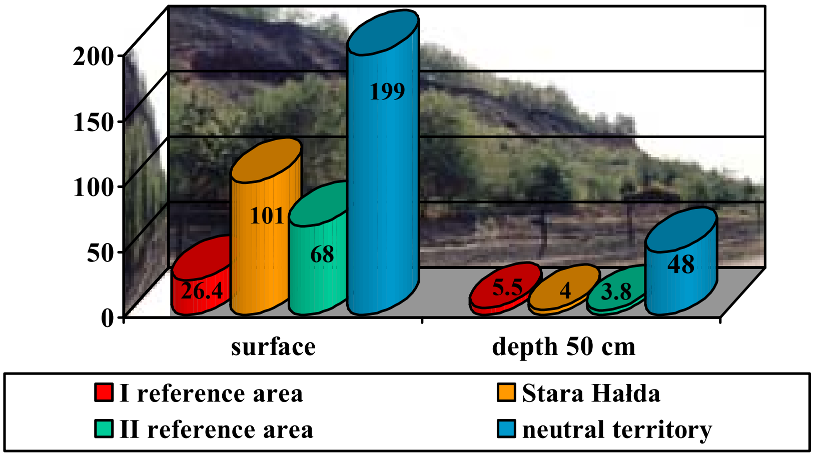

FIG. 5. Specific activity (Bq/g) of ^{137}Cs in waste rocks and soil in the second area of investigation

Based on the measured specific activity, the contribution of each constituent to the total air kerma rate above the ground was calculated. For this purpose, the following assumptions were made:

- The natural uranium and thorium series were in secular equilibrium. This fact was proven by the measurement of particular elements and isotopes included in the uranium and thorium series, namely: ^{214}Bi, ^{214}Pb, ^{228}Ac, ^{212}Pb, ^{212}Bi, ^{208}Tl.
- The average gamma radiation energy was 504 keV for the uranium series and 550 keV for the thorium series, respectively. Taking into account the ratio of the activity concentrations of ^{226}Ra and ^{228}Ra, the contribution of the 1460.75 keV energy peak from ^{40}K and, where necessary, the 661 keV energy peak from ^{137}Cs, the average energies for all investigated sites varied across the range 530–545 keV.
- An adequate approximation of the radiation source distribution is that of an infinite half space with a homogenous source concentration in the horizontal plane and where possible variations occur only with depth in soil or waste. For natural radionuclides, as proven, the uniform activity concentration distribution with depth was true. For ^{137}Cs, the model of decreasing exponential profile with depth was considered as the best.
- For the component coming from radionuclides occurring in the atmosphere at ground level, namely radon isotopes and their progeny, and beryllium, the simplest model, based on a semi-infinite cloud with uniform distribution in air was used.

The component of total kerma rate caused by natural radionuclides was then calculated using the following coefficients recommended in ICRP Publication 53:

- 0.462 μGy/h per Bq/g for the uranium series,
- 0.604 μGy/h per Bq/g for the thorium series,

- 0.041 μGy/h per Bq/g for ^{40}K.

The results are shown in Table II. For the sites where it was applicable, the ^{137}Cs contribution was estimated on the basis of relaxation mass (ICRP Publication 53). The results are presented in Table III.

TABLE II. THEORETICAL CONTRIBUTION OF NATURAL RADIONUCLIDES TO THE TOTAL AIR KERMA RATE 1 m ABOVE GROUND LEVEL

Site of investigation	Contribution to the total air kerma rate (nGy/h)
First area, series I	94.15
First area, series II	119.69
Reference area I	33.78
Stara Hałda	58.83
Rejon D	99.01
Reference area II	36.06
Neutral territory	36.04

TABLE III. CONTRIBUTION OF ^{137}Cs TO THE TOTAL AIR KERMA RATE

Site of investigation	Ground density (g/cm^3)		Specific activity of ^{137}Cs (Bq/g)		Relaxation mass (g/cm^2)	Kerma rate (nGy/h)
	Depth 10 cm	Depth 50 cm	Depth 10 cm	Depth 50 cm		
Stara Hałda	0.56	0.75	0.101	0.004	16	8.02
Reference area I	1.09	1.06	0.026	0.0055	32	3.15
Reference area II	0.81	1.09	0.068	0.0038	18	6.07
Neutral territory	1.08	1.24	0.1993	0.0475	36	26.20

Since all the investigated sites lay at a similar height above the sea level, the contributions from cosmic rays were assumed to be the same, at 33.8 nGy/h [13]. The impact of radionuclides dispatched in air was calculated from the results obtained during permanent control of air pollution that had been carried out for several years by a station located in CMI, Katowice. Although this was about 50 km from the investigated sites, there was no evidence to suggest any difference. The highest observed concentration of beryllium, 10^{-4} nGy/h, was used in the calculation. A similar approach was applied for the potential component of external radiation coming from radionuclides in dust suspended in air. The derived concentration of radionuclides was a few becquerels per cubic metre, so the contribution to the total kerma rate was less than the kerma rate calculated for beryllium.

The radon concentrations at the investigated sites were at normal levels (see Section 6), so the estimation of this constituent was based on measurements conducted in Katowice. Again, the highest observed value of radon progeny concentration was used in the calculation. Even then, the evaluated value of this kerma rate component was less than 7 nGy/h, where the average was 1.2 nGy/h. The kerma rates for all the calculated components are shown in the Fig. 6. The calculated values were compared with the average measured values. The results are presented in Fig. 7. Generally, the measured values agree closely with the calculated ones. Only in two cases — Reference area II and Stara Hałda — were the differences greater than the measurement uncertainty. This can be explained by attenuation of radiation by trees overgrowing these areas.

Taking into consideration all estimated constituents, it was possible to calculate the impact of the investigated spoil banks on the potential risk at their surfaces excluding all local conditions. The net values of total air kerma rate on all the investigated waste rock dumps are presented in Fig. 8.

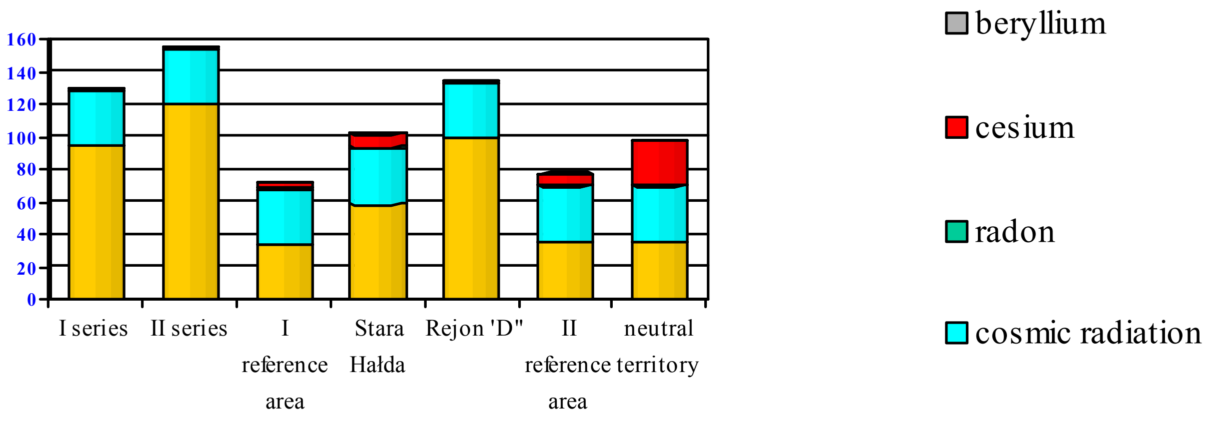

FIG. 6. Components of the air kerma free-on-air rate at 1 m above ground level (nGy/h)

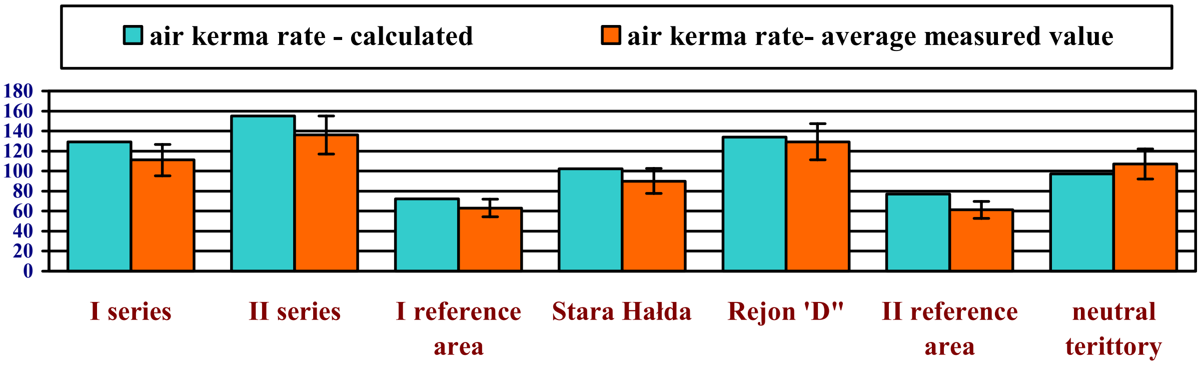

FIG. 7. Comparison of average measured value of air kerma rate with values calculated using specific activities of individual radionuclides (nGy/h)

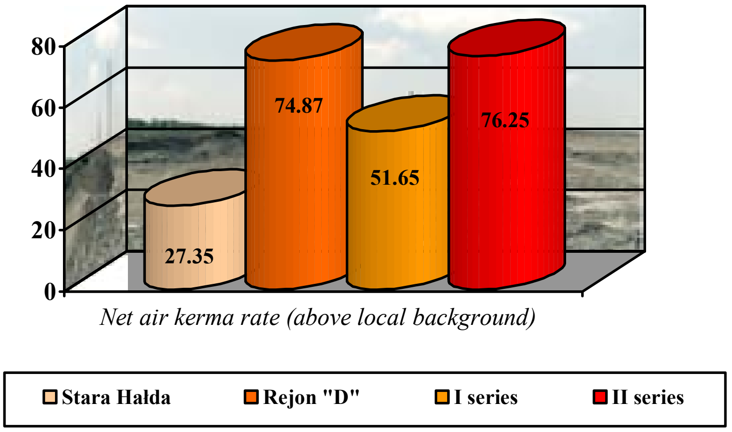

FIG. 8. Relative increase of air kerma rate on investigated spoil banks [nGy/h].

The largest observed increment of air kerma rate on the waste rock dump in comparison with the relevant reference area was 76.25 (nGy/h). Making the following assumptions:

- The exposure time was one year (365 × 24 h),
- The risk was that associated with an adult person,
- The way of exposure conformed to the ROT (rotational geometry) model,
- The average gamma radiation energy was 600 keV,

and taking into account the reference values for converting air kerma rate to effective dose [14], the possible annual effective dose was as follows:

$$E = 0.814 \times \Delta \, \mathrm{d}K/\mathrm{d}t = 0.542 \text{ mSv}$$

That represents about 20% of the medium annual effective dose caused by natural radioactivity in the territory of Poland. On the other hand, however, the calculated value is five times greater than the part derived from natural terrestrial outdoor radiation, which is reported to be less than 0.1 mSv [15].

6. RADON POTENTIAL

Measurements of the radon concentration in soil gas indicated that there was no clear relationship between the ^{226}Ra concentration and occurrence of radon in soil. Indeed, higher radon concentrations were observed in soil gas samples taken from the reference area, as shown in Fig. 9.

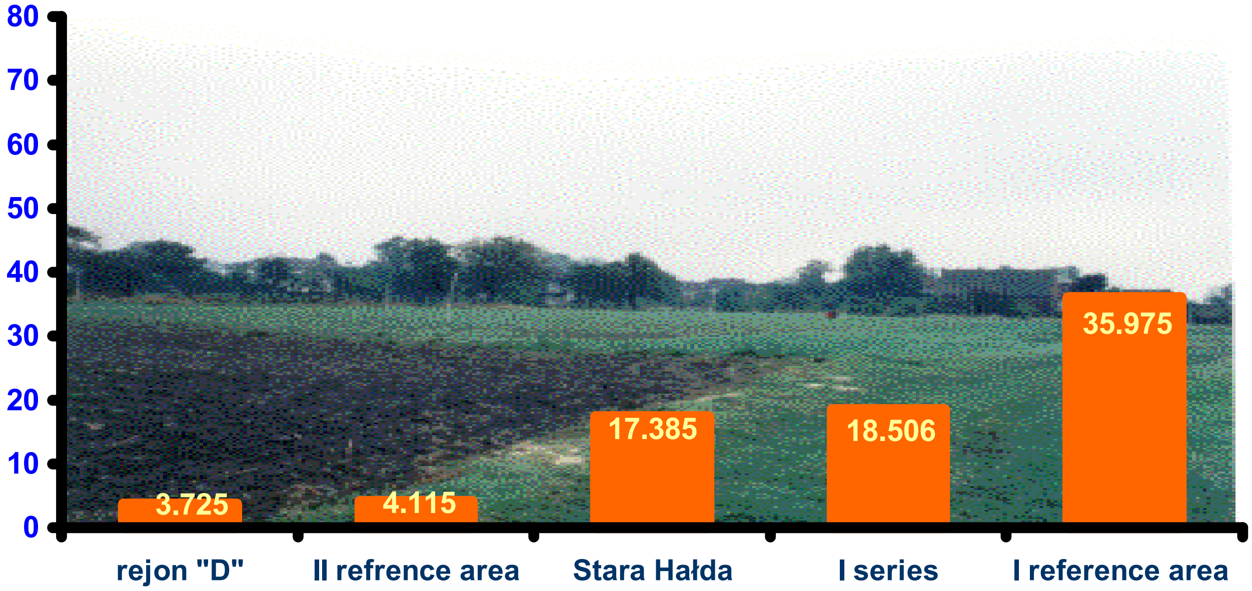

FIG. 9. Radon concentration in soil gas (kBq/m^3)

This result showed that, in this instance, the influence of ground properties such as permeability or porosity was much more significant than the influence of the specific activity of ^{226}Ra. In spite of a very wide range of radon concentration values observed, all of them were below 50 kBq/m^3, which is regarded as a criterion for high potential radon risk [16].

7. NATURAL ISOTOPES IN WATER

As shown in Fig. 10, all radium concentrations measured in water were very low, close to the lower limit of detection for the analysis method applied. All results obtained were below the maximum acceptable level for potable water of 0.1 Bq/L. In addition, the potential seasonal differences related to the amount of rainfall were not observed. The results obtained showed that even where was a certain impact of waste rock on radium concentration in the permeating water, the final effect was not noticeable.

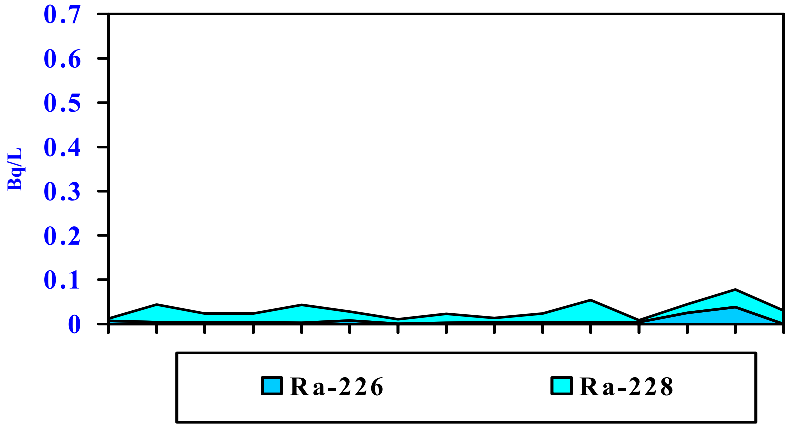

FIG. 10. Radium isotopes in surface water in the vicinity of the waste rock dump

8. CONCLUSION

Among all the investigated components of radiation risk, only external radiation derived from a slightly enhanced activity concentration of natural radionuclides was noticeable. The remaining components such as radon and radon progeny and possible leaching of radionuclides to ground water did not differ significantly from the values observed in the relevant reference areas. The calculated potential increment of effective dose should be taken into account during the planning the development of sites where waste rock was or will have been used as landfill.

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NATURAL RADIOISOTOPE LEVEL DIFFERENTIATION IN ARABLE AND NON-CULTIVATED SOILS AT ŁĘCZNA-WŁODAWA LAKE DISTRICT

A. Komosa*, S. Chibowski, M. Reszka

Department of Radiochemistry and Colloid Chemistry, Maria Curie-Sklodowska University, Lublin, Poland

Abstract

The Pojezierze Łęczyńsko-Włodawskie district located in eastern Poland is used as a recreation area, but mainly it is an agriculture area producing ecological food. Due to the lack of industry, this area is relatively uncontaminated. An exception is the Bogdanka coal mine located 20 km north of Łęczna in the vicinity of the Poleski National Park. Radioactivity levels, despite compliance with legal and technical regulations, may be disadvantageous for the environment in future. A potential hazard may be caused by the accumulation of natural radionuclides in soil and bottom sediments, resulting from an increase of the waste storage area (up to 83 ha in future) and disposal of coal mine water to the Świnka river. In this paper, the results of comparative studies of the concentrations of some natural radionuclides in cultivated and uncultivated areas are presented. The samples were collected from a surface layer at seven points on the Poleski National Park border. The concentrations of gamma-emitting radionuclides were measured using a Silena-Canberra semiconductor (HPGe) spectrometer with Genie 2000 software for quantitative analysis of the radionuclides. The results obtained enable an estimation of the health hazard by natural and anthropogenic (^{137}Cs) gamma-emitting radionuclides.

1. INTRODUCTION

The Łęczna-Włodawa Lake District (Pojezierze Łęczyńsko-Włodawskie) located in eastern Poland is used as recreation ground, but mainly it is an agriculture area producing ecological food. This area is relatively uncontaminated due to the absence of industry. Bogdanka coal mine located 20 km north of Łęczna in the vicinity of the Poleski National Park is the only industrial plant. Radioactivity levels, despite compliance with legal and technical regulations, may be disadvantageous for the environment in future. A potential hazard may be caused by the accumulation of natural radionuclides in soil and bottom sediments, resulting from an increase of the waste storage area (up to 83 ha in future) and disposal of coal mine water to the Świnka river [1].

It is also well known that use of phosphate and potassium fertilizers introduces additional amounts of natural radionuclides such as ^{238}U contained in phosphate ore and phosphogypsum, and ^{40}K.

The aim of present research was the investigation of the activity levels and vertical distribution of some natural gamma-emitting radionuclides in cultivated soils, and a comparison of the results with those obtained from uncultivated soils. Additionally, attention was paid to the anthropogenic isotope ^{137}Cs, which, being the result of radioactive fallout, may be treated as a marker of the migration rate of isotopes in environment. An evaluation of the transfer coefficients of some radionuclides from soil to selected plants, and a

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* E-mail: akomosa@hermes.umcs.lublin.pl

determination of the purity of soils under study, in relation to the content of anthropogenic elements was attempted.

Data relating to the concentration of radionuclides and their vertical distribution in cultivated soils are not often encountered in the literature. Usually, uncultivated soils are studied, where isotope migration, being the result of natural phenomena (the change of physical, chemical and atmospheric conditions etc.), may be observed [2]. However, for determination of the possible transfer of contamination from soil to plants and the radiochemical purity of soil, investigations of cultivated terrain are necessary. In comparison with uncultivated terrain, the main difference in the condition of migration is created by mechanical mixing of the surface layer of soil as well as the introduction of some radioisotopes with fertilizers as mentioned above.

2. MATERIALS AND METHODS

Profile samples of cultivated soils to a 40 cm depth (each layer 5 cm) and the surface layer (0–5 cm) of the uncultivated soil were taken in September 2003. Sampling points were selected in the vicinity of seven villages in the Łęczna-Włodawa Lake District: Świerszczów (marked as SWI), Krzczeń *(*KRZ*)*, Kulczyn *(*KUL*),* Wola Wereszczyńska *(*WOW*),* Turno *(*TUR*),* Ludwin (LUD) and Pieszowola (PIE). For each sample, a grain-size distribution as well as the content of elements was determined. The soils were qualified as follows: bog soils (SWI, KRZ and KUL), black-earth (WOW, TUR and LUD), and alluvial soil (PIE) [3].

To investigate the soil-to-plant transfer coefficients, samples of vegetables cultivated on this terrain, i.e. beetroot (beta vulgaris) and potato (solanum tuberosum) as well as their green parts, were taken. Measurements of the concentrations of gamma-emitters in the samples were made spectrometrically with the Silena-Canberra spectrometer equipped with an HPGe crystal of active volume 70 cm^3 and relative efficiency 13.5 %.

A quantitative analysis was executed with Genie 2000 computer program (Canberra). All measured results were related to the dry weights of the samples of soils and plants. The contents of main and trace elements in the samples were determined by the ED-XRF method with isotope excitation (^{109}Cd) using a Canberra spectrometer with an Si(Li) detector.

3. RESULTS AND DISCUSSION

Basing on gamma spectrometric measurements, three representative isotopes, being components of the natural radioactive series ^{210}Pb and ^{226}Ra (^{238}U series), as well as ^{212}Pb (^{232}Th series) were chosen for comparison. The concentration of these isotopes in Bq/kg is presented on Figures 1–7 for respective layers of the soil profiles.

As can be seen from Figs 1–7, the distribution of these natural radionuclides in the soil profiles is even. A comparison was made with the concentrations of the same radionuclides in a surface layer of uncultivated terrain.

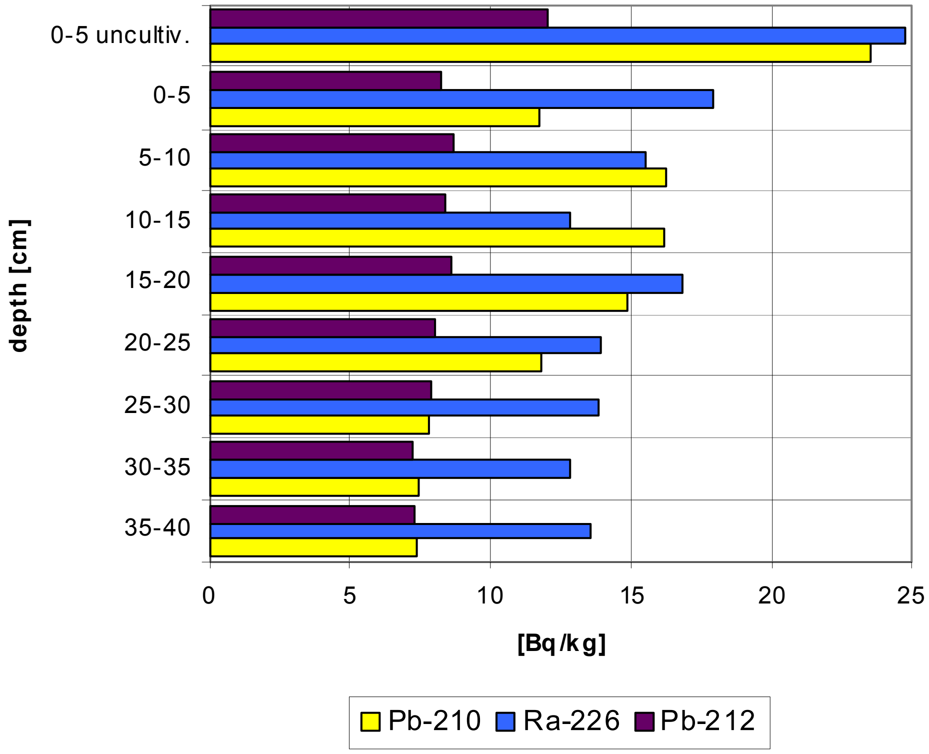

FIG. 1. Concentrations of ^{210}Pb, ^{226}Ra, and ^{212}Pb in layers of Świerszczów (SWI) soil

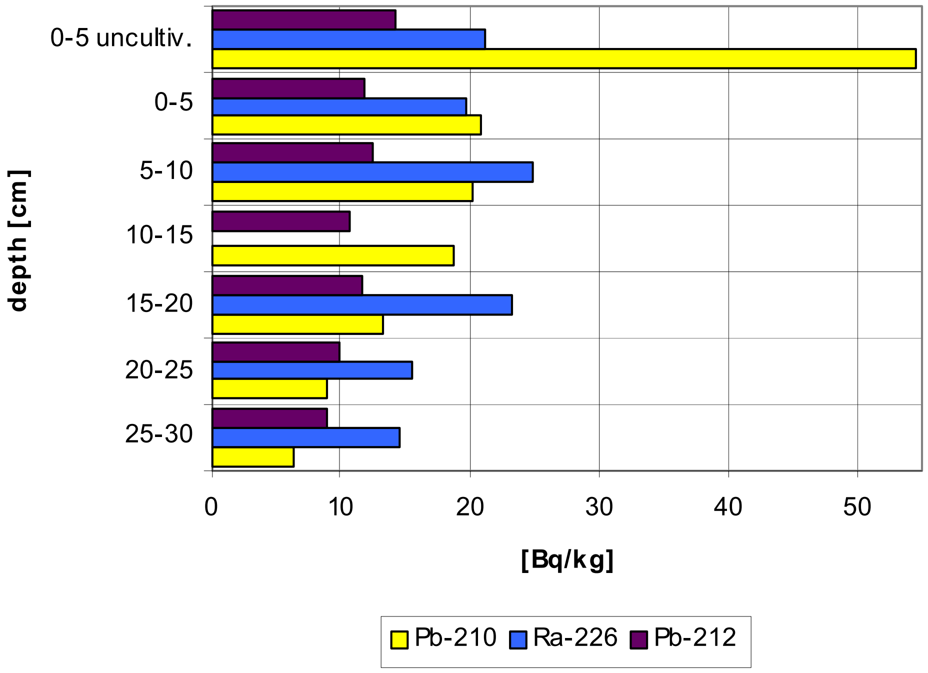

FIG. 2. Concentrations of ^{210}Pb, ^{226}Ra, and ^{212}Pb in layers of Krzczeń (KRZ) soil

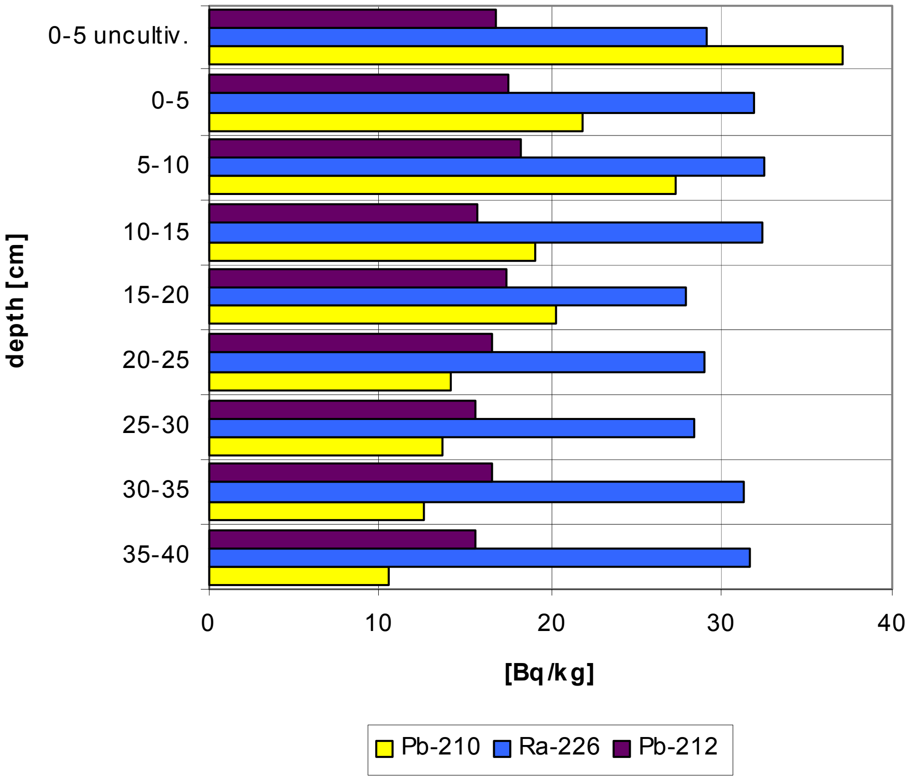

FIG. 3. Concentrations of ^{210}Pb, ^{226}Ra, and ^{212}Pb in layers of Kulczyn (KUL) soil

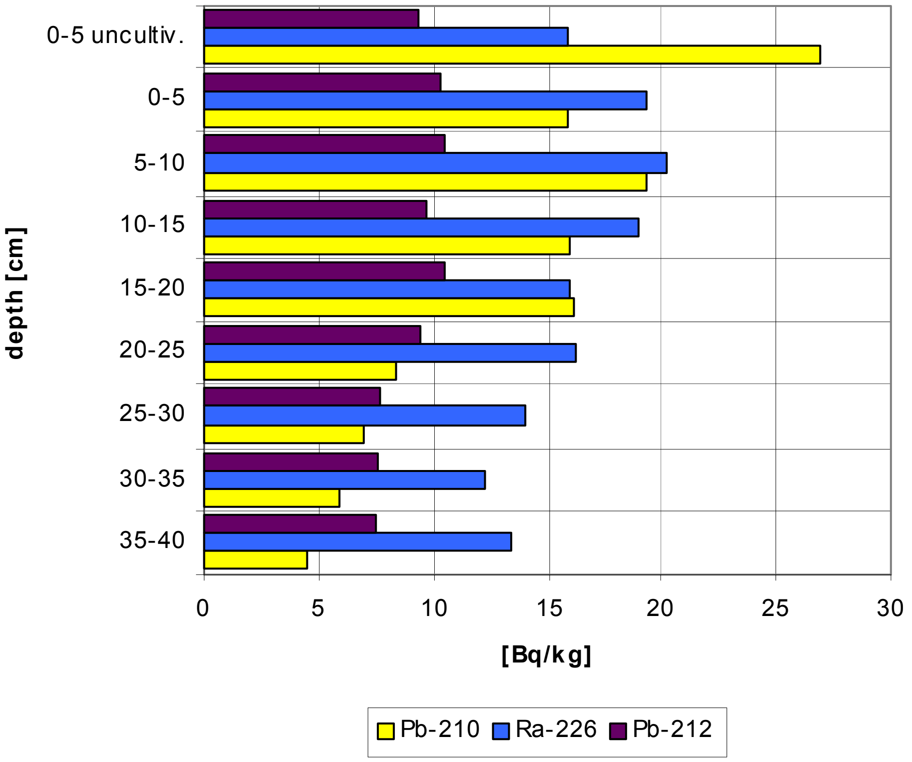

FIG. 4. Concentrations of ^{210}Pb, ^{226}Ra, and ^{212}Pb in layers of Wola Wereszczyńska (WOW) soil

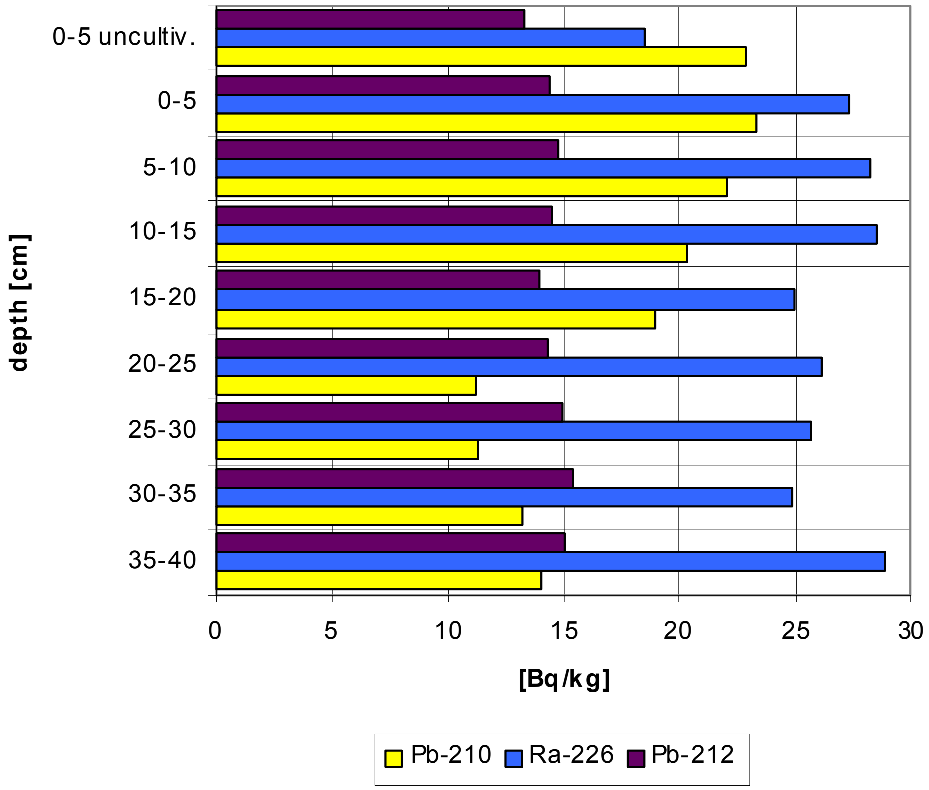

FIG. 5. Concentrations of ^{210}Pb, ^{226}Ra, and ^{212}Pb in layers of Turno (TUR) soil

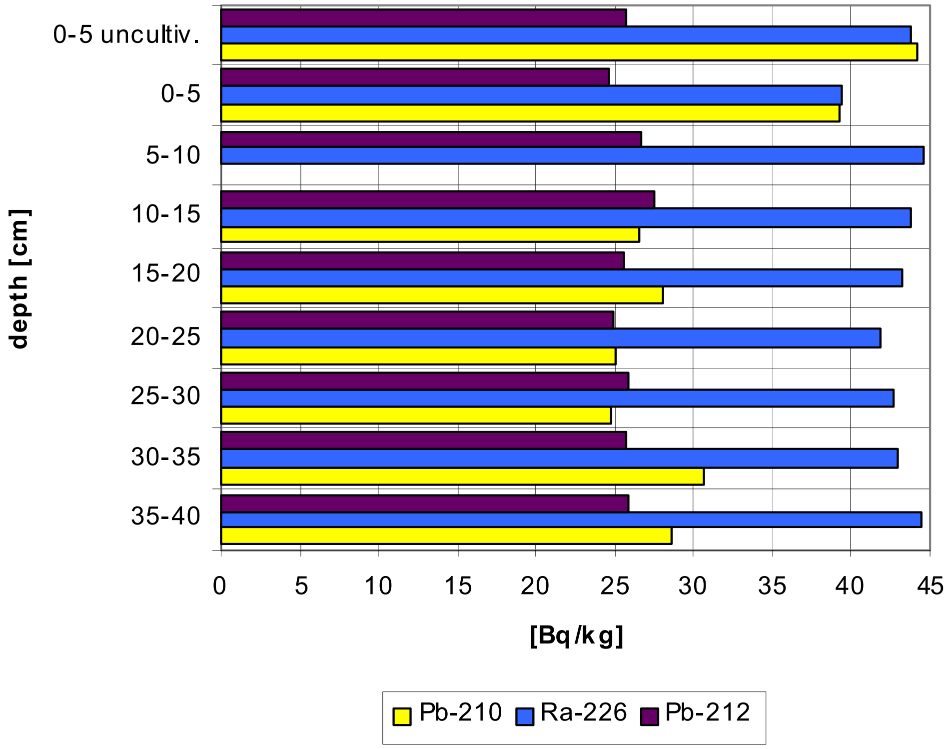

FIG. 6. Concentrations of ^{210}Pb, ^{226}Ra, and ^{212}Pb in layers of Ludwin (LUD) soil

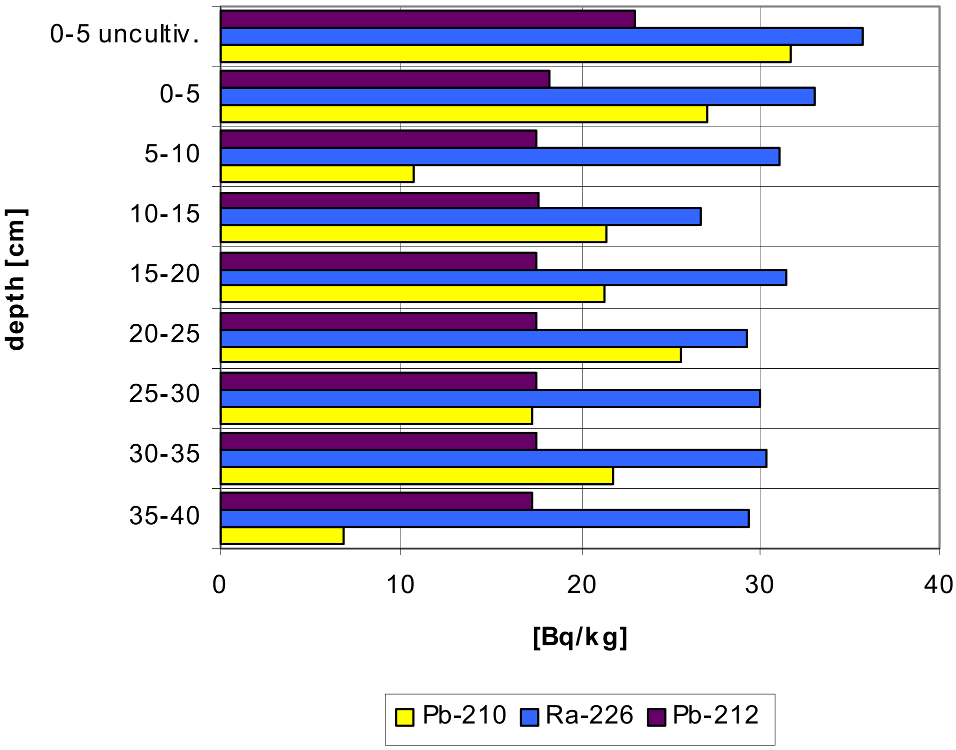

FIG. 7. Concentrations of ^{210}Pb, ^{226}Ra, and ^{212}Pb in layers of Pieszowola (PIE) soil

The concentration of ^{210}Pb was in most cases higher in the uncultivated soil due to the presence of this radionuclide in air and its accumulation on the surface of the soil. An intense mixing of the soil during cultivation dilutes this isotope because its concentration in deeper layers is low. In cultivated soil the concentrations of the two natural isotopes ^{226}Ra and ^{212}Pb were the same (KRZ, KUL and LUD samples), lower (SWI and PIE) or higher (WOW and TUR) than those in an uncultivated layer of the same soil.

It is to be expected that where mineral fertilizers are not used, the concentrations of natural radionuclides in a cultivated area will be similar to or lower than those in an uncultivated area. Such an effect is produced by impoverishment of the soil by crops. On the other hand, mineral fertilization will cause an increase in the concentration of natural radionuclides in soil. The typical case was met for WOW and TUR soils.

In Figs 8 and 9, the changes in concentration with soil depth of the natural radionuclide ^{40}K, as well as ^{137}Cs introduced as radioactive fallout, are shown. The level of ^{40}K activity is different for samples from various sites, as a result of different chemical compositions of the soils involved. However, the ^{40}K concentration does not change significantly over the whole depth range of the cultivated soil, and is similar to values obtained for uncultivated soils. The changes in ^{137}Cs concentration in the depth profile, shown in Fig. 9, are different from that observed for ^{40}K (Fig. 8). The ^{137}Cs appeared as the result of radioactive fallout and has migrated downwards from the surface layer where its concentration was greatest. In uncultivated soils, its concentration diminished in an exponential manner with increasing depth, achieving a background value at 15–30 cm (depending on physicochemical condition, soil composition etc.) [2]. For cultivated soils, one can observe the same concentration level of ^{137}Cs down to a depth of about 25 cm, followed by a progressive lowering at depths of 25–40 cm. The concentration of ^{137}Cs in the surface layer (0–5 cm) is smaller than that in the same layer of the cultivated soil. The equalization of isotope concentrations observed in the 0–25 cm layer results from ploughing of the soil and mixing it to just such a depth. Samples marked as LUD and PIE show a somewhat different pattern of ^{137}Cs concentration changes.

The sharp decrease of concentration in the 25–40 cm layers was not observed. Most probably this was connected with the presence of a relatively high concentration of potassium, reaching as much as 2% of the dry weight of the soil, as determined by the XRF method.

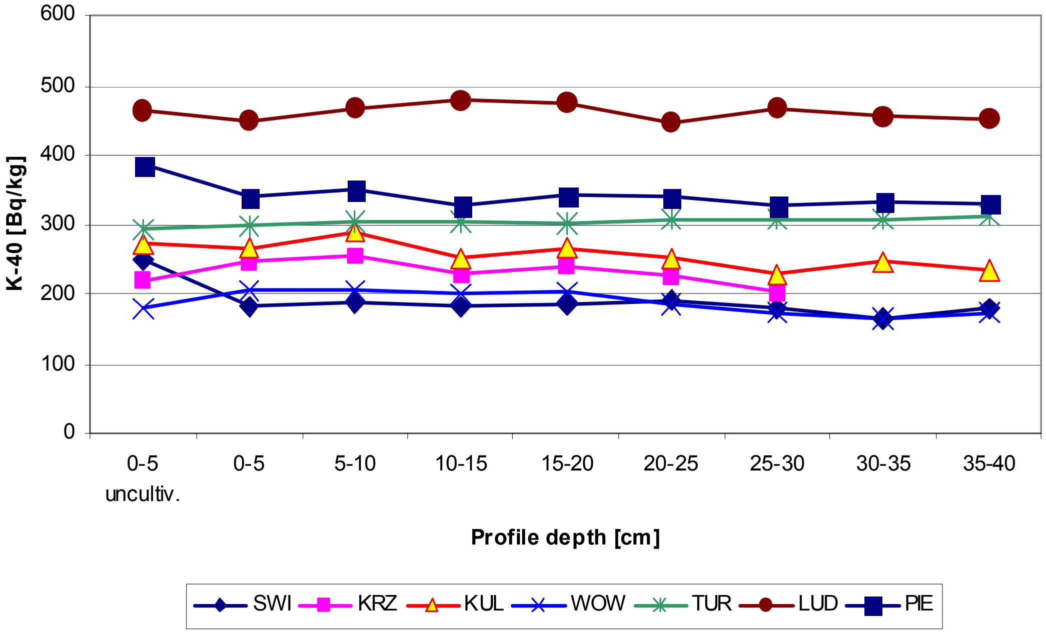

FIG. 8. ^{40}K concentration changes along the depth profile of soils

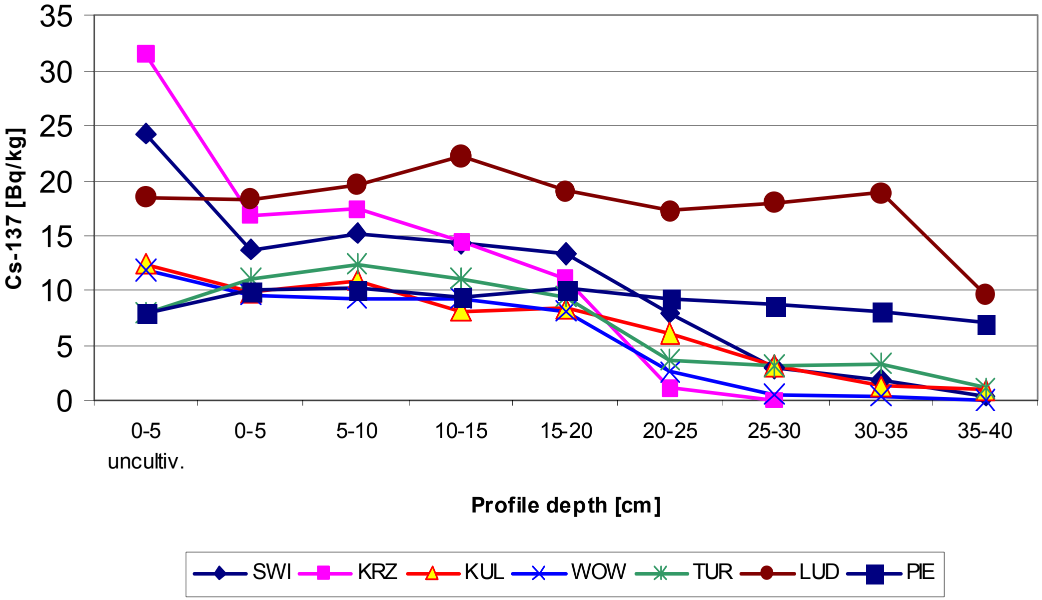

FIG. 9. The ^{137}Cs concentration changes along the depth profile of soils.

In the next stage of the study, the concentrations of gamma-emitting radionuclides in samples of beetroot, potato and green parts of these plants were determined. The data were used to calculate the transfer coefficients (*TF*) of selected isotopes: ^{210}Pb, ^{214}Pb and ^{226}Ra (^{238}U series), ^{212}Pb (^{232}Th series), as well as ^{40}K and ^{137}Cs. The samples were collected in every sampling place where soil samples were taken.

The transfer coefficient *TF* was defined as the quotient of the radionuclide concentration in plant (per dry mass) to its concentration in soil. The *TF* values of the above-mentioned radionuclides for beetroot, potato tuber and green parts of potato are listed in Table I.

TABLE I. MEAN VALUE OF TRANSFER COEFFICIENTS (*TF*) OF THE CHOSEN ISOTOPES FROM SOIL TO BEETROOT, POTATO TUBER AND GREEN PARTS OF POTATO

Crop		Transfer coefficient					
		Uranium series			Thorium series (^{212}Pb)	^{137}Cs	^{40}K
		^{210}Pb	^{214}Pb	^{226}Ra			
Beetroot	Mean ± SD	0.12 ± 0.10	0.12 ± 0.10	—	0.03 ± 0.02	0.14 ± 0.09	4.25 ± 1.89
	Median	0.07	0.10		0.01	0.15	3.57
	Minimum	0.05	0.04		0.01	0.02	1.81
	Maximum	0.29	0.32		0.08	0.32	7.25
Potato (tuber)	Mean ± SD	0.07 ± 0.09	0.18 ± 0.18	0.06 ± 0.03	0.03 ± 0.02	0.07 ± 0.04	2.84 ± 0.84
	Median	0.02	0.10	0.07	0.02	0.07	2.36
	Minimum	0.01	0.04	0.006	0.004	0.02	1.72
	Maximum	0.22	0.60	0.09	0.07	0.16	4.29
Potato (green parts)	Mean ± SD	2.54 ± 0.55	0.78 ± 0.27	0.29 ± 0.30	0.53 ± 0.14	0.70 ± 0.19	5.22 ± 1.95
	Median	2.61	0.73	0.12	0.59	0.71	5.20
	Minimum	1.88	0.48	0.05	0.32	0.36	2.10
	Maximum	3.61	1.15	0.87	0.69	0.91	7.88

One can notice that the *TF* values vary to a large extent. The highest values of ^{40}K in potato and beetroot edible parts confirm the accumulation of potassium by plants. Other radionuclides do not accumulate in edible parts of the studied plants. Considerably higher values of *TF* were calculated for green, inedible potato parts. In this case, a much larger accumulation of ^{40}K than in tuber was observed and also a significant accumulation of ^{210}Pb. This long-life isotope comes from radon decay and its presence in the green parts results probably from direct sorption from air. The ^{137}Cs comes from radioactive fallout but its concentration in the atmosphere is not significant nowadays. It is transported to green parts of plants by the root system because it appears in air as result of soil resuspension only. The *TF* for ^{137}Cs in green parts is close to unity, which means that the ^{137}Cs concentration in soil is approximately the same.

Analyzing the gamma spectra of the green parts of potato and beetroot, the presence of the cosmogenic isotope ^{7}Be at concentrations of 30–90 Bq/kg was observed. This isotope does not exist in soil, and its concentration in the surface layer of atmosphere amounted to about 3.6 mBq/m^3 in 2003. For this reason, one may conclude that the presence of ^{7}Be in the green parts of plants proves a direct assimilation of this isotope from air by stalks and leaves.

To evaluate the level of anthropogenic contamination of the soils, the enrichment factor (*EF*) was calculated, defined as follows [4]:

$$EF = \frac{(C_x / C_{Fe})_{in\ sample}}{(C_x / C_{Fe})_{in\ lithosphere}}$$

where: C_x is the concentration of a given element and C_{Fe} is the concentration of iron. The concentrations of main and trace elements in soil samples were determined by the XRF method. Calculated values of *EF* are shown in Fig. 10. For these calculations, the mean concentrations of the relevant elements in the earth's crust were used [6]. The more the value of *EF* exceeds unity, the more pronounced is the negative influence of man on the soil.

The *EF* value of all analyzed soils for all the studied elements was higher than unity, which proved enrichment of the soil by these elements. The accumulation of some elements in surface soil in comparison to bedrock is well-known. Such a phenomenon is due to the decay of rocks and other soil-forming processes. Some elements, such as manganese, strontium, or lead demonstrate higher values of *EF*, ranging from 3.5 to 5 [4, 5]. In the case of the studied soils, as can be seen from Fig. 10, zirconium and lead show a relatively high enrichment, i.e. mean values of *EF* of 32 and 48 respectively. Considering lead, this value is more than ten times higher than expected [4, 5] whereas a lack of literature data for zirconium makes such a comparison impossible. In the case of copper and zinc, values two to three times higher than those expected for soils can also be observed, which may be attributed to man's influence on the environment.

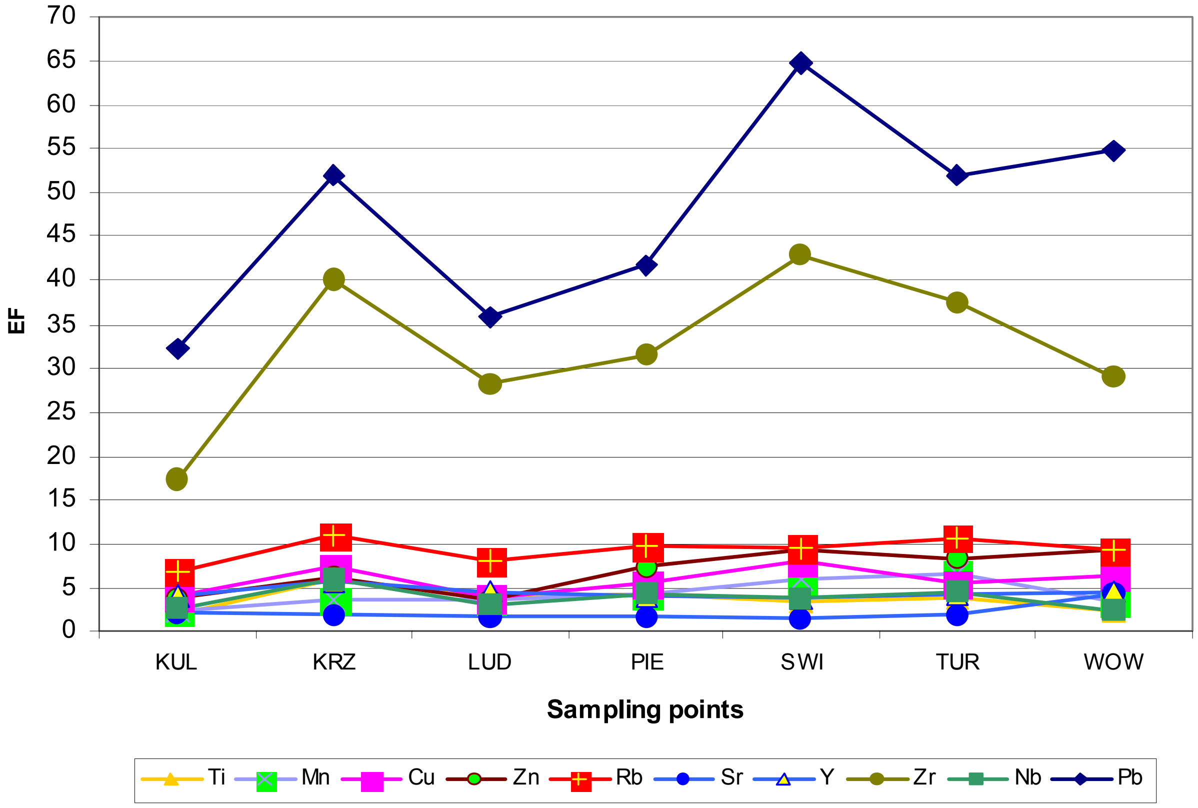

FIG. 10. Enrichment factors of elements in soils

4. CONCLUSIONS

Using gamma spectrometry, the distribution of selected natural radionuclides was determined in soil profiles of cultivated soils and compared with those in uncultivated soils. It was observed that in most cases (except for two samples) the average concentration of radionuclides in the profile layers is smaller than in surface layer of uncultivated soil, which proves no fertilization at the studied site. The concentration changes of ^{137}Cs in soil profiles resulted from the ploughing of the soil to an average depth of 25 cm and mixing of the layers. The calculated soil-to-plant transfer coefficients of the radionuclides studied revealed the high concentration of ^{40}K in the edible parts of beetroot and potatoes as well as in their green parts. A relatively high concentration of ^{210}Pb was also found in the leaves and stalks of these plants. The XRF method of elemental analysis demonstrated a significant enrichment of the surface layer of soil with zirconium and lead, as compared with the average content in the lithosphere. To a lesser extent, the soils were also disadvantageously enriched with copper and zinc.

ACKNOWLEDGEMENT

This study was supported by the Polish Committee of Scientific Research (KBN) with Grant No. 4T09D 05824.

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ENVIRONMENTAL ASSESSMENT OF THE MATERIAL DEPOSITED ON THE FORMER URANIUM MINING DISPOSAL DUMP IN RADONIÓW

A. Żak[1], M. Biernacka[1], P. Lipiński[1], K. Isajenko*[1], T.J. Sibiga[2]

[1]Central Laboratory for Radiological Protection, Warszawa, Poland
[2]MOSTOSTAL Warszawa SA, Warszawa, Poland

Abstract

Radoniów is a small town in the district of Lubomierz near Jelenia Góra (south-western Poland). From the end of World War II up to the end of the 1960s, uranium mining activities were carried out near the town. The uranium deposits were almost entirely exploited, leaving traces of the mining activities in the form of waste disposal dumps on the east side of Mount Głębiec. The area of the terrain is 6.85 ha. The district authorities plan to use the material on the dumps (containing significant quantities of uranium) as a bedding for the construction of a road around the town (PHARE contract). The measurements performed by the Central Laboratory for Radiological Protection (CLOR) and ordered by MOSTOSTAL-Warszawa (the developer of the road) were aimed at assessing the usability of the dumped material for road construction. The assessment programme consisted of environmental measurements at the disposal site, an assessment of the usability of the materials from the disposal site for the construction of the road, and an analysis of the risk to workers exposed to the material deposited on the dumps. The following tasks were performed: (a) measurement of the whole area using a mobile spectrometric laboratory (creating a radiological map of the area); (b) measurement of the beta activity and gamma dose rate at the surface of the material deposited on the dumps at 41 measurement locations using an RKP-1 radiometer; (c) measurement of the gamma dose rate at the 41 locations using an Exploranium GR-130; (d) measurement of the gamma dose rate at 5 locations using an ionization chamber; (e) measurement of the gamma spectra at 3 locations on the dumps and at 2 locations representative of local background; and (f) sampling for further analysis at CLOR by gamma spectrometry using natural radioactive contamination analyzers AZAR-90 and MAZAR-95. The following samples were taken: 41 samples of the surface material of the dump (10 cm depth); 10 samples from the deep layers of the dump (taken by the specialized geological company Geological Services); and 2 samples representing the local natural environment. The sampling results were averaged over 5 to 7 subsamples collected from the central point at each location and from surrounding points 2 m away. A detailed description of the measurement methods, the results and their interpretation are presented.

1. INTRODUCTION

Radoniów is a small town in the district of Lubomierz near Jelenia Góra (south-western Poland). From the end of World War II up to the end of the 1960s, uranium mining activities were carried out near the town. The uranium deposits were almost entirely exploited, leaving traces of the mining activities in the form of waste disposal dumps on the east side of Mount Głębiec. The area of the terrain is 6.85 ha. The district authorities plan to use the material on the dumps (containing significant quantities of uranium) as a bedding for the construction of a road around the town (PHARE contract). The measurements performed by the Central Laboratory for Radiological Protection (CLOR) and ordered by MOSTOSTAL-Warszawa

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[*] E-mail: isajenko@clor.waw.pl

(developer of the road) were to assess the usability of the dumped material for road construction.

2. DESCRIPTION OF THE AREA

The plan of the area, which comprises several dumping mounds, is presented in Fig. 1. The main part of the dump is surrounded by the field road. North of this part of the dump, idle land is situated. On this area, next to Shaft No. 9, a small steep dumping mound with an irregular top (A) is located. The eastern part of the dumping site is bounded by a high dumping mound (B) stretching along the south-north axis. This mound is connected to two smaller ones (C) having flat tops and three steep stony dumping mounds (D) in the direction of a concrete construction (E). At the foot of the high stony dumping mound (D), a sandy flattened dumping mound covered with birch forest (F) is situated. On its west side, a circular re-entrant is seen (G). In the south-west part of the area, close to the road, a narrow sickle-shaped embankment (H) is located, and further north a flattened part (I) going into a small valley, behind which there is promontory in the form of a sandy dumping mound. A small dumping mound a few metres high (J) is located in the western part of the area. Between the concrete construction and the external road there is a long dumping mound having a plain ridge (K).

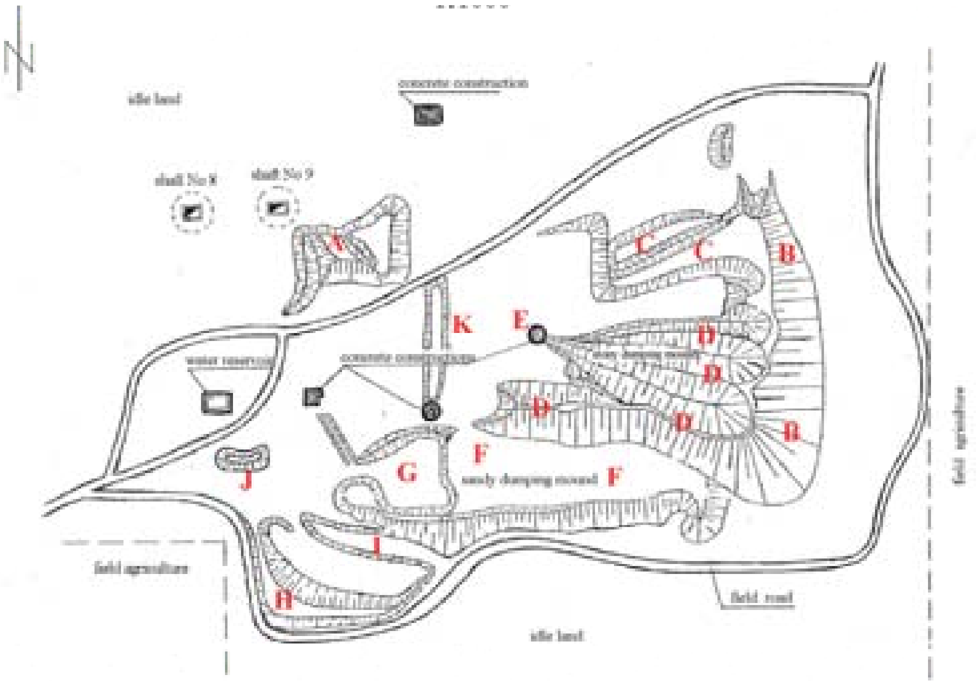

FIG. 1. Plan of disposal dumps at Radoniów

3. MEASUREMENT PROGRAMME AND METHODS

The assessment programme consisted of:

- Environmental measurements at the disposal site;
- Assessment of the usability of the materials from the disposal site for the construction of the road;
- Analysis of the risk to workers exposed to the material deposited on the dumps.

The tasks performed are described below.

3.1. Radiological mapping of the area

The whole area was measured using a mobile spectrometric laboratory based upon a Toyota Land Cruiser GX90. A scintillation detector type Exploranium GPX-256 with an NaI(Tl) crystal having a volume of 4 L (dimensions 40×10×10 cm) was mounted on the roof of the car. The detector was placed in an aluminum container and covered with polyurethane foam. Its function was to permanently measure the environmental gamma spectra, both along the measuring route and while standing. The mobile laboratory was also equipped with a GR-660 system mounted on the back seat of the car in a special shockproof container. The GR-660 system consisted of an on-board computer with touch screen connected to a computer with a long cable. Such a connection enabled the operator to sit on the front seat of the car. The computer stored the collected measurement data and performed the on-line visualization. The second element of the GR-660 system was an Exploranium GR-320 256-channel spectrum analyzer connected to the detector placed on the roof of the car. In addition, the car was equipped with a differential geographic positioning system (DGPS), enabling the position of the car to be determined very precisely (within 0.5 m). The results from the GPS were transferred to the on-board computer, enabling the measuring route to be presented on the screen and radiological maps to be prepared.

The GR-660 spectrometer enabled the concentrations of natural radionuclides to be determined down to the following levels:

- ^{40}K: 0.13% (40 Bq/kg),
- Uranium: 1.6 ppm (20 Bq/kg),
- Thorium: 1.0 ppm (4 Bq/kg).

The results were stored on the hard disk drive of the on-board computer. Further processing of the data was performed in the laboratory using specialized software for detailed spectra and auxiliary data analysis, e.g. the creation of radiological maps of the investigated area.

3.2. Gamma measurements at specific locations using a spectrometer

Gamma dose rates were measured at 41 measuring locations and gamma spectra were measured at 5 locations (3 in the investigated area and 2 at ‘neutral points’ representing natural background), using an Exploranium GR-130 hand-held spectrometer equipped with an NaI(Tl) detector. A GM detector was used for measurements in high dose rate areas. When the dose rate became high, the device automatically switched to the GM for dose rate measurement. The gamma spectra were stored in the memory of the device for onward transfer to the computer and analysis for radionuclide identification.

3.3. Beta and gamma measurements at specific locations using a radiometer

Using a standard RKP-1 radiometer calibrated with a ^{90}Sr source, the radiation above the dumped material was measured by counting the pulses from beta and gamma radiation while the detector window was open and then counting the pulses with the detector window closed. The difference gave the count rate associated with beta radiation. The gamma dose rate was measured with the detector window closed and the device switched to the dose rate mode.

3.4. Gamma dose rate measurements at specific locations using an ionization chamber

Gamma dose rate was measured at 5 locations using a current-type pressurized ionization chamber. The chamber comprised a 5 L high-pressure steel tank with a wall thickness of 4 mm. The pressure of argon gas was 35 atmospheres. The tank was covered by 1.5 mm of aluminum to prevent noise. The self-counting (the background) of the chamber was 2 nGy/h. A VA-J-51 electrometer equipped with a dynamic capacitor powered by 220 volts AC or an accumulator (in the field) was used to measure the current. The calibration of the instrument was performed assuming that terrestrial background gamma radiation was 70% equivalent to a ^{226}Ra source filtered by 0.5 mm of platinum and 30% equivalent to a ^{131}I source. The calibration procedure took into account the influence of scattered radiation, directional anisotropy of the ionization chamber and the attenuation of the radiation in air.

The background dose rate 1 m above ground, D (in nGy/h), was calculated from following equation:

$$D = VK - D_0$$

where: V is the velocity of the rise of charge (mV/s), given by $V = z/t$, z being the voltage rise on the capacitor during measurement and t being the voltage rise time (the time of measurement — average of 5 readings);

K is the calibration coefficient (nGy/h per mV/s) determined during the calibration procedure;

D_0 is the self-counting of the chamber (nGy/h).

The dose rate was determined with an error of ± 10%.

3.5. Measurement of radionuclide activities in material samples using gamma spectrometry

The following samples were taken for analysis in the Dosimetry Department of CLOR:

- 41 samples of the surface material of the dump (10 cm depth);
- 10 samples from the deep layers of the dump (taken by the specialized geological company Geological Services);
- 2 samples representing the local natural environment.

Each surface material sample was averaged from 5–7 sub-samples taken from the central point and from the circumference of a 2 m diameter circle around that point.

The method used for determining the activity of the samples was based on a comparison of the concentrations of the natural radionuclides ^{40}K, ^{226}Ra and ^{228}Th. It entailed the analysis of the count rate registered in three channels — separately for the examined sample and three volume calibration sources of potassium, radium and thorium. The count rate was measured using a scintillation detector with AZAR-90 and MAZAR-95 three-channel amplitude analysers. The scintillation detector was located in a lead shielding chamber. The walls of the shielding were 50 mm of lead and 2 mm of steel. The Marinelli beaker containing the sample (1.7 L) was placed inside the chamber. The function of the chamber was to reduce the external gamma background. Such geometry allowed more counts to be achieved in the defined measurement time. The detector was powered by a stabilized high voltage power supply. Energy peaks from the detector were processed by a linear amplifier and passed to one of three single-channel analyzers. In addition, inside the chamber there was a ^{137}Cs source for controlling the slope of the calibration curve. Each single-channel analyzer was set to its energy range:

- Range I: 1.26–1.65 MeV covering potassium ^{40}K with an energy peak of 1.46 MeV;
- Range II: 1.65–2.30 MeV covering mainly the energy peak of 1.76 MeV for bismuth ^{214}Bi from the ^{238}U series;
- Range III: 2.30–2.85 MeV covering mainly the energy peak of 2.62 MeV for ^{208}Tl from the ^{232}Th series.

The peaks from the outputs of each analyzer were counted separately, and the results were stored in three memory groups. The device was powered by a 230 V AC electrical supply. The measurement technique for ^{40}K, ^{226}Ra and ^{228}Th is described in detail in the *Guidelines on the Determination of Natural Radioactivity in Raw and Building Materials*, Instruction 234/2003 of the Institute of Building Technology. Based on the measured concentrations of ^{40}K, ^{226}Ra and ^{228}Th, the radioactivity indices f_1 and f_2, and the dose rate above a flat infinite plane of a thick layer (a few metres) of the measured material were calculated.

4. RESULTS OF MEASUREMENTS

The distribution of the measurement points and sampling points (surface and deep) is presented in Fig. 2.

FIG. 2. Measurement and sampling points

4.1. Surface beta radioactivity measurements

The results of the surface beta radioactivity measurements fell within the range 0.16–1.92 Bq/cm^2, with an average of 0.52 Bq/cm^2. All measured values were less than 3.7 Bq/cm^2, i.e. the limit value for beta surface radioactivity for laboratories applying beta radionuclides. The comparison is due to a lack of standards on the permissible beta activity values in the natural environment.

4.2. Natural radionuclide concentrations in samples taken from the dumping mounds

Measurements of the environmental samples were performed at the Natural Radioactivity Section of the Dosimetry Department of CLOR. The measured concentrations of the natural radionuclides ^{40}K, ^{226}Ra and ^{228}Th are presented in Table I, along with the radioactivity indices f_1 and f_2, calculated from the measured radionuclide concentrations in accordance with the Regulation by the Council of Ministers of 3 December 2002 (Law Gazette No 220/2002 pos. 1850).

TABLE I. RADIONUCLIDE CONCENTRATIONS AND RADIOACTIVITY INDICES IN SURFACE-LAYER SOIL SAMPLES

	Samples from waste dumps		Samples from 'neutral points'	Location of maximum value[1]
	Average	Range		
Radionuclide concentration (Bq/kg)				
^{40}K	1627	782–5704	740; 686	a, b, c
^{226}Ra	2172	252–8726	95; 49	b, c
^{228}Th	95.3	37.5–782.4	38.5; 36.0	a, b, c
Radioactivity index				
f_1	8.26	2.33–34.90	0.76; 0.57	b, c
f_2 (Bq/kg)	2172	252–8726	95; 49	b, c

4.3. Gamma dose rates

The gamma dose rates measured in the dumping area are given in Table II. The measurements were performed using the ionization chamber at certain points confirmed the correctness of the results obtained by other methods.

TABLE II. GAMMA DOSE RATES

Instrument	Dose rate (nGy/h)			Location of maximum value[1]
	Waste dumps		'Neutral points'	
	Average	Range		
Radiometer RKP-1	680	300–1800	—	a, b, c
Exploranium GR-130	662	288–1988	142; 117	a, b, c

Additional environmental spectrometric measurements were made using the mobile spectrometric laboratory. The measurements were performed along roads that were negotiable by all-terrain vehicle. The concentrations of potassium, thorium and uranium were measured.

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[1] Location 'a': between road and concrete construction near water reservoir; location 'b': between road and water reservoir; location 'c': west part of dumping mound A, at its top.

The detector was situated 2 m above the ground, so the measurements do not represent point values but are averaged from a larger area. Thus the results are approximate, and indicate those places having elevated natural radionuclide concentrations.

5. ANALYSIS OF RESULTS

5.1. Possible application of the materials for construction

5.1.1. Legal basis

In Poland, for the purpose of evaluating raw materials and building materials for use in various types of construction, the criteria given in the Regulation of Council of Ministers of 3 December 2000 "*on natural radioactive isotope content in raw and building materials used in buildings for population and livestock, as well as in industrial wastes used in construction, and monitoring of the concentration of these isotopes*", Law Gazette No 220/2002 pos. 1850 (the 'Regulation') are applied. According to the Regulation, the concentrations of natural radionuclides in raw materials and building materials, as well as wastes, are used to calculate:

- The activity coefficient f_1 defined by the equation

$$f_1 = \frac{S_{\mathrm{K}}}{3000} + \frac{S_{\mathrm{Ra}}}{300} + \frac{S_{\mathrm{Th}}}{200}$$

- The activity coefficient f_2, defined as

$$f_2 = S_{\mathrm{Ra}}$$

where S_{K}, S_{Ra} and S_{Th} are the concentrations of ^{40}K, ^{226}Ra and ^{228}Th in Bq/kg. It is stated in §3 of the Regulation that f_1 and f_2, cannot exceed 20% of the following:

> *"1. f_1 = 1 , f_2 = 200 Bq/kg related to raw and building materials applied in construction for public or livestock;*
>
> *2. f_1 = 2, f_2 = 400 Bq/kg related to industrial wastes used in surface constructions situated on the ground and built on the inhabited (used) areas or devoted to construction in local urbanization plans, and for leveling of such terrains;*
>
> *3. f_1 = 3,5, f_2 = 1000 Bq/kg related to industrial wastes for constructions situated on the ground not mentioned above and for leveling of the terrains not mentioned above;*
>
> *4. f_1 = 7, f_2 = 2000 Bq/kg related to industrial waste used in underground parts of constructions mentioned in point 3 and in underground constructions such as railway and road tunnels excluding industrial wastes used in underground mining galleries."*

In addition, §4 of the Regulation requires that while using industrial wastes for the leveling of the terrain quoted in §3 pt. 2 and 3, and for construction of road, sports and recreation objects it should be assured that achievement of the required values of f_1 and f_2 will cause the absorbed dose rate at 1 m above the terrain, road or object to be less than 300 nGy/h, in particular by placing an additional layer of another material.

The recommended procedures on sampling and preparation of samples, measurement, and elaboration of the results can be found in the "*Guidelines on the Determination of Natural Radioactivity in Raw and Building Materials*", Instruction 234/2003 of the Institute of Building Technology.

5.1.2. Analysis of the measurement results

The activity coefficients f_1 and f_2 obtained (Table I) demonstrated that:

- None of the samples complied with §3 pt. 1 of the Regulation;
- 2 samples complied with §3 pt. 2;
- 12 samples did not comply with §3 pt. 2 but satisfied §3 pt. 3;
- 19 samples did not satisfy §3 pt. 3 but satisfied §3 pt. 4;
- 18 samples did not satisfy §3 pt. 4.

The activity coefficients f_1 and f_2 are presented in Figs 3 and 4 respectively, and show that there are probably two groups of materials present in the area:

- A first group, with f_1 ranging from 0 to 9 and f_2 from 0 to 2500 Bq/kg;
- A second group, with f_1 ranging from 9 to 16.4 and f_2 from 2500 to 4332 Bq/kg.

In addition, there are two 'hot spots' in the sites described as b and c in Footnote 1 (for point b: f_1 = 27.9; f_2 = 7083 Bq/kg; and for point c: f_1 = 34.9; f_2 = 8724 Bq/kg). It is possible that the area contains other hot spots (having diameters of a few metres) that were not included in the sampling. Thus, it is recommended that the site be checked with simple dosimeter.

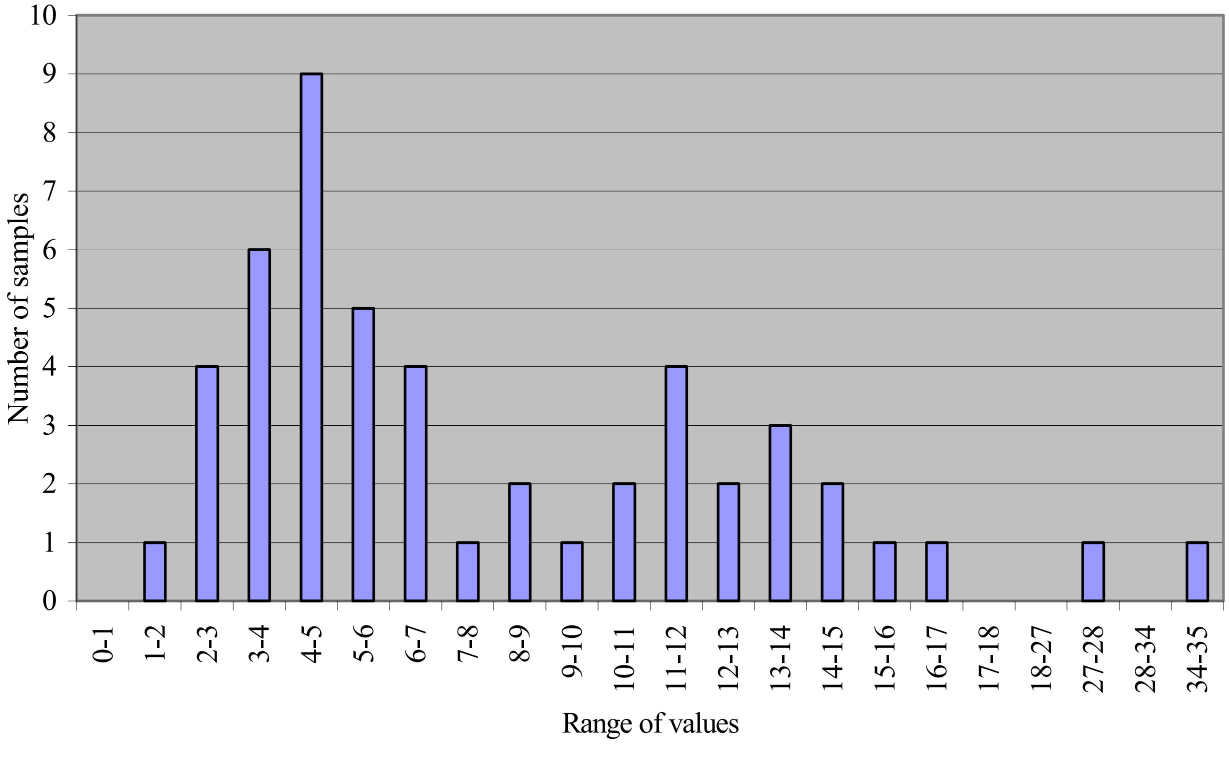

FIG. 3. Activity coefficient f_1

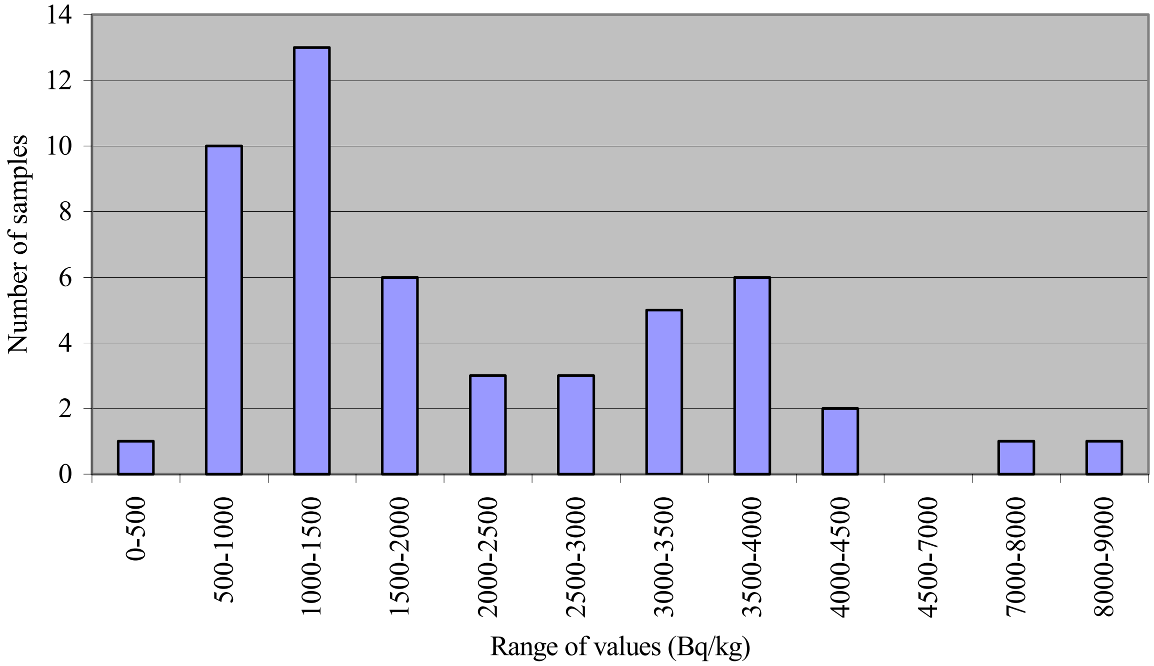

FIG. 4. Activity coefficient f_2

5.2. Risk to workers exposed to the materials from the dumps

5.2.1. Legal basis

The fundamental legislation is the Atomic Law of 29 November 2000. This Act is a set of general regulations. Article No. 13 is the most important in this case:

> "Art. 13
>
> 1. *The dose limit is the sum of the doses from external and internal exposure.*
> 2. *The dose limit does not include exposure to natural radiation, when not increased by human activities; in particular, it does not include exposure to radon in dwellings, exposure to natural isotopes in the human body, cosmic radiation at ground level, and exposure at the surface of the earth from radioactive isotopes present in the undisturbed earth's crust."*

The dose limits for ionizing radiation for specific population groups are given in the Regulation by Council of Ministers of 28 May 2002 *"on limiting doses of ionizing radiation"* (Law Gazette no 111 pos. 969). The values given in §5 of the Regulation apply to the individuals working on the road construction. According to the Regulation, the dose limit for such persons is 1mSv effective dose per calendar year. This dose can be exceeded during the year if during the following 5 year period its value does not exceed 5 mSv in total.

5.2.2. Worker exposures in the examined area

Exposure to beta and gamma radiation was taken into account. For this analysis workers employed on the dump and the construction of the road were divided into two main groups:

- Employees working in cabins (excavators, bulldozers, trucks etc.),
- Employees directly on the dump and road (non-shielded).

The following assumptions were made:

- A nominal exposure time of 2100 working hours in a year;
- Wearing of overalls and rubber boots;
- Surface beta activity and gamma dose rate at the maximum values (excluding hot spots).

The results are presented in Table III. The dose was 0.90–2.54 mSv/a. The most exposed workers were those working directly on the dump in places not satisfying the Regulation by Council of Ministers of 3 December 2002 §3 pt. 4. The least exposed workers were those in cabins either on the dump or on the road in places conforming to the above point of the Regulation. It should be stressed that all exposure values (for specified groups of workers and workplaces) were calculated assuming the maximum values of exposure factors, so the real doses would be lower. The analysis did not include exposure of persons at hot spots.

TABLE III. RESULTS OF ANALYSIS OF EXPOSURE OF WORKERS

Shielding by vehicle cabin	Type of work	Compliance with §3 pt. 4	Surface beta activity (Bq/cm^2)	Gamma dose rate (nGy/h)	Exposure time (h/a)	Effective dose (mSv/a)		
						Beta	Gamma	Total
No	Dumps	No	1.36	1064	2100	1.17	1.56	2.54
		Yes	0.64	742	2100	0.55	1.09	1.45
	Road construction	Yes	0.64	742	2100	0.55	1.09	1.45
Yes	Dumps	No	Negligible	1064	2100	1.17	0	0.98
		Yes	Negligible	742	2100	1.09	0	0.9
	Road construction	Yes	Negligible	742	2100	1.09	0	0.9

5.2.3. Environmental protection

The concentration of radium on the dump (excluding hot spots) exceeded that in the vicinity of the dump by 3–50 times. Thus, it is recommended that the environment be protected from contamination by the dump material by the following measures:

- Maximum suppression of dust during excavation of the material;
- Prevention of material losses during transport, by:
  (a) Sprinkling the transported material with water, or
  (b) Covering the transported material with foil;
- Maximum suppression of dust during construction of the road;
- Avoid the organizing of intermediate dumps.

6. CONCLUSIONS

The following conclusions are drawn, based upon the measurements on site, the samples collected from the dumps and analysis of the exposure of workers:

- The material on the disposal dumps is inhomogeneous with respect to the concentration of natural radionuclides, particularly ^{226}Ra (252–8724 Bq/kg). Neighbouring points with totally different concentrations of ^{226}Ra were found. The highest concentration of radium was at so-called hot spots. This material must not be reused in any applications, and must be recultivated on site. The remaining material can be used for road construction after mixing with material having a low natural radionuclide concentration so that the final product complies with the Regulation of 3 December 2002 (§3). It must be stressed that the road built using this material must comply additionally with the requirements of §4, i.e. reducing the absorbed dose rate at 1 m above the road surface to a value not exceeding 300 nGy/h;

- The exposure of workers employed directly on the dumps and road construction (not shielded by cabin walls) will result in a dose of 1.45–2.54 mSv (based on 2100 h of work per year), so it will exceed the prescribed value of 1 mSv/a. However, according to the Regulation of Council of Ministers "on dose limits", the dose limit of 1 mSv in a calendar year can be exceeded, provided that in the following five year period a summed dose of 5 mSv would not be exceeded. Thus, for a period of road construction of less than 2 years, a limitation of working hours below 2100 h is not mandatory. The exposure will not exceed 1 mSv for the workers employed as operators of special construction vehicles.

RADIONUCLIDE CONTAMINATION OF NATURAL ENVIRONMENT OF ABSHERON PENINSULA (AZERBAIJAN)

S. Aliyeva[*]

Geology Institute of Azerbaijan National Academy of Sciences,
Baku, Azerbaijan

Abstract

The territory of Azerbaijan due to its geographical situation, diversity of natural climatic zones and industrial potential, is a unique object of ecological research. One of the most ecologically problematic regions of Azerbaijan is the Absheron Peninsula. The main factors of pollution in the development of oil deposits are oil and oil products. The normal radioactive background in the Absheron Peninsula varies from 4 to 10 μR/h. The problem of pollution of oil-producing areas by radionuclides of natural origin arose recently. Surfaces and oil industry equipment polluted by radionuclides are discovered at almost all exploration fields surrounding the large industrial centre, Baku. Anomalous areas were determined where the intensity of gamma radiation reached 600 μR/h. In addition, within the Absheron Peninsula there are iodine plants, the surroundings of which are also polluted by radionuclides of natural origin. Identification of the radionuclides showed that they were from the uranium-radium group, reaching high concentrations. One method of reducing the impact of the oil fields on the ecology can be the utilization of underground salt brines and, probably, their use for medical purposes. During oil and gas field exploration (especially in the offshore area of the Caspian Sea) it is necessary to take environmental protection measures involving the study of the radiation background of the coastal-shelf zones and radioactivity of bottom sediments prior to embarking on geological exploration work. At present there is a large body of experience of radioecological work that can be used for the establishment of radiation monitoring in Azerbaijan.

1. INTRODUCTION

The territory of Azerbaijan Republic is a unique object of ecological research, due to its geology, structure, geographical situation, diversity of natural climatic zones and industrial potential. One of the most ecologically problematic regions of Azerbaijan is the Absheron Peninsula (total area 2500 km^2). The Absheron Peninsula is not only a highly populated area but also the main agricultural and oil- and gas-producing region of the Republic, where oil and gas exploration has been carried out for more than 150 years. The main factors of pollution here are the oil products from the exploration fields.

2. NATURAL BACKGROUND RADIATION

The land area of the Absheron Peninsula is composed of weakly radioactive rocks, closely related to its geotectonic evolution. Throughout the Absheron Peninsula, the intensity of gamma radiation varies from 3.5 to 7 μR/h [1]. At the Shakhov spit and north coast beaches, it decreases to 3 μR/h. On the other hand, at the fields of mud breccia [1], at the areas of young travertine accumulations and within the areas of Maykopian rocks outcrops it increases

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[*] E-mail: aliyevas@yahoo.com

[1] 1 R = 2.58 × 10^{-4} C per kg of air.

to 9–30 μR/h. Statistical parameters demonstrate a normal radioactivity distribution with an average of 6 μR/h (equivalent to a dose of 0.5 mSv/a), i.e. it is within a level favourable for human residence (Fig.1). Comparison of these data with the results of studies conducted in France, Germany, Italy, Japan and USA demonstrated that nearly 95% of population live in places where the radiation dose is in a similar range: 0.3–0.6 mSv/a.

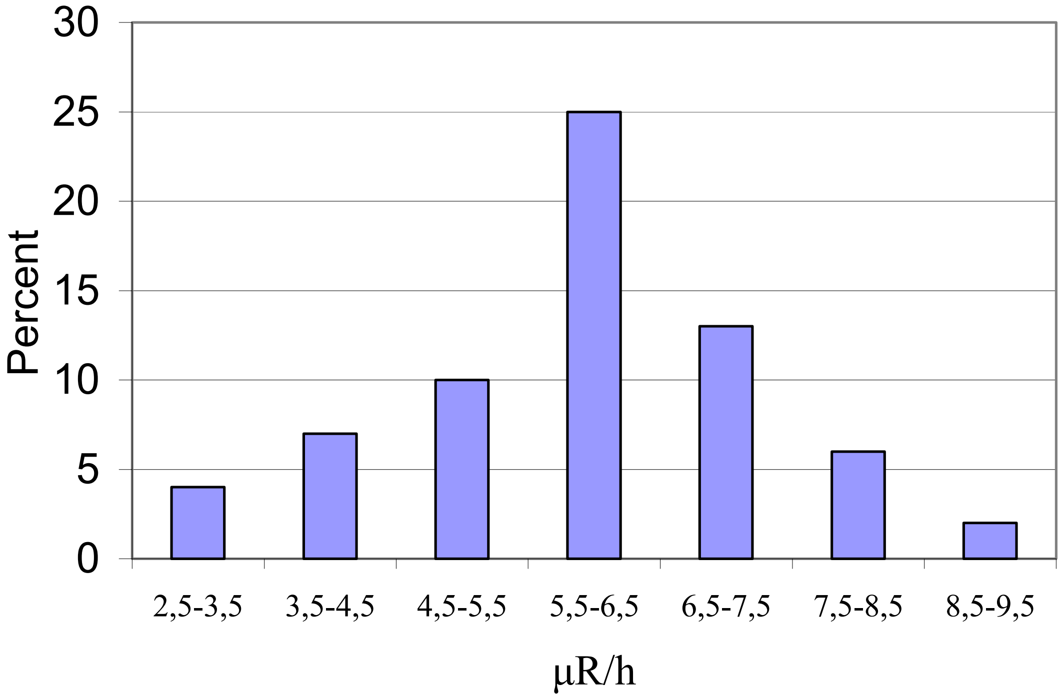

FIG. 1. Radioactivity distribution for the Absheron Peninsula

3. RADIONUCLIDE CONTAMINATION AT THE OIL FIELDS

The problem of pollution of oil-producing areas by radionuclides of natural origin has arisen recently. Surfaces and oil industry equipment contaminated by radionuclides were discovered at almost all exploration fields surrounding Baku, the capital city and a large industrial centre of Azerbaijan [2]. Anomalous areas were found there, where the intensity of gamma radiation reached 600 μR/h (Fig. 2). Soils at several oil fields are heavily contaminated by radionuclides and sometimes are probably subject to disposal as radioactive waste. It was determined that intensive contamination of equipment, pipelines, reservoirs and the surrounding environment occurs during the production, processing, transportation and preservation of oil and oil products.

A large amount of contaminated equipment (pipes, pumps, etc.) with long term radioactive background 'crusts' (Fig. 3) was discovered in the area of the oil fields. It represents a high risk also because sometimes this equipment is recycled or simply used by local inhabitants (for example, radioactive pipes serve as fences in kindergartens, schools, etc.). Products made from such metal are very hazardous especially if they are used for the construction of buildings [3].

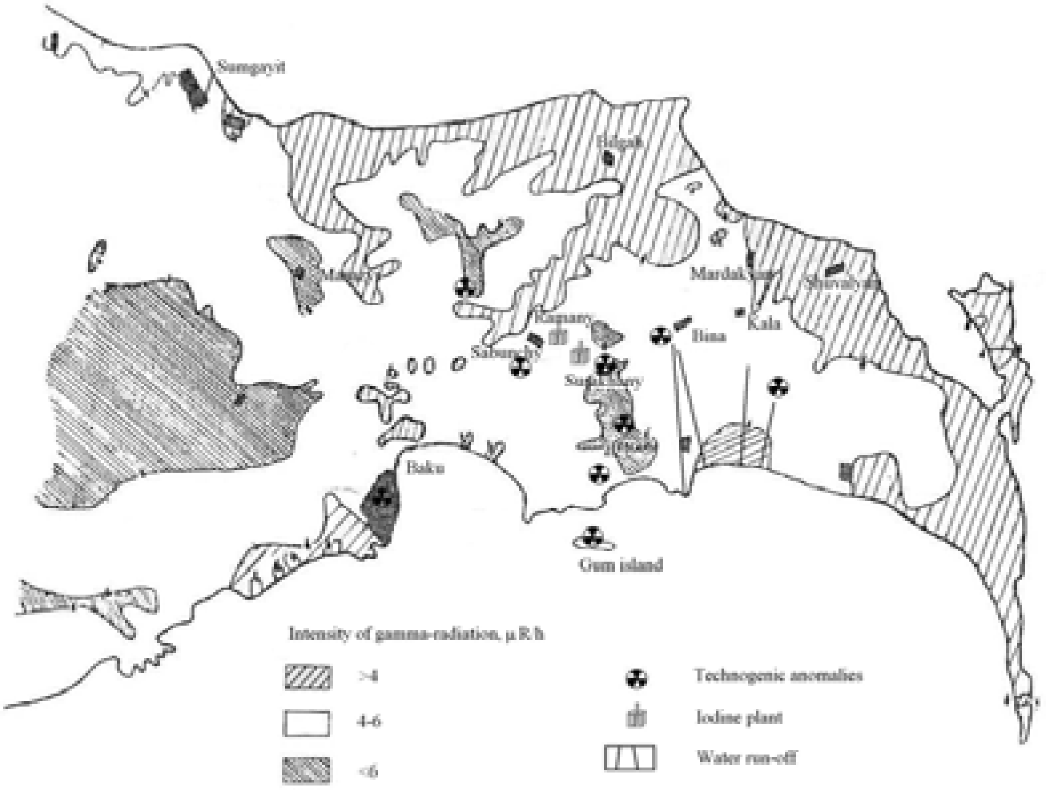

FIG. 2. Location of zones with increased radioactivity on the Absheron Peninsula

FIG. 3. Contamination of the oil field area

3.1. Radionuclides in waters from the oil fields

The main contaminants at oil fields are radium and uranium, depending on the type of groundwater accompanying the oil. By their chemical composition, formation water in the Absheron Peninsula is divided into two main types [4, 5]:

- Hard chlorine-calcium-sodium,
- Alkaline-hydrocarbonate-sodium.

Hard formation water at oilfields, in contrast to other types of water widespread in the earth's crust, are carriers of the highest concentration of radium. The most common concentration of radium in such water varies from 3×10^{-11} to 8×10^{-11} percent, exceeding by a thousand times the concentration in seawater (2×10^{-14} percent). With rare exceptions, the concentration of radium in mineral spring water reaches only the lower limit of the concentration of radium in oilfield water. One can observe a dramatic deviation above and below the average amount. The highest amount of radium is 2×10^{-8} percent. In oilfield water, the concentration of some isotopes of the thorium series (mainly ^{228}Ra, ^{224}Ra) is also very high. As a result of numerous investigations, it was determined that high-mineralized hard sulphate-free water of the chlorine-calcium-sodium type containing high amounts of alkaline earth elements is enriched by radium and its isotopes [6]. Oilfield waters became radium bearing due to the leaching of radium from rocks containing normal concentrations of radium. In the dispersed state, radium is always present in rocks. Radium seeps into formation waters by means of capillary and fracture water. Radium is accumulated in sulphate-free chloride brines during exchange desorption from clayey particles of rocks during its presence in a layer of metamorphized water of marine sedimentation.

Water of the second type (alkaline water) differs by having a low concentration of radium, but it is most favourable for the concentration of uranium. Uranium is found in all formation water in the oilfields in the Absheron Peninsula. The concentration of uranium in the alkaline water does not drop below a few micrograms per litre (for hard waters it is less than a few tenths of a microgram per litre). Any rigorous regular relationship between mineralization of hard waters and uranium concentration has not yet been determined [7, 8].

Hard water in comparison with seawater is lower in uranium by 5 times on average. The enrichment of uranium in alkaline water depends on many factors, including the form of uranium present in the water and rocks and the character of its distribution in the oil–water system. The minimum and maximum concentrations of uranium in the alkaline formation water of oilfields differ by a factor of 100 or more (Table I).

TABLE I. RADIOELEMENT CONCENTRATIONS IN THE MAIN HYDROCHEMICAL TYPES OF WATER IN THE ABSHERON PENINSULA OIL FIELDS

Hydrochemical type of water	Concentration (g/L)		
	Uranium	Radium	Thorium
Alkaline	5×10^{-6}	7×10^{-11}	1×10^{-7}
Hard	4×10^{-7}	2.5×10^{-11}	1×10^{-7}

A typical feature of radioactive contamination of the Absheron Peninsula area is that the contamination comprises radionuclides that are naturally occurring but resulting from technogenic processes. The dynamics of such oilfield contamination can be modelled rather simply.

Radioelements are brought to the earth's surface by formation and produced waters. Areas within and surrounding the oilfields are the most contaminated. Together with water and sand, oil goes to a terminal via pipes. After initial separation, the oil is removed and sent to the oil refinery in pipes. The water is discharged into artificial reservoirs where large quantities of radioactivity are deposited in the form of silty, muddy deposits. The contamination of new areas occurs rather quickly. Monitoring has shown, for example, that in 5 years the gamma field changed from 4 μR/h to 600–700 μR/h at an absolutely clean area of the island Gum (a shallow marine area of the Caspian Sea) [7, 8].

The existence of mobile contact between water, rocks and oil during production plays a significant role in the formation of contaminated areas in oilfields.

One of the methods of reducing the ecological impact of the oilfields can be the purification and reutilization of subsurface waters and underground salt brines, followed, probably, by their use for medical purposes.

4. RADIONUCLIDE CONTAMINATION IN THE VICINITY OF IODINE PANTS

In addition, there are two iodine plants within the Absheron peninsula, the vicinity of which is also polluted by radionuclides of natural origin. Extraction of iodine and bromine from the formation waters is associated with the accumulation of radium in the activated charcoal. In the coarse of time, the charcoal accumulates in the vicinity of plants (Fig. 4). Wind and precipitation spread radionuclides around the plants and contaminate the populated areas nearby. The levels of gamma radiation within such areas sometimes reach 1000 μR/h (with a background of 6 μR/h). In the areas polluted by iodine plants (beyond the immediate plant areas), the amount of radium in surface layers exceeds the background by 1000–2000 times [9]. Identification of the radionuclides showed the presence of uranium–radium in high concentrations.

FIG. 4. Environmental contamination by iodine plants. Accumulations of highly radioactive activated charcoal can be seen on the left

5. CONCLUSION

Different mechanisms for the generation of anomalies depend on numerous geological and hydrogeological factors. The results of investigations have demonstrated that mitigation of contamination or its removal is a difficult task, and first of all it is necessary to examine the hydrogeochemical environment in different areas.

During the exploration of oil fields it is necessary to take environmental protection measures even before embarking on geological exploration work. In particular, it is almost obligatory to conduct research linked with the study of the radiation background.

There is great potential for the above-mentioned problems to be solved, and different leading oil companies (such as BP) understand this as well. Radiation safety should be provided by the adoption of specific control measures and by the observation and implementation of the requirements of the ‘Law on Radiation Safety’ adopted in 1997.

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NORM IN INDUSTRY

METHODS FOR ASSESSMENT OF THE OCCUPATIONAL EXPOSURE AT WORKING PLACES OF DIFFERENT TENORM INDUSTRIAL BRANCHES

D. Weiss[1], H. Biesold[2], P. Jovanovic[3], L. Juhàsz[4], A. Laciok[5], K. Leopold[6], B. Michalik[7], H. Moravanská[5], A. Poffijn[8], M. Popescu[9], C. Rădulescu[9], P. Szerbin[4], J. Wiegand[6]

[1] Gesellschaft für Anlagen- und Reaktorsicherheit (GRS) mbH, Germany
[*2]GRS, Germany
[3] Institute of Occupational Safety (ZVD), Slovenia
[4] Frederic Joliot-Curie National Research Institute of Radiobiology and Radiohygiene (NRIRR), Hungary
[5] Nuclear Research Institute (NRI), Czech Republic
[6] University of Essen, Germany
[7] Central Mining Institute, (GIG), Poland
[8] University of Ghent, Belgium
[9] Research and Design Institute for Rare and Radioactive Metals (ICPMRR), Romania

Abstract

Within the TENORMHARM project one task concerns an assessment of the radiation dose to workers in different TENORM industries that are of some relevance within the participating EU and candidate countries. This assessment is based upon information and data collected at the beginning of the project and, if existing, on national regulations and compared with EU standards. The most relevant industries of each participating country where TENORM occurs were reported and compared, from which each participant selected one branch where an occupational exposure of more than 1 mSv/a could be expected. Subsequently, the calculation of the radiation dose was carried out independently by each participating country. Also, the real situation at the considered working place, i.e. the use of respiratory protection or indoor air cleaning measures, was considered. The results of the dose calculation obtained by each contractor for the selected exposure scenario were compared with the same or a similar scenario described in a European Commission report. This comparison demonstrated that the applicability of reference levels for regulatory control of workplaces given in the report was limited because the considered scenarios do not reflect sufficiently the recent work conditions. Moreover, any scenarios described by the contractors had no applicable counterpart in the report. The results of this comparison will be presented and proposals for realistic dose assessments at different working places where TENORM occurs will be given.

1. INTRODUCTION

Within the TENORMHARM project, one task concerns the assessment of the radiation dose to workers of different TENORM industries which are of some relevance within the participating EU and candidate countries. This assessment is based upon information and data collected at the beginning of the project and, if existing, on national regulations and compared with EU standards. The most relevant industries of each participating country where TENORM occurs were reported by contractors. Each participant selected one branch where an occupational exposure of more than 1 mSv/a could be expected. Subsequently, the

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[*] E-mail: wem@grs.de

calculation of the radiation dose was carried out independently by each participating country. The results of the dose calculation obtained by each contractor for the selected exposure scenario were then compared with the same or a similar scenario described in the European Commission report ‘Radiation Protection 107’ (RP107) [1].

2. METHODOLOGY

2.1 Selection of industries and working places

The following working places were selected for the assessment of occupational exposure by each participating country:

- GRS, Germany: oil & gas industry
    - Storage of tubes and drilling equipment
    - Handling of separated scales
    - Removal of scales from tubes
    - Cutting of tubes
- NRI, Czech Republic: titanium dioxide pigment industry
    - Ilmenite feedstock
    - Material in vats
    - Radium bearing scales
- NRIRR, Hungary and ZVD, Slovenia: coal fired power plant (ash and slag repository)
- ICPMRR, Romania: bauxite processing (red sludge repository)
- UGENT, Belgium: phosphate fertilizer production
    - Phosphate ore stockpile
    - Waste dumps
- UESSEN, Germany and GIG, Poland: coal mining (sediments from pit water discharge)

2.2 Exposure pathways and work conditions

According to the specific features of the above-mentioned working places, in most cases the following exposure pathways were considered

- External exposure to gamma radiation;
- Inhalation of dust;
- Inhalation of ^{222}Rn and progeny.

In the case of coal mining in Poland and the titanium pigment industry in Czech Republic, direct ingestion was also taken into account. In addition, NRI included the exposure by skin contamination because they used the same approach as described in RP107.

The considered scenarios are based on realistic work conditions, as appropriate. That means all measures to avoid or reduce occupational exposure at each working place were taken into account, e.g. installation of dust suppression systems or air filters.

2.3 Dose calculation procedure

For the dose calculation procedure in any participating countries, legal framework conditions or at least recommendations exist.

In Germany, the dose calculation procedure is described in two regulations on the prediction of dose resulting from uranium mining and milling activities [2, 3]. Nevertheless, some changes of the described dose calculation procedures are necessary in the case on hand. That concerns the consideration of nuclides of the thorium decay chain that occur in some TENORM and non-equilibrium conditions within and between the natural decay chains, especially in the oil and gas industry.

In the Czech Republic and Romania, no regulation on dose calculation procedures exists for TENORM industries. While NRI applied the calculation procedure according to RP107, ICPMRR developed a special procedure for the calculation of dose to an individual staying on or around a dry red sludge pond.

The Hungarian approach is based on measured values of gamma dose rate and ^{222}Rn concentration in air (calculated from Rn exhalation). ZVD (Slovenia) used for dose calculation the measured values of gamma dose rate, the ^{222}Rn concentration in air, radionuclides in aerosols, and fallout.

The dose calculation applied by GIG is based on the new Polish Atomic Act, which came into force in January 2002. According to this regulation, the assessment of dose related to natural radiation has to be carried out in underground mines by means of dosimetric measurements in the work environment.

In principle, the following procedure for the calculation of the annual effective dose (D) was applied:

- External exposure to gamma radiation:

$$D_\lambda = H_\lambda \, f_\lambda \, t_{\mathrm{exp}} \qquad (1)$$

where H_λ is the photon-equivalent dose rate (gamma dose rate) (nSv/h);

f_λ is the conversion factor from dose rate to effective dose (0.6 for adults);

t_{exp} is the annual exposure time (h).

- Inhalation of radon and progeny:

$$D_{Rn} = k(\mathrm{Rn})_{\mathrm{A}} \, F \, C_{\mathrm{Rn}} \, t_{\mathrm{exp}} \qquad (2)$$

where $k(\mathrm{Rn})_{\mathrm{A}}$ is the coefficient pertaining to the dose convention following ICRP Publication 65 (7.9×10^{-6} for workers) (mSv per Bq·h·m^{-3});

F is the equilibrium factor (0.4);

C_{Rn} is the Rn concentration (Bq/m^3).

- Inhalation of contaminated dust:

$$D_{\mathrm{LLA}} = t_{\mathrm{exp}} \, V \sum g_{\mathrm{inh},r} C_r \qquad (3)$$

where V is the breathing rate (1.2 m^3/h for workers);

$g_{\mathrm{inh},r}$ is the inhalation dose coefficient for radionuclide r (Sv/Bq);

C_r is the ambient activity concentration of radionuclide r (Bq/m^3).

- Direct ingestion of contaminated soil or dust:

$$D_{\mathrm{ING}} = t_{\mathrm{exp}} \, U_{\mathrm{S}} \sum g_{\mathrm{ing},r} C_{\mathrm{S},r} \qquad (4)$$

where U_{S} is the soil ingestion rate (kg/h);

$g_{\text{ing},r}$ is the ingestion dose coefficient for radionuclide r; (Sv/Bq)

$C_{\text{S},r}$ is the activity concentration of radionuclide r in the fine-grained fraction of the soil (Bq/kg).

In most cases the direct ingestion of contaminated particles can be neglected if the principles of radiation and work protection are followed.

The total annual dose was obtained by summing the doses for each exposure pathway.

3. COMPARISON OF EXPOSURE SCENARIOS USED BY CONTRACTORS WITH THOSE DESCRIBED IN RP107

3.1 Applied scenarios defined in RP107

RP107 reported on the establishment of reference levels for regulatory control of workplaces where materials containing enhanced levels of naturally occurring radionuclides are processed. The exposure pathways according to RP107 are the same as those described above. In addition, skin contamination is considered. The reference levels in RP107 corresponding to specified dose levels were derived from ‘normal assumptions’ and ‘unlikely assumptions’, defined for two different exposure scenarios for each exposure pathway. In contrast, the dose calculations carried out by the contractors of the TENORMHARM project are mostly based upon measurements of dose rate and radionuclide concentration at a working place or another location of interest. As far as possible the following scenarios defined in Ref. RP107 are taken into account for comparison:

(i) Exposure from stockpiles

This scenario considers the exposure of a worker to a large pile of material in a warehouse.

(ii) Exposure from scales and residues

This scenario considers the exposure of a worker to chemically or physically concentrated radionuclides, where the following two basic assumptions are met:

- volatilization of Po (and sometimes Pb) in high temperature furnaces,
- enrichment of radium in pipe scales in certain oil and gas fields.

(iii) Exposure from process vessels and pipes

In this scenario, workers are exposed only to external radiation from a shielded source.

Deviating from these scenarios, the national reports include exposure situations at outdoor working places.

Because RP107 is directed towards establishing reference levels for the regulatory control of workplaces, the dose calculation procedures are sometimes different from that applied by the contractors. Therefore, the calculation of the dose for each pathway in RP107 is based on the ratio between the annual effective dose (Sv/a) and the radionuclide activity concentration (Bq/g). Subsequently, the dose coefficient is expressed as Sv/h per Bq/g, instead of the dose per activity unit (Sv/Bq). The dose calculation for skin contamination is based on the ratio between dose rate (Sv/h) and surface activity concentration (Bq/cm^2).

3.2 Data and assumptions used for comparison

According to RP107, the classification of a workplace would be carried out using the reference levels given in Table 7b in RP107 for ‘normal assumptions’ corresponding to ≤ 1 mSv/a and ‘unlikely assumptions’ corresponding to ≤ 6 mSv/a. Afterwards, the measured individual radionuclide concentrations would be compared with the reference levels for a particular reference point (in this case the reference point of 1 mSv/a for normal assumptions) given by the formula:

$$A_i = \sum_{n=1}^{N} \frac{conc_n}{reflevel\ ^i n}$$

where $conc_n$ is the concentration of radionuclide n;

$reflevel\ ^i n$ is the reference level for radionuclide n and reference point i.

Only if $A_i \leq 1$ does the material contain concentrations below those corresponding to the specified reference point. The reference levels correspond to a dose of 1 mSv/a if the material-specific scenarios and parameters are used as described in Chapter C4 of RP107. Thus, if a parameter used by a contractor for dose calculation did not correspond with the relevant value specified in RP107, corrections were necessary. Differences between exposure times were eliminated by dividing the applied exposure time by the corresponding exposure time given in RP107.

The comparison of external exposure was more complicated because in RP107 the ratio between dose and specific activity (Sv/h per Bq/g) is calculated for a distance of 1 m from the source. For some scenarios described in the national reports, other distances to the source were used. The relationship between the gamma dose rate (nSv/h) and different distances to the source is given in a German national report [5].

Where a reported scenario had no counterpart in RP107, the applied dose calculation procedure was compared with the methods of calculating dose according to section 3.5 in RP107 using the same exposure time for both calculations.

4. RESULTS AND DISCUSSION

Table I gives an overview of the results of the comparison for selected scenarios and workplaces described in Ref. [4]. Table I illustrates that the dose calculated by the contractors sometimes deviated from that calculated according to RP107. The main reasons for these deviations are summarized in Table II.

The applicability of the RP107 reference levels for regulatory control of workplaces seems to be limited because the scenarios used for deriving the reference levels do not reflect sufficiently the current work conditions. Moreover, many scenarios described by the contractors have no applicable counterparts in RP107.

Except for the Czech contractor no party calculated the dose via ingestion of dust and by contamination of skin. According to modern work conditions and measures required to prevent the ingestion of contaminated dust, this exposure pathway can be neglected in most cases. The same concerns the contamination of skin.

TABLE I. COMPARISON OF THE RESULTS OF DOSE CALCULATIONS BETWEEN CONTRACTORS AND RP107

Exposure pathway	Reported by contractors		According to RP107	
	Effective dose (mSv/a)	Calculation parameters	Effective dose (mSv/a)	Calculation parameters
Scales in pipes (at drilling platform), GRS				
External exposure (direct contact with pipes)	1.20	^{226}Ra: 200 Bq/g ^{228}Ra: 68 Bq/g ^{228}Th: 80 Bq/g t_{exp}: 400 h/a	20.88	External dose coefficient: Table C1 (pipe scale) × 3.33 (direct contact) t_{exp}: 400 h/a
Removal of scales (by sandblasting), GRS				
External exposure	0.51	^{226}Ra: 200 Bq/g ^{228}Ra: 68 Bq/g ^{228}Th: 80 Bq/g t_{exp1}, t_{exp2}, t_{exp3} as in Ref. [4]	0.14	External dose coefficient: Table C1 (pipe scale) × 3.33 (direct contact) × 0.17 (5 m) t_{exp1}, t_{exp2}, t_{exp3} adapted
Inhalation of dust	18.4	^{210}Pb: 0.45 Bq/m^3 ^{210}Po: 0.45 Bq/m^3 ^{226}Ra: 1.80 Bq/m^3 ^{228}Ra: 0.61 Bq/m^3 ^{228}Th: 0.72 Bq/m^3 t_{exp}: 500 h/a	27.8	Inhalation dose coefficient: Table D9 AMAD: 5 μm
Disposal of ash and slag (from coal fired power plant), ZVD				
External exposure	0.0012	^{226}Ra: 0.25 Bq/g ^{228}Ra: 0.03 Bq/g ^{228}Th: 0.035 Bq/g	0.047	External dose coefficient: Table C1 (pyrochlore feedstock)
Radon inhalation	0.16	^{222}Rn: 50 Bq/m^3	0.11	Rn dose coefficient: Section F3.3
Inhalation of dust	0.00062	^{226}Ra: 0.001 Bq/m^3 ^{210}Pb: 0.06 Bq/m^3 ^{210}Po: 0.06 Bq/m^3	0.15	Inhalation dose coefficient: Table D9 AMAD = 5 μm
Disposal of red sludge, ICPMRR				
External exposure	0.27	Background included		Comparable to 'exposure from stockpiles'
Radon inhalation	^{222}Rn: 0.56 ^{220}Rn: 4.70	0.1 m above ground: ^{222}Rn: 248 Bq/m^3 ^{220}Rn 6270 Bq/m^3	^{222}Rn: 0.084 ^{220}Rn: 0.71	Assume Rn conc. 1 m above ground is 10% of value at 0.1 m
Inhalation of dust	0.112	U_{nat}: 0.0018 Bq/m^3 Th_{nat}: 0.0025 Bq/m^3	0.088	Inh. dose coefficient: Table D9. AMAD: 5 μm
Flood plain soils affected by pit water discharge from coal mines, UESSEN				
External exposure	0.72	t_{exp}: 200 h/a	0.11	'Exposure from stockpiles', ext. dose coefficient: Table C1

TABLE II: REASONS FOR DIFFERENCES IN THE RESULTS OF DOSE CALCULATIONS BETWEEN CONTRACTORS AND RP 107

Scenario and exposure pathway	Reasons for deviation
Scales in pipes	
External exposure	Dose coefficients derived in RP 107, Table C1 do not sufficiently consider real conditions (e.g. self-absorption of gamma radiation by $BaSO_4$ and its non-linear relationship to scale thickness, or the consideration of a pipe as a shielded linear source) and lead to a dose 10 times higher
Removal of scales	
External exposure	Smaller deviation compared with 'scales in pipes' results from better fitting of theoretical assumptions to natural conditions for unshielded volumetric sources
Inhalation of dust	Significantly higher inhalation dose coefficient used in RP 107
Disposal of ash and slag	
External exposure	Possibly the use of external dose coefficients for pyrochlore feedstock (Table C1)
Radon inhalation	No significant deviation
Inhalation of dust	Possibly significant differences in dose coefficients
Disposal of red sludge	
External exposure	See Table I
Radon inhalation	Use of Rn concentration measured 0.1 m above ground by Romanian contractor
Inhalation of dust	No significant deviation
Flood plain soils affected by pit water discharge from coal mines	
External exposure	Smaller deviation compared with 'scales in pipes' results from better fitting of theoretical assumptions to natural conditions for unshielded volumetric sources. Use of external dose coefficients (Table C1) for Ra sludge removal could also influence result

In contrast to RP 107, the TENORMHARM contractors excluded ^{40}K from the project work. This approach is justified because the dose resulting from ^{40} K is unavoidable and the ratio between stable potassium and ^{40} K remains constant all over the world.

Table C1 of RP107, containing external dose coefficients for different industries and materials, is highly complicated and its practical application is limited. In practice, the use of results from site-specific gamma dose rate measurements is much more suitable for external dose calculations because the theoretical approaches in RP107 do not reflect the natural conditions sufficiently. Furthermore, these data are not really hard to reconstruct. Table C1 presents external dose coefficients for all long-lived naturally occurring radionuclides and for a lot of different materials. Most of the listed radionuclides can be neglected for external dose estimation purposes. Only certain decay products of ^{226}Ra and ^{228}Ra/^{228}Th (and ^{40}K) contribute to the external dose through gamma radiation.

The same is true for the reference levels in Tables 7a–7d of RP107. In the case of those raw materials in which equilibrium of the natural decay chains is preserved, it is always the radionuclide with the highest contribution to the dose that defines the activity level of interest, and the ratio between ^{238}U and ^{235}U series radionuclides is unchanged. This scheme is also questionable for non-equilibrium conditions. Consider, for example, the reference levels of ^{228}Ra and ^{228}Th in radium scales where the value of ^{228}Th is one order of magnitude lower than that for ^{228}Ra. If ^{228}Ra is acting as the starting point of the segment of the thorium decay chain, the activity concentration of ^{228}Th will rise, in theory, to 1.46 times that of ^{228}Ra after a certain time and, in parallel, will decay with the half-life of ^{228}Ra.

5. SUMMARY AND CONCLUSIONS

(i) In most of the investigated cases of TENORM at workplaces, occupational exposure cannot be reliably assessed by automatically applying standardized factors. Only the possible pathways can be listed and general rules of assessment prepared.

(ii) In each case, the assessment should be based on the direct measurement of particular risk factors. Only in this way can all influencing features be considered (particular work conditions, geometry, attenuation, individual protection, respiratory protection, etc.).

(iii) Only external exposure and the inhalation of radon and dust contribute significantly to the total occupational exposure. The dose via direct ingestion of particles and skin contamination is avoidable by common radiation protection and hygiene measures.

(iv) All investigated practices should be additionally assessed by considering their impact on members of the public.

(v) When evaluating the significance of risk occurring in all the investigated branches of industry, the concepts of clearance, exemption and exclusion should be applied according to European Commission guidance [6].

ACKNOWLEDGEMENT

The work was funded and carried out in the EU 5th FP, Nuclear Fission and Radiation Protection, Contract No. FIGM-CT-2001-00174.

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DISMANTLING OF A NORM CONTAMINATED PHOSPHORIC ACID PLANT IN THE NETHERLANDS

R. Rentmeester[1*], **R. Janssen**[2**]
[1]Hydro Agri BV (Norsk Hydro), Vlaardingen, Netherlands
[2]Radiation Protection Services, Rontgen Technische Dienst BV, Rotterdam. Netherlands

1. INTRODUCTION

The Netherlands does not have phosphoric acid plants anymore. The last two plants, operated by Norsk Hydro (Hydro Agri, Rotterdam BV) and Kermira BV respectively, ceased production in 2000, after which their dismantling was started. In the Netherlands the production of phosphoric acid started at the beginning of the last century, and this has been continued during the whole century. In the 1970s it was observed that, with the production of phosphoric acid, radioactive deposits could occur in the production installations. The type and extent of the depositions depended on the chemical process applied, the phosphate ores used and a number of physical parameters.

Sedimentary phosphate ores contain only small concentrations of ^{238}U in equilibrium with its decay products, amongst which is ^{226}Ra. The concentration depends on the origin and composition. As a result of the chemical process, salts with ^{226}Ra come into being that are deposited in certain parts of the process installation. Because of the process, ^{238}U remains in solution and is found in the phosphoric acid. The radioactivity problem was reduced considerably by adjusting the chemical process and the process parameters, and changing the type of phosphate ore used. The older installations exhibited radiation levels up to 100 μSv/h and activity concentrations of ^{226}Ra up to 1500 Bq/g.

2. NO NEW GENERATION

At the end of the 1970s and beginning of the 1980s, more and more attention was drawn to the risk of exposure from ionizing radiation, including the exposure from naturally occurring radioactive materials (NORM). In the 1990s, the risk to the public due to exposure to NORM was also investigated. In the second half of the 1990s, the first regulations were drawn up for non-nuclear industries. Companies from these industries had to obtain a licence if the activity concentration of the depositions in their installations was higher than 100 Bq/g. A change in policy by the Dutch government in the area of waste and problems with the sale of by-products such as gypsum on the open market led to considerable problems. As a consequence, the companies no longer invested in the modernization of their phosphoric acid plants. In the Netherlands at least, there were no good prospects anymore for the future.

In accordance with European Council Directive 96/29/Euratom of 13 May 1996, a new Dutch Radiation Protection Ordinance came into force on 16 July 2001. A chapter was introduced in this new ordinance applicable exclusively to work activities involving NORM. It is expected that a regulation based on this chapter will come into force by the end of 2004.

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[*] E-mail: rinus.rentmeester@yara.com
[**] E-mail: r.g.c.janssen@rtd.nl

The proposed regulation was sent to the European Commission for verification at the beginning of 2004.

3. DISMANTLING OF THE PHOSPHORIC ACID PLANT OF HYDRO AGRI ROTTERDAM BV

3.1. Plan of action

Problems can occur with the maintenance and dismantling of process installations in which NORM deposits exist as a result of the use of radioactive raw materials. Exposure to these radioactive substances can lead to health risks for the personnel involved as a result of inhalation, ingestion, and external exposure. Therefore, in the Netherlands a licence to perform these work activities is required in accordance with the Radiation Protection Ordinance.

Because of the need for specific knowledge of the process and the risks involved with these NORM contaminated installations, such installations are generally dismantled by the personnel of the owner. Permission is required from the Dutch authorities before dismantling can take place. The company that carries out the dismantling has to have a licence. The licence can be revoked only after the completion of the dismantling and fulfilment of all the obligations in the licence.

Before the dismantling takes place, a plan of action has to be drawn up with a description of the most important health and safety aspects and the impact on the environment, taking economic aspects into account. Such a plan of action contains the following:

- The necessary preparations (flushing, termination of operation);
- The organization of health and safety, and responsibilities;
- The method of disposal of radioactively contaminated installation components and radioactive substances;
- The method of dismantling of the installation;
- The method of use of technical equipment in the dismantling of the installation;
- The method in which the (radioactive) waste is treated;
- The disposal of the waste.

The plan of action must contain a risk inventory in which the exposure of workers and the public are estimated. Moreover, a description of how this exposure is to be kept as low as reasonably achievable must be given. During the dismantling, the plan of action has to be adjusted in the event that the information used in drawing up the original plan is superseded.

3.2. The final report as a dossier

At the end of the dismantling, a report with the following contents has to be presented:

- Historical information and references;
- A summary of the whole project;
- The organization with respect to responsibilities and supervision;
- The applicable licences;
- The results of the preliminary inventory;

- An overview of the contaminated installation components identified;
- An overview of the methods applied for treating these components;
- The plan of action for each method;
- An overview of the ultimate release of contaminated components;
- An overview of the release of equipment used;
- An overview of the tools and aids applied and released;
- A calculation of the dose received by workers and the public;
- An overview of the quantities and temporary storage of the (radioactive) waste produced;
- The transfer of radioactive substances to third parties for the purpose of further processing.

The report must be available for at least 15 years. The document may be used in evidence.

3.3. Technical approach

When dismantling a NORM-contaminated installation, it is advisable to start by conducting a radiation survey. During the survey the whole installation has to be measured and all the radiation levels have to be recorded and collated. With this information, the sources of the highest radiation levels, and the possibility of such levels limiting the radiation survey of the other parts of the installation, are identified.

The installation components that can be either dismantled or decontaminated elsewhere can now be selected. Next, a plan is drawn up to remove or clean objects with the highest radiation levels. As a result, the radiation level in a certain area is lowered and other objects with enhanced radiation levels can be identified in a second survey. With the information from this second survey, the objects with the highest radiation levels can again be removed, and ‘new’ contaminated objects become ‘visible’.

Radioactively contaminated metal objects that cannot be decontaminated properly can be transferred to a metal foundry that has a licence to melt such objects. In the Netherlands, the export of such objects for this purpose is permitted. On-site decontamination is the best option for objects that can be decontaminated or that cannot be transferred to a metal foundry. It is known from experience that the radioactive deposits that occur with the production of phosphoric acid can generally be removed using high pressure or ultra high pressure (>2500 bar) water jetting. In general, the radioactive substances (scales) released are not very soluble in water.

During decontamination with water, particles with diameters from 0.1 μm to several millimetres are generated. The activity concentration as a function of the diameter is generally constant. This means that the used water can be cleaned with available separation techniques. In most cases, the water remains contaminated with non-radioactive components. Because of this, discharge of the used water into surface water bodies is not permitted in the Netherlands.

Installation components that come into contact with acid are normally protected by a coating or rubber lining. As a result of the contact with the acid, radioactive deposits occur in the top layer of the coating and the rubber. During the dismantling project, the rubber also has to be decontaminated with high pressure water jetting. Using this method, a long rubber belt from the belt filter system, including the accompanying transportation reel, could be treated. The radioactive contamination could be ‘milled’ away by applying a suitable combination of nozzles, pressure and water quantity.

The reactor vessels and acid storage tanks also have protective layers. The reactor vessels had a layer consisting of rubber on carbon stones that were glued to each other. The acid storage tanks had a rubber coating. Because of the long period for which the vessels and tanks had been used, the surfaces had become contaminated with deposits containing ^{226}Ra. With the use of a robot, the surfaces were decontaminated with high pressure water jets. The robot could be moved horizontally and vertically across the surfaces to which it was attached by producing a vacuum that was used also to drain away the water with the radioactive particles to a storage tank. The radioactive particles were removed from the water afterwards. A mist occurs when using water at high pressure. This mist was removed through a filter system by a vacuum installation. Discharge of the water–air mixture was done using a demister and an absolute filter. Because of these measures, discharge of radioactivity to the environment was very limited.

4. RESULTS

4.1. Exposure of workers and members of the public

The following doses received by workers were determined:

- Wet decontamination workers: 1.2 mSv
- Dry decontamination workers: less than the minimum detectable level (MDL)
- Dismantling/construction workers and assistants: <1.7 mSv
- Supervisors: <MDL

The maximum dose received by a member of the public outside the plant site was determined to be <0.4 μSv (corresponding to a risk of $<10^{-8}$)

4.2. Work activities associated with the removal and disposal of radioactive substances

4.2.1. Wet decontamination

The following objects could be decontaminated using high pressure water jetting:

- Reactor vessel (transformation);
- Reactor ‘defluorizing’;
- Storage tank for soft acid;
- Stainless steel frame and transport reels of a belt filter system;
- Rubber belt of the belt filter, with the exemption of the centre strip of 10 cm;
- Buffer tank (spilled acids);
- Seal tanks and table filter;
- Remaining part of the tilting-pan-filter;
- Metal constructions, machine frames and smooth parts of the installation;
- Ceramic floor tiles;
- Drains and gutters;
- Carbon (stones) from the coating of the reactor;
- Some drain wells.

4.2.2. Dry decontamination

The decontamination of filter plates, funnels and a 20 000 kg table filter was attempted using stainless steel grit blasting. The results were disappointing because of distortion of the objects, and the decontamination of these objects by grit blasting has now been abandoned.

4.3. Other work activities

Other work activities involved the dismantling, transport, storage, etc. of pipes, pumps and funnels.

5. TREATMENT AND TRANSFER OF RADIOACTIVELY CONTAMINATED OBJECTS AND WASTE BY THIRD PARTIES

5.1. Melting

The following radioactively contaminated installation parts made of steel were identified as suitable for melting:

- Parts of the tilting-pan filter,
- All steel pipes (with rubber lining),
- Seal tanks,
- Separators,
- Buffer tank.

These parts, with a total mass of 62 t and total activities of 1.9 GBq ^{226}Ra and 0.5 GBq ^{210}Pb, were packed into 7 closed IP-1 containers and transferred to the German company Siempelkamp for melting. Objects that were too large, such as tanks, were cut into pieces before being packed.

5.2. Radioactive waste

Carbon waste, NORM scales, and rubber waste with a total mass of 6711 kg and a total ^{226}Ra activity of 7 GBq were packed into 118 barrels (each of 100 L) and transferred to the Dutch Central Organization for Radioactive Waste (COVRA). The ‘HEPA’ filters used during the decontamination were also transferred to COVRA. In order to meet the COVRA specification that the liquid content be <1%, the waste was dried by an infrared installation before packing.

5.3 Industrial waste

An amount of 447 990 kg of water containing radioactive particles as a result of its use in the high pressure water jetting system was collected in 16 tank cars. The water was first treated (cleaned) by an industrial waste company and then handed over and treated as chemical waste because of the other chemical (soluble) components present. The residual ^{226}Ra activity concentration was <1 Bq/L. An amount of 750 000 kg of scales (gypsum) with a ^{226}Ra activity concentration of <1 Bq/g were also treated as chemical waste.

6. STOCK OF RAW MATERIAL

The stock of phosphate ores has been sold.

7. RECYCLING OF OTHER MATERIALS

An amount of 2213 t of scrap metal was transferred to scrap metal traders in 129 containers. Some activity was detected in two of these containers by a portal detector at a scrap yard entrance.

8. TRANSFER OF MACHINES TO THIRD PARTIES (SALE)

A belt filter installation (without rubber belt and filter cloth) was sold within the Netherlands. A table filter was sold to Greece.

9. HEALTH, SAFETY, AND ENVIRONMENTAL INFORMATION

9.1. Water and air filtration systems

The following filtration systems were used for the produced mist and used air:

- Step 1: demister
- Step 2: absolute filter (HEPA)

The following filtration systems were used for the water from the high pressure water jetting:

- Step 1: several pre-filters
- Step 2: settling tank
- Step 3: filter units: 100 μm, 1 μm, 0.5 μm
- Step 4: recirculation with addition of coating <0.5 μm

9.2. Air measurement with filters, type GF/B15:

The maximum measured alpha activity concentration was 1.8 Bq/m^3. The total calculated discharge to the atmosphere was <34 kBq.

10. INCIDENT REPORTS (DECONTAMINATION)

- There were no personal incidents;
- A small leakage occurred from the filter system, involving neither personal nor financial risk;
- One person did not receive proper instructions;
- Two containers with radioactively contaminated scrap were transferred to a scrap metal trader, in contravention of the Nuclear Energy Act;
- A leaking pump necessitated extra cleaning of the area, involving a small personal risk and a small financial risk;
- The overflow of a tank necessitated extra cleaning of the area, involving no personal risk and a small financial risk.

RECYCLING OF ^{232}Th-CONTAMINATED TUNGSTEN SCRAP

U. Quade, R. Kreh, W. Müller*

Siempelkamp Nukleartechnik GmbH, Krefeld, Germany

Abstract

In Krefeld, Germany, Siempelkamp operates a melting plant to treat metal scrap contaminated with natural radioactivity, mercury and other chemical and toxic substances. The so-called GERTA plant is licensed according to the German BImSchG (federal law on protection against environmental pollution). The facility is equipped with a mains frequency induction furnace and has an annual licensed capacity of 2000 t. The purpose is to decontaminate metal scrap for recycling in the steel cycle without any limitations. So far the input has been carbon or stainless steel with contamination of ^{226}Ra as the main radionuclide in the case of NORM contamination, or mercury from oil and gas producing facilities or from chlorine electrolysis. In a recent project, over 130 t of tungsten and molybdenum alloyed with thorium oxide from welding electrodes and filaments production have been successfully decontaminated and converted into a Fe-W-Mo alloy, which could be marketed as a high value product. In this way, up to 25 wt-% of tungsten–molybdenum could be solved in an iron melt and the thorium oxide could be transferred to the slag. The slag could be released by the 1 mSv/a criterion for workers and population in accordance with the German Radiation Protection Ordinance. In an expert opinion it was found out that, according to the typical distribution of throughput in the GERTA plant, specific activities up to 65 Bq/g ^{232}Th and 87 Bq/g ^{226}Ra can be accepted when 100 t/a of slag are recycled to road construction material. This paper describes the 'tungsten project' in terms of metallurgy, radiation protection and legislation.

1. SIEMPELKAMP´S MELTING FACILITIES

Since 1883, the Siempelkamp group has operated a foundry with a current capacity of more than 60 000 t/a of ductile cast iron at their main site in Krefeld, Germany. At the beginning of the 1980s, the Siempelkamp foundry developed a process to melt moderately radioactively contaminated scrap originating from maintenance and decommissioning projects of nuclear power plants. The so-called CARLA facility (central facility to recycle low radioactive materials) is licensed according to the German Radiation Protection Ordinance since 1989 and is still unique in Germany. The treating of metals is limited to a specific activity of up to 200 Bq/g with the exemption of 2000 Bq/g for low beta emitters (^{3}H, ^{14}C, ^{55}Fe and ^{63}Ni) and 1000 Bq/g for scrap contaminated by naturally occurring radioactive materials (NORM). The value for contamination with fissile radionuclides is limited to 15g per 100 kg of scrap in accordance with the German atomic law.

The aim of melting radioactive scrap is to minimize the volume of scrap to be disposed of as radioactive waste, to decontaminate the metal and to homogenize the remaining radionuclides in the melt. Depending on the remaining activity, the options for reuse of the produced CARLA ingots are as follows:

- Ingots below the release limits can be used as input for conventional recycling paths;

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* E-mail: wolfram.mueller@siempelkamp.com

- Ingots above these limits are reused for manufacturing casks or shielding for application in the nuclear cycle.

Should ingots not be qualified for recycling, they would have to be stored for decay before release or for final disposal once an atomic repository comes into operation.

In 1998, the GERTA facility (large scale melting plant for recycling hazardous wastes) started operation at the site in Krefeld. Siempelkamp developed this recycling process in 1996 as a spin-off from the CARLA process specifically to treat scrap cross-contaminated with NORM and mercury. The GERTA plant is licensed according to the German BImSchG (federal law on protection against environmental pollution) and can process chemically/toxically contaminated scrap (e.g. scrap contaminated by mercury, asbestos, PCB, furanes, dioxines) as well as NORM contamination up to 500 Bq/g. The final metal product is completely free of all contamination and can be released to the steel cycle without any limitations [1].

2. USE OF TUNGSTEN-MOLYBDENUM-THORIUM ALLOYS

The use of tungsten and its alloys covers a wide variety of applications due to its properties such as high density (19.25 g/cm³), a melting point of 3410°C and a hardness of 4.5–8 (Moh´s scale). Examples for the different basic and final products include:

- Ferro–tungsten (70–85 wt.-% W) as an additive for alloy steel;
- Tungsten powder (99.99 %) as an additive for non-ferrous alloys;
- Tungsten carbides (W_2C, WC);
- Filaments, welding rods (tungsten–molybdenum–thorium alloys).

Fig. 1 shows examples of the production residues of W-Fe-Th materials.

FIG. 1. Filament and pressed powder residues.

Filaments and welding rods are made of a W-Fe-Th alloy. Up to 4 wt.-% of radioactive ThO_2 and a certain amount of molybdenum are sintered with tungsten powder to enhance the properties of tungsten for use in filaments and welding rods [2]. This leads to activity levels of up to 65 Bq/g Th-232sec for the particular alloy. The average activity of the residues processed at Siempelkamp in the current project was 12 Bq/g. Accordingly, the treatment of the thorium-contaminated material as well as the production residues (grinding sludge, filament fragments, pressed powder etc.) needs special monitoring according to Appendix XI,

§96 respectively §102 of the German Radiation Protection Ordinance. According to current legislation, the recycling of tungsten–thorium alloys is not permitted without prior decontamination, whereas tungsten ferrous and non-ferrous alloys and carbides can be handled as conventional material for recycling.

3. CHEMICAL AND RADIOLOGICAL ASPECTS OF THE MELTING PROCESS

After 5 years of experience with steel scrap contaminated with products of the uranium and radium decay chain, Siempelkamp invented a process to decontaminate tungsten–thorium alloys and to transform the tungsten into a reusable product. It takes place in a net frequency induction furnace with a capacity of 8 t per batch. The melting process has to be started with a 3 t sump of liquid iron followed by a batch of 5 t of scrap. The furnace can be operated in the temperature range 1350–1500°C. The average melting time is 4 h, which leads to a capacity of 30 t/day. Additives like silica-carbides and carbon amount to 4 wt-% of the input. Fig. 2 shows schematically the GERTA melting plant.

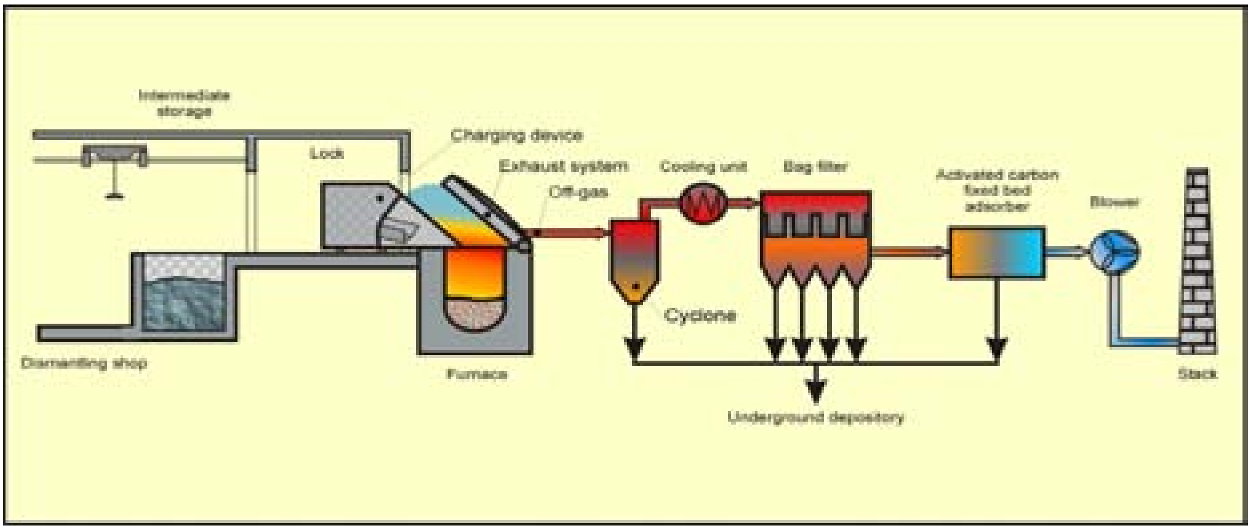

FIG. 2. GERTA melting plant

Concerning the melting point of tungsten, Siempelkamp uses the eutectic 17–25 wt.-% tungsten, 65–75 wt.-% iron, 1–4 wt.-% additives in order to process the tungsten at temperatures of 1450–1500°C [3]. During the melting process the W-Fe-Th-alloy is solved and the main elements and components behave in different ways:

- The thorium and its daughter products are almost totally transferred into the slag, which is gripped from the surface of the melt.
- Tungsten and molybdenum remain in the melt and are mostly transformed into carbides according to the high carbon content [4].

The output of the melting process is metal, slag and dust. While the weight distribution amounts to 90–95 wt.-% metal, 4–10 wt.-% slag and 1–2 wt.-% dust, the main radionuclides of the thorium decay chain remain in the slag and very quickly attain equilibrium with their daughter radionuclides. The daughter radionuclides transferred into the dust are present only for a short time, due to their short half-life. The distribution of the radionuclides is shown in Table I [5]. Besides radionuclides, organic impurities are totally destroyed or evaporated. The transfer of the radionuclides into the slag results in a decontaminated melt that is reusable. The ferro-tungsten product (17-25 wt.-% W) is used as an additive for alloyed steel. Fig. 3 shows typical Siempelkamp ferro-tungsten ingots and details of the alloy structure.

TABLE I. DISTRIBUTION OF RADIONUCLIDES AFTER MELTING

Radionuclide	Melt	Slag	Dust
^{238}U, ^{235}U	1 %	98 %	1 %
^{232}Th, ^{234}Th	<1 %	>98 %	1 %
^{226}Ra, ^{228}Ra	—	98 %	2 %
^{210}Pb	—	7 %	93 %
^{210}Po	—	2 %	98 %

FIG. 3. Ferro-tungsten ingots and details of the metal structure.

4. HANDLING OF SLAGS AND DUST — LICENSING AND LEGISLATION

The slag is free of any toxic impurities but contains a certain amount of thorium. The German Radiation Protection Ordinance stipulates the monitoring of NORM-contaminated material according to Appendix XI, §96 respectively §102 if there is a possibility of the dose to an individual exceeding 1 mSv/a. To check this, exposure calculations were carried out by an accredited radiological expert team and all possible paths of exposure for the waste disposal, from recycling to final disposal, were taken into consideration [6]. The calculation was based on an assumed slag production from NORM-contaminated scrap of 100 t/a. Table II shows the results of the calculation. This is linked to the condition of blending the slag at a ratio of 1 to 4 with slag from the conventional foundry and using it as road construction material or disposing of it in a near-surface facility. Since starting the operation of the GERTA melting plant, 100% of the slag could be recycled by this path.

TABLE II. ACTIVITY CONCENTRATION LIMITS FOR WASTE DISPOSAL

Radionuclide	Activity concentration (Bq/g)
U-238sec	87
Th-232sec	65
Ra-226+	99
Pb-210++	161

Only 1–2 wt.-% of the input material is retained as dust in the bag filter and in the cyclone. Both kinds of dust are mixed with quicklime and then transferred to storage drums. In other melting campaigns, up to 1 wt.-% of mercury can be detected in the dust. The chemical contamination of the dust, in particular the content of mercury coming from different melting campaigns, prevents recycling, so the dust is blended with the lime and is firmly bound and sent to underground storage. Underground storage in rock salt mines up to a depth of 200 m offers a disposal solution for hazardous waste in Germany that has long been regarded as safe for the environment. Drums are stored and subsequently covered by layers of anhydrite and clay originating from salt refining. The remaining hollow space is filled with rock salt and each cavern is sealed hermetically. The radiation exposure of mine workers and the public has to be less than 1 mSv/a. Additionally, the filter dust must not be radioactive in the sense of the former ADR regulation for transport — that means that the total activity concentration of ^{210}Pb and ^{210}Po must be below 70 Bq/g.

5. ACTIVITY MEASUREMENTS

The determination of the total activity concentration of incoming material is most problematic. A direct measurement of the activity concentration is usually not possible due to the different geometry and density of the material. It is necessary to calculate the activity concentration from measurements of surface contamination or dose rate. A method that is quite simple for measuring the activity of individual radionuclides is gamma-spectroscopy. For this method, no chemical processing is necessary before measurement. Only the geometric characteristics and the density of the sample are important for determining the activity. Siempelkamp uses two high-purity germanium (HPGe) detectors and analysis software of EG&G Ortec. One of the detectors is equipped with a carbon window at the top. This allows the detector to measure gamma energies down to about 5–6 keV, which is necessary for detecting the gamma energy of ^{210}Pb at 46.5 keV with sufficient efficiency. For gamma analyses, different calibrations such as Marinelli beakers and wipe tests are used.

6. DOSE MEASUREMENTS DURING TUNGSTEN–THORIUM MELTING CAMPAIGN

The dose coefficient for ^{232}Th is considerably more than two orders of magnitude higher than that for ^{238}U. For that reason, special staff dose measurements were carried out in three different ways: local dose, personal dose and aerosol. The local dose was measured with thermo-luminescence dosimeters (TLDs) and the personal dose was measured with electronic dosimeters EDW150A from Graetz:

- The TLDs were installed near the workplaces and the measured results provided only an average dose for a given work area. The ‘weighted man’ value considers that on a shift the staff are present for only several hours or minutes at the various working places. The results are listed in Table III and show no significantly increased doses for the time spent handling the contaminated scrap.
- The EDWs for personal dose measurement were positioned at the front of the worker’s body, mostly aligned to the contaminated material. Fig. 4 shows the dose measured for 15 workers who mainly dealt with the material. The displayed doses are corrected by subtracting the background at the Siempelkamp site and also show the average value (red line) for these workers and the standard deviation.

The average dose during the whole project amounted to 35 μSv. Taking into account that the measuring period was 30 shifts, an annual dose for handling exclusively this kind of material would be about 250 μSv.

TABLE III: LOCAL DOSES DURING THE TUNGSTEN PROJECT

No.	Exposure time (h)	Local dose (mSv)						
		Furnace control panel	Scrap bunker	Shear	Melting shop	Exit dismant. facility	Weighted man value	
							(mSv)	(μSv/day)
1	201	0.00	0.07	0.09	0.05	0.02	0.042	0.21
2	180	0.09	0.20	0.07	0.07	0.07	0.098	0.54
3	186	0.07	0.04	0.04	0.04	0.05	0.054	0.29
4	188	0.07	0.11	0.06	0.06	0.06	0.070	0.37
5	141	0.30	0.06	0.00	0.00	0.00	0.130	0.92
Mean value		0.107	0.095	0.051	0.044	0.039	0.08	0.47
Standard deviation		0.103	0.056	0.029	0.024	0.024	0.03	0.25

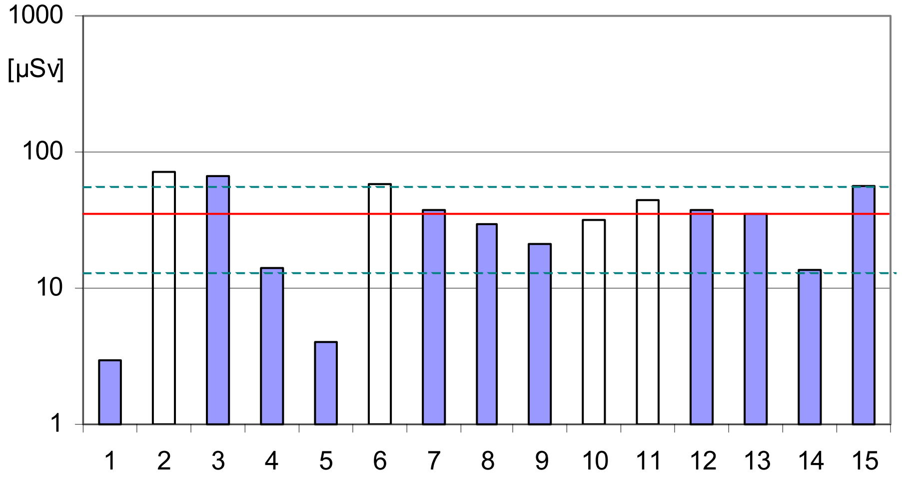

FIG. 4. Personal dose of staff (15 persons) during tungsten project (background corrected)

In addition to the personal dose measurements of the staff, aerosol measurements with an aerosol sampling device were carried out. The samples were taken at different workplaces, such as the decanting and sorting areas of the delivered raw material and the operation area of the furnace. Table IV shows the average values for the different operations and workplaces.

TABLE IV. AVERAGE VALUES OF AEROSOL MEASUREMENTS

Operation/workplace	Decay chain activity (Bq)		^{228}Ac+ activity concentration (Bq)	Decay chain activity ratio ^{228}Ac+ / ^{210}Pb+
	^{228}Ac+	^{212}Pb+		
Decanting of material	12.1	20.1	0.2	0.6
Furnace handling	13.8	49.5	2.4	0.28
Furnace exhaust system	9.7	792.0	258.7	0.01

The most significant dose when working with thorium-contaminated material is received through incorporation. In particular, inhalation of ^{232}Th and some of its daughters can cause high organ doses and effective doses. To check for possible incorporation of thorium, urine measurements using the HR-ICP-MS method were conducted for four workers directly in contact with the contaminated scrap. It could be proved that, assuming the use of a personal dust filter, the incorporated activity was less than the minimum detectable activity by the HR-ICP-MS method.

7. CONCLUSION

In 2002, Siempelkamp Nukleartechnik invented a process to decontaminate and reuse tungsten scrap alloyed with thorium oxide. Experience with the melting of 130 t of this tungsten scrap has shown that:

- The scrap could be decontaminated and transformed into a marketable ferro-tungsten product;
- The slag is reusable according to German legislation;
- The dose received by workers is far below 1 mSv/a, the dose limit for members of the public.

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INDUSTRIES GIVING RISE TO NORM DISCHARGES IN THE EUROPEAN UNION — A REVIEW

T.P. Ryan[1*], A. Janssens[1], E. Henrich[1], J.-L. Daroussin[2], Z.K. Hillis[3], E.I.M. Meijne[4]

[1]European Commission, DG TREN, H4, Radiation Protection, Luxembourg
[2]IRSN/DEI/SARG/LERAR, Fontenay-aux-Roses Cedex, France
[3]NNC Limited, The Renaissance Centre, Warrington, Cheshire, United Kingdom
[4]NRG, Petten, Netherlands

Abstract

The focus of this paper is the identification of industries giving rise to discharges or residues of naturally occurring radioactive material (NORM) that are potentially significant in terms of public exposure and therefore may require regulatory control as set out in Title VII of the European Union Council Directive 96/29/Euratom. The industries have been identified and assessed as part of a study commissioned by the European Commission with a view to assisting Member States in implementing the aforementioned Directive in this area. Information was gathered largely on the basis of data supplied by regulatory authorities in Member States, by means of a questionnaire as well as through published reports and direct contacts with organizations such as trade associations. It is evident that available information on wastes and discharges both in terms of volume and content are limited. Furthermore, there are few reliable monitoring data for NORM radioactive substances probably as a consequence of the absence of previous regulatory control. The industries considered in this paper include fossil fuel power stations, oil and gas extraction, metal processing, phosphate processing and production, titanium oxide pigment production, rare earth processes, and cement production. A brief description of the processes involved in each is presented including the waste production pathways, activity concentrations, typical emissions and annual throughput, where available. It is noted that the characteristics of discharges and residues, even from the same type of industry and production process, have been found to differ widely because of variations in raw materials and processing methods. This is particularly pertinent in respect of differences in treatment of liquid wastes and off-gases prior to discharge. It is possible that for some of the NORM industries studied, controls already in place to prevent non-radioactive pollution may have the additional benefit of controlling the radioactive discharges. However it must also be highlighted that restricting discharges may increase the amount of radioactivity retained in residues such as sludge and dust.

1. INTRODUCTION

The main objective of this paper is to summarize the main findings of the study carried out on behalf of the European Commission (EC) into those industries giving rise to discharges or residues of naturally occurring radioactive material. The full report of the study has been published by the EC as Radiation Protection 135 [1]. The interested reader is directed to the full report in order to access the complete data set.

NORM is the acronym for naturally occurring radioactive material. Most materials contain trace amounts of ^{238}U, ^{235}U and ^{232}Th; however, when these materials are processed, concentration or enhancement of the levels of these radionuclides may occur. Enhancement is

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[*] E-mail: thomas.ryan@cec.eu.int

said to have occurred when a naturally occurring radioactive material has its composition, concentration, availability or proximity to people altered by human activity [2]. NORM can be defined as all naturally occurring radioactive materials where human activities have increased the potential for exposure in comparison to the unaltered situation. However, activity concentrations in the end product may or may not be increased [3].

The industries covered by the current review include:

- Fossil fuel power stations;
- Oil and gas extraction;
- Metal processing — iron and steel production in particular but also tantalum and niobium;
- Phosphate industry;
- Titanium oxide pigment production;
- Zircon, refractory products, ceramics and brick manufacture;
- Cement production.

The water industry, including waterworks and water purification, has been cited in the past as an industry giving rise to potentially significant NORM wastes. A recent report focused on the radiological impact due to wastes containing radionuclides from the use and treatment of water and concluded that such wastes did not give rise to concern [4].

It should be emphasized that the characteristics of discharges and residues, even from the same type of industry and production process, have been found to differ widely because of the variation in raw material used, differences in process methodologies as well as differences in the treatment of liquid wastes and off-gas prior to discharge. It is also possible that existing controls in place to prevent non-radioactive pollution may have the additional benefit of controlling the radioactive discharges from these NORM industries as a by-product of controlling discharges generally. However, it should also be noted that restricting discharges such as those from stacks might increase the amount of radioactive residues contained in solid wastes, sludges and dusts.

A summary of the potentially significant NORM industries, together with an identification of waste streams and a statement of the presence or otherwise of the industry in the European Union (EU), is presented in Table I.

2. THE INDUSTRIES

2.1. Fossil fuel power stations

Fossil fuels such as coal, lignite, oil and natural gas are used to produce energy by combustion. These fuels contain varying amounts of natural radioactivity often depending on the area from which they are mined or extracted. When coal and oil are burned, the radioactivity is transferred largely to the ash except where volatile radionuclides are released to the atmosphere along with a proportion of the ash. Where ^{210}Po and ^{210}Pb are volatized in the process they may condense on the fly ash. Enrichment factors increase with decreasing particle size. It has been observed that the type of coal used has a very significant effect upon the activity discharged into the environment, as does the plant design [5].

TABLE I. SUMMARY OF POTENTIALLY SIGNIFICANT NORM INDUSTRIES

Industry or work activity	Potentially significant solid residues	Potentially significant discharges		Is such a facility present in EU Member State?														
		Liquid	Aerial	B	DK	D	EL	E	F	IRL	I	L	NL	A	P	FIN	S	UK
Onshore oil/gas	Sludges, scales	Produced water, scales, but not if reinjected	None	—	Yes	Yes	—	—	Yes	—	Yes	No	Yes	Yes	—	—	No	Yes
Offshore oil/gas	Sludges, scales	Produced water, scales	None	—	Yes	Yes	Yes	Yes	No	Yes	Yes	No	Yes	—	No	—	No	Yes
Phosphoric acid	Phosphogypsum, if stockpiled	Phosphogypsum, if discharged	None	Yes	—	—	Yes	Yes	Yes	—	—	—	—	—	—	—	—	—
Phosphate fertilizer[1]	Depends on process	Depends on process	None	Yes	Yes	Yes	Yes	Yes	Yes	—-	Yes	—	Yes	—	Yes	Yes	Yes	—
Thermal phosphorus	Calcined dust, slag	^{210}Po, ^{210}Pb	^{210}Po, ^{210}Pb	—	—	—	—	—	—	—	—	—	Yes	—	—	—	—	—
TiO$_2$ pigment	Solids from liquid waste treatment	Depends on process	None	—	—-	Yes	—	Yes	Yes	—	Yes	—-	Yes	—	–	Yes	—	Yes
Steel	Blast furnace and sinter dust	Depends on waste water treatment	^{210}Po, ^{210}Pb	Yes	Yes	Yes	Yes	Yes	Yes	—	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Cement	None	None	^{210}Po, ^{210}Pb	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Coal fuelled power plants	Bottom and fly ash	None	None	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Bricks and roofing tiles	None	None	^{210}Po	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Tin smelters (closed down)	Slag, slag wool (historical)	None	^{210}Po, ^{210}Pb	—	—	—	—	—	–	—	—	—	—	—	—	—	—	—
Metal extraction from tin slag	Slag	None	^{210}Po, ^{210}Pb	—	—	Yes	—	—	—	—	—	—	—	—	—	—	—	—
Lead/zinc smelter	Cobalt-cake	None	^{210}Po, ^{210}Pb	Yes	—	Yes	Yes	Yes	Yes	—	Yes	—	Yes	—	Yes	Yes	Yes	Yes
Copper smelter	?	None	^{210}Po, ^{210}Pb	Yes	—	Yes	—	Yes	Yes	—	—	—	—	—	—	Yes	Yes	—

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[1] Includes production using phosphoric acid produced elsewhere

The ash content of coal is typically about 16% [6], with that of peat at 2–6% and that of fuel oil at 0.1% The enrichment of the activity concentration from coal to ash is dependent on the ash content but is typically of the order of a factor of seven. Lignite (brown coal) has a lower ash content than other coal and this results in a higher enrichment factor, but it has considerably lower activity concentrations [7].

The application of coal ash in building materials is regarded as the most significant practice from a radiological point of view because it may affect indoor dose from external radiation and inhalation of radon decay products [8].

Liquid wastes may arise from the desulphurization of flue gases, which generates water along with the gypsum. Often the liquid waste is used to carry the ash away and then the slurry is stored in ponds. Alternatively, the water can be recycled to the plant as part of a closed loop [5]. It is unlikely, however, that there is a significant liquid discharge of NORM radionuclides from fossil fuel power stations. Fly ash emissions from the stacks of coal-fired power stations depend on the efficiency of the flue gas cleaning by electrostatic precipitators, scrubbers, and desulphurization systems and so the discharge will vary between plants. It is unlikely that for modern plants there is a significant aerial discharge of NORM radionuclides from fossil fuel power stations. This is consistent with the conclusion from studies in the UK [6] and the Netherlands where coal fuelled power plants are not considered to have significant aerial discharges. These installations, however, typically install efficient filter systems in order to prevent the aerial discharge of fly ash.

Typical concentrations of natural radioactivity in fossil fuels are presented in Table II with mean concentrations of radionuclides in certain ashes in Table III and typical annual emissions from coal and gas fired power stations in Table IV.

TABLE II. TYPICAL ACTIVITY CONCENTRATIONS IN FOSSIL FUELS

Material	Radionuclide activity concentration	
	^{238}U series	^{232}Th series
Coal (global average) [9]	20 Bq/kg	22 Bq/kg
Natural gas [10]	340 Bq/m^3 (^{222}Rn)	—
Peat (global average) [11]	40 Bq/kg	—

TABLE III. ACTIVITY CONCENTRATIONS IN CERTAIN TYPES OF ASH

Material	Arithmetic mean of radionuclide activity concentration (Bq/kg)							
	^{238}U	^{232}Th	^{228}Th	^{228}Ra	^{226}Ra	^{210}Pb	^{210}Po	^{40}K
Escaping fly ash (coal)	200	70	110	130	240	930	1700	265
Bottom ash (coal) [12]	240	240	—	—	240	151	138	653
Fly ash (coal) [12]	200	200	—	—	200	220	220	670
Peat fly ash [13]	268–1048	—	—	—	<215	—	—	<1480

TABLE IV. ANNUAL EMISSIONS FROM 'TYPICAL' COAL- AND GAS-FIRED POWER STATIONS [12]

Plant	Emitted activity (GBq/a)					
	^{238}U	^{232}Th	^{226}Ra	^{222}Rn	^{210}Pb	^{210}Po
Coal-fired (600 MW e)	0.16	0.08	0.11	34	0.4	0.8
Gas-fired (400 MW e)	-	-	-	230	-	-

2.2. Oil and gas extraction

According to Ref. [14], there are no 'typical' discharges for an oil or gas production plant. Discharges of natural radionuclides depend strongly on the type of reservoir, specific production conditions and number of years of exploitation of a reservoir. Production of oil and gas is accompanied by water, which is co-produced from the well and so is known as 'produced water'. The ratio between the rate of water production and oil production is variable, affected by the age of the well and production conditions. The variability is even greater for gas extraction. Produced water contains radionuclides which have been mobilized from the reservoir rocks and in addition to being present in the produced water, they may also be deposited as scales on pipes, valves and vessels. These pipes may be descaled offshore or at onshore descaling facilities. For the most part, releases of NORM from offshore oil and gas production originate from the following:

- Produced water released offshore (^{228}Ra, ^{226}Ra, ^{210}Pb);
- Scale from offshore mechanical descaling released offshore (^{228}Th, ^{228}Ra, ^{226}Ra, ^{210}Pb);
- Scale from coastal descaling site discharged into the sea or disposed on land (^{228}Th, ^{228}Ra, ^{226}Ra, ^{210}Pb).

There is a very large variability in the radionuclide concentrations in sludges and scales from different wells because of the differences in the nature of the reservoirs and other conditions [15]. Activity concentrations in sludges and scales vary from virtually zero up to several hundred becquerels per gram. Production rates of sludges and scales may vary considerably between installations. While no specific data were available at the time of the current study, it is anticipated that the amounts of sludge arising from a given amount of oil production are not significantly lower than for gas production.

A recent study of marine discharges [14], including discharges from the offshore oil and gas industry, reference ratios for oil and gas production and produced water were estimated together with reference concentration values. However, concentrations of ^{228}Ra, ^{226}Ra and ^{210}Pb in produced water vary between production wells and over the production period, by several orders of magnitude.

Onshore production installations can be assumed to discharge produced water by reinjection into the reservoir, although some installations are known to discharge produced water into a public sewer after pre-treatment. The typical practice for offshore installations is to discharge produced water overboard.

Order-of-magnitude estimates of discharges of natural radionuclides from offshore oil and gas production platforms are presented in Table V.

TABLE V. ROUGH ESTIMATES OF DISCHARGES OF NATURAL RADIONUCLIDES FROM OFFSHORE OIL AND GAS PRODUCTION PLATFORMS[2]

Product		Water discharge		
Type	Assumed production (million m^3/a)	Quantity discharged (million m^3/a)	Activity concentration (Bq/L)	Emitted activity (GBq/a)
Oil	1	3	10 (^{226}Ra and ^{228}Ra)	30 (^{226}Ra and ^{228}Ra)
Gas	3000	0.15	10 (^{226}Ra) 5 (^{228}Ra and ^{210}Pb)	1.5 (^{226}Ra) 0.75 (^{228}Ra and ^{210}Pb)

2.3. Metal processing

The basic process by which metals and alloys are produced from metal-rich ores is that of smelting. The activity concentrations in the raw materials vary depending on the region of origin. There are currently smelters for aluminium, copper, iron, steel, lead and zinc within the EU [16]. However, tin ore appears to be no longer produced or processed within the EU. Typical activity concentrations of natural radioactivity in certain ores are presented in Table VI and production figures for selected EU metal processing operations in 2000 are presented in Table VII.

TABLE VI. ACTIVITY CONCENTRATIONS IN CERTAIN ORES

Ore	Radionuclide activity concentration (Bq/kg)	
	^{238}U	^{232}Th
Bauxite (aluminium)	37–530	41–527
Iron ore [9]	<50	<50
Pyrochlore (ferro-niobium) [17]	6000–10 000	7000–80 000
Tin ore [17]	1000	300

Slags, dross, fly ash, furnace coal ash and scales may be produced as a result of the smelting process. There are also likely to be stack emissions of fly ash and gases; each metal processing operation involving high temperatures is a potential source of emissions of ^{210}Po and ^{210}Pb to air. The radioactivity of the feedstock or ore is largely transferred to the slag. Although figures were not available for the current paper, zinc production from zinc ore results in cadmium, copper and cobalt-cake and the latter is understood to be enriched in uranium.

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[2] The actual annual discharges at a given platform in a particular year may be quite different from the figures derived from normalized data. Discharges of ^{210}Pb from oil producing platforms have not been estimated, as the radium isotopes are likely to be the dominant radionuclides in the discharges. However, ^{210}Pb cannot be assumed to be absent.

TABLE VII. PRODUCTION FIGURES FOR SELECTED METAL PROCESSING ACTIVITIES IN EU MEMBER STATES

Country	Production in 2000 (kt) [16]								
	Iron and steel		Aluminium		Copper, primary (refining)[3] [metal content]	Lead, primary (refining)[3]	Tin, primary (smelting)[3]	Titanium, metal sponge	Zinc, primary (smelting)[3]
	Pig iron[4] and direct-reduced iron [metal content]	Crude steel [gross weight][5]	Alumina	Primary metal					
Belgium	8472	11 637	0	0	236	98	0	0	252
Denmark	0	783	0	0	0	0	0	0	0
Germany	30 846	46 376	600	644	335	210	0	0	325
Greece	0	1056	600	163	0	0	0	0	0
Spain	4059	15 844	1200	366	265	0	0	0	391
France	13 661	21 002	400	441	0	100	0	0	348
Ireland	0	375	1200	0	0	0	0	0	0
Italy	11 223	26 544	950	190	0	75	0	0	168
Luxembourg	0	2571	0	0	0	0	0	0	0
Netherlands	4969	5667	0	302	0	0	0	0	215
Austria	4318	5725	0	0	2	0	0	0	0
Portugal	382	1060	0	0	0	0	0	0	4
Finland	2983	4096	0	0	100	0	0	0	223
Sweden	3146	5227	0	100	105	38	0	0	0
UK	10 989	15 306	100	305	1	166	0	0	99
TOTAL EU	95 048	163 269	5050	2511	1044	687	0	0	2025

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[3] Primary production also includes undifferentiated (primary and secondary) production for those countries listed.

[4] Pig iron is primary iron melted into a standard pyramidal mould or trapezoidal mould, ~ 4.5 and 6.5 kg respectively. Primary iron production (blast furnace iron) figures are those relevant to emissions and residues.

[5] Crude steel can be produced from primary iron and scrap in a basic oxygen furnace (converter) or from recycled steel in an electric arc furnace. Crude steel production figures are therefore higher than primary iron production figures as the latter are included in the former.

2.3.1. Iron and steel production

The main sources of emissions and residues are the installations for production of sinters and pellets from iron ore and the production of iron in blast furnaces from these sinters and/or pellets.

(a) Sinter plants

Iron ore sinters are produced from mixtures of ore, dolomite, cokes and recycled dust. The activity concentrations of most of the radionuclides from the decay chains of ^{238}U and ^{232}Th in the feed mix are of the order of 15 Bq/kg. The concentrations of ^{210}Po and ^{210}Pb can be somewhat higher because of the recycling of enriched dust. The sinters are fired with gas and temperatures reached in the combustion zone are of the order of 1400°C. As a consequence, ^{210}Pb and ^{210}Po, with boiling points of 1740 and 962°C respectively, are volatilized and condense on dust particles, which are carried by the off-gas. Dust from sintering is enriched in ^{210}Po relative to ^{210}Pb and strongly depleted in all other natural radionuclides from the raw materials. The off-gas is cleaned with electrostatic precipitators or high-pressure water scrubbers. The small particles emitted after passing through the cleaning system are enriched in ^{210}Po and to a lesser extent in ^{210}Pb. Emissions to the air depend on the efficiency of the off-gas cleaning system and emissions to water depend on post-treatment of water from the scrubbers.

(b) Pellet plant

Ore preparation for input into the blast furnaces is also carried out in a pelletizing plant. Ore mixes are dried and ground, sieved, mixed with water and bentonite and formed into wet pellets. The pellets are fired into hard pellets and cooled with air. The hot air is fed into the firing zone and to the ore dryer and then fed through low-pressure-water dust scrubbers. As in the sinter process, ^{210}Po and ^{210}Pb are volatilized and condense on dust particles carried by the off-gas. Solids collected from the wash water are refed into the pelletizing process and the water is treated in the biological water treatment system.

(c) Blast furnace

Primary iron is produced from sinters (and pellets), coal and cokes in blast furnaces. They produce iron and slag, both fluid and blast furnace gas carrying dust. Because of the high temperature, ^{210}Pb, and ^{210}Po still present in the feed materials, as well as zinc, are volatilized and condense preferentially on the small particles carried by the gas. ^{210}Pb concentrations in this dust are higher than those of ^{210}Po because the latter radionuclide would have been, to a large extent, already removed in the sintering or pellet process due to its significantly lower boiling point. Wet scrubbers are used to remove the solids from the gas. The coarse material is recycled into the sintering and/or pellet process. The finer fraction, zinc-rich filter cake, is stored for disposal. The cleaned gas is used as fuel elsewhere in the production process or sold as an energy source for electric power production.

2.3.2. Tantalum and niobium

Tantalum (Ta) is a refractory metal that is highly corrosion resistant, a good conductor of heat and electricity and is used on a large scale in capacitors in all kinds of electronic equipment. Niobium (Nb) is used as an alloying element in steels and super alloys for aircraft turbine engines. The primary sources of these elements are the tantalum- and niobium-bearing ores mined in Australia, Brazil, Canada, Thailand, China and Africa. Prospecting for tantalum is currently underway at sites in Ireland and Finland [18]. The minerals in niobium-bearing ores (pyrochlore and columbite) contain enhanced levels of the decay chains of ^{238}U and ^{232}Th. Tantalum occurs in combination with niobium and usually with tin, iron, manganese and rare earths. The processing of the ores into metal concentrates, carbides, oxides and metal powder starts with a wet process involving dissolution of the ore with strong acids and removal of impurities by liquid–liquid extraction. These production facilities are located outside the EU. A specific source of tantalum is the slag from tin production. The tin slag originates mainly from Thailand and contains enhanced levels of natural radionuclides. Typical concentrations encountered in tin slag from past tin production in the Netherlands and the UK were 4 Bq/g ^{238}U and 11 Bq/g ^{232}Th and daughters.

No information was available on natural radionuclides in the tin slag process nor on the processing methods involved. Potentially the processing may involve discharges into the air of ^{210}Pb and ^{210}Po. However, the tin slag is most probably significantly depleted in ^{210}Pb and ^{210}Po because of the high temperatures in the tin smelting process. The solid waste from the tantalum extraction probably contains virtually all of the other radionuclides of both decay chains.

2.4. Phosphate industry

There are four main processes for producing phosphate fertilizers and phosphorus:

- The wet acid process using sulphuric acid;
- Hydrochloric acid treatment;
- Nitric acid treatment;
- Thermal processing.

In the sulphuric acid, hydrochloric acid and nitric acid processes the chemical reaction is similar i.e. acidification of the ore. However, the waste products and by-products are markedly different with differing implications for NORM waste production. Across the EU there have been significant changes in the industry, with a move away from the production of phosphoric acid from phosphate ore and its associated production of large amounts of phosphogypsum. Discharges of phosphogypsum by EU member States are in fact historical.

The thermal process uses high temperatures to reduce the phosphate to produce phosphorus, calcium silicate slag and calcinate. An elemental phosphorus plant is in operation in the Netherlands [19].

In the EU, 90% of the phosphate rock was originally treated by the sulphuric acid method [20]. However, changes in the industry have moved much of the phosphoric acid production, with its associated waste of phosphogypsum, to areas where the phosphate rock is mined, i.e. Morocco and other North African countries. Where the industry remains within the EU, phosphogypsum is largely recycled or stored on land. Approximately 15% of phosphogypsum is recycled into building material [20].

The hydrochloric acid process produces predominately a calcium fluoride sludge at a rate of 0.5 t for each tonne of processed P_2O_5. This sludge is stored on land where the combination of the radium sulphate precipitate and the calcium fluoride means that the sludge contains 90% of the radium inventory, resulting in radium levels of 8 to 10 Bq/g [3].

There is one phosphor plant within the EU that uses the thermal process. The refined process in operation at the plant results in no radionuclide enhancement of the silicate slag. However, the calcined dust contains 95% of the ^{210}Pb with a typical activity concentration of 1000 Bq/g [19].

Indicative activity concentrations of natural radionuclides in ore and waste products from the phosphate industry are presented in Table VIII, with estimates of P_2O_5 production in the EU presented in Table IX.

TABLE VIII. INDICATIVE ACTIVITY CONCENTRATION IN ORE AND WASTE PRODUCTS OF THE PHOSPHATE INDUSTRY

Material or process	Radionuclide activity concentration (Bq/kg)[6]			
	^{238}U+	^{232}Th	^{226}Ra+	^{210}Pb+
Raw material				
Ore[7] [21]	1400	160	1400	1400
Sulphuric acid process:				
Phosphogypsum [21]	200	17	850	200
Hydrochloric acid process:				
Calcium fluoride (solid) with radium sulphate precipitate (from $BaCl_2$ precipitate step) [3]	—	—	8000–10 000 (^{226}Ra)	—
Calcium chloride (effluent) [3]	—	—	2 Bq/L (^{226}Ra)	—
Nitric acid process:				
Calcium carbonate (recycled)			(no data)	
Thermal process:				
Calcium silicate slag [21]	2700	310	2300	270
Calcined dust [21]	—	—	—	1 600 000

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[6] The data are as cited in the source material and may be for the selected chain and radionuclide only.

[7] It is important to note that phosphate ore of igneous origin is lower in radioactivity than that of sedimentary origin and the range of ^{238}U+ measured in ores is quoted in Ref. [21] as being in the range 40–5000 Bq/kg.

TABLE IX. ESTIMATED PHOSPHATE PRODUCTION IN EU MEMBER STATES [19]

Country	P_2O_5 production		Phosphate fertilizer production	
	kt/a	% of total EU	kt/a	% of total EU
Belgium/Luxembourg	270	14	340	14
Germany	0	0	220	9
Greece	200	11	120	5
Spain	530	28	180	7
France	250	13	930	39
Italy	250	13	330	14
Netherlands	120	6	290	12
Austria	55	3	—	—
Finland	240	12	—	—
TOTAL EU	1900	100	2410	100

2.5. Titanium oxide pigment production

Titanium oxide pigment is produced from the ores rutile (TiO_2) and ilmenite ($TiO_2 \cdot FeO$). In addition, tin slag may be used as the raw material. In the original sulphuric acid process, ilmenite is dried, ground, mixed with concentrated sulphuric acid and heated until an exothermic reaction commences between the titanium raw material and the sulphuric acid. The resulting solid reaction cake is composed mainly of titanium and iron sulphates. The reaction cake is dissolved in acid, and ferric iron in solution is reduced to the ferrous form in separate reduction tanks using scrap iron as the reducing agent. The reduced solution settles and is filtered to remove unreacted solids. Much of the iron is removed by cooling and crystallization into hydrated ferrous sulphate (copperas, $FeSO_4 \cdot 7H_2O$). After removal of the copperas by centrifuging, the solution is concentrated by vacuum evaporation followed by preferential precipitation of TiO_2 from the iron and titanium basic sulphate ($TiOSO_4$) liquor as white titanium oxihydrate. The titanium oxihydrate is filtered from the dissolved sulphates and extensively washed to remove impurities. The pure white precipitate is calcined in a kiln at about 1000°C to form the TiO_2 crystals of the required size and shape. This traditional production process is being phased out in favour of the cleaner chloride process, but it is unlikely to disappear completely as it is currently also used to produce anatase.

In the chloride process, rutile, cokes and chlorine react at about 1000°C to form a mixture of chlorides including the highly volatile $TiCl_4$. The other chlorides are separated from $TiCl_4$ in a series of condensation steps. After purification by distillation, the $TiCl_4$ is oxidized to TiO_2 and 'finished' into pigment. About 70% of EU production is from the chloride process.

Typical mean activity concentrations in the rutile are found to be around 400 and 600 Bq/kg for the ^{238}U chain and ^{232}Th chain radionuclides respectively. However, it is important to emphasize the potential variability of concentrations in such minerals. It is assumed that both chains are in secular equilibrium, which is not necessarily the case for synthetic rutile produced from ilmenite in which the iron content of the ilmenite is strongly reduced. The process, involving reductive roasting with coal in a kiln, magnetic separation and acid leaching of the ilmenite (the Becher process) not only removes non-radioactive impurities, but may also preferentially remove certain members of the ^{238}U and ^{232}Th decay chains either in the roasting or leaching step. On the basis of this process, the annual activity throughput for a typical TiO_2 production plant is of the order of 40 GBq for each of the radionuclides from the ^{238}U chain and 60 GBq for the members of the ^{232}Th chain.

The highly purified TiO_2 pigment is practically free of the natural radionuclides contained in the ore. Emissions to the atmosphere, excluding those of radon, are negligible. Consequently, all radioactivity from the ore appears in the liquid effluent and solid wastes. Solid wastes arise as blow-over of cokes and ore from the reactor and as precipitates from the treatment of acidic solutions of chlorides separated from $TiCl_4$ in the condensation steps. This acidic solution of chlorides contains the majority of the radioactivity contained in the ore. The partitioning of the radionuclides between solid waste and discharged waste water depends on the treatment of the acidic liquid waste stream. This treatment involves the precipitation of the cations as hydroxides by increasing the pH. Radionuclides of the elements radium and lead tend to remain in solution if the pH endpoint is not high enough.

A summary of the titanium dioxide industry in the EU including the processes and capacities is presented in Table X, with typical discharges of natural radionuclides from a TiO_2 pigment plant presented in Table XI.

TABLE X. TITANIUM DIOXIDE INDUSTRY IN EU MEMBER STATES, 2000–2001

Country	Site	Company	Process	Capacity (kt/a)
Belgium	Langerbrugge	KRONOS	Chloride	69
	Antwerp	Kerr-McGee	Sulphate	?
Germany	Uerdingen	Kerr-McGee	Sulphate	130
	Leverkusen	KRONOS	Sulphate	30
	Leverkusen	KRONOS	Chloride	100
	Nordenham	KRONOS	Sulphate	62
	Duisburg	Sachtleben	Sulphate	100
France	Le Havre	Millennium	Sulphate	110
	Thann	Millennium	Sulphate	28
	Calais	Huntsman Tioxide	Sulphate	100
Italy	Scarlino	Huntsman Tioxide	Sulphate	80
Netherlands	Rotterdam	Kerr-McGee	Chloride	80
Finland	Pori	Kemira Pigments	Sulphate	130
UK	Greatham	Huntsman Tioxide	Chloride	80
	Grimsby	Huntsman Tioxide	Sulphate	80
	Grimsby	Millennium	?	150

TABLE XI. ACIDIC LIQUID EFFLUENT FROM A TiO_2 PIGMENT PLANT[8]

Radionuclide	Annual discharged activity (GBq/a)
^{228}Ra	38
^{226}Ra	22
^{210}Pb	9
^{210}Po	3

2.6. Zircon, refractory products, ceramics and brick manufacture

Zircon ($ZrSiO_4$) is a zirconium ore used mainly for high temperature purposes in steel and iron foundries, in refractory materials as well as in fine ceramics. Minor quantities are used as additives in special types of glass. Other uses of zircon and the associated minerals of zirconia and zirconium include abrasive products, catalysts, paints, fuel cladding and structural materials in nuclear reactors [8].

Zircon is not mined in the EU but approximately 350 000 t/a are imported. The Italian ceramics industry is probably the largest consumer of zircon in the EU. Italy imports about 170 000 t/a of zircon sand, of which 70% is used in the ceramic industry [22]. However, the zirconium is fixed in the glaze.

Zirconium ore processing locations and capacity in the EU are summarized in Table XII, and mean activity concentrations of natural radionuclides are summarized in Table XIII.

TABLE XII. ZIRCONIUM ORE PROCESSING IN EU MEMBER STATES [23]

Country	Production (kt/a)
Belgium/Luxembourg	3
Germany	45
Greece	—
Spain	52
France	40
Italy	98
Netherlands	—
Austria	—
Finland	—
TOTAL EU	238

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[8] Chloride process, 90 000 t/a, rutile feedstock with average activity concentrations of 400 Bq/kg (^{238}U sec) and 600 Bq/kg (^{232}Th sec).

TABLE XIII. RADIOACTIVITY IN ZIRCONIUM ORES

Ore	Average activity concentration (Bq/kg)				
	^{238}U	^{226}Ra	^{232}Th	^{228}Th	^{228}Ra
Zircon [9]	6800	8300	11 000	—	—
Baddeleyite [24]	7000	—	300	200	6000

Zircon milling, which is a physical process involving crushing, grinding and sizing, is carried out at various sites in the EU including the Netherlands, UK, Germany, Italy and Spain. The main waste issue associated with the process is that of dust, which can be kept to a minimum by good housekeeping. Typically, there is a loss of between 0.1% and 1% of the turnover by this pathway. However, it must be emphasized again that there is a high potential for variability in activity concentrations of natural radionuclides in such minerals. Comparatively small amounts of waste are produced at zircon mills, and are usually disposed of at landfill sites. Quantities of up to 200 t/a (1% of turnover) have been reported for one plant using dry milling [9].

In the UK, one plant makes fused zirconia for high specification refractory products and dielectrics. Baddeleyite ore (ZrO_2) is heated in a furnace to extract the zirconia. Sources of waste from this process include liquid effluent from floor washing, dust from the ventilation system and atmospheric discharges from the furnace. Approximately 20 t/a of solid powder from the filters are produced from the production of 2000 t of refractory material, representing approximately 1% of the feed ore. The waste from floor washings is assumed to be about 20 kg/a, with dust emissions at approximately 5 kg/a [5]. Other processes with minor waste production include rare earth glass polish and factories producing refractory bricks where again the waste is likely to be floor washings.

The firing temperature of the ovens used in the production of bricks and roofing tiles is 1000–1200°C. The feed clays usually have concentrations of radionuclides from the decay chains ^{238}U and ^{232}Th of the order of 35 Bq/kg. Between 40 and 100% of the ^{210}Po is volatilized in the firing process. The fraction of the throughput of ^{210}Po emitted depends on the extent of the off-gas cooling and cleaning to abate dust and HF emissions. An upper estimate of the aerial discharge of ^{210}Po from a brick factory can be based on the following assumption: typical production 30 kt/a, average concentration in clay 35 Bq/kg, volatilization 100%, trapping in off-gas 0%. The maximum annual emission for such a plant is 1 GBq.

2.8. Cement production

Production of cement involves the calcining and sintering of blended and ground raw materials, typically limestone, clay or shale to form clinker (partially fused residues). This clinker burning takes place at a temperature of 1450°C in kilns. The clinker is ground and mixed with small amounts of gypsum to make cement. In addition, blended cements are produced from cement clinker with blast furnace slag and fly ash. Large cement plants produce of the order of 4000 t/day of cement (1.5 million t/a). Production capacities in the EU are presented in Table XIV.

Because of the very high temperature of the raw materials in the kilns, volatilization of ^{210}Po and ^{210}Pb is the main potential source of aerial discharge. Estimates of ‘typical’ discharges provided in Annex B of Ref. [10] are based on Ref. [12], and are reproduced in Table XV. In the figures quoted, the fact that blast furnace slag, which can be used in blended cements as mentioned above, is considerably depleted in ^{210}Pb and ^{210}Po has been taken into account. The discharge figure for ^{210}Po is based on the assumption that 50% of the polonium escapes from the thermal process in analogy with the assumption used for the production of bricks and roofing tiles. No other source of activity emission data has been identified.

TABLE XIV. CEMENT PRODUCTION IN EU MEMBER STATES, 1998

Country	Production (million t/a)
Belgium	8
Denmark	2.528
Germany	36.61
Greece	15
Spain	27.943
France	19.5
Ireland	2
Italy	35
Luxembourg	0.65
Netherlands	3.2
Austria	3.85
Portugal	9.5
Finland	0.903
Sweden	2.105
United Kingdom	12.409
TOTAL EU	179.198

TABLE XV. AERIAL DISCHARGES FROM A 'TYPICAL' CEMENT PLANT [12]

Radionuclide	Activity discharged for a production rate of 2 million t/a of different cement types (GBq/a)
^{238}U	0.2
^{228}Th	0.05
^{226}Ra	0.2
^{222}Rn	157
^{210}Pb	0.2
^{210}Po	78
^{40}K	0.4

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CHARACTERIZATION OF SCALE FROM A FORMER PHOSPHORIC ACID PROCESSING PLANT

H. Beddow[1*], **S. Black**[1], **D. Read**[2,3]

[1]Environmental Radioactivity Research Group, School of Human & Environmental Sciences, University of Reading, Reading, United Kingdom
[2]Enterpris Ltd, University of Reading, Reading, United Kingdom
[3]Chemistry Department, University of Aberdeen, Old Aberdeen, United Kingdom

Abstract

A wide variety of industries extract and/or process ores and minerals containing naturally occurring radioactive material (NORM). In many cases the industrial processing of natural feedstock results in radioactive material becoming concentrated in (by-) products, wastes and plant installations. The main sources of NORM are members of the ^{238}U and ^{232}Th decay chains. The radioelements of greatest concern are radium, lead and polonium, due to their radiological and toxicological properties when inhaled and/or ingested. Scale samples were collected from a phosphoric acid processing plant, which is currently in the process of being demolished. These materials were analysed to determine the nature and concentration of NORM retained in the pipework and process plant. Three areas of the site were investigated: 1) the 'green acid plant', where crude acid was concentrated; 2) the green acid storage tanks; and 3) the 'purified white acid plant', where inorganic impurities were removed. The scale samples predominantly comprise: fluorides (e.g. malladrite, iron oxide fluoride), calcium sulphate (e.g. bassanite) and an assemblage of mixed fluorides and phosphates (e.g. iron fluoride hydrate, calcium phosphate) respectively, which can be related to the process occurring at each of these locations. The radioactive inventory is dominated by ^{238}U and its decay chain products and significant fractionation along the series occurs. Compared to the feedstock ore, elevated concentrations of ^{238}U ($\leq$ 8.8 Bq/g) in equilibrium with its daughter ^{234}Pa were found in installations where the process stream was rich in fluorides and phosphates. Enriched levels of ^{226}Ra ($\leq$ 11 Bq/g) were found in association with precipitates of calcium sulphate. Levels of ^{210}Pb in excess of its parent ^{226}Ra were also noted in many materials from the PWA plant, which may be attributed to the purification process in this installation.

1. INTRODUCTION

Enhanced concentrations of naturally occurring radioactive material (NORM) arise in industry where radioisotopes become mobile and subsequently accumulate in (by-) products, wastes and plant installations [1]. The main sources of NORM are from parent actinides ^{238}U and ^{232}Th, which decay to stable lead through a series of intermediate radioactive daughters [2]. The daughters of greatest radiological concern are ^{226}Ra, ^{228}Ra, ^{222}Rn, ^{210}Pb and ^{210}Po, due to their radiological properties and potential to invade the human environment by inhalation and/or ingestion, thereby becoming a health hazard [3]. It is therefore necessary for this radioactive material to be disposed of responsibly so that it remains sufficiently isolated from the human environment [4].

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[*] E-mail: h.l.beddow@reading.ac.uk

The need to dispose of diffuse NORM waste will have environmental and regulatory implications that so far have not been fully appreciated [5]. For example, contaminated installations require disposal, or decontamination and disposal, of the resultant waste. Both options are accompanied by loss of production and considerable costs are incurred. In addition, by-products and waste streams are produced in large volumes and are frequently dumped on site or go to landfill. Furthermore, in many cases the wastes were produced a long time ago, and were disposed of as non-radioactive materials, thereby occupying valuable land needed for construction and/or agriculture. At the root of the problem is a lack of understanding of:

(1) The extent of NORM-contaminated land,

(2) The concentration of NORM in these industrial sites,

(3) The quantity of NORM to be disposed of under the current directives.

In order to investigate the extent of radionuclide-contaminated land, a database of UK sites contaminated by NORM was compiled. Sites were characterized according to the nature of the industry, the radionuclides present, the aerial extent of the contamination, and whether the site is under institutional control. In addition, information was gathered on the nature of the hazard i.e. whether the radioactivity is in installations, buried, in (by-) products etc. (Table I). From this database, a phosphoric acid processing works was selected in order to investigate the extent and nature of radionuclide contamination.

2. THE PHOSPHATE INDUSTRY

2.1. Background

A phosphate processing plant on the north west coast of England has produced phosphoric acid since 1954. Until mid-1992, the company imported phosphate ore of sedimentary origin from Morocco and Israel, containing approximately 1490 Bq/kg (120 ppm) of uranium [6]. This ore was reacted with sulphuric acid to produce a ‘green acid’, using the Norsk Hydro hemidihydrate wet phosphoric acid production process, and was then further purified to produce food, technical and salts grade phosphoric acid. The waste product from this process was phosphogypsum slurry, the insoluble fraction resulting from the initial digestion of the ore with sulphuric acid, and an acid waste stream resulting from further processing of the green acid. The combined wastes were discharged into the sea under UK authorization [6].

In 1992, the company significantly modified its manufacturing procedure. Two main changes in operations occurred:

(1) The on-site manufacture of phosphoric acid from phosphate ore was abandoned, and instead crude phosphoric acid (green acid, with a uranium activity of 744 Bq/kg) was imported from Morocco and Mexico and purified at the works;

(2) The introduction of a treatment plant, which treated the liquid raffinate waste with quicklime (CaO) to produce a solid comprising calcium sulphate and calcium hydroxyapatite [7]. The calcium hydroxyapatite has a crystal structure similar to that of natural phosphate rock in which the heavy metals are locked into the insoluble lattice. The uranium, along with other metals, primarily cadmium [8], is said to be permanently encapsulated within the solid, called Ufex, which was landfilled on site. Consequently, discharge to the sea ceased.

TABLE I. SUMMARY OF SELECTED SITES FROM DATABASE OF UK NORM-CONTAMINATED SITES

Industry	Location	Contamination	Extent	Institutional control	Hazard
Coal-fired power station	Drax and Eggborough, Leeds	^{238}U, ^{232}Th and decay products; ^{210}Pb, ^{210}Po follow airborne pathways	Unknown	Emissions to air considered below the UK regulations; possible future restrictions on use of ash	Contamination concentrated in furnace flue; coal ash (fly ash, bottom ash, boiler slag)
Mineral processing	Cornwall, Devon	^{226}Ra, ^{228}Ra	Various process plants	Managed site	Insoluble Ra-substituted barite plated out on process installations
Defence	Fife	^{226}Ra	Beach, foreshore	Managed site	Incinerated Ra-luminized dials
Oil and gas.	Aberdeen	^{226}Ra, ^{228}Ra, ^{210}Pb, ^{210}Po	Unknown	Managed site	Macerated solid material discharged to sea
Paint manufacturer	Gowkthrapple, Wishaw, Scotland	^{226}Ra	Areas within 6 ha	Managed site	Buried radium paints
Phosphoric acid	Northern England	^{238}U, ^{232}Th and decay chain products	Unknown	Managed site	Liquid slurry discharged to sea; Ufex and radioactive plant landfilled on site
Radium extraction	Loch Lomond	^{226}Ra	‘Hot spots’ within 30 x 50 m area	Managed site	Ra extraction company
Refractory metals	Brighton	^{238}U, ^{232}Th	Unknown	Unknown	Rare earth oxide particles produced during grinding of electrodes
Special precautions burial	Whittle Hill quarry, Preston	^{238}U	Unknown	Unknown	Solid waste (drums used for transporting U ore, contaminated brickwork, laboratory ware, etc.)

2.2. Current status

The phosphoric acid processing plant ceased operation in 2002. Installations from the phosphoric acid purification process are currently being demolished and this is due to be completed by mid-2004. The company is working with the regulator on a remediation plan for the site. The Ufex will remain on site in engineered clay-lined landfills capped with a waterproof membrane and 1 m of soil. Leachate from the Ufex cells is monitored by the regulator twice a year under its radioactive monitoring programme, and the results published in an annual report [9]. The leachate is discharged via the former phosphogypsum waste pipe into the sea. The radioactive discharge authorization is still extant.

2.3. Aims and objectives

It has long been known that in the process of phosphoric acid production, radionuclides in the uranium decay chain become partitioned into products and by-products [10], [11]. However, in a study conducted in 1992 at the UK chemical works it was suggested that a proportion of the radionuclides were retained on site in the pipework and process plant [6]. Should this be the case, the industry would be faced with decontamination/disposal issues when maintaining or demolishing processing plant.

Thus, the aim of this study was to characterize scale, from selected stages of the processing stream, in terms of mineralogy and radioactivity. The overall objectives of this characterization programme were to:

(a) Establish the process areas, if any, which accumulate radioactivity and the fractionation that had occurred along the natural decay series chains;

(b) Quantify the form and nature of the material that was being disposed of.

3. SOURCES OF CONTAMINATION

3.1. Materials produced on the site

The chemical composition of phosphate ores varies between sources (see Table II), with sedimentary deposits tending to have the highest uranium concentrations. The phosphate minerals in both igneous and sedimentary ores are of the apatite group, of which the most commonly encountered variants are: fluorapatite ($Ca_{10}(PO_4)_6(F,OH)_2$) and francolite ($Ca_{10}(PO_4)_{6-x}(CO_3)_x(F,OH)_{2+x}$). Fluorapatite predominates in igneous phosphate rocks and francolite predominates in sedimentary phosphate rocks [12]. However, in sedimentary rocks replacement of PO_4^{3-} by CO_3^{2-} may reach several percent, and SO_4^{2-}, CrO_4^{2-} and SiO_4^{4-} may also replace the phosphate. Fluorine may be replaced by hydroxyl and chlorine ions. In addition, the calcium ions may be substituted by sodium, magnesium, potassium, strontium, rare earths and uranium [13].

At the works investigated in this study, phosphoric acid was produced by the 'wet' process, in which the phosphate rock is converted, by reaction with concentrated sulphuric acid, to phosphoric acid and an insoluble calcium sulphate salt (phosphogypsum).

$$Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 2H_3PO_4 + 3CaSO_4 \qquad (1)$$

3.2. Areas investigated

Widespread scaling of the process plant and storage tanks was observed. However, due to the ongoing demolition work, samples were taken from only a limited number of areas. These areas were as follows:

TABLE II. CHEMICAL ANALYSIS OF PHOSPHATE ROCK (From Ref. [12])

	Igneous rock			Sedimentary rock		
	CEI Russia	Phalaborwa, South Africa	Certified Standard	Khouribga, Morocco	Florida, USA	Senegal
Composition (wt. %)						
P_2O_5	38.9	36.8	36.04	33.4	34.3	36.7
CaO	50.5	52.1	55.74	50.6	49.8	50
Na_2O	0.4	0.1	0.1	0.7	0.5	0.3
MgO	0.1	1.1	0.83	0.3	0.3	0.1
Al_2O_3	0.4	0.2	<LLD[1]	0.4	1.1	1.1
SiO_2	1.1	2.6	0.37	1.9	3.7	5.0
K_2O	0.5	0.1	<LLD	0.1	0.1	0.1
Fe_2O_3	0.3	0.3	<LLD	0.2	1.1	0.9
CO_2	0.2	3.5	NR[2]	4.5	3.1	1.8
SO_3	0.1	0.2	NR	1.6	0.1	NR
F^-	3.3	2.2	NR	4.0	3.9	3.7
Cl^-	NR	NR	NR	0.1	NR	NR
Organics	NR	0.1	NR	0.3	0.5	NR
Organ. C	0.1	NR	NR	NR	0.2	0.4
Trace elements (ppm)						
Rare earth elements	6200	4800	5745	900	600	NR
As	10	13	24	13	11	18
Cd	1.2	1.3	<LLD	15	9	53
Cr	19	1	<LLD	200	60	6
Cu	37	102	76	40	13	NR
Hg	33	0.1	NR	0.1	0.02	0.2
Ni	2	2	15	35	28	NR
Pb	NR	11	20	10	17	5
Sr	29 000	3000	4000	1000	NR	NR
U	11	134	189	185	101	124
Zn	20	6	<LLD	200–400	70	NR

(i) The green acid plant, where the acid was concentrated by vacuum evaporation with forced circulation. The plant was utilized both pre- and post-1992 for concentrating the acid. Two scale samples were taken from a pipe that linked the concentrator with the ejector, which was used to pull the vacuum. This was positioned at the top of the building, but has since been dismantled.

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[1] LLD = Lower limit of detection.

[2] NR = Not reported.

(ii) The green acid storage tanks, used in both processes for storing concentrated phosphoric acid from the green acid plant, and for pre-concentrated acid from Morocco/Mexico. The tanks were installed with agitators to keep the solids in suspension. A scale sample was taken from one of the agitators and also from the inside of one of the tanks.

(iii) The purified white acid (PWA) plant, where inorganic impurities are removed by means of an extraction process in which pre-purified acid was contacted with a solvent (methylisobutyl ketone) in several stages. Together with small amounts of impurities, the phosphoric acid was transferred to the organic phase, while most of the impurities remained in the aqueous phase. In order to achieve a higher yield of P_2O_5, the underflow from the solvent reaction vessel was transferred to a second extraction column, and reacted with sulphuric acid so that the cationic impurities remained in the aqueous phase as sulphates [14]. This waste stream then went to the raffinate treatment plant prior to landfill. The purified acid from both columns underwent further processing in additional plant installations to remove arsenic and fluorine, thereby producing a food grade phosphoric acid. Six samples were taken from the PWA plant at various locations as illustrated in Fig. 2.

4. MINERALOGY

All samples were prepared for analysis by drying in an oven at 70ºC for 24 h. The samples were then ground to a fine powder (~ 5 μm) using a 'Tema' disc mill, as required for X-ray analysis. A certified standard of igneous phosphate rock from South Africa was also analysed in order to determine the precision and accuracy of the sample data (Table II). The mineralogy of the samples was obtained by X-ray diffraction (XRD) analysis and is summarized in Table III.

A sub-set of samples was also examined by scanning electron microscope (SEM). A JOEL JXA840 was used with a Link AN10000 attachment for energy-dispersive X-ray analysis, in order to characterize the morphology of the samples and obtain compositional information. Stubs with sample mounts were coated with carbon and gold, the latter providing better definition for photographic reproduction.

The results of these analyses are discussed below according to sampling location.

4.1. The green acid plant

Sample HB/03/001 (Fig. 3(a)) was taken from the opposite end of the pipe to sample HB/03/002 — both scales were 10–15 mm thick. The samples were light green in colour, but HB/03/002 had a botryoidal surface expression (Fig. 4(a)) and was therefore divided laterally into upper and lower parts labelled HB/03/002a and HB/03/002b, respectively, in order to examine any differences in mineralogy.

The pipework at the top of the green acid plant was subject to fluorine-rich effluent, which appears in the vapours exhausted from the evaporators when the acid is concentrated. Fluorine is initially liberated as hydrogen fluoride but in the presence of silica this readily reacts to form fluosilicic acid (H_2SiF_6), which, in the presence of other components, forms pachnolite ($NaCaAlF_6H_2O$) [15] and precipitates known in the phosphate industry as 'alkali fluorosilicates' [16]. This latter material was found to be in all three samples in the form of an alkali silica hexafluoride, malladrite (Na_2SiF_6). In addition, the samples contain sodium magnesium aluminium fluoride ($NaMgAlF_6$), ralstonite ($NaMgAlF_6 \cdot H_2O$), a sublimate mineral, and iron oxide fluoride (FeOF).

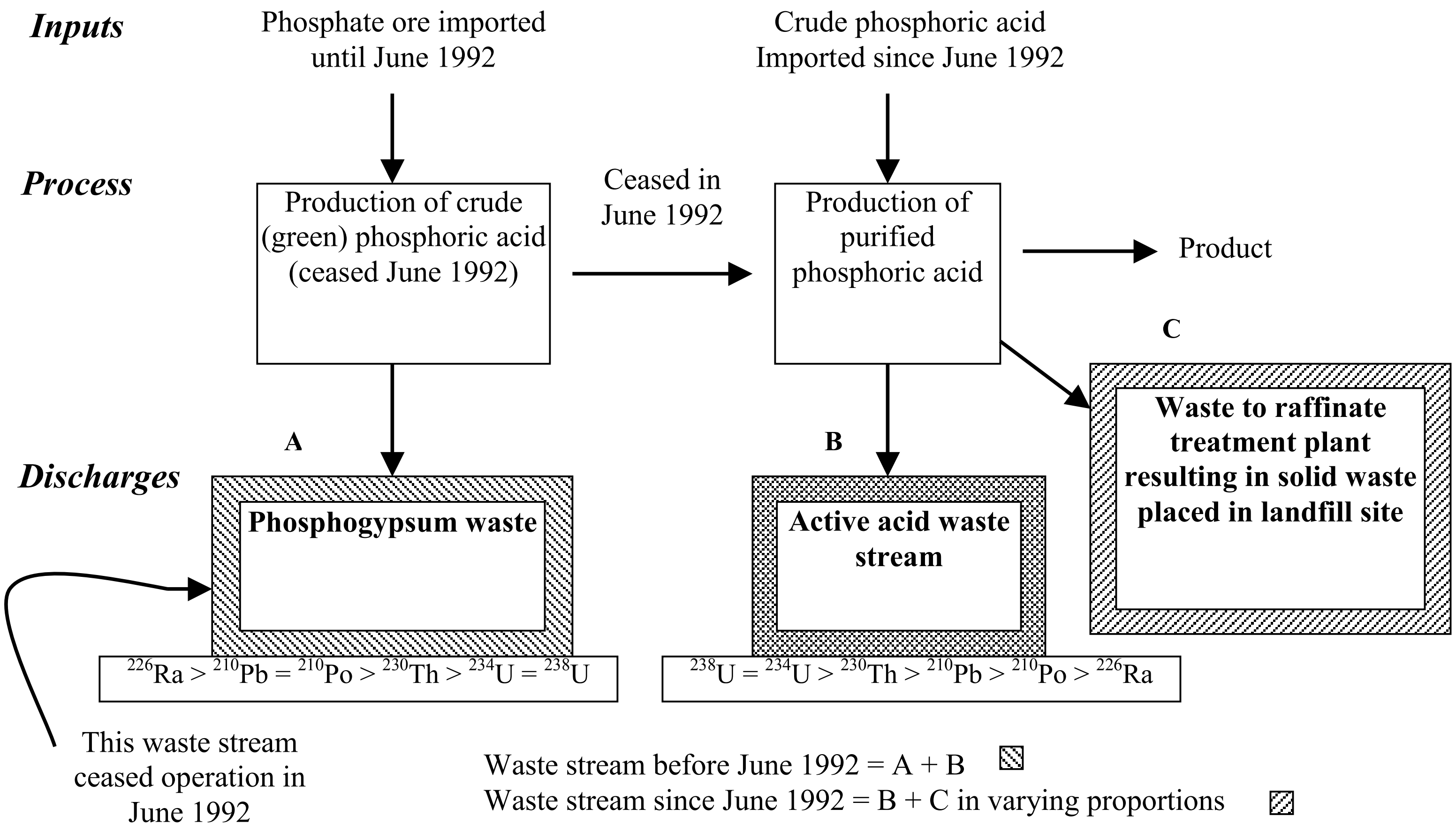


FIG. 1. Flow diagram of the radioactive inventory before and after changes at the chemical works [6].

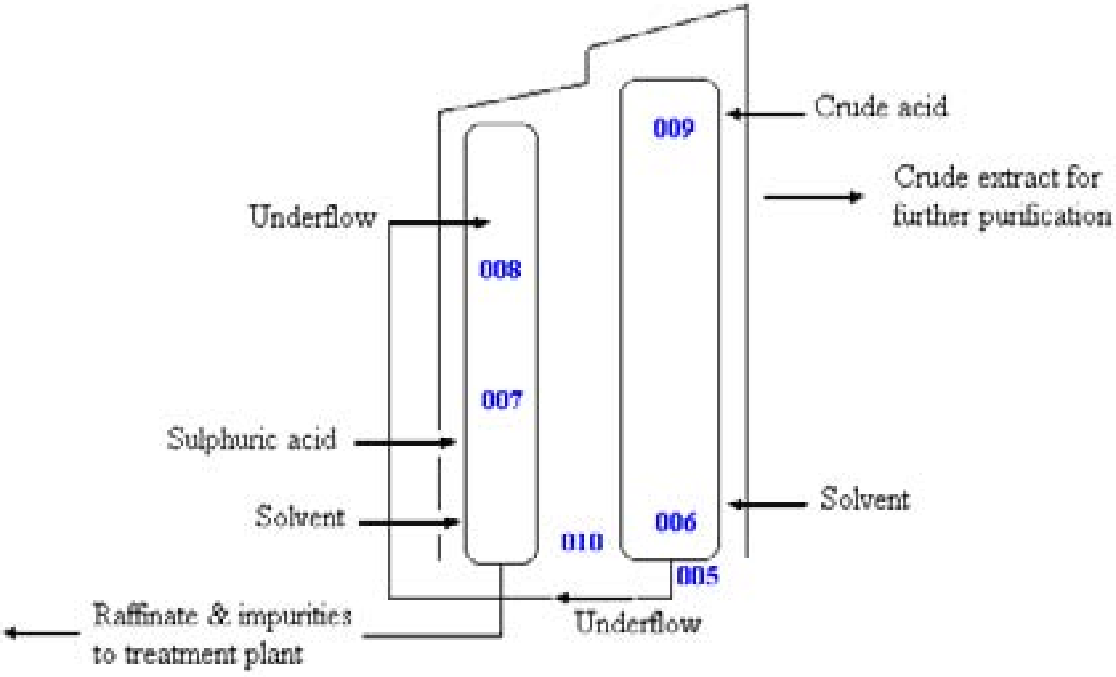


FIG. 2. Schematic diagram of the PWA plant. Sample numbers HB/03/005 to 010 taken from the locations as indicated.

Under the SEM, sample HB/03/001 appears as an aggregate of small spherical particles (Fig. 3(b)). Of note are the diameters of these smaller particles, which are within the respirable range (<10 µm) — these particles are therefore a potential health hazard if inhaled. Sample HB/03/002b has a more open structure than that of HB/03/001, and is also composed of particles <10 µm in diameter together with angular crystals growing on their surfaces (Fig. 4(b)). An additional image taken of HB/03/002b (Fig. 4(c)) shows rhombohedral crystals >30 µm in diameter, indicating the sample to be heterogeneous. The chemistry obtained by point analysis would suggest that these crystals are malladrite.

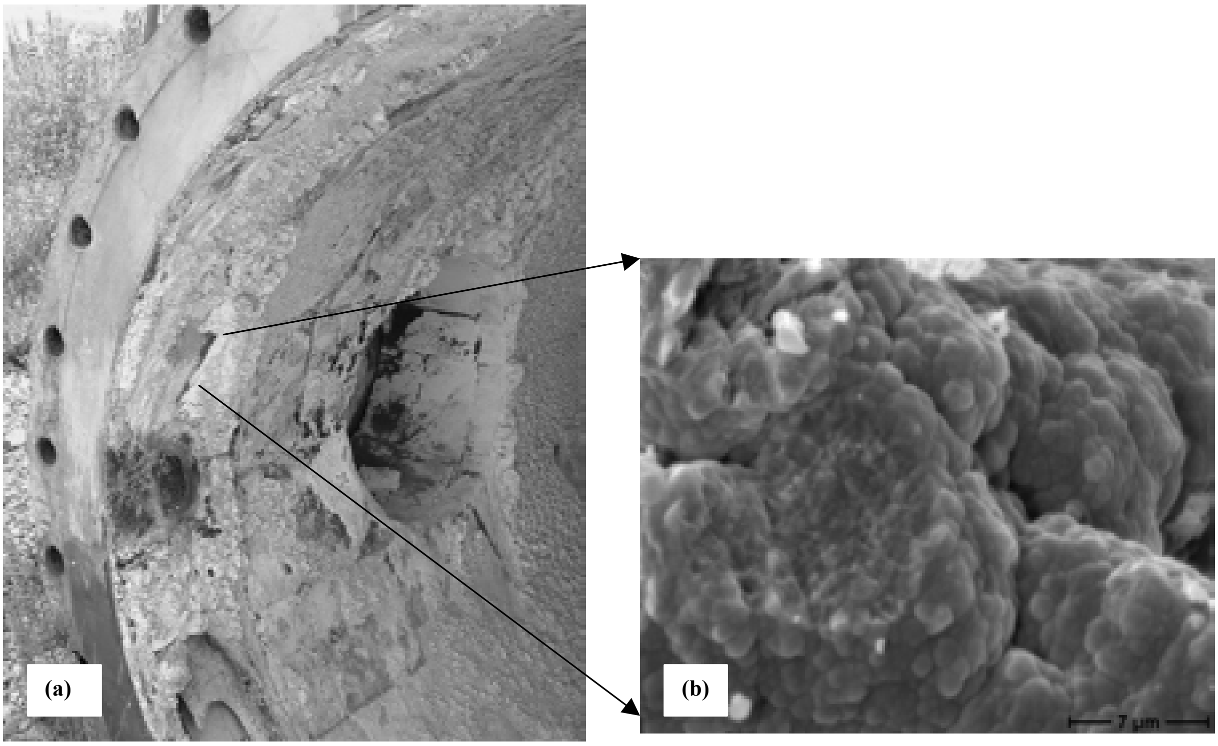
4.2. The green acid storage tanks

Scale sample HB/03/003 was taken from an agitator that had originally been installed in one of the storage tanks (Fig. 5 (a)). This sample was hard, and displayed well-defined layering of grey and black minerals; the sample was therefore split laterally in order to separate these two minerals for analysis, and the parts were labelled HB/03/003a and HB/03/003b respectively. Both samples were found to be predominantly gypsum ($CaSO_4{\cdot}2H_2O$). Sample HB/03/003b also contains small quantities of anhydrite ($CaSO_4$) and bassanite ($CaSO_4{\cdot}\frac{1}{2}H_2O$), the latter known in the phosphate industry as hemihydrate.

Under the SEM, an unseparated sample of HB/03/003 showed ‘flattened’ calcium sulphate crystals >20 µm in diameter (Fig. 5 (b)). However, these crystals had, in places, become fragmented into respirable-sized particles (<10 µm).

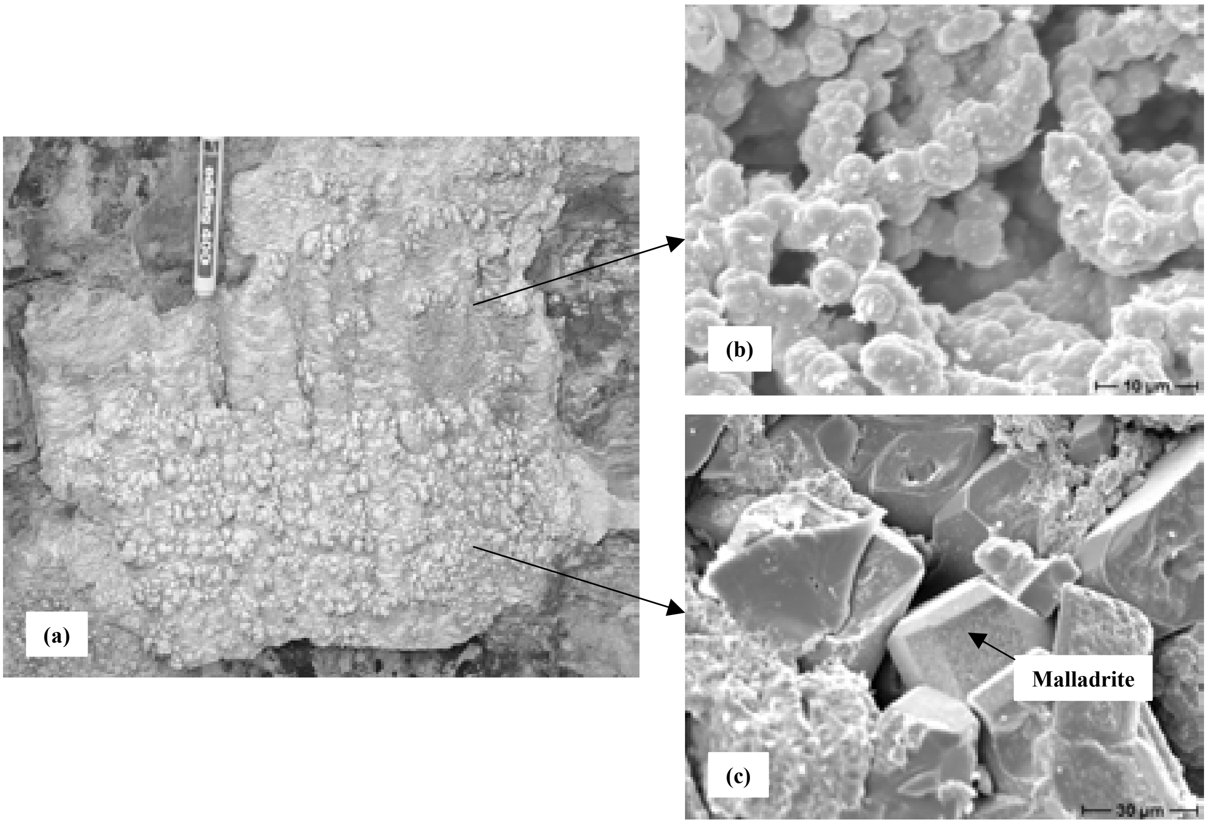
TABLE III. SUMMARY OF THE MINERALOGY OF THE SAMPLES

Location	Green acid plant			Storage tanks			PWA plant						
HB/03/-	001	002a	002b	003a	003b	004	005	006a	006b	007	008	009	010
Sodium magnesium aluminium fluoride	•	•	•					•		•			
Ralstonite ($NaMgAlF_6{\cdot}H_2O$)	•	•	•							•			
Malladrite (Na_2SiF_6)	•	•	•										
Iron oxide fluoride	•	•	•										
Gypsum ($CaSO_4{\cdot}2H_20$)				•	•	•							
Bassanite ($CaSO_4{\cdot}$ $0.5H_20$)					•			•			•		
Anhydrite ($CaSO_4$)					•			•			•		
Calcium magnesium aluminium fluoride silicate						•		•					
Sodium magnesium aluminium silicate fluoride						•							
Sodium aluminium silicate						•							
Magnesium chloride						•							
Ammonium magnesium aluminium fluoride						•					•		
Calcium phosphate							•		•				•
Iron hydrogen phosphate							•		•				•
Iron (III) fluoride							•		•				•
Collinsite ($Ca_2(Mg,Fe)(PO_4)_2{\cdot}2H_2O$)							•		•				•
Wagnerite ($(Mg,Ca,Fe)_2(PO_4)F$)							•		•				•
Iron (II) fluoride							•		•				•
Iron fluoride hydrate							•		•				•
Iron phosphate							•	•					•
Magnesium phosphate hydrate							•						•
Aluminium chloride hydroxide hydrate								•					
Aluminium hydrogen phosphate hydrate								•					
Ammonium iron phosphate hydrate												•	
Sodium magnesium phosphate												•	
Iron fluoride hydrate												•	



(a) Photograph (b) SEM image

FIG. 3. Images of sample HB/03/001



(a) Photograph of HB/03/002a (b) and (c) SEM images of HB/03/002b

FIG. 4. Images of samples HB/03/002a and HB/03/002b

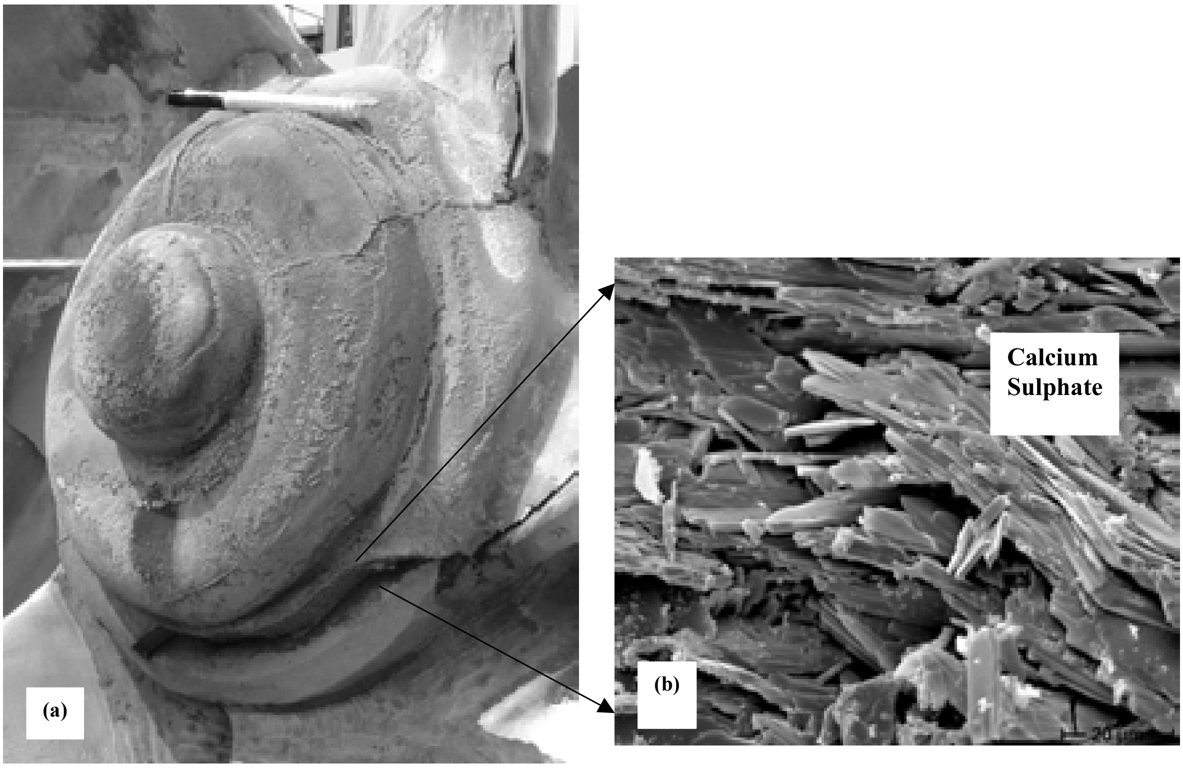
As part of the demolition programme, the storage tanks had been cut open and the scaling scraped out and deposited around the tanks (Fig. 6 (a)). This scale, HB/03/004, was extensive and >10 cm thick. The material is light grey in colour, and appears porous and inhomogeneous. XRD analysis found the sample to be composed of gypsum, calcium magnesium aluminium fluoride silicate ($CaMg_6Al_2Si_6O_{20}F_4$), sodium magnesium aluminium silicate fluoride ($NaMg_3AlSiO_4F_6$), sodium aluminium silicate ($NaAlSiO_4$), magnesium chloride ($MgCl_2$), and ammonium magnesium aluminium fluoride ($(NH_4)MgAlF_6$).

SEM analysis of HB/03/004 showed a mix of large (>30 μm) gypsum crystals and small (<3 μm) granular particles, which were determined from point analysis to be calcium magnesium aluminium fluoride silicate (Fig. 6 (b)).

4.3. The PWA plant

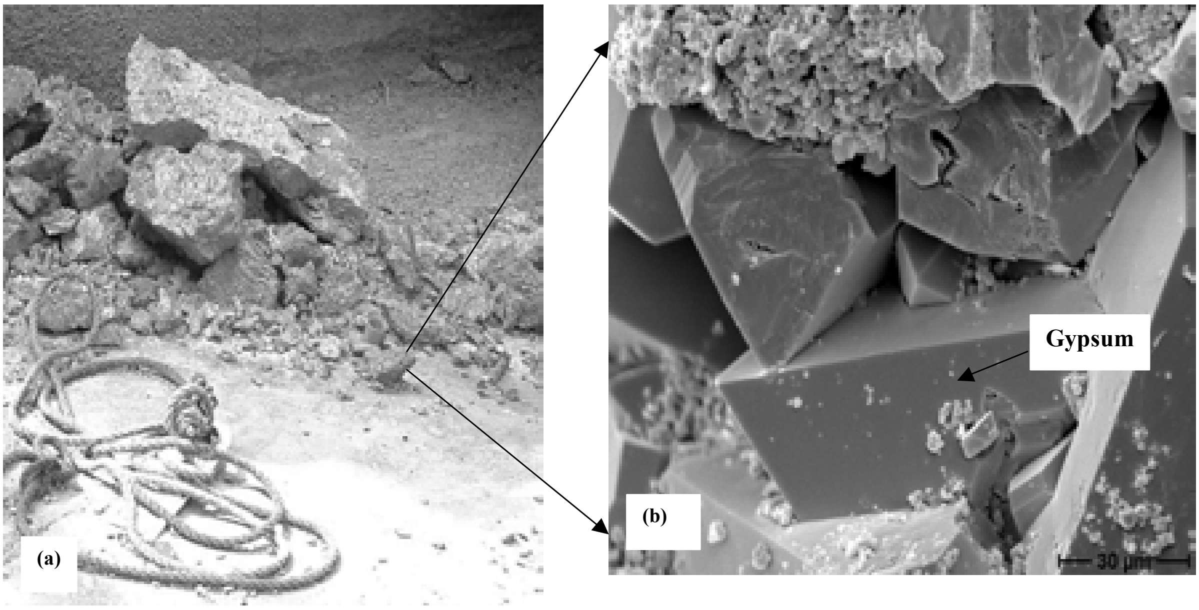
Sample HB/03/005 was taken from the base of the right-hand extraction column as shown in Fig. 2. This soft material was found encrusted around pipework, and was light green in colour. From XRD analysis it was found that the material is composed of a variety of phosphate and iron compounds. These compounds are calcium phosphate ($Ca(PO_3)_2$), iron hydrogen phosphate ($FeH_2P_3O_{10}$), iron fluoride (FeF_3), collinsite ($Ca_2(MgFe)(PO_4)_2 \cdot H_2O$), wagnerite ($(Mg,Ca,Fe)_2(PO_4)F$), iron fluoride ($FeF_2$), iron fluoride hydrate ($FeF_2 \cdot 4H_2O$), iron phosphate ($FePO_4$) and magnesium phosphate hydrate ($Mg_3(PO_4)_2 \cdot 5H_2O$).

Sample HB/03/006a was taken from inside the extraction column, adjacent to the solvent outflow pipe, and sample HB/03/006b from the access door. Both samples were hard and undulate in appearance, and approximately 2–3 mm thick. HB/03/006a was cream coloured, whereas HB/03/006b was green.



(a) Photograph (b) SEM image

FIG. 5. Images of sample HB/03/003 (not separated)



(a) Photograph (b) SEM image

FIG. 6. Images of sample HB/03/004

HB/03/006a was found to be composed of all three hydration states of calcium sulphate encountered previously, i.e. gypsum, bassanite and anhydrite. Additional compounds that were identified were iron phosphate ($FePO_4$), aluminium hydrogen phosphate hydrate ($AlH_3(PO_4)_2{\cdot}H_2O$), aluminium chloride hydroxide hydrate ($AlCl(OH)_2{\cdot}2H_2O$), and sodium magnesium aluminium fluoride ($NaMgAlF_6$).

Sample HB/03/006b had the same assemblage of compounds as HB/03/005 and HB/03/010 except that HB/03/006b lacked magnesium phosphate hydrate and iron phosphate ($Fe\ PO_4$). This similar chemical composition may be attributed to the fact that all three samples were taken from outside of the reaction vessel and at a similar level in the purifying tower (Fig. 2). Sample HB/03/010 had the same appearance as HB/03/005 and was found encrusted around a stop tap.

HB/03/007 was taken from inside of the second reaction vessel (Fig. 2), where it was found coating pipe work as a hard, undulate, cream coloured deposit approximately 4 mm thick. XRD analysis showed that this material comprised sodium magnesium aluminium fluoride ($NaMgAlF_6$) and ralstonite.

HB/03/008 was an inhomogeneous, grey/black scale, 5– 10 mm thick and deposited on the inside rim of the access hatch. The XRD trace obtained had a high background level, suggesting the presence of an X-ray amorphous phase that would mask this mineral's identification. However, other minerals that were identified were bassanite, anhydrite and ammonium magnesium aluminium fluoride.

Sample HB/03/009 was taken from inside the reaction vessel as indicated in Fig. 2. Only a small (>1 g) quantity of HB/03/009 was available for sampling, as just a 'dusting' of vivid green crystals were found at this point. Due to the lack of material, XRD analysis was obtained by smearing the ground sample, mixed with isopropanol, onto a silicon slide. Compounds of ammonium iron phosphate hydrate ($(NH_4)Fe_3P_6O_{20}{\cdot}10H_2O$), sodium magnesium phosphate ($Na_2Mg(PO_3)_4$), and iron fluoride hydrate ($Fe_2F_5{\cdot}7H_2O$) were found.

5. RADIOACTIVITY

Radioactivity was determined using gamma spectrometry, which utilizes a large (3800 mm^2 active area) Harwell Instruments, Broad Energy Germanium Detector with a computer equipped with software for quantitative analysis, control of data acquisition and spectral analysis. The detector was calibrated against a mixed radionuclide standard covering an energy range of approximately 50–2000 keV.

In this characterization study, the following radionuclides were analysed (half-life $t_{½}$ given in parentheses):

- From the ^{238}U series: ^{238}U (4.468 × 10^9 a), ^{234}Pa (1.18 min), ^{226}Ra (1600 a), ^{210}Pb (22 a);
- From the ^{232}Th series: ^{228}Ra (5.75 a), ^{212}Pb (10.64 h), ^{208}Tl (3.1 min).

Samples were prepared in the same manner as for X-ray analysis (see Section 4), and then sealed in plastic containers. Results for members of the ^{238}U decay chain are given in Table IV. The majority of the detected radioactivity is essentially from the ^{238}U decay series. None of the samples contain significant activities of ^{232}Th series radionuclides due to the feedstock phosphate ore having low ^{232}Th activity (<0.01 Bq/g) [6].

TABLE IV. RADIONUCLIDE ACTIVITIES IN THE SAMPLES

Location	Sample	Activity concentration (Bq/g) (± %)			
		^{238}U	^{234}Pa	^{226}Ra	^{210}Pb
Green acid plant	HB/03/001	8.62 (0.79)	9.35 (3.10)	0.37 (1.31)	< LLD
	HB/03/002a	0.04 (2.66)	< LLD	0.03 (0.92)	0.03 (2.00)
	HB/03/002b	1.16 (1.22)	1.44 (8.38)	0.38 (1.00)	0.12 (4.22)
Storage tanks	HB/03/003a	0.22 (8.35)	< LLD	7.21 (0.23)	2.90 (0.62)
	HB/03/003b	0.21 (15.75)	< LLD	11.11 (0.37)	11.55 (0.98)
	HB/03/004	0.48 (10.89)	< LLD	5.27 (0.34)	0.96 (7.57)
PWA plant	HB/03/005	2.84 (0.94)	4.69 (7.36)	0.03 (6.25)	0.19 (8.37)
	HB/03/006a	0.58 (9.38)	< LLD	2.42 (0.60)	3.08 (3.00)
	HB/03/006b	0.14 (12.76)	< LLD	1.11 (1.21)	4.55 (1.47)
	HB/03/007	< LLD	< LLD	2.16 (0.57)	1.04 (6.37)
	HB/03/008	1.56 (3.14)	1.98 (12.89)	1.93 (0.60)	1.68 (3.81)
	HB/03/010	1.37 (1.33)	2.17 (11.81)	0.04 (5.56)	0.52 (3.59)
—	Standard	0.10 (2.59)	< LLD	0.12 (0.66)	0.05 (2.44)

As discussed earlier, scale from the pipe sampled in the green acid plant was subject to fluorine-rich effluent, and consequently the scaling was found to comprise fluoride-rich compounds. Uranium is readily complexed by both PO_4^{3-} and F^- ions [16], which was borne out by the ^{238}U activity found in sample HB/03/001 (8.62 Bq/g). At this location, ^{238}U had been concentrated to levels above the 1.49 Bq/g level encountered in the feedstock ore [6]. As expected from its short half-life, ^{234}Pa was found to be in equilibrium with its parent ^{238}U (taking into account the statistical uncertainty). The concentration of ^{226}Ra was found to be enhanced in the materials from this location, and in particular in samples HB/03/001 and HB/03/002b — 0.37 Bq/g and 0.38 Bq/g respectively. The radionuclide ^{210}Pb was depleted relative to ^{226}Ra and, with a half-life of ~22 a, would take approximately 100 a to reach secular equilibrium — it takes approximately five half-lives of the daughter isotope to attain secular equilibrium with its parent.

Samples taken from the green acid storage tanks comprised predominantly calcium sulphate. Consequently, due to the similar chemistry of radium and calcium, these materials were enriched in ^{226}Ra. In sample HB/03/003b, ^{226}Ra and ^{210}Pb were approximately in equilibrium, as these isotopes had not been fractionated from one another during storage of the acid. Therefore, it may be concluded that both isotopes were co-precipitated with calcium sulphate, which, in this material, was present in its three hydration states. In both samples HB/03/003a and HB/03/004, however, ^{226}Ra had been fractionated, as it was found in excess of its daughter ^{210}Pb (Fig. 7), which may be attributed to the slight differences in mineralogy compared with HB/03/003b (Table III). In addition to the enhanced ^{226}Ra level, sample HB/03/004 was a fragmentary material (Fig. 6 (a)), which had been removed from the tanks and deposited over a large area around the storage facility.

Various phosphate and fluoride compounds that had complexed ^{238}U dominated the deposits collected throughout the PWA plant; this was particularly apparent in samples HB/03/005 and HB/03/010, both of which had the same chemical composition (Table III). It was noted earlier that HB/03/006b also shared a similar composition with the aforementioned materials. However, as seen from the profiles of all three samples in Fig. 7, HB/03/006b had a much lower ^{238}U content. This distinction is likely to be associated with its lack of iron phosphate and magnesium phosphate hydrate, which were present in both HB/03/005 and HB/03/010. Also, of particular interest is that these three samples, together with sample HB/03/006a, had an excess of ^{210}Pb relative to its parent ^{226}Ra (Fig. 7). The activity concentration ratios of ^{210}Pb to ^{226}Ra for samples HB/03/005, HB/03/006a, HB/03/006b and HB/03010 were 6.33, 1.27, 4.09 and 13 respectively. This ^{210}Pb excess must be due to direct precipitation related to the chemical reactions occurring at the corresponding stage of the purification process.

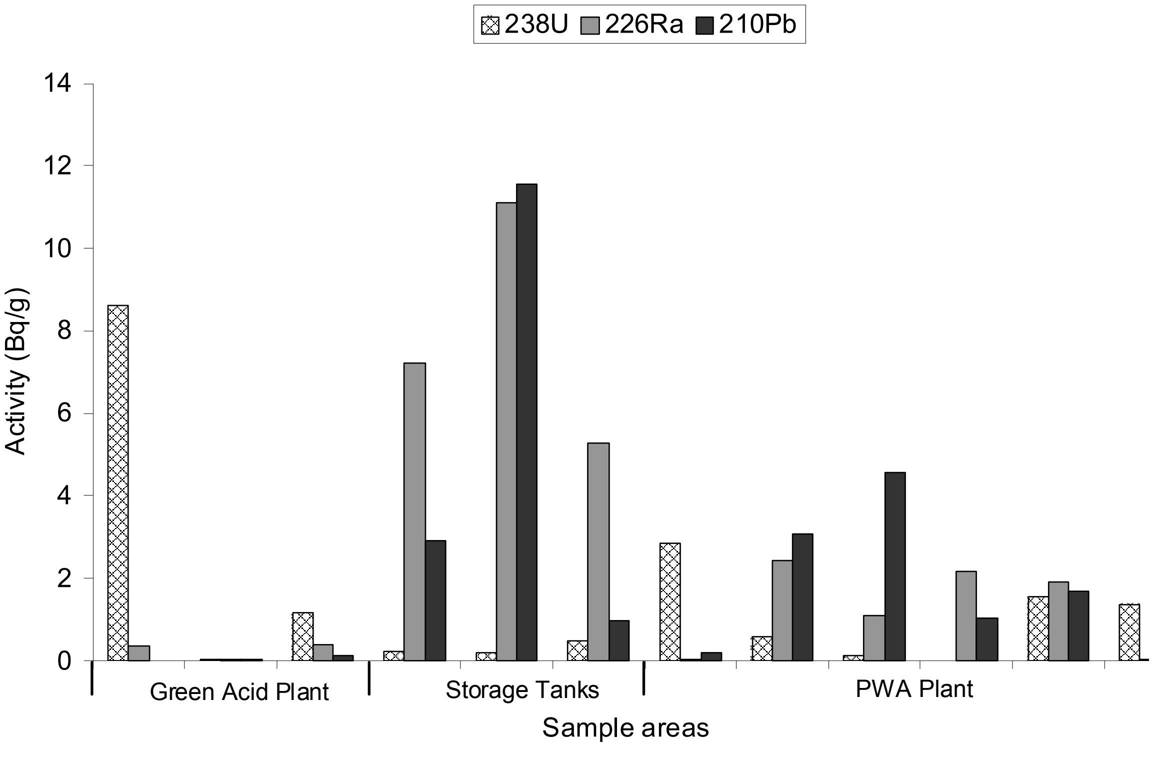


FIG. 7. Summary of the radioactivity inventory of the scales

6. CONCLUSIONS

Scale samples from the green acid plant, the storage tanks and the PWA plant have been characterized mineralogically and radioactively. The materials comprise predominantly fluorides, calcium sulphate and an assemblage of fluorides and phosphates respectively, which can be related to the process occurring at each of these locations.

The radioactive inventory is primarily all from ^{238}U and its decay chain products. ^{238}U and its daughter ^{234}Pa were found to be retained in installations where the process stream was rich in fluorides and phosphates, namely the green acid plant and the PWA plant. High levels of ^{226}Ra were found in association with precipitates of calcium sulphate in the storage tanks and to a lesser extent in scales from the PWA plant. However, it was noted that many of materials from the PWA plant had ^{210}Pb activity levels in excess of its parent ^{226}Ra (Fig. 7), which may be attributed to the purification process occurring in this installation.

Total inventories for radioactive elements, assuming short-lived (<2 a) equilibrium between some daughter isotopes, were:

- Uranium: 0.0–17.24 ± 0.07 Bq/g;
- Radium: 0.11–11.12 ± 0.02 Bq/g;
- Lead: 0.13–22.70 ± 0.08 Bq/g.

This variation is a result of fractionation within the manufacturing process and represents differences of 0.04–6.70 over the original starting materials.

These data show the detailed nature of the mineralogical and radioelement associations and are vital prerequisites for understanding the potential solubility and hence, future mobility of the elements associated with them.

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PRESENCE OF TECHNOLOGICALLY-ENHANCED NATURALLY-OCCURRING RADIOACTIVE MATERIALS IN THE CZECH REPUBLIC

H. Moravanska[*]**, A. Laciok**

Nuclear Research Institute Rez (NRI), Waste and Environmental Management Department, Czech Republic

Abstract

NRI Rez participates in the TENORMHARM project within the 5th EU Framework Programme. NRI´s effort is focused on evaluation of the NORM inventory and assessment of radiation dose and health risks to workers and members of the public. In the case of phosphate fertilizer production, three major factories provide for Czech consumption at present. Nowadays, generally less radioactive raw materials are used, such as yellow phosphorus, phosphoric acid, Kola apatite concentrate and AMOFOS. Only the Kola apatite concentrate contains higher quantities of ^{238}U, ^{226}Ra and ^{228}Th (several tens of becquerels per kilogram), but even in this case the resulting annual effective dose received by workers does not exceed the regulatory limit. Titanium dioxide pigments are produced in only one factory. Ilmenite from Ukraine (approximately 140 Bq/kg ^{238}U and 80 Bq/kg ^{228}Th) is used as the raw material. The final product (rutile-TiO_2) contains only negligible quantities of these radionuclides. The majority of the radioactivity content thus remains in the various wastes; for example, the concentrations of ^{210}Pb and ^{226}Ra are up to 1000 Bq/kg in sludges. Currently, one factory processes zirconium refractory material (EUCOR). Only zirconium-containing bricks (with a ^{226}Ra activity concentration of approximately 1700 Bq/kg) discarded from glass factories are used for EUCOR production. The current consumption of approximately 200 t of zirconium input material (bricks) means reprocessing of 340 000 kBq of ^{226}Ra. Coal exploitation and use represents one of the most important industries concerning NORM. The concentrations of uranium and thorium in Czech brown coal are 5–16.3 ppm and 0.2–30.2 ppm respectively; the hard coal contains 2–9 ppm uranium. The majority of the coal is used for energy production. The uranium and thorium concentrate mostly in the ash and slag (<12 ppm U and about 20 ppm Th); the concentration of all radionuclides in gypsum produced in the desulphurization process is negligible. The majority of oil and gas used in Czech industry is imported. Measurements of samples of oil sludge from cleaning of the IKL and Druzba pipelines and from oil tanks exhibited only negligible concentrations of all radionuclides (tenths of a becquerel per kilogram). A similar range of activity has been found in samples from domestic oil exploitation. Evaluation of radioactivity in sludges resulting from the 68 ground and surface water treatment installations was performed by NRPI. An average ^{226}Ra activity concentration of 200 Bq/kg was identified in groundwater treatment sludges.

1. INTRODUCTION

NRI Rez participates in the TENORMHARM project within the 5th EU Framework Programme. NRI´s effort is focused on evaluation of the NORM inventory (identification of priority areas, detailed studies of technological schemes, measurement of selected materials), assessment of radiation dose and health risks to workers and members of the public and ranking NORM on the basis of its radioactivity, the quantity of managed material and type of industry and/or process. NORM is present in two general branches of industry:

(i) Industries based on imported materials:

- Phosphate fertilizer production;

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[*] E-mail: moh@ujv.cz

- Production of titanium dioxide pigments;
- Oil and gas transport and processing;
- Production of zirconium refractory materials;
- Thoriated electrodes manufacturing.

(ii) Industries based mainly on domestic raw materials:

- Coal mining and its use;
- Ground water treatment sludge.

2. PHOSPHATE FERTILIZER PRODUCTION

During the history of phosphate fertilizer production, various raw materials were utilized — most were imported from Russia (Kola apatite) and the remainder from several North African countries (Morocco, Algeria, Egypt, etc.). At present, only three major factories provide for Czech consumption of fertilizer (Table I). The technologies used currently do not produce waste and all by-products are recycled. Nowadays, generally less radioactive raw materials are used such as yellow phosphorus and phosphoric acid imported from Ukraine, Kola apatite concentrate, and AMOFOS (a mixture of hydrogen and dihydrogen ammonium phosphate) from Russia.

TABLE I. PHOSPHATE FERTILIZER PRODUCERS IN THE CZECH REPUBLIC

Factory	Raw material
FOSFA	‘Yellow phosphorus’ (Ukraine)
Synthesia	Kola apatite concentrate (Russia) AMOFOS (Russia)
Lovochemie	Kola apatite (Russia) AMOFOS (Russia)

Only the Kola apatite concentrate contains non-negligible quantities of ^{238}U, ^{226}Ra and ^{228}Th, but even utilizing this material the resulting annual effective dose of workers does not exceed the guidance level (1 mSv/a) as confirmed by exposure measurements. A detailed characterization of the Lovochemie factory was performed, including quantification of selected radionuclides (Table II) and exposure measurements.

TABLE II. GAMMA SPECTROMETRIC ANALYSIS OF SAMPLES FROM THE LOVOCHEMIE FACTORY

Radionuclide	Activity (Bq/kg)				
	^{40}K	^{228}Ac	^{228}Th	^{226}Ra	^{238}U
Kola apatite	37	115	95	38	64
Insoluble residue	366	435	183	142	190
NPK fertilizer	3626	31	33	12	—

The higher value of ^{40}K in NPK fertilizer is caused by the KCl content.

An effective dose rate of 0.04–0.26 μSv/h was measured at various places (natural background: 0.2 μGy/h). The highest values were detected in the KCl storage facility and in the area where the insoluble residue returns to the main process stream. The actual measurement of the dust has not been carried out so far. Assuming that the dust level does not exceed 5 mg/m^3 and that the air inhalation is 2000 m^3/a, the effective dose received by workers would not exceed 0.1 mSv/a. Therefore, negligible dose could be also expected for members of the public. Detailed measurements of various deposits, including those containing ^{210}Pb and ^{210}Po, have not been performed, but utilization of relatively low activity raw materials indicates that such measurements are of secondary importance.

In the FOSFA factory, a sample of phosphogypsum from disused sludge lagoons was collected and measured (Table III). As expected, the phosphogypsum (used for the production of fertilizer and construction materials) contained only negligible amounts of radioactivity.

TABLE III. GAMMA-SPECTROMETRIC ANALYSIS OF A PHOSPHOGYPSUM SAMPLE

Radionuclide	Activity (Bq/kg)		
	Mean	Standard deviation	Detection limit
^{40}K	<11.0	—	11.0
^{210}Pb	21.7	±2.1	4.0
^{226}Ra	27.5	±1.1	0.30
^{228}Ra	28.9	±1.3	1.1
^{227}Ac	<1.4	—	1.4
^{228}Th	32.7	±1.4	0.35
^{230}Th	<51.0	—	51
^{231}Pa	<10	—	10
^{235}U	<0.48	—	0.48
^{238}U	<4.0	—	4.0

3. TITANIUM DIOXIDE PIGMENT PRODUCTION

Titanium dioxide pigments are produced only in the Precheza factory situated in Prerov. TiO_2 production is at present about 65 000 t/a. This factory formerly used ilmenite imported from Finland, then in 1996–2001 a 1:2 mixture of Norwegian and Ukrainian ilmenites, respectively, and since 2002 only ilmenite from Ukraine. Ukrainian ilmenite represents a material with relatively high concentrations of uranium and thorium (about 11 ppm U and 20 ppm Th); the Norwegian mineral contains only about 0.1 ppm U and 0.3 ppm Th.

The titanium dioxide manufacturing process is based on the digestion of ilmenite with sulphuric acid (‘sulphate technology’). A simplified process schematic is shown in Fig. 1.

Selected materials from the Precheza factory were analysed (Table IV) and the dose rate was measured in the potentially problematic work areas (Table V) — the data were used for the evaluation of the radiation risk for workers.

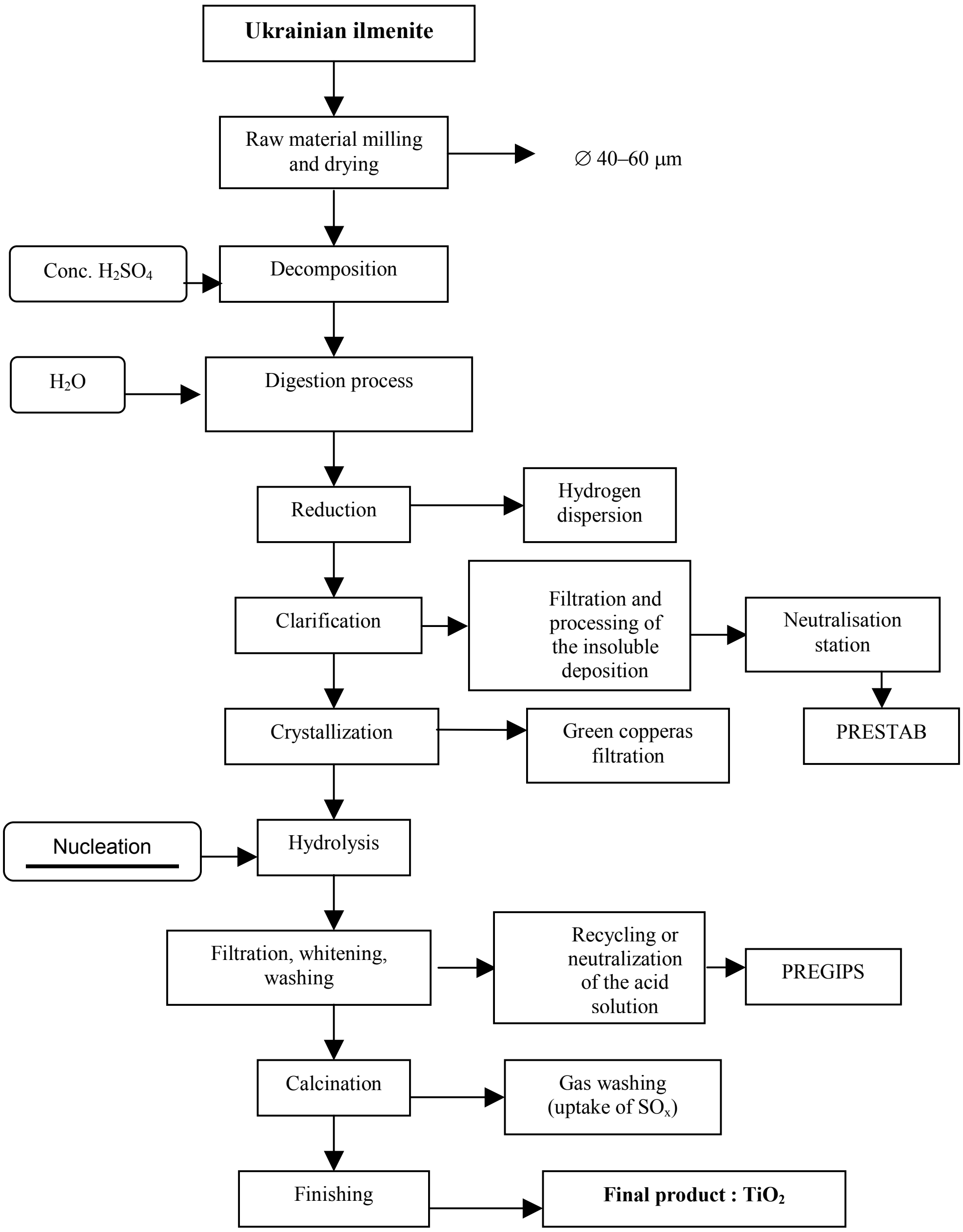

FIG. 1. Process schematic of titanium dioxide pigment production

TABLE IV. GAMMA-SPECTROMETRIC ANALYSIS OF SELECTED MATERIALS AT THE PRECHEZA FACTORY

Sample	Measure-ment	Radionuclide activity concentration (Bq/kg)										
		^{40}K	^{210}Pb	^{226}Ra	^{228}Ra	^{227}Ac	^{228}Th	^{230}Th	^{234}Th	^{231}Pa	^{235}U	^{238}U
Ilmenite	NRPI[1]	5.8±1.5	65.0±11.0	165.0±5.5	79.1±3.0	7.19±0.57	80.4±2.8	140.0±18.0	75.6±9.0	<13	6.5±1.0	—
Ilmenite	SONS[2]	<5.0	—	208±19	—	—	86.0±5.0	—	—	—	—	58.0±11.0
Sludge, liquid phase[3]	NRPI	<5.2	<2.6	<5.0	<0.97	<0.65	10.78±0.38	26.1±4.5	19.0±1.1	<5.4	0.86±0.10	—
Sludge, solid phase[3]	NRPI	<190	807±35	1292±80	557±25	23.6±4.4	53.4±3.6	<400	<90	<123	<9.6	<200.0
PREGIPS	NRPI	<8.2	<4.4	<1.5	1.45±0.34	1.46±0.21	16.5±1.0	44±12	14.3±1.3	<7.5	0.69±0.12	14.60
PRESTAB	NRPI	<14.8	81.5±5.6	120±10	44.4±1.9	3.49±0.32	42.8±1.7	90.0±19.0	—	<12.0	5.30±1.0	80.90±5.7
PRESTAB	SONS	<4	—	216±19	—	—	54.0±4.0	—	—	—	—	62.0±24.0
TiO_2 (rutile)	NRPI	45.2±3.7	2.90±0.78	4.09±0.26	1.99±0.29	<0.52	<0.32	<16	2.74±0.33	15.1±1.2	<0.24	<5.1
TiO_2 (anatase)	SONS	64.0±3.0	—	5.0±2.0	—	—	1.0±0.3	—	—	—	—	4.0±3.0
Green copperas, new	NRPI	<10.5	<5.0	<3.6	<2.0	<1.3	0.70±0.19	<33.0	<4.5	<8.8	<0.25	<5.3
Green copperas, old	NRPI	<7.5	<3.4	<2.5	<1.6	<0.90	<0.52	<22	<2.8	<6.4	<0.24	<5.1
MONOSAL	NRPI	<4.4	<2.7	<1.78	<0.84	<0.54	0.63±0.11	<16.0	<2.15	<4.0	<0.25	<5.3
HEPTASAL	SONS	<2.0	—	<2.0	—	—	<1.0	—	—	—	—	<4.0
Deposit from drainage	NRPI	43.6±4.0	59.0±3.5	295.4±9.2	105.2±3.6	<5.2	93.4±3.0	<106	—	<16	<2.6	12.8±2.2
Waste water	SONS	1.3±0.1	—	<0.1	—	—	0.02±0.01	—	—	—	—	<0.15

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[1] Laboratory of the National Radiation Protection Institute.

[2] Laboratory of the State Office for Nuclear Safety.

[3] Sludge from clarification.

TABLE V. DOSE RATE MEASURED AT SELECTED WORKPLACES OF THE PRECHEZA FACTORY

Workplace	Dose rate (μSv/h)	Characterization of the measurement place
LIS-FIKA 310	1.4	Filtration of sludge resulting from clarification (filter press)
Storage tank 375	1	$TiOSO_4$ solution with Pearlite to eliminate residual impurities
LIS-KOFI 377 A, B	1.2–1.5	Filtration of residual sludge after addition of Pearlite
Storage tank 417C	2.5	Final solution after hydrolysis — $TiO(OH)_2$ Dose rate at 1m — 1.05 μSv/h
Storage tank 417D	3.4	Final solution after hydrolysis — $TiO(OH)_2$
I° Moore filter, empty	13–21	Step 1 of Moore filtration after hydrolysis (vacuum filtration)
I° Moore filter, full of $TiO(OH)_2$	8	Step 1 of Moore filtration after hydrolysis (vacuum filtration) Dose rate at 1m — 3 μSv/h

Concerning the storage tanks, there is only a low radiation risk to the workers because of their relatively short occupation time there; only in exceptional cases (e.g. during maintenance activities) can the radiation risk be higher. For example, a worker would have to in the close vicinity of storage tank 417D for at least 40 day/a to receive the guidance level dose (1 mSv/a), and such a situation is highly improbable. In addition, these tanks are not usually full and therefore the actual effective dose rates are considerably lower. Also the total annual effective dose for an employee working near LIS-FIKA and LIS-KOFI filter presses does not exceed the guidance level (estimates are 0.87 mSv/a for LIS-FIKA and 0.80 mSv/a for LIS-KOFI). The only exception is the situation of an employee working near the vacuum filter (I° Moore filter), where an annual effective dose around 14 mSv/a can be received, thus considerably exceeding the established guidance level. According to the assessments performed, the filtration equipment serving as the first step of vacuum filtration (which follows after the hydrolysis step: $TiO(OH)_2$) represents a workplace with a possible higher radiation risk. The reasons are the absorption properties of the cloth filters in I° Moore filter unit and the relatively long periods between their replacement. Due to the relatively high cost of the cloth material used, the filters are regenerated by concentrated HF. The expected effective dose rate in the vicinity of tanks with this liquor is relatively low (around 0.14 μSv/h) due to the dilution factor.

In the light of the assessments performed, the following corrective safety measures are proposed:

- Implementation of personal dosimetry;
- Shortening of the cloth exchange period;
- Adaptation of the working time.

The evaluation of selected materials from the point of view of discharge into the environment was also carried out. According to the relevant Czech legislation (SONS Decree No. 307/2002 Coll.), the clearance level for discharge of natural radionuclides into the environment from workplaces with the potential for significant exposure to natural sources is established in the form of a mass activity index, I, derived from the activity concentrations, a, of ^{40}K, ^{226}Ra and ^{228}Th in units of Bq/kg according to the following formula:

$$I = \frac{a_{K\text{-}40}}{3000} + \frac{a_{Ra\text{-}226}}{300} + \frac{a_{Th\text{-}228}}{200} \qquad (1)$$

The mass activity index should be lower than 2 for unrestricted release to the environment. The mass activity index exceeds twice the clearance level only in the case of sludge from clarification (solid phase) and therefore this material cannot be discharged into environment without the approval of the State Office for Nuclear Safety. Actually, this material is not directly discharged to the environment — the volume of sludge is firstly reduced by a press and then is repumped to the neutralization plant. After neutralization by lime and calcite, a construction material is produced — PRESTAB (brown gypsum with admixtures of iron oxides). During the sludge treatment the concentration of the radioactivity is decreased (due to the addition of the lime and calcite) and the mass activity index of the PRESTAB product reaches a value of around 0.8.

4. ZIRCONIUM REFRACTORY MATERIALS PRODUCTION

Currently, zirconium refractory materials are only processed at Eutit Ltd in Stara Voda. The melted basalt and EUCOR are the main products of this factory. EUCOR is basically a three-phase system containing 48–50 % corundum, 30–32 % baddeleyite and 18–20 % glass phase. The zirconium-containing bricks discarded from glass factories (with a ^{226}Ra activity concentration of approximately 1700 Bq/kg, see Table VI for a detailed characterization) are used exclusively for the production of EUCOR. The current consumption of approximately 200 t of zirconium input material means processing of 340 000 kBq of ^{226}Ra.

TABLE VI. GAMMA-SPECTROMETRIC ANALYSIS OF USED ZIRCONIUM REFRACTORY MATERIAL

Radionuclide	Activity concentration (Bq/kg)		
	Mean	Standard deviation	Detection limit
^{40}K	107	35	65
^{210}Pb	214	25	34
^{226}Ra	1680	110	25
^{228}Ra	252	13	7.2
^{227}Ac	87	8.3	5.5
^{228}Th	243	10	2.1
^{230}Th	1850	340	180
^{231}Pa	106	24	4.2
^{235}U	76.9	6.2	2.0
^{238}U	1480	110	15

5. COAL MINING AND COMBUSTION

Coal exploitation and use represents one of the most important industries concerning NORM. Coal mining production, reaching more than 130 million t/a in the past, is at present 70 million t/a. The majority of the Czech coal exploited is used for energy production. In the process of coal combustion, various radionuclides are concentrated, mainly in the combustion products — ash, slag and ‘energo-gypsum’.

5.1. Brown coal mining and combustion

The most important deposits are situated in west and north Bohemia — the Sokolov basin and the North Bohemian basin. In the Sokolov basin, the concentration of uranium is 3.1–16.3 ppm and that of thorium is 5.0– 30.2 ppm; the activity concentrations of the relevant radionuclides are shown in Table VII. The highest thorium concentration (about 30 ppm) was detected in the Anezka seam and the highest uranium concentration in the Josef seam (15.5 ppm). In the North Bohemian basin, the radioactivity concentrations are lower — uranium 0.5–4.1 ppm and thorium 0.2–8.9 ppm. Table VIII shows the activity concentrations of selected radionuclides in 2 mining areas of the North Bohemian basin. On combustion of brown coal, the uranium and thorium become concentrated mainly in the ash and slag, as shown in the Table IX.

TABLE VII. RADIOACTIVITY IN BROWN COAL, SOKOLOV BASIN

Radionuclide	Activity concentration (Bq/kg)	
	Range	Mean
^{226}Ra	30–62	46
^{232}Th	<10–47	25
^{40}K	<10–78	Not determined

TABLE VIII. RADIOACTIVITY IN BROWN COAL, NORTH BOHEMIAN BASIN

Radionuclide	Activity concentration (Bq/kg)	
	Most area	Chomutov area
^{226}Ra	15–30	≤ 20
^{232}Th	15–25	≤ 10
^{40}K	Not determined	≤ 10

TABLE IX. RADIOACTIVITY IN BROWN COAL COMBUSTION PRODUCTS

Radionuclide / radioelement	Concentration of radionuclide (Bq/kg) or radioelement (ppm)							
	North Bohemian Coal Co.			Most Coal Co.			Sokolov Coal Co.	
	Ash	Slag	Gypsum	Ash	Slag	Gypsum	Ash	Slag
^{226}Ra	92.8	66.8	9.2	83.5	69.5	< 4.0	138.5	81.0
^{232}Th	80.5	63.5	< 9.0	76.5	61.5	< 6.0	92.0	50.0
^{40}K	324.2	280.5	< 26.0	354.5	288.5	< 13.0	169.2	< 28.0
Uranium	7.6	5.5	0.8	6.8	5.7	< 0.3	11.4	6.6
Thorium	19.9	15.7	< 2.3	18.9	15.2	< 1.5	22.7	12.3

5.2. Hard coal mining and combustion

The most important basin concerning production of hard coal is the Upper Silesian basin situated in Northern Moravia. The concentration of uranium in the Upper Silesian basin hard coal is between 2–9 ppm. As with brown coal, uranium and thorium become concentrated in the ash and slag, while the gypsum contains negligible levels of radioelements as shown in the Table X.

TABLE X. RADIOACTIVITY IN HARD COAL COMBUSTION PRODUCTS

Radionuclide / radioelement	Concentration of radionuclide (Bq/kg) or radioelement (ppm)		
	Ash	Slag	Gypsum
^{226}Ra	128.5	78.0	< 6.0
^{232}Th	82.0	58.5	< 9.0
^{40}K	698.5	637.0	< 13.0
Uranium	10.5	6.4	< 0.5
Thorium	20.2	14.4	< 2.1

6. OIL AND GAS EXPLOITATION, TRANSPORT AND STORAGE

The majority of oil and gas used in Czech industries is imported from Russia (Druzba pipeline) and Norway (IKL pipeline). Measured samples of oil sludge from the cleaning of pipelines and oil storage tanks revealed only negligible concentrations of radionuclides; a similar level of activity has been found in samples from domestic oil exploitation (Table XI).

TABLE XI. RADIOACTIVITY IN OIL AND OIL SLUDGE

Sample	Activity concentration (Bq/kg)									
	^{40}K	^{210}Pb	^{226}Ra	^{228}Ra	^{227}Ac	^{228}Th	^{230}Th	^{231}Pa	^{235}U	^{238}U
Transport and storage of imported oil										
Druzba pipeline	<8.7	<3.9	0.75	<1.1	<0.91	<0.35	<27	<7.1	<0.3	<2.2
IKL pipeline	<13	<4	0.32	<1.2	<0.9	<0.33	<38	<7.3	<0.31	<2.6
Oil sludge, storage tank	5.9	47.5	43.1	15.5	<1.2	11.9	<50	<10	<0.6	<3.5
Oil sludge, IKL pipeline	<11	60.8	13.4	6.6	<1.2	3.5	<74	<10	<0.51	<3.1
Domestic oil exploitation, MND Hodonin Co.										
Crude oil	<8.6	<2.9	<0.59	<1.32	<1.06	<0.37	<22.9	<5.9	<0.21	<1.59
Purified oil (degassed, dewatered)	<7.9	<2.64	<0.53	<1.18	<0.97	<0.34	<22	<5.6	<0.2	<1.4
Oilfield water	122	<1.6	<0.3	<0.65	<0.5	<0.0	<12	<2.7	<0.11	<0.86
Sludge from oilfield water	243	7.7	55.6	34.4	<2.9	22.2	<51	<9.6	<1.7	7

7. WATER TREATMENT SLUDGE

The State Radiation Protection Institute performed an evaluation of the radioactivity in sludges resulting from 68 ground and surface water treatment installations, using gamma spectrometric analysis. As expected, significantly higher activities were found in the sludge from ground water treatment (Tables XII and XIII).

TABLE XII. RADIOACTIVITY IN SLUDGE FROM THE TREATMENT OF SURFACE WATER

Radionuclide	Number of samples	Activity concentration, (Bq/kg)		
		Arithmetic mean	Geometric mean	Maximum
^{40}K	20	249	128	1330
^{210}Pb	17	55	41	111
^{226}Ra	20	21	17	84
^{228}Ra	20	27	19	103
^{227}Ac	8	—	—	11
^{228}Th	20	17	12	61
^{235}U	6	3.1	2.5	6.5
^{238}U	15	84	66	354

TABLE XIII. RADIOACTIVITY IN SLUDGE FROM THE TREATMENT OF GROUND WATER

Radionuclide	Number of samples	Activity concentration, (Bq/kg)		
		Arithmetic mean	Geometric mean	Maximum
^{40}K	26	158	65	714
^{210}Pb	32	64	36	208
^{226}Ra	34	230	93	1290
^{228}Ra	32	212	87	1102
^{227}Ac	16	11	11	11
^{228}Th	34	65	36	316
^{235}U	17	21	11	66
^{238}U	21	116	63	425

8. CONCLUSION

Most of the Czech industrial companies processing materials with enhanced levels of naturally occurring radioactivity have recently made great efforts to minimize the potential negative health impacts. Some raw materials are no longer used — in some cases, the original raw materials have been replaced by alternative materials with negligible concentrations of radioactive elements (e.g. the phosphate fertilizer industry). Coal seams with a relatively high radioactivity content are excluded from mining.

The current assessments indicate that potentially significant radiation risks for workers from the processing of NORM occur during TiO_2 pigment production, but effective doses can be controlled by low cost measures. Higher concentrations of radionuclides were also detected in input material (zirconium-containing bricks) used for the production of EUCOR, but only around 200 t of this material is processed per year, usually during a single production run, and therefore the radiation risk is low.

A special problem arises from the remnants of disused production lines, abandoned milling and chemical processing tailings and dumps, or even closed factories. The monitoring, decontamination and disposal of waste from such sites constitutes an important task.

ACKNOWLEDGEMENT

The authors are grateful for partial financial support from the European Commission (the TENORMHARM project) and the Czech Radioactive Waste Repositories Authority. The authors also appreciate the co-operation with the State Radiation Protection Institute and the State Office for Nuclear Safety.

IDENTIFICATION OF ENHANCED CONCENTRATIONS OF ^{210}Pb AND ^{210}Po IN IRON ORE INDUSTRY

J. Döring[1], J. Gerler[1], M. Beyermann[1], U.-K. Schkade[1], J. Freese[2]

[1]Federal Office for Radiation Protection, Berlin, Germany
[2]Arcelor Group, Eisenhuettenstadt, Germany

Abstract

A study was initiated to investigate the naturally occurring radioactivity in by-products of the industrial iron ore reduction process such as sinter dust and blast furnace dust. In the first step, dust samples obtained from the air stream cleaning procedure at one production place were investigated. Enhanced concentrations of ^{210}Pb and ^{210}Po radionuclides were found through measurements of the emitted gamma and alpha radiations. Thus, these materials have to be handled according to the regulations outlined in the German Radiation Protection Ordinance, Part 3, Appendix XII, i.e. recycling and disposal of these materials are controlled by law. In this paper, the measurements performed, the results, as well as the specific regulations that have to be applied to these materials are given.

1. INTRODUCTION

The German Radiation Protection Ordinance, in place completely since January 2004, contains in Part 3 special regulations regarding the recycling and disposal of residues and/or by-products with enhanced natural radioactivity (ENORM). Such material may occur in several industries, for example in the iron ore industry in by-products of the pig iron production process. Thus, a study was initiated to investigate the naturally occurring radioactivity in by-products such as sinter dust and blast furnace sludge. The assessment of the radionuclide content of these materials is important, since about 200 000–300 000 t of dust and/or sludge are obtained each year at the seven production sites in Germany [1] and, depending on the specific activities, radiation protection controls may be required.

2. INDUSTRIAL PROCESS

The process of converting iron ore into iron centres on the blast furnace. The raw materials — iron ore and other ingredients (sinter, coke, scrap iron) — used in the conversion process contain, besides iron, many elements in low concentrations. They are fed into the top of the furnace and pre-heated air is blown into the base of the furnace to burn the coke and to generate the high temperature needed for the chemical processes. Liquid iron is removed from the bottom, whereas the gas (with dust) passing through is taken off from the top and cleaned for reuse, e.g. as fuel. For optimal operation of the furnace, the raw materials must be of a certain size. However, some material is too fine, and thus has to be sintered prior to use. In this sinter process, as well as in the blast furnace melting and reduction process, the raw materials are heated to temperatures above 1600ºC. At this high temperature, elements with low melting and boiling points such as lead and/or polonium are vaporized and partly taken out with the hot gas stream. The gas is subsequently cooled down and in this process the volatile Pb and Po atoms get attached to the dust particles inside the gas stream. In the sinter facility, a multi-step dry air cleaning procedure is applied and a large fraction of the dust particles are recycled as ingredients to the sinter process. The dust from the last cleaning step only is taken out as waste and was analyzed in this study.

The hot gas from the blast furnace is also cooled down and cleaned in a multi-step process. First, the coarse-grained fraction of the dust, which contains large concentrations of carbon and iron, is filtered out and recycled into the sinter process. Second, the fine-grained fraction undergoes a special wet cleaning procedure using water as the cleaning substance for the dust particles. Thus, this fraction of the dust is converted into a sludge and contains many elements with low melting and boiling points, i.e. mainly heavy metals such as Zn, Cd, Pb and Po (and hence also radioactive ^{210}Pb and ^{210}Po) in enhanced concentrations. Even though the concentrations of Pb and Po are very low in the raw materials, the large amount of material used in the pig iron production process generates a considerable amount of waste that is deposited in authorized and fenced areas. Samples of this sludge were taken and analyzed too.

3. ANALYSIS TECHNIQUES

In the first step of the study, several samples obtained from the sinter and blast furnace gas cleaning facilities at one production plant were investigated. The samples were analyzed by two methods:

- Gamma spectrometry,
- Alpha particle counting after radiochemical processing of the sample material.

3.1. Gamma spectrometry

The samples were dried in an oven at a temperature of about 80ºC, well below the melting and boiling points of Pb and Po. Subsequently, the material was put into cylindrical containers made out of aluminum with gas-tight tops to keep the radon and its decay products inside. The containers were stored for about 23 days to achieve a radioactive equilibrium between ^{226}Ra and its decay products.

The radionuclide ^{210}Pb with a half-life of 22.3 a undergoes beta decay to ^{210}Bi. During this decay, 84 out of 100 events proceed to the level at 46.5 keV excitation energy in ^{210}Bi, which in turn decays via a 46.5 keV gamma ray to the ground state. Thus, the activity concentration of ^{210}Pb can be directly determined from the measurement of this low energy gamma transition. We used a well-shielded n-type high-purity Ge detector of about 40 % relative efficiency to detect this gamma ray. A typical measuring time of about 40 000 s was used, which is reasonable for our geometry. Special care was taken to correct the intensity of the 46.5 keV line with regard to the self-absorption in the sample material. For this purpose, a series of measurements with different amounts of sample material was performed.

Besides the determination of ^{210}Pb, the gamma spectrometry method also provides reliable information on the specific activity of many other radionuclides such as ^{40}K, ^{228}Ra, ^{228}Th, ^{226}Ra and ^{238}U. The concentrations of these radionuclides were determined as well, according to our measuring instructions [2]. The activity concentration of ^{40}K can be measured directly. In the case of ^{226}Ra, the gamma rays associated with the beta decay of the short-lived daughter products ^{214}Pb and ^{214}Bi were analyzed while, for the determination of ^{228}Ra, the decay of the short-lived daughter ^{228}Ac was studied. To deduce the ^{228}Th concentration, the gamma rays accompanying the decay of the short-lived daughter products ^{212}Pb and ^{208}Tl were determined, while for ^{238}U the gamma rays from the decay of the daughter nuclides ^{234}Th and ^{234m} Pa were analysed.

3.2. Alpha spectrometry

The radionuclide ^{210}Po with a half-life of 138.4 days is a pure alpha emitter; it cannot be measured using gamma spectrometry. Thus, we measured the alpha particles after sample preparation using a radiochemical method. The sample dissolution was achieved by treating 100 mg portions with nitric and hydrochloric acids in a first step, and with perchloric acid in a second step. Finally, ^{210}Po in 0.5 M hydrochloric acid solution was spontaneously deposited in a thin layer on a small nickel disk. The alpha particles emitted from this layer were measured with a calibrated low-background proportional counter. A typical measuring time of 60 000 s was used for each sample.

4. RESULTS

The results of the analyses are given in Table I. The measured concentrations of radionuclides in our samples show remarkably enhanced concentrations of ^{210}Pb and ^{210}Po. In the sinter-dust samples, the content of ^{210}Po is about three times higher than that of ^{210}Pb, whereas in the blast furnace sludge samples the ^{210}Po concentration is slightly lower than that of ^{210}Pb. The concentrations of the other radionuclides such as ^{226}Ra and ^{238}U are within the expected range for normal environmental samples.

TABLE I. RADIOACTIVITY IN PROCESS MATERIALS

Sample	Typical average activity concentration and 95% confidence level (2σ) measured in dry sample material (Bq/kg)	
	Sinter dust	Furnace sludge
^{40}K	4000 ± 800	280 ± 60
^{228}Ra	7.6 ± 1.5	28 ± 6
^{228}Th	7.3 ± 1.4	12 ± 3
^{226}Ra	23 ± 5	74 ± 15
^{238}U	24 ± 6	41 ± 9
^{210}Pb	15 200 ± 2600	33 000 ± 6000
^{210}Po	50 300 ± 5300	22 200 ± 2500

To evaluate the mobility of the radionuclides, i.e. the capability to leave the solid material, watery extracts were made according to DIN 38414, Part 4 [3] and analyzed by radiochemical methods. It was shown that only about 0.001–0.002% of the ^{210}Pb and ^{210}Po is available in an easily leachable form, and relevant amounts of radionuclides in seepage water at disposal areas are very unlikely to occur.

As a consequence of the high ^{210}Pb and ^{210}Po radionuclide concentrations, the materials investigated have to be handled according to the regulations outlined in the German Radiation Protection Ordinance, Part 3, §§97–102, i.e. recycling and disposal of these materials are subject to radiation protection control.

5. EXPOSURES

A case study was performed [4] to estimate the dose expected for workers handling the sludge waste during the disposal process, and for the population living close to the disposal area. Several scenarios for possible paths of the exposure were considered, such as external exposure due to gamma radiation, internal exposure due to inhalation of dust, exposure due to direct ingestion of material and exposure due to food produced locally. A possible distribution of the radionuclides via the water paths (surface water, ground water) was also considered.

The different scenarios for estimating the occupational dose received by workers handling the blast furnace sludge show that the exposure due to inhalation of dust particles is the most important contribution. The reference dose value of 1 mSv/a is not exceeded for the workers as long as the specific activities are below the value of about 50 Bq/g. The expected exposure of a person from the general population is small and can be neglected compared with that of the workers depositing the material. Thus, as long as the specific activities are below the value given above, the material can be released from radiation protection control by the authorities.

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INVESTIGATION OF THE PEAT-FIRED POWER GENERATION IN IRELAND

C. Organo[1*], E. M. Lee[2], G. Menezes[2], E.C. Finch[2]

[1]Radiological Protection Institute of Ireland, Dublin, Ireland
[2]Department of Physics, Trinity College, Dublin, Ireland

Abstract

Annually, approximately 15% of Ireland's electricity requirement is provided through the combustion of 3 million t of peat. While literature on coal-fired power generation is quite abundant, studies on the peat-fired power generation industry from the radiological point of view are scarce. A study of the largest Irish peat-fired power plant was initiated to review the potential occupational radiation exposures arising from the occurrence of naturally occurring radioactive material (NORM) at different stages of the industrial process. Ambient gamma dose rate measurements, radon measurements, quantification of the occupational exposure from inhalation of airborne particles and gamma spectrometry analysis of peat, peat ash and effluent samples from the ash ponds were undertaken. The results indicate that the plant workers are unlikely to receive a radiation dose above 300 μSv/a over typical working hours.

1. INTRODUCTION

Around 90% of human radiation exposure arises from natural sources such as cosmic radiation, exposure to radon gas and terrestrial radiation. However, some industries processing natural resources may concentrate radionuclides to a degree that they may pose risk to both humans and the environment if they are not controlled. In May 2000, legal controls were introduced in Ireland covering work activities where the presence of natural radioactivity could lead to the risk of a significant increase in exposure to workers or members of the public. These controls are set out in the Radiological Protection Act, 1991 (Ionizing Radiation) Order. Statutory Instrument 125 of 2000 [1], hereinafter referred to as S.I. 125 of 2000, implements the European Council Directive 96/29/Euratom [2]. Article 3 of S.I. 125 of 2000 in particular provides for the regulation of naturally occurring radioactive material in the workplace, mostly of terrestrial origin and hereinafter referred to as NORM, if it is liable to give rise to a radiation dose greater than 1 mSv/a. In 2001, the Radiological Protection Institute of Ireland (RPII) initiated a programme to identify industries currently active in Ireland, which, on the basis of the literature, were considered liable to involve work activities resulting in exposure to diffuse NORM sources. To date, they include the gas extraction industry, fossil fuel (peat and coal) power production and a range of industrial processes using bulk materials with enhanced levels of natural radioactivity (e.g. bauxite refining). A joint study was designed in collaboration with the Physics Department of Trinity College Dublin to determine the radioactivity levels in Irish peat and peat ash, compare the results with similar studies in other countries and with national and international legislation, and investigate the extent of any radiation exposure of workers arising from the handling, burning and storage of peat ash. Environmental exposure to elevated levels of radionuclides resulting from the gaseous emissions from the stack was not investigated.

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[*] E-mail: corgano@rpii.ie

2. IRISH PEAT-FIRED POWER GENERATION

Until recently, up to nine peat-fired power plants were in operation in Ireland. By the end of 2004, this generation of power stations built between 1950 and the early 1980s will be replaced by two newly-built power plants processing between them just over 2 million t/a of peat. This study was undertaken at the largest existing peat-fired power station in the country, Shannonbridge. It is located in the Midlands region (Fig. 1) and has been operating since 1965. The current plant consumes approximately 1.1–1.2 million t/a of peat and produces 125 MW of electricity. On average, 20 000–25 000 t of peat ash are produced every year (a third of the total ash produced by all the Irish peat-fired plants). Five million t of ash are currently landfilled on site at the plant. The Irish Peat Board (Bord na Móna) supplies the milled peat to Shannonbridge from a local bog where it is mechanically harvested by scraping the top of the bog to a depth of up to 30 cm, milled (72 mesh), solar dried and transported to the power station by light rail. Each convoy of 15 wagons carries 75 t of peat. On arrival at the plant a 'tippler' unloads each wagon sequentially into a hopper from where the peat is transferred by conveyor belts into the plant. At this stage, the peat is milled further into a fine dust and blown into the furnaces for combustion in suspension at about 1000–1100 °C. Approximately 5–10% of the total ash produced falls below the furnace as 'bottom ash'. The remaining 90–95% passes into the flue gas stream as 'fly ash'.

This gaseous-particulate mixture leaves the furnace and is drawn through a series of grit arrestors designed to retain about 90% of the fly ash and any unburnt carbon. At furnace temperatures, some elements originally contained in the peat are partly or completely evaporated. Between the furnace and the grit arrestors, the gas and fly ash stream passes over banks of tubes containing water or air to give a more efficient removal of the heat from the gas prior to its emission to atmosphere. As the flue gases cool down from 1000 to 200°C, the volatilized elements condense onto the fly ash particles, giving rise to an enrichment of their concentrations in the fly ash trapped by the grit arrestors. Only a small fraction of the fuel gases containing small quantities of radionuclides in gaseous form passes through the grit arrestors and is discharged through the stack to the atmosphere. Sampling of fly ash is possible only when the boilers are not in operation. The number of samples that could be obtained was therefore limited. In Shannonbridge, the bottom ash is disposed of in wet or dry conditions. 'Dry' bottom ash is produced by two of the three furnaces in operation. It is transported in a trailer attached to a tractor to a dry ash pile. 'Wet' bottom ash from the third furnace is hydraulically piped out by flexible tubing to two nearby wet ash ponds together with the totality of the fly ash trapped in the grit arrestors. In the ponds, the ash resides in a 50% minimum aqueous environment to minimize the production of airborne particles.

3. MATERIALS AND METHODS

Gamma spectrometry analysis of peat, peat ash and effluent samples collected at the plant, airborne peat dust analysis, aerial radon gas measurements, and ambient gamma dose rate measurements were carried out. Samples for gamma spectrometry analysis were counted in Marinelli geometry and analysed using a low background n-type HPGe GMX gamma-ray detector (relative efficiency 34%, resolution 2 keV (FWHM) at 1.33 MeV). Each sample was counted for 24 h. Activity concentrations of ^{238}U series radionuclides, ^{232}Th, ^{40}K and ^{137}Cs were determined. Activities of ^{226}Ra were ascertained using the two gamma-ray lines at 93 and 186 keV, corrected for the interference of ^{235}U at 186 keV. Thorium-232 was determined from the gamma-ray emissions at 911, 969, 338, 965, 795, and 463 keV from ^{228}Ac. The activities of ^{40}K and ^{137}Cs were determined from their respective lines at 1461 and 662 keV.

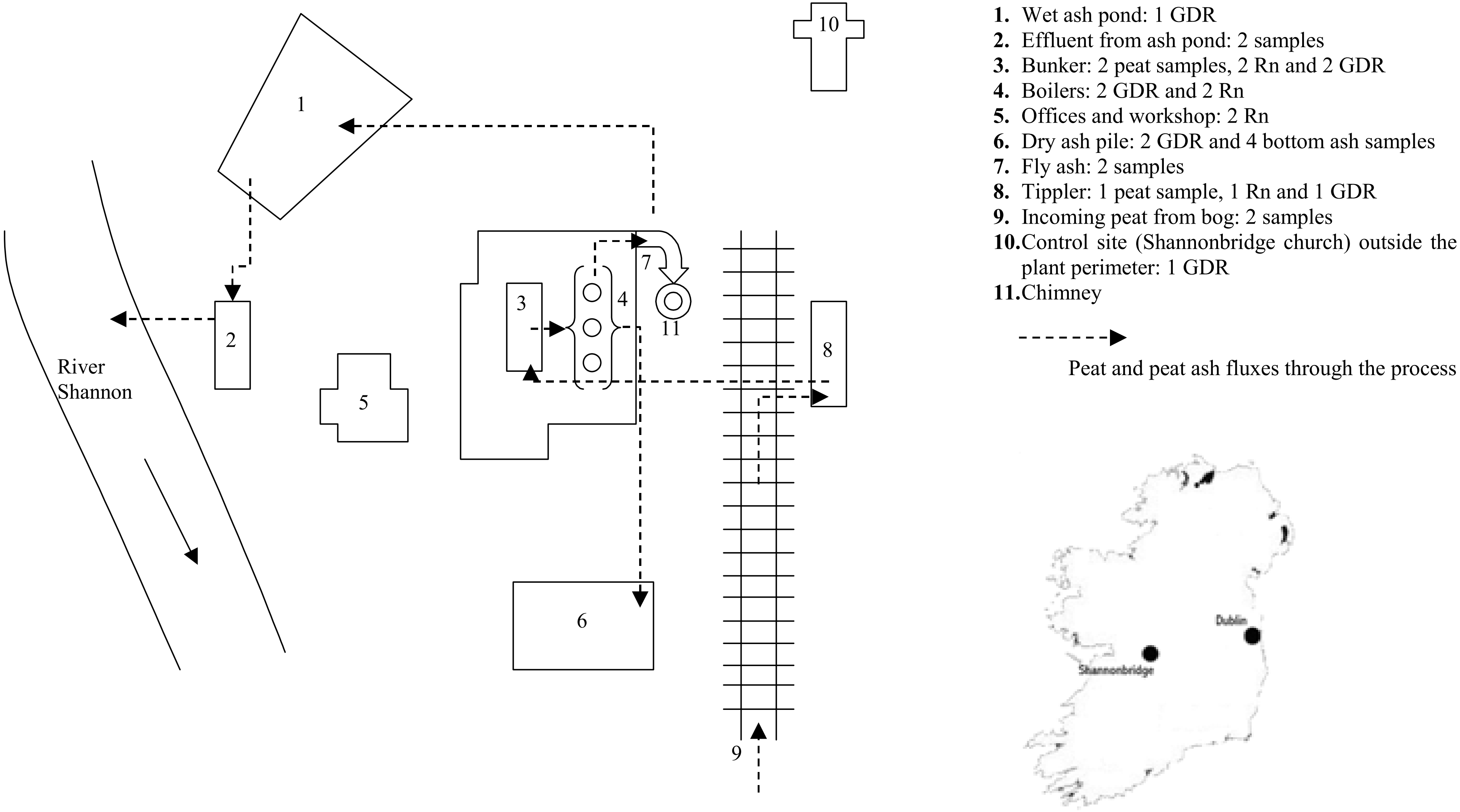

FIG. 1. Schematic sketch of the Shannonbridge peat-fired power plant with locations of the measurements undertaken and samples analysed during this study (objects not to scale)

GDR = gamma dose rate measurement, Rn = radon measurement. A map of Ireland is inserted to show the location of Shannonbridge

Airborne peat dust concentration was measured in the plant to assess the potential radiation dose through inhalation of airborne particles. A filtration sampling method (AEA Technology filter holder, Casella London Ltd.) was used, where a known volume of air is drawn through a pre-weighed glass fibre filter paper (25 mm diameter, pore size 80 μm) by means of an air pump. On site, the filter holder was placed in a static position at approximately 1.6 m high (breathing zone height). The flow rate of the pump was set at 2L/min and the pump was allowed to run from 9.30 am until 5.15 pm (standard work shift). Passive long-term radon measurements were carried out to determine if the concentrations exceeded the national Reference Level for workplaces, 400 Bq/m^3 averaged over a minimum period of three months. Passive alpha track detectors consisting of a two-part polypropylene holder and a CR-39 (polyallyl diglycol carbonate) detection plastic were used. Upon completion of the measurements the tracks recorded on the plastics are analysed and counted using a Leitz Ergolux AMC microscope coupled to a Leica Quantimet Q520 image analysis system. A track density is determined for each plastic and converted into radon concentration C (Bq/m^3) after subtraction of a fixed background value and taking into account a predetermined calibration factor as well as the exposure duration. A seasonal correction is applied to C when the detectors are exposed for less than twelve months [3]. Gamma dose rate measurements were carried out using an NE Technology portable gamma dose rate meter (type PDR1) and a Mini Instruments integrating Geiger Müller Background Monitor Type 6-80 (GM6-80). Instantaneous gamma dose rate readings were taken with the PDR1 meter and an average value was calculated from the lowest and highest readings. The GM6-80 meter was fixed to a tripod at each location for 1000 s. The readings were converted to an ambient gamma dose rate (in units of microsievert per hour) using a calibration conversion table relevant to the instrument.

4. RESULTS

4.1. Peat, peat ash and effluent from the wet ash pond

If the activity concentrations of radionuclides present in the ash are significant there could be a potential for increased radiation exposure to workers handling and working with the ash. Radionuclide analysis of peat, bottom ash and fly ash from Shannonbridge indicates a great variability of activity concentrations (Table I). In general, fly ash presents significantly higher concentrations than the bottom ash in the U series, while the bottom ash contains more ^{40}K than the fly ash. Table II shows that there is a wide range of activities between the fly ash produced at different peat-fired power stations in Ireland [8]. Compared with other types of NORM or with the average Irish soils, it is clear that the peat and the peat ash produced in Shannonbridge contain lower levels of naturally occurring radionuclides.

With regard to the radioactivity enhancement in the fly ash and the bottom ash arising from the combustion process, some radionuclide concentrations could be enhanced by a factor of 20–25 compared with concentrations in the original peat as indicated in Ref. [15]. Lead-210 shows the largest enrichment onto small fly ash particles (< 1.3 μm) according to Ref. [4], indicating a volatile behaviour at the furnace temperature. Enrichment factors EF for different radionuclides can be calculated using the formula:

$$EF = \frac{[c_r]_{\text{ash}}}{[c_{\text{Ra}-226}]_{\text{ash}}} \Bigg/ \frac{[c_r]_{\text{peat}}}{[c_{\text{Ra}-226}]_{\text{peat}}} \qquad (1)$$

where c_r and $c_{\text{Ra}-226}$ are the activity concentrations of a potentially enriched (or depleted) radionuclide r and of ^{226}Ra, respectively. Radium-226 is used as a reference radionuclide because of its non-volatile nature at furnace temperature [4]. To simplify the calculations, a single activity concentration for each radionuclide in the peat, in the fly ash and in the bottom ash was assumed by rounding up to the maximum concentration measured (conservative end of the range of concentrations measured). The values are displayed in italics in Table I. Values of *EF* in the fly ash were calculated to be 1.4, 4, 2, 1 and 0.5 for ^{210}Pb, ^{238}U, ^{232}Th, ^{40}K and ^{137}Cs, respectively. For the same radionuclides, *EF* values in the bottom ash are 2.5, 3.3, 2.5, 10 and 3.75.

TABLE I. RADIONUCLIDE ACTIVITY CONCENTRATIONS IN PEAT, PEAT ASH AND ASH POND EFFLUENT

Sample Type	Activity concentration (Bq/kg) on a dry weight basis[1]							
	^{238}U	^{234}Th	^{226}Ra	^{214}Pb	^{210}Pb	^{232}Th	^{40}K	^{137}Cs
Peat								
Entering plant	2.8±0.4	4.3±0.6	2.6±0.4	4.4±1.0	18.8±1.5	BDL[2]	6.1±5.7	4.2±0.1
Entering plant	4.0±0.3	2.0±0.2	1.8±0.1	0.5±0.1	5.0±0.6	0.4±0.0	BDL	2.2±0.1
In tippler	10.9±5.3	14.1±1.0	6.3±3.1	3.8±0.6	27.3±1.6	BDL	6.5±2.9	12.3±0.3
In bunker	7.4±3.9	10.8±1.0	5.4±2.8	2.2±0.4	37.8±2.6	BDL	BDL	11.5±0.3
Dust in bunker	BDL	3.8±0.4	4.3±0.2	1.6±0.1	23.8±1.6	BDL	BDL	BDL
Maximum	*15*	*15*	*10*	*5*	*50*	*1*	*10*	*20*
Fly ash								
	301.2±13.9	306.3±5.8	28.9±1.4	59.2±0.9	225.9±10.4	7.27±0.4	66.5±2.0	67.5±1.0
	52.1±1.4	115.1±7.6	32.2±0.9	41.7±6.3	297.0±14.9	BDL	BDL	BDL
Maximum	*300*	*300*	*50*	*70*	*350*	*10*	*50*	*50*
Bottom ash								
	77.1±13.8	33.0±0.9	14.9±1.4	3.8±0.1	13.9±0.8	BDL	7.6±0.8	4.8±0.1
	67.9±2.9	19.6±1.1	7.2±0.3	13.5±0.4	211.1±9.1	4.2±1.3	185.0±19	104.0±1.6
	32.1±3.2	29.3±2.9	19.3±2.0	9.8±0.2	167. 3±6.0	2.8±0.8	121.0±30	92.3±1.4
	9.1±0.6	7.1±0.8	6.3±0.4	0.3±0.1	8.2±1.0	0.59±0.1	BDL	BDL
Maximum	*100*	*50*	*20*	*20*	*250*	*5*	*200*	*150*
Effluent								
	0.31±0.1	2.9±0.5	BDL	0.5±0.1	3.0±0.3	BDL	BDL	0.6±0.0
	BDL	1.1±0.1	0.7±0.1	BDL	0.27±0.2	BDL	BDL	BDL

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[1] Errors quoted are the counting uncertainties at one standard deviation from the mean count.

[2] Below detection limit of 0.19 Bq/kg.

TABLE II. COMPARISON OF THE RESULTS FROM THIS STUDY WITH OTHER REFERENCES IN THE LITERATURE

Sample Type	Activity concentration (Bq/kg)							Reference
	^{238}U	^{234}Th	^{226}Ra	^{210}Pb	^{232}Th	^{40}K	^{137}Cs	
Raw material								
Irish peat	***15***	***15***	***10***	***50***	***1***	***10***	***20***	*This study*
Finnish peat	16	—	11	30	5.3	28	27	[4]
Coal Moneypoint	19 (5–45)	—	30 (6–67)	14 (4–27)	8 (2–13)	61 (20-100)	—	[5]
Coal UK	15	15	15	15	7.5	144	—	[6]
Coal world average	24	—	—	—	22	100	—	[7]
Fly ash								
This study	***300***	***300***	***50***	***350***	***10***	***50***	***50***	
Peat Shannonbridge	133	—	71	—	7	32	130	[8]
Peat Ferbane	290	—	121	—	11	112	20	[8]
Peat Lanesborough	74	—	68	—	14	263	79	[8]
Peat Rhode	121	—	127	—	8	57	127	[8]
Peat Bellacorick	38	—	31	—	10	153	47	[8]
Peat Finland	—	—	120	—	46	390	—	[9]
Coal Moneypoint	110	—	156	79	68	445	—	[5]
Coal UK	100	100	100	100–200	50	900	—	[5]
Bottom ash								
This study	***100***	***50***	***20***	***250***	***5***	***200***	***150***	
Coal Moneypoint	73	—	84	23	43	307	—	[5]
Coal world average	—	—	85	—	61	510	—	[6]
Other NORM								
Bauxite Boké	—	—	78	—	110	—	—	[10]
Bauxite	400–600	—	—	—	400–600	—	—	
Red mud	260–540	—	—	—	340–500	—	—	[11]
Red mud	—	—	250	—	300	—	—	[12]
Phosphogypsum	—	—	1000	—	—	—	—	[13]
Phosphate ore	—	—	30–5000	—	20-2000	3-200	—	
Zircon sands	—	—	3000–4000	—	10000	—	—	
Average Irish soils	—	—	46	—	25	418	—	[14]

4.2. Airborne dust concentration

The dustiest location of the plant was found to be the bunker, an indoor-type of warehouse where a 4 h supply of milled peat is temporarily stored at any time before it is fed into the mills. In this area, employees carry out dry sweeping duties of spilled peat dust, regularly generating large amounts of fine airborne dust. A single air sampling experiment over an 8 h working shift was carried out during which the dust concentration was measured at 25.6 mg/m^3. This is very significant in terms of occupational dust exposure (the Irish occupational exposure limit for nuisance dust is set at 10 mg/m^3 [16]). Employees working in this area are required to wear personal protective equipment (PPE) including protective clothing and a face dust mask. They also only work in this location for very short periods of time.

4.3. Radon gas

In industries dealing with diffuse NORM, an important radiation exposure pathway can be the inhalation of radon and radon daughters arising from the storage of large volumes of materials. This is because these materials are often crushed or powdered before they are processed (allowing radon to escape more easily from the matrix) and may be stored in poorly ventilated spaces (allowing radon concentrations to build up). The associated radiation dose may vary substantially, as it is strongly dependent on a wide range of parameters such as the emanation fraction, the equilibrium factor, the dose coefficient, the ventilation rate, the room size, the surface-to-volume ratio, and the diffusion coefficients [12]. Two radon surveys were carried out in Shannonbridge over the last eight years and the results are displayed in Table III. Not only are all the measurements below 400 Bq/m^3, but they are all similar to outdoor radon concentrations commonly measured in Ireland. As such, they are of no radiological significance from the point of view of radon occupational exposure.

TABLE III. PASSIVE LONG-TERM RADON MEASUREMENTS CARRIED OUT IN THE SHANNONBRIDGE PEAT-FIRED POWER PLANT, AND ASSOCIATED EFFECTIVE DOSES

Location	Measurement period	Radon concentration (Bq/m^3)	Assumed exposure duration[3] (h/a)	Effective dose from radon inhalation[4] (µSv/a)
Maintenance room	02/1995–05/1996	17	2000[5]	110
Conference room	02/1995–05/1996	33	20	2
Tippler area	12/2002–03/2003	11	100	3
Bunker	12/2002–03/2003	12	100	4
Control room in bunker	12/2002–03/2003	10	Unoccupied	0
Boiler 1	12/2002–03/2003	10	680	32[6]
Boiler 2	12/2002–03/2003	15		

4.4. Ambient gamma dose rate measurements

The locations of the measurements carried out are displayed in Fig. 1 and the results are shown in Table IV. The values given by the two dose rate meters are in good agreement and range from 0.06 to 0.18 µSv/h. They are not significantly different from the ambient gamma dose rate recorded outside the perimeter of the plant and used as a control measurement of the natural background (0.07–0.13 µSv/h). More than likely, the readings given by the GM6-80

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[3] Based on the characteristics of each work practice on site.

[4] Using ICRP65 dose coefficients [17] and an equilibrium factor of 0.4.

[5] Employees in the maintenance room spend the whole working year at this location.

[6] Assuming a maximum radon concentration of 15 Bq/m^3 in the boiler room.

(0.07 µSv/h on average) give a better idea of the real situation as these are integrated counts over 20 min instead of instantaneous values given by the PDR1 (0.10 µSv/h on average). In Ireland, the average absorbed dose rate in air is 33 nGy/h, with a range of 2–110 nGy/h [14]. Using a conversion factor of 1 Sv/Gy [7], it leads to an average effective dose for adults of 0.03 µSv/h (range: 0.002–0.11 µSv/h). Therefore, the dose rates measured in Shannonbridge are within the range of natural variations, although clearly in the upper part of this range.

TABLE IV. AMBIENT GAMMA DOSE RATE MEASUREMENTS AT THE SHANNONBRIDGE PEAT-FIRED POWER PLANT AND ASSOCIATED EFFECTIVE DOSES

Location	Dose rate (µSv/h)		Assumed exposure duration[7] (h/a)	Effective dose (µSv/a)
	PDR1	GM6-80		
Tippler area	0.06	0.06	100	6
Bunker area	0.08	0.06	100	8
Boiler 1, bottom ash area	0.12	0.07	340	41
Boiler 2, bottom ash area	0.18	0.07	340	61
Bottom ash pile (inactive disposal area)	0.08	0.07	50	4
Bottom ash pile (active disposal area)	0.08	0.07	500	40
Wet ash pond	0.13	0.06	400	52
Control measurement (outside plant)	0.13	0.07	2000	260
Irish average [14]	0.03 (absorbed dose rate in air 33 nGy/h)		2000	66

5. DISCUSSION

5.1. Peat harvesting

Radiation dose arising from exposure to external gamma radiation of terrestrial origin for workers involved in the harvesting of the peat all year round should be lower than the natural background value. It should also be lower than the dose arising from a ‘normal’ outdoor work activity. This is because activity concentrations measured in the raw peat are lower than in average Irish soils. Harvesting is carried out in the open air by machinery, and workers are wearing face masks and protective clothing to protect them from any windborne peat dust. The radiation dose arising from inhalation of peat dust is therefore minimized.

5.2. Enrichment factors

Enrichment factors calculated in this study are not significant compared with other published values [15]. It is recognized that the levels of enhancement of radionuclide concentrations in ash are very variable. This is mostly due to differences in the raw peat, the type of furnace, the combustion temperature and the operational characteristics of the plant [6]. For example, the temperature in the furnace at Shannonbridge is 1000–1100ºC, which is lower than the combustion temperature of 1250–1350ºC quoted in Ref. [4].

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[7] Based on the characteristics of each work practice on site.

5.3. Inhalation of airborne peat dust in the bunker

Radiological assessments usually refer to the inhalation of contaminated dust as a major pathway by which workers dealing with NORM are likely to receive the largest radiation dose. Calculations were undertaken to determine the committed effective dose arising from inhalation of peat dust likely to be received by an employee in the bunker over the working year. A sample of airborne peat dust that had settled on shelving adjacent to the personal sampling pump was collected and analysed by gamma spectrometry. This enabled the amount and type of radionuclides likely to be in the airborne peat dust to be determined (see Table I, dust in bunker). The committed effective dose from inhalation of peat dust was calculated using the formula:

$$D_{\mathrm{inh}} = t_{\mathrm{exp}} \times V \times \sum \left(g_{\mathrm{inh},r} \times c_r \right) \qquad (2)$$

where t_{exp} is the exposure duration (assumed to be 100 h/a), V is the breathing rate (1.18 m^3/h for light work [6]), $g_{\mathrm{inh},r}$ is the inhalation dose coefficient (Sv/Bq) for radionuclide r [18], and c_r is the ambient air activity concentration (Bq/m^3) for radionuclide r. The results of the calculations are shown in Table V. The committed effective dose resulting from inhalation of peat dust in the bunker over the working year is less than 1 µSv (0.89 µSv/a) and therefore insignificant. It should be noted that this dose is the maximum likely to be received by any worker as it was calculated assuming no PPE.

5.4. Radon and radon daughter inhalation

Another significant exposure pathway in workplaces where NORM materials are processed is radon inhalation from storage of important quantities of materials in a warehouse [19]. In our case, it could be possible that the peat (bunker area) and peat ash (bottom ash in the boiler area) stored on the site may contribute significantly to the total occupational exposure due to the quantities involved. Another exposure situation, which would arise from large quantities of fly ash stored in an enclosed space, would be the cleaning of the grit arrestors or the freeing of blockages in the hoppers. The radiological assessment of these work activities was not carried out, as they did not occur at the time of our site visits. This maintenance work would arise 3 times in a year approximately, would take up to 5 days to be completed, and would be undertaken under very strict conditions (obligation to wear respiratory equipment, overclothing, gloves, etc) using water sprays for dust suppression. The annual effective dose from inhalation of radon and radon daughters at different locations throughout the plant (Fig. 1) was calculated for the levels measured across the plant and by taking into account the exposure duration at each location (Table III). The highest dose calculated would be received in the maintenance room and is 0.11 mSv/a, which is only 10% of the annual limit under S.I. 125 of 2000.

5.5. Exposure to external gamma radiation in the plant and on the landfill sites

The annual effective dose arising from exposure to external gamma radiation was calculated on the basis of the maximum dose rate measured at each location in the plant (Fig. 1) multiplied by the exposure duration at each location (Table IV). They are all below the annual effective dose calculated for the control site (Shannonbridge church).

TABLE V. COMMITTED EFFECTIVE DOSE FROM INHALATION OF AIRBORNE PEAT DUST IN THE BUNKER AREA

Quantity	Value	
Assumed activity concentration of radionuclide *r* in peat dust[8]		
^{226}Ra	15	Bq/kg
^{210}Pb	50	Bq/kg
^{210}Po	50	Bq/kg
^{228}Ra	1	Bq/kg
^{228}Th	1	Bq/kg
Dust concentration[9]	25.6	mg/m^3
Ambient air activity concentration for radionuclide *r* (c_r) [10]		
^{226}Ra	3.8×10^{-4}	Bq/m^3
^{210}Pb	12.8×10^{-4}	Bq/m^3
^{210}Po	12.8×10^{-4}	Bq/m^3
^{228}Ra	2.6×10^{-5}	Bq/m^3
^{228}Th	2.56×10^{-5}	Bq/m^3
Inhalation dose coefficient for radionuclide *r* ($g_{\text{inh},r}$) [11]		
^{226}Ra	1.2×10^{-5}	Sv/Bq
^{210}Pb	1.1×10^{-6}	Sv/Bq
^{210}Po	7.1×10^{-7}	Sv/Bq
^{228}Ra	1.7×10^{-6}	Sv/Bq
^{228}Th	2.3×10^{-5}	Sv/Bq
The product ($g_{\text{inh},r} \times c_r$) for radionuclide *r*		
^{226}Ra	4.6×10^{-9}	Sv/m^3
^{210}Pb	1.4×10^{-9}	Sv/m^3
^{210}Po	9.1×10^{-10}	Sv/m^3
^{228}Ra	4.3×10^{-11}	Sv/m^3
^{228}Th	5.9×10^{-10}	Sv/m^3
The sum $\sum(g_{\text{inh},r} \times c_r)$ for all radionuclides	7.5×10^{-9}	Sv/m^3
Exposure duration (t_{exp})	100	h/a
Breathing rate (V)	1.18	m^3/h
Committed effective dose (D_{inh})	**0.89**	**µSv/a**

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[8] See Table I. ^{210}Pb and ^{210}Po are assumed to be in equilibrium.

[9] The quotient A/V where A is the amount of peat dust inhaled during an 8 h shift (23.78 mg) and V is the flow rate of the pump (2 L/min) multiplied by the duration of the experiment (465 min) and divided by 1000.

[10] The product of the assumed activity concentration and the dust concentration.

[11] 5 µm AMAD [18].

6. CONCLUSIONS

Table VI summarizes all the doses arising from different pathways calculated in the framework of this study.

TABLE VI. OCCUPATIONAL RADIATION DOSE CALCULATED FOR A WORKER AT SHANNONBRIDGE

Location	Annual exposure time (h)	Annual effective dose (μSv)			
		Inhalation		External gamma irradiation	Total
		Dust	Radon and progeny		
Tippler	100	—	3	6	9
Bunker area	100	0.89	4	8	13
Boiler area	680	—	32	102	134
Bottom ash pile (inactive)	50	—	3 [12]	4	7
Bottom ash pile (active)	500	—	32 [12]	40	72
Wet ash pond	400	—	25 [12]	52	77
Maintenance duties	170	Not determined			
TOTALS	2000	0.89	99	212	312

The total annual effective dose likely to be received by a worker involved in the processing of the peat and handling of the peat ash in Shannonbridge is approximately 0.3 mSv (312 μSv). The exposure pathways taken into account are the peat dust inhalation in the bunker area, the inhalation of radon and radon progeny and the external gamma irradiation at different locations in the plant. Therefore, most of the exposure situations where workers are involved on a regular basis are covered, with the exception of maintenance duties such as the cleaning of the hoppers and the freeing of blockages in the grit arrestors. These duties are the only ones where workers are directly in contact with the peat fly ash. One would not expect the annual effective dose associated with these duties to be significant, as this type of work is always carried out with PPE, is undertaken in wet conditions, occurs non-routinely (three times per year) and is usually completed within a week. Another exposure situation not covered in this study is the inhalation of peat ash dust on the landfill sites arising from the generation of windborne ash on the ash pond. However the top layer of the pond, when dried out, usually forms a crust underneath which the ash is trapped. It is therefore unlikely to be wind blown.

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[12] Assuming an outdoor radon concentration of 10 Bq/m^3 [7] and an equilibrium factor of 0.8 (instead of 0.4 indoors).

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EVALUATION OF OCCUPATIONAL RADIOLOGICAL EXPOSURES ASSOCIATED WITH FLY ASH FROM FRENCH COAL POWER PLANTS

J.-P. Degrange[*], **S. Lepicard**

Centre d'étude sur l'Evaluation de la Protection dans le domaine Nucléaire (CEPN),
Fontenay-aux-Roses Cedex, France

Abstract

The French Ministry of Health is preparing a series of decrees for transposing into French regulation Title VII of the European Council Directive 96/29/Euratom concerning in particular the work activities where natural radioactive substances are handled and used, but not for their radioactive, fertile or fissile properties. Coal power stations belong to a list of industrial sectors potentially concerned by this transposition and the decrees' calendar of preparation includes a consultation period allowing the collection of information about the possible dosimetric impacts on various population groups of these industrial sectors. At the request of the two French operators of coal power stations, Electricité de France (EDF) and the National Company of Electricity and Thermics (LA SNET), CEPN has evaluated occupational radiological exposures resulting from industrial activities that bring into play fly ash produced by the French coal power stations. In a first step, the various stages of the French fly ash cycle were studied, namely production, handling and transport, storage, and recycling (mainly in building materials and road works). In a second step, reference groups of workers likely to receive significant doses were identified. Finally, a series of exposure scenarios, aiming to be both conservative and realistic, were described on the basis of realistic exposure data (when available) together with generic values and simplifying assumptions. In the absence of dosimetric measurements, individual exposures were evaluated using appropriate models for external irradiation, dust and radon inhalation, ingestion and transfer in the biosphere. Estimated annual individual doses range from fractions to hundreds of microsieverts per year and maximum doses are associated with situations (tailings works, road construction) where external contribution is slightly dominating. Sensitivity analyses were performed to evaluate the impact on dose estimates of possible variations of the calculation parameters. This study should provide both industrial and regulatory bodies with a methodological approach enabling to pinpoint situations in the French context that may be calling for particular attention in terms of radiation protection. This paper summarizes the assessment methodology as well as the characteristics and associated individual doses of the most important scenarios.

1. INTRODUCTION

The French Ministry of Health is currently preparing a series of decrees for transposing in French regulation the European Council Directive 96/29/Euratom, particularly Title VII relating to work activities where natural radioactive substances are handled and used, not for their radioactive, fertile or fissile properties [1–3]. The calendar of preparation of these decrees has envisaged a consultation period in order to collect information about the dosimetric impacts of such activities on various population groups (workers and members of the public). In this context, Electricité de France (EDF) and the National Company of Electricity and Thermics (LA SNET), the two French operators of coal power stations, have

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[*] E-mail: degrange@cepn.asso.fr

asked CEPN to evaluate occupational and public radiological exposures resulting from the French industrial activities which bring into play fly ash produced by coal power stations. In this paper, only occupational exposure situations are presented [4].

As a first step, the various stages of the French fly ash cycle (from production to storage or final use) were studied, namely handling and transport, storage, physicochemical transformations, and recycling (mainly in building materials and road constructions). For each stage, the sources, exposure places and physical/chemical properties of fly ash and its by-products were described. As a second step, different reference groups of workers likely to receive significant doses were identified. A series of exposure scenarios, aiming to be both conservative and realistic, were defined on the basis of actual data (when available) together with generic parameter values and simplifying assumptions.

Complementary sensitivity analyses were performed in order to identify the main calculation parameters, i.e. those, the variation of which would have the greatest impact on the dose estimates.

2. DATA USED FOR THE ASSESSMENT

2.1. French fly ash cycle

The combustion of coal in French power stations produces each year an estimated volume of about 2 million t of fly ash that varies according to the energy demand. At present, all of the produced fly ash is recycled, and even tips are regularly reprocessed. As shown in Table I, coal fly ash is largely used in building materials and road works. It can be sent from the power station immediately after being produced, but the seasonality of road works (especially in winter) may require fly ash to be temporarily stored. In that case, fly ash is humidified and then deposited in basins (short transit storage) or on tips, and further retrieved according to the demand.

TABLE I. PRODUCTION AND USE OF FLY ASH IN FRANCE [5]

	Average quantity, 1996–2000 (kt/a)	
Production	1930	
Use	1802	
Concrete + prefabricated material	749	(42%)
Cement	425	(24%)
Road works	392	(22%)
Embankments	157	(9%)
Other	79	(3%)

2.2. Physical and chemical properties of fly ash

The physical and chemical properties of fly ash depend upon the composition of the coal and the combustion process by which fly ash is formed. In France, power stations currently use mostly coal imported from South Africa in ‘classical’ fluidized wet-bottom boilers — the use of lignite in the single remaining power station of Gardanne is to be stopped soon. Chemically, the fly ash is of the silicate-aluminate type, with low calcium oxide content.

2.3. Radionuclide content of fly ash

The radioactivity of fly ash comes mainly from ^{40}K, and from the ^{238}U and ^{232}Th decay chains (the maximum values were found to be 1700, 250 and 200 Bq/kg respectively). The radionuclide content of fly ash varies according to the origin of the coal. For the present study, 20 fly ash samples from French power stations were investigated. Taking account of the various measurement limitations, the activity concentrations of radionuclides that were either not measured or below the detection limit, as well as values measured with a relative uncertainty greater than 50%, were replaced by values derived from a secular equilibrium hypothesis. Three types of typical fly ash were derived artificially from these 20 samples, which will be referred in the following as: 'low-level' where the radionuclide concentrations were all set to the lowest measured values, 'high-level' where the radionuclide concentrations were all set to the highest measured values and 'mean-level'. The results showed that, for each radionuclide, the maximum activity concentration values were roughly four times higher than the minimum values (Table II).

TABLE II. RADIONUCLIDE CONTENT OF FLY ASH CONSIDERED IN THE STUDY

Radionuclide	Activity concentration (Bq/kg)			
	Low-level	High-level	Mean-level	Standard deviation
^{238}U	54	246	133.9	59.1
^{234}Th	54	246	133.9	59.1
^{234m}Pa	54	360	160.3	90.8
^{234}Pa	0.2	1.2	0.5	0.3
^{234}U	54	246	133.9	59.1
^{230}Th	38	246	118.3	60
^{226}Ra	44	260	138	75.6
^{218}Po	44	260	138	75.6
^{218}At	44	260	138	75.6
^{214}Pb	47	231	117.5	58.8
^{214}Bi	45	231	112.2	57
^{214}Po	47	231	117.5	58.8
^{210}Pb	29	274	116.8	64.8
^{210}Bi	29	274	116.8	64.8
^{210}Po	29	274	116.8	64.8
^{232}Th	66	173	119.3	39.2
^{228}Ra	66	173	119.3	39.2
^{228}Ac	66	173	119.3	39.2
^{228}Th	66	190	12,6	42.4
^{224}Ra	66	190	123.6	42.4
^{216}Po	66	190	123.6	42.4
^{212}Pb	65	180	128.2	39.7
^{212}Bi	73	200	133.5	42.6
^{212}Po	42	122	79.2	27.2
^{208}Tl	23	62.3	44.7	14.4
^{40}K	170	1703	955.6	481.7

3. METHODOLOGY AND ASSUMPTIONS

3.1. Methodology

The methodology consisted of:

(a) The identification of exposure situations within thermal coal power stations and within the major fly ash recycling industries in the building materials and road works sectors;

(b) The elaboration, for these situations, of exposure scenarios for reference groups of persons;

(c) The calculation of individual exposures associated with those scenarios.

In the absence of direct dosimetric measurements, individual exposures were evaluated using models requiring, for each scenario, particular information relating mainly to:

- Sources: physical form, geometry, air dust concentration, release rate from power station stack, radionuclide contents of stack emissions, effective release height, meteorological conditions;
- Exposure places: location/distance to the radioactive source, time spent at this place, existence of possible radiological protection measures (natural or artificial protective shields against external irradiation, respiratory protection);
- Physicochemical properties of fly ash and by-products: specific activity, chemical composition, particle size distribution, density, porosity, permeability.

In this paper, only occupational exposure situations are presented.

3.2. Exposure situations

Workplaces potentially leading to a significant radiological exposure due to proximity to fly ash were identified: five of them were associated with thermal coal power stations and four were associated with the fly ash transport/recycling industries. The pertinence of these situations has been confirmed during a visit to a French coal power station. The following exposure situations were considered:

In coal power stations:

(i) *Boiler ash box*, used for retrieving bottom ash, filled with water, in front of which a person is assumed to work periodically to remove ash from it;

(ii) *Plant silos*, storage silos for dry fly ash beside which an ash handling agent is assumed to spend time during fly ash truck loading or during fly ash humidification before loading;

(iii) *Hoppers under electrostatic precipitators*, beside which a person is assumed to spend time when conducting surveillance rounds, or during repair or maintenance operations;

(iv) *Electrostatic precipitators*, inside which a person is assumed to spend time for repair or maintenance operations;

(v) *Tip works*, involving a person in a vehicle on the fly ash tip for continuous ash-levelling or truck loading.

In the transport/recycling industry:

(vi) *Truck*, beside which a person is assumed to spend time during loading/unloading operations and transport of dry or wet fly ash from power plants to fly ash recycling industries;

(vii) *Concrete factory*, where a person is assumed to be exposed to fly ash storage silos and to loaded concrete trucks during his duties;

(viii) *Road works*, where a person is assumed to be exposed to fly ash used as embankments or as aggregates in road sub-layers;

(ix) *Building materials factory*, where a person is assumed to work close to a pile of building material containing fly ash as a partial substitute for cement.

For each situation, external irradiation was taken into account. Ambient dose rates associated with the radionuclides contained in the fly ash were calculated using the Microshield software package [6], considering adequate protective shields where necessary. Where relevant, inhalation of airborne dust was evaluated considering — in the absence of more precise information — an air dust load of 10 mg/m^3, this conservative value corresponding to the French occupational regulatory limit of airborne dust concentration without the compulsory wearing of respiratory protective equipment [7]. Radon inhalation was also considered where relevant.

3.3. Annual exposure scenarios

The exposure situations identified above were combined with annual work durations associated with different jobs, in order to elaborate realistic exposure scenarios. Conservative assumptions of annual work duration were made where this information could not be obtained precisely, in particular for repetitive tasks for which several operators could be involved over a whole year, rather than a single one. Details of the exposure scenarios are given in Table III.

4. RESULTS

4.1. Individual doses

For all the scenarios described above, the annual individual doses calculated for the ‘mean-level’ fly ash radioactivity content are less than or equal to 500 μSv/a. The highest individual doses were associated with works in the vicinity of large volumes of fly ash, with a major contribution of external irradiation:

- Tip works: 500 μSv/a (60% from external irradiation);
- Road works: 310 μSv/a (54% from external irradiation).

4.2. Exposure routes and radionuclide contributions

In situations where the person was exposed to a large volume of fly ash, external irradiation predominated over the other sources of exposure (it represented about 60% of the total exposure in road and tip works). In other situations involving relatively smaller volumes of fly ash, airborne dust inhalation became the predominant exposure route, keeping in mind that the air dust load (10 mg/m^3) was a crucial parameter in this evaluation.

TABLE III. DESCRIPTION OF EXPOSURE SCENARIOS

Exposure situation		Scenario	Exposure duration for one operation	Annual duration for a single person
(i)	Boiler ash box	Emptying of boiler ash box	2 h per emptying, every 24 h	Maximum 178 operations over a year, i.e. 356 h/a
(iii)	Hoppers under electrostatic precipitators	Round in room under electrostatic precipitators	10 min per round; 2 rounds per 8 h period	Maximum 178 rounds over a year, i.e. 60 h/a
(iii)	Hoppers under electrostatic precipitators	Maintenance in room under electrostatic precipitators	80 h over a year	40 h/a for a single person
(iv)	Electrostatic precipitators	Maintenance inside electrostatic precipitators		88 h/a for a single person
(ii)	Plant silos	Loading/unloading trucks	½ h per operation, twice a day	For truck driver, 2 h/day, 200 day/a, i.e. 400 h/a
(vi)	Truck	Transport of fly ash	3 h per round (half of it with empty truck)	For truck driver, twice a day, 200 day/a, i.e. 600 h/a
(ii)	Plant silos	Humidification of fly ash	½ h per truck, 4 trucks per day	40 day/a, i.e. 80 h/a
(v)	Tip works	Ash-moving on tips	8 h/day	200 day/a, i.e. 1600 h/a
(vii)	Concrete factory	Concrete factory	8 h/day	200 day/a, i.e. 1600 h/a
(viii)	Road works	Road works	8 h/day	200 day/a, i.e. 1600 h/a
(ix)	Building materials	Building materials factory	8 h/day	200 day/a, i.e. 1600 h/a

The radionuclides associated with the ^{232}Th decay chain contribute mainly to the external exposure (segments [^{228}Ra, ^{228}Ac] and [^{228}Th to ^{208}Tl] represent approximately half of the total external exposure). The segment [^{226}Ra to ^{214}Po] of the ^{238}U decay chain represents about 30% of the external exposure, and ^{40}K represents 23%.

Similarly, radionuclides associated with the ^{232}Th decay chain contribute mainly to the exposure from airborne dust inhalation (^{228}Th, ^{232}Th and ^{224}Ra represent about 60% of the total exposure from airborne dust inhalation). ^{40}K does not contribute significantly to this exposure route.

Radon inhalation contributes significantly to the total exposure (maximum 25% of total) only when the person is exposed indoors (as compared with open air situations). This is the case for the employee of a building materials factory.

4.3. Sensitivity analysis of the results

The exposure scenarios presented in this study were elaborated on the basis of hypotheses that seemed realistic in the French context, but were nevertheless designed to be conservative. To provide quantitative elements to better evaluate the situation in a wide range of possible contexts, a sensitivity analysis of the results to the various calculation parameters was performed. A synthesis of this analysis is presented in Table IV. The following paragraphs present the application of the major sensitivity analysis results to the two exposure scenarios associated with the highest individual doses estimated in this study, i.e. the ash-moving on tips and the road works.

One of the critical parameters used is the radionuclide content of fly ash, which may vary. However, even if one considers the 'high-level' radioactivity fly ash content derived from the 20 samples considered in this study, the maximum annual individual dose would remain below the French regulatory limit of 1000 μSv/a for non-exposed workers.

As far as tip works are concerned, keeping in mind the respective contributions of the major exposure routes — 54% from external irradiation for a 0.3 cm cabin steel thickness and 45% from airborne dust inhalation — the sensitivity of calculated doses to the exposure parameters is as follows:

- Increasing the *steel thickness* of the cabin from 0.3 to 0.6 cm would reduce the exposure from external irradiation by a factor of about 1.4;
- The *distance to the source* has no significant effect;
- The *size of the tip* has no significant effect as soon as its surface is greater than an equivalent 20 m radius disc and its depth is greater than 0.4 m;
- The contribution of *radon* to the exposure may be neglected;
- The dose associated with dust inhalation is directly proportional to the considered *airborne dust concentration*.

As far as road works are concerned, keeping in mind the respective contributions of the major exposure routes — 64% from external irradiation and 40% from airborne dust inhalation for an ash content of 10 wt.-% in road aggregates and an airborne dust load of 10 mg/m^3 — the sensitivity of the calculated doses to the exposure parameters is as follows:

- The *size* of the embankment or road aggregate sub-layer has no significant effect as soon as the surface is greater than an equivalent 5 m radius disc and the depth is greater than 0.4 m;
- The contribution of *radon* to the exposure can be neglected;
- Exposures from external irradiation and airborne dust inhalation are directly proportional to the *fly ash content of aggregates*;
- The dose associated with dust inhalation is directly proportional to the considered *airborne dust concentration*.

TABLE IV. DETAILED RESULTS OF SENSITIVITY ANALYSIS

Parameter and value	Sensitivity
All exposure routes	
Fly ash activity concentration	Annual dose directly proportional (according to relative contribution of each radionuclide)
Exposure duration	Annual dose directly proportional
External radiation	
Thickness of steel — silo 1 cm, cabin of tip ash-moving machine 0.3 cm	Quasi linear — at 1 m from source, dose rate decreases 1.4× when steel thickness doubles; less pronounced as distance to source increases
Height of fly ash — tip 10 m, silo (axial) 15 m, aggregates in road sub-layers 0.4 m, road embankments 6 m	• Beyond 1 m height, no influence on dose rate • <1% difference between 1m and 0.4 m
5 m axial distance from source under a 5 m radius silo	Dose rate increases 2.4× going from 5 to 1 m decreases 3× going from 5 to 10 m
2 m axial distance from source under a 1 m radius hopper, 2 m from axis	Dose rate increases 1.5× going from 2 to 1 m
1 m radial distance from source beside a 5 m radius silo (i.e. 6 m from axis)	Dose rate decreases 2.3× going from 1 to 5 m decreases 3.8× going from 5 to 25 m
1 m radial distance from source beside a hopper 1 m radius, 2 m high	Dose rate decreases 1.5× going from 1 to 2 m decreases 4.6× going from 1 to 5 m
1 m distance from tip surface	<3% difference going from 1 to 3 m
100 000 m^2 tip surface area	No effect above 1000 m^2 (i.e. 20 m radius disc)
10 wt.-% fly ash content of material (road aggregates and building materials)	Dose rate directly proportional
Dust inhalation	
10 mg/m^3 airborne dust concentration	Dose rate directly proportional
10 wt.-% fly ash content of material (road aggregates and building materials)	Dose rate directly proportional
Radon inhalation	
5×10^{-7} m^2/s effective diffusion coefficient	Exhalation rate: • Increases 1.3× when coefficient increases 2× • Decreases 2.3× when coefficient decreases 5×
100 000 m^2 tip surface area	Outdoor radon air concentration: • Increases 3× when surface increases 10× • Decreases 10× when surface decreases 100×
Source density of 1	Exhalation rate directly proportional
10 m source depth (tip)	No effect on exhalation rate beyond 4 m, even for highest diffusion coefficient
Room-to-source volume ratio of 4 (pile of building materials)	Indoor radon concentration inversely proportional

5. CONCLUSION

This study enabled the estimation of radiological exposures associated with fly ash produced by thermal coal power stations in France. The occupational exposure scenarios that were considered tackled various exposure situations. Five of them dealt with activities within thermal coal power stations (jobs situated near significant volumes of fly ash, directly connected to the moving of fly ash, transport and stocking operations). Four specific additional scenarios were studied in fly ash recycling industries (building and road works).

For each situation, the following exposure routes were considered (where relevant): external irradiation, inhalation of airborne dust and inhalation of radon. These predominant exposure routes were selected on the basis of data extracted from the literature and from the preliminary estimates performed within the framework of this study involving EDF and LA SNET.

The annual individual doses estimated for the various persons concerned by the scenarios considered in this study are less than the French regulatory dose limit for non-exposed workers (1 mSv/a). The highest value (0.5 mSv/a) — associated with fly ash, the 'mean-level' radioactivity content of which was derived from the analysis of 20 fly ash samples supplied by EDF and LA SNET — relates to ash-moving tip works.

It should be noted that the estimated doses rely on parameters that influence the results in a direct way, such as:

- The annual exposure duration and the level of radioactivity of fly ash: the total annual dose is directly proportional to these parameters. The annual exposure duration was voluntarily estimated very conservatively in this study;
- The airborne dust concentration: the exposure by inhalation is directly proportional to this parameter. In the absence of more realistic data, the value considered in this study is the French regulatory limit of 10 mg/m^3, which seems to be a very conservative estimate. In this context, the inhalation represents 45% of the total annual dose for an employee on fly ash tips.

It could be envisaged that complementary measurements be made of the radioactivity in fly ash according to the place of production and to the origin of the coal in order to get a better assessment of the French situation, as well as in situ measurements of ambient dose rate and airborne dust concentration to validate the major assumptions made in this study.

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A STUDY CONCERNING NORM IN REFRACTORIES INDUSTRIES

C. Zampieri[1], F. Trotti[1], D. Desideri[2], G. Jia[3], E. Caldognetto[1], G. Torri[3], A. Tacconi[1], G. Clauser[4], M. Facchinelli[4], L. Filipozzi[1], M. Lanciai[1]

[1]ARPA Veneto*: Regional Agency for the Environmental Protection of Veneto, Verona, Italy
[2]Institute of General Chemistry, Urbino University, Urbino, Italy
[3]APAT: National Agency for Environmental Protection and Technical Services, Roma, Italy
[4]APPA Trento: Provincial Agency for the Environmental Protection of Trento, Trento, Italy

Abstract

A specific study concerning refractories industries has been performed by a group of Italian Regional Environmental Protection Agencies together with the National Agency for Environmental Protection and Technical Services. The aim of this study was to evaluate the environmental impact for some activities dealing with NORM. A radiological survey was carried out in a company in northern Italy. Activity concentration measurements by gamma spectrometry (of the more relevant gamma-emitting radionuclides of the natural decay chains) and radiochemical analysis (^{210}Pb, ^{210}Po) on raw materials, finished products, residues and treatment water were made. Information and technical data related to the present working cycle were collected by means of specific questionnaires sent to most of the involved factories selected from the sector association's database. An estimate of collective effective dose based on a simplified model is made by the combination of the radiological results of the companies survey with information from the questionnaires.

1. INTRODUCTION

A study project about NORM is being developed by the National Topic Centre on Physical Agents (CTN–AGF), a co-ordination of Regional Agencies for the Environmental Protection (ARPA), which supports the National Agency for Environmental Protection and Technical Services (APAT) in collecting environment quality information as far as physical pollutants are concerned. Among the relevant work activities, the refractories industries have been chosen for detailed study because they may use zircon sands (or zircon flour) and semi-finished products based on zircon sands as raw material, and it is well known that zircon sands may contain elevated concentrations of natural radionuclides.

This study has two working plans:

- To evaluate the environmental radiological significance for a specific refractories industry by the determination of ^{40}K and some radionuclides of the ^{238}U and ^{232}Th decay chains, and to estimate the collective effective dose by a simplified model;
- To give an overview of the general situation of Italian refractories industries through data from specific questionnaires sent to selected refractories factories.

Three laboratories were involved in this project: ARPAV (Regional Agency for the Environmental Protection of Veneto), APAT (National Agency for Environmental Protection and Technical Services) and the University of Urbino.

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* E-mail: czampieri@arpa.veneto.it, ftrotti@arpa.veneto.it

2. NORM IN A SPECIFIC REFRACTORIES INDUSTRY

2.1. Description of manufacturing cycle

The most widespread components of refractories materials are alumina, zirconia and silica. The typical manufacturing cycle can be described by the following:

- Raw materials preparation (casting into moulds of sand, graphite or metal);
- Fusion in an electric arc furnace;
- Grinding and finishing.

The raw materials may be zircon sands/silicates or semi-finished components based on zircon silicates (for instance 'mullite-zircon' or scraps). The products are obtained by casting in moulds a mixture that has been melted in an electric arc furnace. During this step the uranium chain may be broken, with consequently ^{210}Pb and ^{210}Po enrichment in residual dust, due to volatilization at the high temperature of fusion. The fusion products are then 'finished' by sand blasting and the scraps are ground in order to enter the manufacturing cycle again — this generates residual dusts. Residues in the form of waste water and sludge coming from the different sections of the factory are also generated. Only dusts produced by sand blasting and waste water treatment are discharged — fusion dusts and sludges are recycled into the manufacturing process.

2.2. Samples and radioanalytical and radiometric measurement methods

In 2003, some activity concentration measurements were carried out in raw materials, products and residues of a selected refractory materials industry. Three laboratories made the analysis: ARPAV, APAT and the University of Urbino. The radionuclides determined were ^{238}U, ^{226}Ra, ^{210}Pb, ^{210}Po, ^{235}U, ^{232}Th and ^{40}K.

ARPAV measurements were performed by gamma spectrometry with high resolution germanium detectors. Uranium-238 was assessed through its decay product ^{234m}Pa. Radium-226 was assessed through its decay products ^{214}Pb and ^{214}Bi — in this case, secular equilibrium was restored by keeping the samples in a sealed aluminium beaker for a month. Determinations of ^{232}Th (through its gamma-emitting decay products), ^{235}U and ^{40}K were also made. Coincidence summing, in particular for ^{214}Bi, and self-attenuation effects were corrected through GESPECOR software.

The determination of ^{238}U, ^{210}Pb and ^{210}Po activity concentrations was carried out by the University of Urbino and APAT. The radioanalytical methods were based on: (a) sample pre-treatment, (b) radionuclide separation and (c) source preparation. Finally, ^{238}U and ^{210}Po were determined by alpha spectrometry and ^{210}Pb by a low background beta counter.

2.3 Results and discussion

Table I shows the activity concentrations of ^{238}U, ^{226}Ra, ^{210}Pb, ^{210}Po, ^{235}U, ^{232}Th and ^{40}K in refractory raw materials, products and residues. The percentage deviations in the analysis of the same samples — on average 14 Bq/kg for ^{238}U and ^{210}Pb, and 10 Bq/kg for ^{210}Po — may represent an estimate of the assessment uncertainty; in effect, they seem to be comparable with single measurement uncertainties.

TABLE I. ACTIVITY CONCENTRATIONS IN RAW MATERIALS, PRODUCTS AND RESIDUES

Sample	Activity concentration (Bq/kg)						
	^{238}U[1]	^{226}Ra[2]	^{210}Pb[3]	^{210}Po[3]	^{235}U[2]	^{232}Th[2]	^{40}K[2]
Zircon sand	3613 (10.2)	3219 (6)	2707 (7.4)	2748.0 (23.3)	137 (7)	517 (6)	0 (36)
Dropping system dust generated by fusion furnace	358.5 (17.6)	147 (6)	21 050 (18.8)	35 000 (57)	20 (10)	27 (6)	10 (17)
Fusion furnace filter	—	—	n.d.	28 000 (25)	—	—	—
Dropping system dust generated by refuse grinding	1191 (21.7)	1046 (6)	1033.5 (4.0)	1293.5 (12.3)	59 (9)	178 (6)	255 (6)
Refuse grinding filter	—	—	n.d.	6100 (25)	—	—	—
Product 1	1701.5 (2.9)	1400 (6)	951.5 (7.3)	1088.5 (7.7)	82 (9)	310 (6)	9 (18)
Product 2	1751 (13.9)	1638 (6)	752.5 (8.7)	684.5 (2.4)	91 (8)	262 (6)	0 (38)
Product 3	1714.5 (7.2)	1481 (6)	1343.5 (10.8)	1352.5 (24.9)	82 (9)	250 (6)	23 (13)
Product 4	19.5 (3.9)	8 (6)	31.3 (43.8)	46.0 (2.0)	1 (31)	2 (7)	81 (6)
Sludges	1635 (3.3)	1496 (6)	1166.5 (14.3)	1176.5 (2.7)	88 (7)	238 (6)	27 (11)
Waste water	—	< 0.38	n.d.	0.0044 (25)	< 0.5	< 0.15	< 1.89

The concentrations of the ^{238}U series radionuclides in zircon sand agree with literature values. Elevated concentrations of ^{210}Pb and ^{210}Po are found in the fusion furnace dust — this enrichment is due to volatilization at the high fusion temperatures. The concentrations of the other natural radionuclides are moderate — this is also attested by the relevant ^{210}Po concentration in the outgoing gas from the fusion furnace filter. The dust generated by refuse grinding shows elevated activity concentrations of all natural radionuclides.

The majority of the finished products contain significant concentrations of ^{238}U series radionuclides, with depletion of ^{210}Pb and ^{210}Po because of their volatilization at high temperatures during the fusion process. In product 4, however, the activity concentrations of all natural radionuclides are moderate, because of the absence of zircon — the product comprises a mixture of alumina and silica.

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[1] The average of ARPAV gamma spectrometry and APAT radiochemical analyses — the percentage deviation of the two values from the average is shown in parentheses.

[2] Gamma spectrometry analysis by ARPAV — the percentage uncertainty at a 68% confidence level is shown in parentheses.

[3] The average of University of Urbino and APAT radiochemical analyses — the percentage deviation of the two values from the average is shown in parentheses.

The activity concentrations in the sludges coming from the water treatment process are elevated, whereas they are negligible in the waste water after treatment.

In general, the concentrations of ^{232}Th chain radionuclides are higher than environmental levels but lower than ^{238}U chain radionuclides.

2.4. Estimate of collective effective dose by a simplified model

An estimate of the collective effective dose received by the population living near the plant due to the emissions of dusts from fusion and grinding stacks has been made, based on the simplified model given in para. 1B, Annex C, pp 111–113 of the UNSCEAR 1982 Report [1]. The model considers two stages of exposure:

(i) Direct inhalation during the passage of the cloud,

(ii) Intake (ingestion of contaminated food and inhalation of resuspended material) and external irradiation, after deposition.

In the first case, the calculation of the inhalation dose for the population living in the plant area was based on the time-integrated activity concentrations in that area from the total radionuclide release. The activity release from the two stacks was calculated by multiplying the dust activity concentrations (Table II) by the annual dust emission from the stacks (191 and 198 kg/a, respectively). For ^{222}Rn, the incremental dose due to the plant release was calculated by comparison with the inhalation dose due to natural emanation from soil — all radon contained in the processed zircon sands (2320 t/a) was assumed to be released into the air. Some parameters were updated with respect to the UNSCEAR 1982 Report: the age-weighted inhalation effective dose coefficients and breathing rates were taken from Table 17 (p. 127) and para. 153 (p. 107) of Annex B of the UNSCEAR 2000 Report [2].

In the second case, the calculation of the dose arising from the deposited activity was performed by comparing with doses resulting from the natural presence of radionuclides in soil. Apart from some fixed parameters [1], the main data used in the calculation were taken from Ref. [2], as follows:

- Natural soil concentrations of 35 Bq/kg for the ^{238}U chain, 30 Bq/kg for the ^{232}Th chain and 400 Bq/kg for ^{40}K;
- Age-weighted committed effective doses for inhalation and ingestion of various naturally occurring radionuclides as in Tables 17 and 18, Annex B of Ref. [2]);
- Age-weighted external radiation dose rates due to the natural content of ^{238}U and ^{232}Th series radionuclides and of ^{40}K in soil as in Table 6, Annex B of Ref. [2]);
- An individual committed effective dose from the inhalation of ^{222}Rn of 470 μSv/a.

The results of the modelling exercise are summarized in Table II and Fig. 1. The total committed collective effective dose arising from the plant emissions is about 0.0012 man·Sv in a year. From the ratio of the collective dose to the population living in the municipality around the plant, the estimated committed effective dose per caput is about 0.3 μSv/a, far below the action level of 300 μSv/a indicated by Italian law [3]. The most significant exposure pathway is the ingestion of contaminated food after deposition — the radionuclides that contribute most to this are (in descending order): ^{210}Po, ^{222}Rn and ^{210}Pb. Given the simplified nature of the model used in this study, more accurate modelling is to be conducted, taking into account the actual site situation near the plant.

TABLE II. COLLECTIVE DOSE ARISING FROM EMISSIONS FROM A REFRACTORY MATERIALS PLANT

Radionuclide	Collective committed effective dose in a year (man·µSv)				
	Passage of the cloud	Deposition			Total
		Ingestion	Inhalation	External irradiation	
^{238}U	3.57	0.0739	0.00621	30.3	11.2
^{234}U	4.29	0.0828	0.00769	—	11.9
^{230}Th	16.1	0.172	0.0142	—	23.9
^{226}Ra	3.34	1.83	0.00594	—	12.7
^{222}Rn	170	—	107	—	278
^{210}Pb	18.7	115	16.4	—	150
^{210}Po	93	573	8.09	—	674
^{232}Th	3.7	0.0165	0.00385	5.27	5.48
^{228}Ra	0.466	0.962	0.000962	—	3.18
^{228}Th	6.53	0.0114	0.0133	—	8.31
^{220}Rn	—	—	1.6	—	1.6
^{235}U	0.195	0.0036	0.000327	—	0.198
^{40}K	—	—	—	0.484	0.484
Total	320	691	134	36	1180

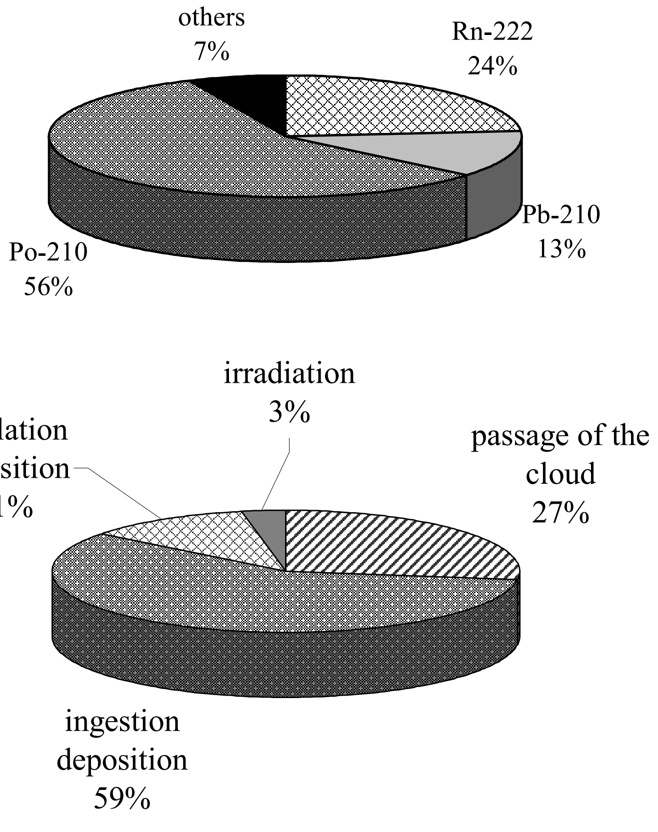

FIG. 1. Exposure contributions of radionuclides and pathways

3. NATIONAL OVERVIEW CONCERNING NORM IN REFRACTORIES INDUSTRIES

The Italian refractories industry is made up of 39 companies, 20 of which have joined the main sector association Assopiastrelle (representing 75% of the market). In 2002 the production of refractories amounted to 556 400 t. The main sector using refractories is the steel industry followed by lime and cement, ceramics, non-ferrous metals, glass, energy and petrochemicals. Ten companies belonging to Assopiastrelle use zircon sands or zircon-based semi-finished components in processing, but only two of them are concerned with the utilization of significant amounts (thousands of tons) of zircon sands [4].

This information and other technical data related to the present working cycle were collected by means of specific questionnaires sent to the relevant factories selected from the sector association's database.

The questionnaire was divided into four forms, concerning:

- Private data of the company and all its plants;
- The type, place of origin, quantity and storage of raw materials involved with zircon sand and silicate;
- The type, quantity and characteristics of the output involved with zircon sand, silicate and osside;
- The quantity of working process residues (dust, sludge and waste water) and technical data on emissions (for instance: temperature, height and flow of stacks).

On the basis of this preliminary survey, the consumption of zircon sand/silicate or zircon-based semi-finished components as raw materials amounted to about 45 000 t in 2003.

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RADIOLOGICAL IMPACT ON THE UK POPULATION OF INDUSTRIES WHICH USE OR PRODUCE MATERIALS CONTAINING ENHANCED LEVELS OF NATURALLY OCCURRING RADIONUCLIDES: ZIRCON SANDS INDUSTRIES

W.B. Oatway[1*], J.A. Jones[1], P.V. Shaw[2], S.F. Mobbs[1]

[1]NRPB, Chilton, Didcot, Oxon, United Kingdom
[2]NRPB, Cookridge, Leeds, United Kingdom

Abstract

As part of its periodic review of radiation doses to the population of the United Kingdom, the National Radiological Protection Board identified the need to estimate the radiological impact of the operation of non-nuclear industries which use or produce materials containing enhanced levels of naturally occurring radionuclides. A number of industries have been considered in the study. For each industry the radiological impact of the primary industry, the waste streams produced and, where applicable, the use of by-products were addressed. Doses to workers in the industries and members of the public were estimated as part of the study. This paper considers the exposures from the production of zirconium compounds from zircon sand, and their use.

1. INTRODUCTION

In the European Union (EU) the revised Basic Safety Standards, as defined in Council Directive 96/29/Euratom [1], provides a regulatory control system for the protection of workers and the public from sources of ionizing radiation. In the case of exposure to natural radiation sources other than radon, national authorities may determine which work activities require control. There is, however, a need for harmonization of the regulatory control of natural radiation sources within the EU. In 1999 the National Radiological Protection Board (NRPB) and the Centre d'Evaluation de la Protection Nucleaire (CEPN) performed a study to identify possible reference levels for the regulatory control of workplaces involved in the production or processing of materials containing enhanced levels of naturally occurring radionuclides [2]. Following this report, NRPB initiated a project to investigate the radiological impact of non-nuclear industries in the UK.

This paper describes the fourth report in the series of reports by the NRPB on the radiological impact of non-nuclear industries within the UK which process or produce materials containing enhanced levels of naturally occurring radioactive material (NORM). It considers the exposures from the production and use of zirconium compounds from zircon sands [3]. The report considers the radiological impact of the primary industry, the waste streams produced, the normal use of the products and, where applicable, the uses of by-products.

The ores from which these chemicals are extracted contain the naturally occurring radionuclides ^{235}U, ^{238}U and ^{232}Th and their decay products. Some of the production processes are such that most of the radioactive material present in the raw materials passes through to the final product, while some products are essentially free of radioactive material. The aim of

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[*] E-mail: wayne.oatway@nrpb.org

the study was to consider all exposures that could arise from the time when the raw material is imported into the UK to the time when all activity has been disposed of.

2. DESCRIPTION OF THE INDUSTRY

Zircon sand is the basic material for a wide variety of uses, particularly in refractory materials and glazes. Natural zircon sand has a particle size that can be up to a few hundred micrometers, which is too coarse for many of the applications. The first step in the processing of zircon is therefore to grind it to an appropriate particle size, producing what is known as zircon flour. This is done using dry processes when producing particle sizes of tens of micrometers, and wet processes for finer particles. These processes are not considered to remove any of the activity from the original raw material. Doses to workers and members of the public from this part of the industry are considered.

Once milled, the zircon flour is packed into bags, which are either exported or used in other manufacturing steps by other companies within the UK. In general, users of zircon flour 'simply' empty the contents of the bags into machines used by their industry. Much of the flour is used as a paste and in general the doses to the workers in these factories are likely to be considerably lower than to those workers in the milling process. However, the doses to workers who empty the bags of zircon flour may not be trivial as there can be a considerable amount of airborne material released during this step of the process. Hence the doses to workers emptying bags of zircon flour are considered in this study, but doses from other stages are not.

Zircon sand is also used as the raw material for the manufacture of zirconium chemicals. The chemical processing essentially removes all the radioactive material from the products and so the doses from the use of the products are extremely small, and are therefore not considered in the report. The radioactive material removed from the product, which has the same relative amounts of different radionuclides as the raw material, is disposed of as waste. Doses to workers in the factory, and to members of the public from waste disposal, have been considered.

Zircon can also be fused with other chemicals to modify some of its properties for some applications. This process (termed fusion) involves heating zircon sand to a high temperature, combining the product with other materials, followed by a grinding process to produce 'flour' at the required particle size. The fusion process raises the temperature to a point where it is likely that the radon, lead and polonium are removed from the product. Air filters installed in the furnace gas treatment plant will trap most of the dust released by this process, but there will be some discharge of material to the environment. Doses from this part of the industry are considered. Doses from the subsequent use of the flour produced are likely to be lower and so are not considered in this study apart from the doses while emptying bags of material during later product manufacturing. In this case, the exposure is considered to be the same as that described above from exposure to emptying bags of zircon flour from the milling process.

The relationships between the various stages of the zircon sand industry, as described above, are presented in Fig. 1. This provides an overview of the industry with arrows indicating the passage of material between the various industrial stages. Also shown are the principal waste streams considered in the report, although for simplicity not all streams are shown.

3. SOURCE TERM

It was assumed that the activity concentration of the material during processing was equal to that of the raw material for most of the assessment calculations, as the activity is considered not to change significantly during milling. From measured activity concentrations in materials that are used in the industry in the UK [4], the typical activity concentrations are:

^{238}U chain members	3000 Bq/kg
^{232}Th chain members	600 Bq/kg
^{235}U chain members	150 Bq/kg

These values are intended to represent material used by the industry in the UK in general and hence some generalization has been made. For comparison, a study by the EU [5], which looked at clearance and exemption within Europe for industries which may have potential problems with naturally occurring radionuclides, found typical activity concentrations of uranium and thorium in zircon sands of 5000 Bq/kg and 1000 Bq/kg respectively. It should be noted that most areas of the industry in the UK are now specifically obtaining raw material from sources that have low activity concentrations.

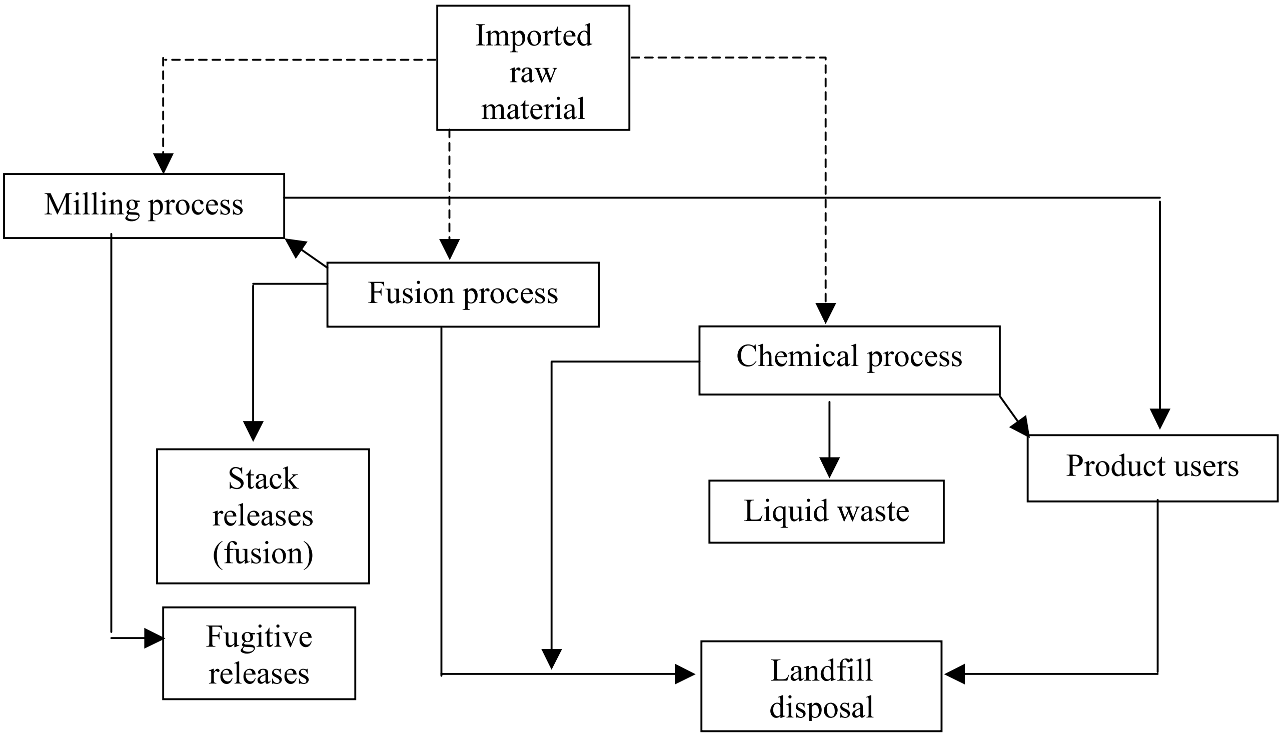

FIG. 1. Schematic overview of the zircon sand industry in the UK showing the main processing and waste stream steps

In a limited number of cases, there will be exposure to material with an activity concentration that, for some radionuclides, is different from that of the raw material. Examples are exposures to material released during the high temperature (fusion) processes. In such processes it is possible that some radionuclides (^{210}Pb and ^{210}Po in particular) will become volatilized and collect in the filter and extraction systems designed to clean the air before it is released to the atmosphere. Material in these situations is considered to exhibit the following activity concentrations [4]:

^{238}U chain members (except ^{210}Pb and ^{210}Po)	1500 Bq/kg
^{210}Pb	10 000 Bq/kg
^{210}Po	10 000 Bq/kg

- ^{232}Th chain members	600 Bq/kg
- ^{235}U chain members	150 Bq/kg

4. EXPOSURE GROUPS CONSIDERED

The study considers the exposure of workers in the industry and to members of the public from disposal or release of waste products. All workers were assessed where it was thought that exposure could not be disregarded from a radiological protection point of view. The workers assessed included those involved in transporting material in lorries and those workers involved in the milling and fusing of material. The exposure times selected were taken to represent the general activities of a single worker throughout the year, and included times spent near bulk material as well as times spent near to machinery or bagging the final product. Doses were also assessed from the dust present on the overalls worn by the workers, including doses received by other people who were involved in cleaning the overalls.

Exposures to members of the public are from three waste streams. Atmospheric releases were considered for both general wind-blown emissions and for releases from fusing of material. Exposure to liquid wastes was considered when the waste was discharged into a local river where boating may occur. Exposure was also considered for material disposed of into landfill. In this case, doses from exposure for both present day and future site occupants were considered. The exposure groups and the pathways considered are shown in Table I.

TABLE I. EXPOSURE PATHWAYS CONSIDERED

Exposed individual	Pathways considered
Transport worker	External exposure during transport
Raw material process and fusion process workers	External exposure to materials stored and being treated in the plant Inhalation of airborne material Inadvertent ingestion of material being treated in the plant Inhalation of radon from stored materials
Manufacturer worker	External exposure to material being treated in the plant Inhalation of airborne material
Laundry worker	External exposure to contaminated overalls Inhalation of material resuspended from contaminated overalls
Member of public (gaseous releases)	External exposure to plume and fallout Inhalation of plume (including radon) and resuspended fallout Ingestion of food grown on land contaminated by fallout
Member of public (liquid discharges)	External exposure to contaminated water while canoeing Inadvertent ingestion of contaminated water while canoeing
Present day landfill worker (solid waste disposal)[1]	External exposure to material disposed of in the ground External exposure from skin contamination Inhalation of suspended material during disposal Inadvertent ingestion of material during disposal
Future user of landfill site	External exposure, inhalation and ingestion of material from future building construction (excavation) on landfill site External irradiation, inhalation and ingestion of material (including radon) from future residence on landfill site

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[1] Although these people have the title of ‘workers’ they are assessed as members of the public, as they are considered to be unaware of the radioactivity present in the material with which they come into contact.

5. DOSES RECEIVED BY WORKERS FROM THE PROCESSING AND MANUFACTURING OF ITEMS FROM ZIRCON SAND

The doses received by workers are summarized in Table II, which considers doses received by transport and laundry workers and three types of process workers. Also presented in the Table are the dominant pathways for each exposed worker and the percentage contribution that pathway makes to the total dose. The 'raw material process' workers are those workers involved in the milling of zircon sand and any other workers who are exposed for an entire year to material with an activity concentration that is not altered from the raw material. The 'fusion process workers' are those involved in the fusion part of the industrial process. They are exposed for most of the year to material that has an activity concentration equal to the raw material, but are also exposed to material from the fusion dust collection system for limited periods of time. The 'manufacturer workers' are those in subsequent industries (such as end product manufacturers) where the main exposure to radioactive materials comes during the opening of bags of zircon flour or sand and their insertion into a processing line. The item labelled 'laundry workers' refers to the dose received by those who handle dirty work overalls during cleaning.

TABLE II. DOSES RECEIVED BY WORKERS ASSOCIATED WITH ZIRCON SANDS

Exposed individual	Dominant exposure pathway	Particle size (μm)	Contribution of dominant pathway	Annual committed effective dose (mSv)
Transport worker	External	—	100%	0.35
Raw material process worker	External	1	54%	2.1
		5	61%	1.9
		10	84%	1.4
Fusion process worker	External	1	54%	2.1
		5	61%	1.9
		10	70%	1.6
Manufacturer worker	External	1	62%	0.72
		5	70%	0.64
		10	76%	0.58
Laundry worker	Inhalation	1	99%	0.062
		5	99%	0.045
		10	98%	0.033

The workers in each of the classes described above are considered separately, as they work in different parts of the process; hence no summing of the results over different classes of worker is made. The doses presented are thus the total annual dose received by any worker in that part of the industry indicated.

Doses received by workers in each class of (apart from transport) were calculated for three particle sizes. This was intended to represent the range of particle sizes of material that might be encountered in the industry. The doses received by any particular worker can then be selected from those presented, depending on the material to which that worker is exposed.

The highest doses predicted are about 2 mSv/a for raw material and fusion process workers. It must be noted, however, that some pessimistic and many general assumptions have been made to cover a wide variety of work tasks. Because of this, individual factories may not have workers who are exposed to doses of this magnitude. Also, good industrial hygiene and the wearing of face masks or other protective measures will lower the inhaled component of the dose considerably. It is also noted that external exposure is the dominant pathway for most of the workers considered, including those where the dose is above the level of 1 mSv/a. Control of access to storage areas, or the time spent in such areas where bulk material is kept, will decrease the total dose.

6. DOSES RECEIVED BY MEMBERS OF THE PUBLIC FROM DISPOSAL OF MATERIAL

The predicted doses received by members of the public from discharges and disposals from industries processing zircon sand are summarized in Table III. This indicates the annual dose received by members of the public from discharges from the various stages of the industry, and also indicates the dominant pathway and its percentage contribution to the total dose. Doses arising from the normal use of the products are not included as they are considered to be well below those arising from disposal and discharges.

TABLE III. DOSES RECEIVED BY MEMBERS OF THE PUBLIC FROM DISCHARGES AND DISPOSALS FROM THE ZIRCON SANDS INDUSTRIES

Discharge or disposal		Dominant exposure pathway		Dose (μSv/a)
Type	Description/material	Description	Contribution	
Atmospheric release	General processes	Plume inhalation	98%	0.011
	Fusion off-dust	Plume inhalation	96%	0.037
Liquid effluent	Chemical washings	Canoeing, external	62%	0.000016
Landfill disposal	Future site users from general (wet) material disposal	Resident, external	85%	750
	Future site users from fusion off-dust disposal	Resident, external	85%	4.5
	Landfill workers (exposure to fusion off-dust only)	External	98%	15

Two types of atmospheric emissions were considered when calculating the doses received by members of the public living near a factory. The first was the release of material from the fusion process (exposure to fusion off-dust). The second was the release of material from the site by fugitive emissions that included, for example, loose material suspended and blown off the site by wind action (exposure to general processes). For liquid effluent, the doses from likely discharges to a local river of material from the chemical processing of zircon sands were considered; the doses from liquid effluents from other parts of the industry are much smaller than those given here due to the limited amount of material released. The doses from landfill disposal reflect those from the disposal of wastes arising from the fusing of zircon sands (fusion off-dust material) and from the chemical processing of zircon sands (general waste materials). It was assumed that only fusion off-dust was sent to a landfill in a form that could expose a worker. However, doses received by members of the public were not affected by the disposal conditions, so exposure of members of the public from the future use of the landfill site from both waste types was considered. Exposure of future site users was from the excavation of the site for construction work and for residents living on the site in the future. It was assumed that the other processes in the industry produced little or no waste when compared with these two processes, and the doses from their disposals were not considered.

The peak dose from the release of material to atmosphere is 0.037 μSv/a, with the dominant pathway being the inhalation of material from the plume as it passed over nearby houses.

The predicted doses from the disposal of material to local water systems was about 0.000016 μSv/a, resulting mainly from external irradiation while in a canoe. The predicted doses from landfill disposal arose from the disposal of two material types: wet material from the chemical processing of zircon sand and the waste produced by the air filters in the fusion process. In the case of future site redevelopment, a dose of up to 750 μSv/a was estimated for a resident living on a site that had received general waste from the zircon sand industry — this dose was much larger than that calculated for the disposal of fusion off-dust, mainly due to the amount of material being disposed of (20 000 t compared with 50 t).

The dose received by landfill workers was estimated to be 15 μSv/a. This result was based on the assumption that waste was sent to the landfill in a form that could readily expose workers, which is not the case for most of the waste sent to landfill from this industry. For most disposals from this industry, the doses received by landfill workers can be regarded as trivial.

The radon concentration in a home built on a former landfill site and the corresponding inhalation dose received by a resident were estimated to be 210–340 Bq/m^3 and 10.6–16.9 mSv/a, respectively. These results were based on the assumption that the activity concentration of ^{226}Ra (the parent of ^{222}Rn) remained about the same over the period between disposal of the waste and construction of housing on the site. It was also assumed that a 1 m layer of clean soil had been placed over any wastes disposed and that this remained in place after construction. The ranges of values reflect differences in the methodology used. The range of activity concentrations exceeds the action level of 200 Bq/m^3, so any new housing constructed on the site may be required to have some features to reduce the radon level. However, the results are not conclusive as it was assumed that radon was free to leave the disposed sand in a similar manner to that for soil (due to the availability of data for the latter). If the radon was trapped for the most part within the crystal structure of the zircon sand, as is currently believed to be the case, then the levels of radon released would be greatly reduced and hence the activity estimated above would also decrease. It was also assumed that the house had been constructed entirely on an area above zircon waste. Given the relatively small amount of zircon waste disposed of, compared with the volume of the landfill, this represents a pessimistic assumption.

7. APPLICATION OF LEGISLATION TO THE INDUSTRY IN THE UK

In the UK, the Ionising Radiations Regulations 1999 (the IRR99) [6] deal primarily with regulating the radiation exposures that people receive at work. Regulation 3 (Application) indicates that the IRR99 shall apply to “any work with any radioactive substance containing naturally occurring radionuclides”. In fact, the application of the IRR99 to such work depends on the definition of ‘radioactive substance’, as described in Regulation 2(1) and, more specifically, in paragraph 11 of the Approved Code of Practice [7]. According to this, the IRR99 are deemed to apply to work activities where it is likely that persons could receive an effective dose in excess of 1 mSv/a. Where the IRR99 do apply, then appropriate controls are required to limit exposures. From the results presented in this paper, there is a strong indication that this legislation does apply to this industry. However each premises in the industry will require a site-specific assessment that takes into account features that are present rather than relying on general, industry-wide assumptions as in this paper. The application of the IRR99 is seen in some zircon processing premises, where such site-specific assessments have indicated that the regulations do apply.

The Radioactive Substances Act 1993 (RSA93) [8] regulates the holding of radioactive material and the accumulation and disposal of radioactive waste, principally to control doses to members of the public. Under the provisions of RSA93, all undertakings that use radioactive materials need to be registered and the accumulation and disposal of waste authorized, unless the material is excluded or exempted from RSA93. Although RSA93 applies to natural radioactivity, materials that have activity concentrations of naturally occurring radionuclides (other than those involved in the nuclear fuel cycle) lower than the values given in Schedule 1 of RSA93 are not considered to be radioactive. These can therefore be excluded from the provisions of the Act. In addition to this exclusion, there are a number of Exemption Orders (EOs) made under RSA93 that exempt specific materials from certain provisions of RSA93.

The concentrations of radionuclides in zircon sands and in the wastes produced by the zircon sands processing industry in the UK are above the values presented in Schedule 1 of RSA93 for most radioelements. However, they are all below the values given in the Phosphatic Substances (Rare Earths, etc.) Exemption Order [9]. In certain processes, enhancement of some radionuclides may occur (although other radionuclide activity concentrations may decrease). The main example in the zircon sand industry is during the fusion of material where an enhancement of volatile elements in off-gases and dust could occur, with most of this material being collected in filters. However, using the source term for the report, no radioelements from either general or collected filter material exceed the limits of the EO. It is noted that the activity concentrations used in the report are conservative for zircon sands processed in the UK and the materials used in UK industry may have activity concentrations that are significantly lower than those presented here.

8. SUMMARY

The results of a study to investigate the radiological consequences to the UK population of zircon sands plants operating within the UK are presented. The maximum dose to the workers involved in the processing of zircon sand, and in the manufacture of products from this material, is around 2 mSv/a. This is above the level at which the IRR99 require an assessment to be carried out, and this could lead to the implementation of monitoring and control regimes to limit exposure. It is noted that such regimes are in place in zircon sand processing factories where site-specific assessments have shown that they are warranted. The maximum dose from the disposal of wastes from this industry is 15 μSv/a for exposure occurring at the present time. This exposure is associated with landfill workers where no controls over disposal are in place. However, controls are known to be in place for the disposal of most of the wastes generated by the industry so the doses received by the majority of these workers are thought to be considerably below this level. Future exposure to waste disposed of in landfill could result in doses of up to 750 μSv/a being received by individuals living on the site after it has been developed. However, there is considerable uncertainty in this calculation, so the dose could be significantly below this level. The predicted activity concentration of radon in houses constructed on a landfill that has received waste from the industry could be above the radon action level of 200 Bq/m^3. This indicates that features may be required in any new houses built on the site to limit radon concentrations.

To place the above-mentioned doses in context, it is worth noting that the average annual dose to the UK population is of the order of 2.6 mSv, with a wide variation depending on the location [10].

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NATURALLY OCCURING RADIOACTIVE MATERIAL (NORM) ASSESSMENT OF OIL AND GAS PRODUCTION INSTALLATIONS IN NIGERIA

S.B. Elegba[1], **I.I. Funtua**[2*]

[1]Nigerian Nuclear Regulatory Authority (NNRA), Abuja, Nigeria
[2]Centre for Energy Research and Training, Ahmadu Bello University, Zaria, Nigeria

Abstract

Naturally occurring radioactive material (NORM) assessment was carried out at oil production platforms and gas processing units in Nigeria with the aim of establishing baseline levels and problem areas. The assessment consisted of external radiation measurements on production units, from the wellheads to the product outlets, sampling and gamma spectrometric analysis of scales and sludge from pig stations and of replaced pipes and vessels. The NORM levels on the installations and associated equipment ranged from 0.1 to 15 μSv/h and gamma spectrometric analysis indicates the presence of ^{226}Ra, ^{214}Bi and ^{214}Pb in the scales and sludge, having a maximum concentration of 200 Bq/g. The levels may seem low but there is still the need to establish a routine monitoring programme for the industry, which presently is non-existent.

1. INTRODUCTION

The presence of naturally occurring radioactive material (NORM) in the earth's crust is well known. The ^{238}U, ^{235}U and ^{232}Th series are particularly important as they contain a number of radionuclides that are encountered in oil and gas products, produced water and in all sludge and scale deposits in subsurface and/or surface production facilities.

The acronym NORM, strictly speaking, refers to natural materials containing natural radionuclides in non-enhanced concentrations. The acronym TE-NORM, meaning technologically enhanced NORM has been introduced to distinguish NORM in the strict sense from materials with enhanced natural radioactivity as a result of human technology like oil and gas production.

NORM has developed from a little known issue to one that is receiving a large amount of global attention. The main reason for the increasing levels of concern are mostly from the large amount of NORM waste generated and the potential long term hazards resulting from the fact that NORM consists of long-lived radionuclides with relatively high radiotoxicities. Compared with artificial radioactive sources, the activity levels found in NORM are not large, even when elevated in oil and gas production and processing. The potential hazard lies in the enormous quantity generated. In Nigeria there is now a renewed interest and focus on the regulation of radioactivity, including NORM [1], and the oil industry is the most important sector of the economy with oil exports accounting for 95% of Nigeria's export revenue.

A survey to carry out an assessment of NORM in some oil and gas production installations in Nigeria was undertaken in this study. The survey covered 10 manned offshore production platforms and two land terminals. The land terminals are an oil separation

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[*] E-mail: iifuntua@yahoo.com

production unit and a NGL production facility. The locations of the sites for this survey are not disclosed at the request of the site operators.

2. METHODOLOGY

An external gamma ray dose rate (μSv/h) survey was performed at the surface (1 cm) of well heads, production flow lines, separators, pumps, valves, storage tanks, and associated equipment at each location with a portable RADOS RDS-120 Universal survey meter manufactured by RADOS Technology OY, Finland. The instrument has a scintillation probe and in addition to two external probes, a GM probe and an alpha pancake probe. The measurement range is 0.05 μSv/h to 10 Sv/h with an automatic selection of the measurement range. Prior to each set of measurements at a location, a background reading was performed at positions that were expected not to be influenced by NORM contamination. At each of the 12 locations the major production process line was monitored from the wellhead and pumps areas through the inlet pipes, separators, pumps to the outlet pipes and or storage tanks. Pig stations and replaced pipes on the platforms were also monitored and scales and sludge samples were taken. About 300 in-situ measurements were taken from the 12 installations and 20 samples of scales and sludge were taken for laboratory analysis. In the laboratory the samples were oven dried and later sealed in polyethylene vials for three weeks to allow equilibrium of ^{226}Ra with its decay products. The activity concentrations of the natural radionuclides were determined by low background gamma spectrometry using a 12 h counting time with a HpGe detector having a resolution of 1.90 keV and relative efficiency of 20% at 1.33 MeV. The ^{226}Ra concentrations were derived from the weighted mean activities of the two photon peaks of ^{214}Pb (295.2 and 351.9 keV) and the three photon peaks of ^{214}Bi (609.3, 1120.3, 1764.5 keV).

3. RESULTS AND DISCUSSION

Approximately 300 measurements were performed at the surface of various components and equipment. The gamma dose rates ranged from 0.1 to 15 μSv/h with a background value of 0.05–0.10 μSv/h. Most of the measured values were within the background values. In the gas plant the highest value of 0.14 μSv/h was measured at the pentane transfer pump area. This is not surprising, since radon in the NGL facility tends to be higher in pump and valve areas.

The highest measurements of 10–15 μSv/h were found at pig receiver stations and wellheads. These values are lower than most reported values elsewhere [2, 3].

In assessing the occupational doses for workers at the 12 facilities, the most important factors are the dose rates and working time spent during normal activities and repairs. The exposure pathways are external exposure to gamma radiation, internal exposure to radon and radon daughters and inhalation of contaminated dust. The occupancy factors used to assess the occupational doses were 10 and 20 h/a for normal activities and repairs. The annual effective doses for the workers were not significant, at less than 3 μSv/a for most of the locations. Even if the occupancy factors were doubled, the doses to the workers would still have been relatively low.

With the low dose values for the monitored areas, NORM appears not to be an immediate problem but still requires a monitoring programme, since mobilization of NORM increases with the lifetime of operations and the appearance of NORM also varies strongly between reservoirs, individual wells, installations and production conditions.

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NORM IN BUILDING MATERIALS

C. Aliyev[*]

Geology Institute of Azerbaijan, National Academy of Sciences, Azerbaijan

Abstract

According to standards of radiation safety, the 'effective' activity concentration C_{ef} of a building material is defined by the expression $C_{ef} = C_{Ra} + 1.31C_{Th} + 0.085C_K$ and thus depends on the concentrations of selected radionuclides. C_{ef} should not exceed 370 Bq/kg. Gamma-spectrometric investigations in Azerbaijan demonstrated that C_{ef} for building materials manufactured from natural raw materials varied from 30 to 190 Bq/kg. The average C_{ef} for Azerbaijan was 69 Bq/kg. Products made from artificial materials should not contain radionuclides. Investigations demonstrated that C_{ef} sometimes exceeded the standard by 10 times (3800 Bq/kg) because of the increased amount of radium. This increases the hazard associated with the use of the material. Cases are known where sources of ionizing radiation have been lost while manufacturing building blocks of cement and concrete. When incorporated into dwellings they create a hazardous situation. The use of highly radioactive industrial wastes to manufacture bricks or cement for floors was discovered. These findings demonstrate the urgency of having constant control over the quality of the products used in the construction of buildings and dwellings. The most effective and economic technique for quality control of building materials is gamma-spectrometric analysis. This method is scientifically based and has proved to be practical.

1. INTRODUCTION

People in highly developed countries spend most of their time indoors. For this reason it is very important to know how favourable the situation is inside their premises. It is very well known that people are irradiated mainly by natural sources of ionizing irradiation, which exist in all building materials. The amounts of natural radionuclides in these materials vary greatly — from background levels to levels that exceed background by 200 times or more. In industrial countries this problem is being considered very seriously.

In the Former Soviet Union, investigations were conducted in all constituent Republics. The 'effective' activity concentration of natural radionuclides in building materials utilized in Azerbaijan, defined by the expression

$$C_{ef} = C_{Ra} + 1.31C_{Th} + 0.085C_K$$

was, on average, 69 Bq/kg. This was half the value found in some other Republics.

Special investigations relating to standards for radionuclides in building materials were conducted in Azerbaijan[1] As a result, 'Provisional Republic standards of radioactivity of building materials' (PCH 31-93 Gosstroy Az. R) were prepared in 1993. Not withstanding their date of preparation and provisional character, they are still used as standards for building materials. During this time, new brands of cements and imported building materials manufactured from hazardous toxic waste appeared. Gosstroy (the State Construction

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[*] E-mail: radiometry@gia.ab.az

[1] Under the supervision of F.G. Aliev with the participation of M.B. Brodskaya, F.A. Aslanov and others.

Administration) needs to systematically conduct radiometric monitoring and strengthen requirements for the quality of building materials. Items for interior use, such as suspended ceilings, plastic frames, need to be made of materials absolutely free of radioactive materials. If radioactivity exists in the material, it demonstrates improper quality of the initial material and the finished product.

One of the main methods of control over the properties of the initial material and the finished product is gamma-spectrometric analysis. We can illustrate this by results of gamma-spectrometric analysis of building materials carried out in the Radiometry Laboratory of the Geology Institute of ANAS. Table I shows the results of a gamma-spectrometric examination of suspended ceilings.

TABLE I. RADIOACTIVITY IN SUSPENDED CEILINGS

Sample no.	Activity concentration (Bq/kg)			
	U (Ra)	Th	K	C_{ef}
1	0	0	0	0
2	0	0	0	0
3	2.53	0	0	2.53
4	2.93	0	0	2.93
5	5.06	0	0	5.06
6	6.01	0	34.50	8.72
7	44.59	0	382.77	74.60
8	51.97	0	387.03	82.31
9	270	0	36.86	273.09
10	279	0	34.54	283.63
11	386	0	4.01	386.72
12	399	0	39.33	402.44
13	401	0	173.19	415.15
14	417	0	0	417.37
15	421	0	12.51	424.03
16	424	0	15.28	426.1
17	447	0	0	447.98
18	445	0	9.83	445.93
19	452	0	47.89	456.20

According to the Standard of Radioactive Safety 76/87 (SRS 76/87), C_{ef} of natural radionuclides in the building materials should not exceed 370 Bq/kg. Table I demonstrates that C_{ef} exceeded the standard in the many of the samples of suspended ceilings, essentially because of the increased amount of radium in the material. Radium is the source of the radioactive gas radon, which is a human health hazard. According to data from the investigation, these ceilings have a high rate of radon emanation, increasing the radiological risk. Ceilings free of radioactive elements exist. This shows that gamma-spectrometric analysis may be of help in choosing radiologically safe ceilings. Figs 1(a) and 1(b) present spectrograms of uncontaminated ceilings and ceilings contaminated by radioactive elements.

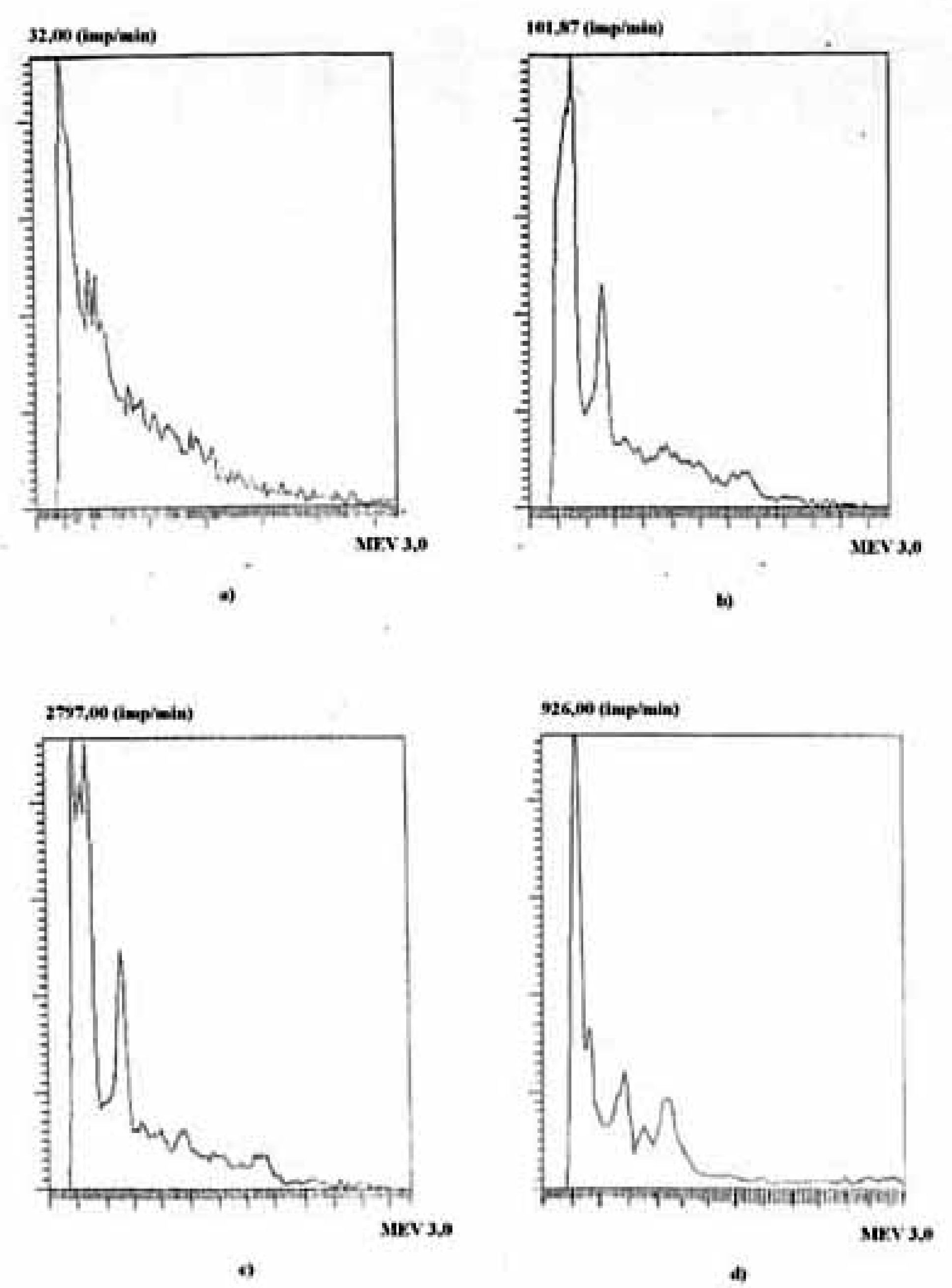

FIG.1. Spectrograms of building materials: (a) suspended ceiling with normal content of radioelements; (b) suspended ceiling with high content of radioelements; (c) brick with high content of radioelements; (d) asbestos pipes polluted by radioelements

Table II presents the results of a gamma-spectrometric examination of bricks. It shows that radioactivity in bricks varies greatly. Since bricks are made of natural materials, they always contain some uranium, thorium and potassium. During the firing of bricks, the concentration of radioactive elements grows. The amount of potassium in the bricks is always increased because they are made of clay containing uranium and thorium. The bricks made of artificial materials with an increased amount of radioactive elements are not suitable for the construction of dwellings and public buildings. Thus, bricks made of 'vinofiline' and industrial waste contain a high amount of uranium and thorium, and this makes the situation more hazardous. These bricks can be used during the construction of pipelines beyond districts. Fig. 1(c) shows a gamma-spectrum of a brick with enhanced thorium content.

TABLE II. RADIOACTIVITY IN BRICKS

Sample no.	Name	Activity concentration (Bq/kg)			
		U (Ra)	Th	K	C_{ef}
1	Pink brick	14.49	2.85	230.35	36.29
2	“Elbrus» brick	17.54	0	488.99	55.88
3	Red brick (Zabrat)	24.18	10.61	477.04	75.49
4	Brick (Geokchai)	41.77	5.84	417.86	82.19
5	Dight-grey brick	35.11	13.92	427.60	86.87
6	Red brick	28.95	21.63	455.08	92.97
7	Light brick (Iran)	70.65	0	446.85	105.68
8	Brick (Salyany)	25.98	21.30	679.00	107.12
9	Brick (Ali-Bayramly)	50.79	9.27	635.85	112.79
10	Red brick (Zykh)	16.74	47.37	695.82	133.36
11	3-sh5 brick light with brown intrusions	49.24	67.97	181.77	152.54
12	Brick (Masalli)	152.47	0	474.68	189.68
13	Vinofiline brick	794.17	207.43	341.65	1092.71
14	Industrial waste brick	1066.93	278.38	420.63	1464.58
15	Vinofiline brick	1146.76	289.62	367.79	1555.00
16	Industrial waste brick	1651.85	430.13	666.04	2267.54
17	Industrial waste brick	1738.76	459.67	636.51	2390.83
18	Industrial waste brick	2200.56	578.3	980.99	3035.05
19	Industrial waste brick	2893.82	648.62	835.23	3808.99

Table III presents the results of gamma-spectrometric analysis of radioactive elements in various other building materials. According to the Table, C_{ef} for tiles varies greatly and depends on the amount of natural radioactive elements within them. The paints are active due to their potassium content. Special attention should be paid to concrete and cement and to goods made of them. There were cases when lost radiation sources were occasionally buried in concrete blocks. People and especially children who lived in flats constructed of such blocks were exposed to strong irradiation with lethal consequences. It is very important to know what cement and concrete are made of. Once we revealed sources of ionizing radiation in cement on the floor of a shop in a student hostel. It turned out that the cement had been manufactured using iodine factory waste, namely activated charcoal containing a high amount of radium. After decontamination of the shop, the radiation levels are at normal background levels. Another source of radiation hazard is the material used for the insulation of the heating system — such objects are asbestos pipes.

TABLE III. RADIOACTIVITY IN OTHER BUILDING MATERIALS

Sample no.	Description	Amount of radioactive elements, Bq/kg			
		U (Ra)	Th	K	C_{ef}
1	Window frame	0	0	0	0
2	White paint	0	0	59.51	4.66
3	White paint STR KO	0	0	126.62	9.92
4	Bulgarian tile	28.14	14.80	194.81	62.80
5	Greenish tile	70.82	62.15	242.37	171.25
6	‘Slavyanski’ tile	96.04	82.55	276.77	225.88

So we tried to present information about unfavourable results of radiometric monitoring of building materials. We would like to attract Gosstroy’s attention to the need for developing standards on the amount of radionuclides in the building materials and to the intensity of radiometric monitoring in this field.

A solution to these problems is possible only by analysing the results of a wide-ranging gamma-spectrometric examination of building materials. Systematic documentation of this examination is available from the Radiometry Laboratory of ANAS.

WATER CONTAMINATION

NATURAL RESTORATION OF A SPANISH ESTUARY AFFECTED BY ANTHROPOGENIC INPUTS OF NORM

M. Villa[1], A. Absi[2], H.P. Moreno[3], G. Manjón[2*], R. García-Tenorio[2], R. Periáñez[4]

[1]Facultad de Física. Universidad de Sevilla, Departamento de Física Atómica, Molecular y Nuclear, Sevilla, Spain
[2]ETS Arquitectura, Universidad de Sevilla, Departamento de Física Aplicada II, Sevilla, Spain
[3]EU Arquitectura Técnica, Universidad de Sevilla, Departamento de Física Aplicada II, Sevilla, Spain
[4]EUI Técnica Agrícola, Universidad de Sevilla, Departamento de Física Aplicada I, Sevilla, Spain

Abstract

The Huelva estuary, located in the southwest of Spain, has been historically affected by waste releases from several factories located in its surroundings and devoted to the production of phosphoric acid and phosphate fertilizers. These wastes, clearly enriched in radionuclides belonging to the uranium series, were stored in open air piles or directly released to the Odiel River. The clear radioactive impact that they have produced in several compartments of the estuary is quite well documented. Fortunately, the waste policy of these factories changed drastically in 1998. Since then, all the wastes are stored in well-protected piles with no interaction with the surrounding environment as before. This means that the input of natural radionuclides from the factories to the estuary has ceased. For that reason, a new time-evolution of the activity concentration of natural radionuclides in these estuarine compartments is expected. In order to analyse the temporal evolution of the contamination in the estuary by natural radionuclides from the interruption time of the releases until the present, the activity concentrations of some natural radionuclides (^{226}Ra, U isotopes, ^{210}Po, ^{210}Pb) in water and sediment samples collected in three different campaigns (1999, 2001 and 2002) have been determined. These results, as well as the activity ratios, are presented in this paper and compared with those determined before 1998, when the releases still occurred. The observed trend shows clearly that the contamination of the estuary by natural radionuclides is decreasing since the change in waste policy, and that the radioactive levels in the waters and sediments are approaching the natural background values of the zone. Consequently, in a few years, a total natural decontamination in natural radionuclides of the Huelva estuary can be expected.

1. INTRODUCTION

The Huelva estuary is located in the southwest of Spain. Two rivers, the Odiel River and the Tinto River, together with a system of channels and several large flat areas affected by tidal flooding, are the main elements of this estuary (see Fig. 1). Anthropogenic enhancements of metals and radioactive elements in the waters and sediments of both rivers have been caused in the past by pyrite mines operating since the Roman Empire period and located on the river heads, and also by an industrial complex located near the mouth of the Odiel River.

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[*] E-mail: manjon@us.es

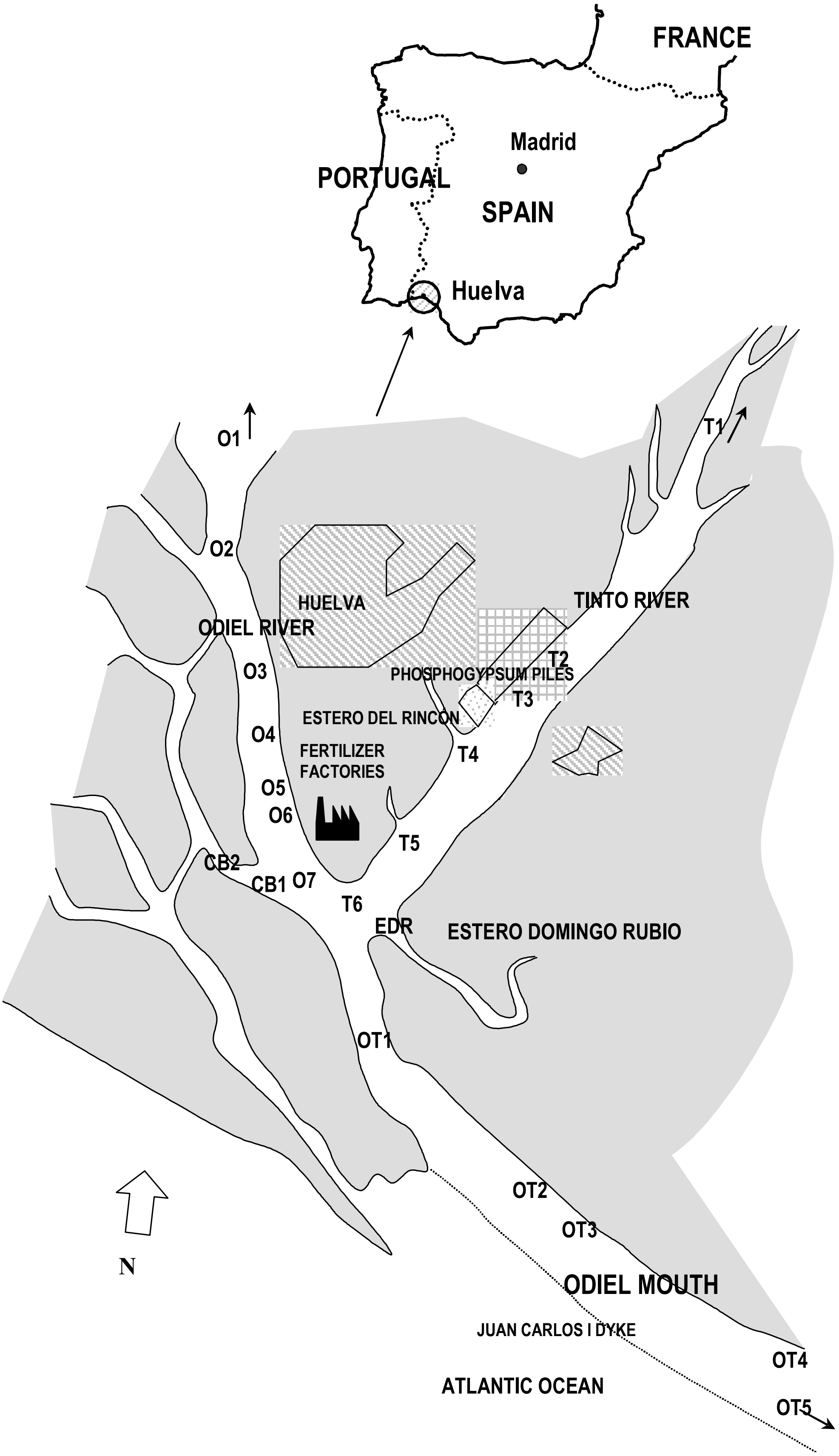

FIG. 1. Map of the estuary of Huelva where the samples of water and sediment were collected

The pyrite mining operations upstream of the Odiel and Tinto rivers have in the past resulted in the formation of H_2SO_4, through oxidation of the natural sulphur deposits, the acidification of the waters and the consequent mobilization of heavy metals from the mining area to the Huelva estuary. Therefore, the sediments located near the mining area are characterized by a low pH (1.9–5.0) and a low concentration of metal due to leaching [1], while high concentrations of heavy metals, i.e. iron and zinc, have been observed in the corresponding waters (pH 1–4) [2]. In contrast, high metal accumulations in sediments are found in large areas of the estuary, where the pH of river waters increase to neutral values due to tidal actions (mixture with sea water) [1]. The sudden change of the water pH to neutral values provokes the precipitation of the heavy metals transported by the waters from the mining areas, and their accumulation in sediments. The spatial heavy metal distribution in this estuary is, on the other hand, not homogeneous, with preferential accumulations in zones where sediments of small grain-size are deposited.

In addition, several industries located along the banks of the estuary have released into the estuary a large amount of heavy metals since the 1960s, increasing the contamination levels of its sediments. Also, two quite large phosphoric acid factories have, since the mid-1960s, produced enormous amounts of phosphogypsum wastes, which were either released directly to the Odiel River (until 1998) or, mainly, were stored in open air piles. For that reason, a total surface area of 1.2×10^7 m^2 of phosphogypsum deposit stretches down to the Tinto River mouth (see Fig. 1). These piles can be considered as an important source of contaminants in the estuary water due to the washing up caused by tidal action.

The direct or indirect releases of phosphogypsum produced radioactive contamination of different compartments of the estuary because these wastes were highly enriched in ^{238}U daughters, i.e. ^{226}Ra, ^{230}Th, ^{210}Pb and ^{210}Po. A considerable fraction of these radioactive contaminants has been then transferred in the past to the estuarine sediments, and spatially distributed by the tidal action. The evolution of this contamination over time has been analysed by studying either $^{226}Ra/^{228}Ra$ or $^{230}Th/^{232}Th$ activity ratio depth profiles in sediment cores [3].

Recently, the phosphogypsum wastes have been stored exclusively in a well-isolated pile that is protected against the tidal leaching, and direct releases into the Odiel River are forbidden. According to this new waste management policy, since 1998 lower radioactive levels can be expected in the estuary.

The radioactive impact in the Odiel estuary has been studied continuously since 1988 [4–7] and for that reason the time-evolution of this impact, before the change in waste treatment policy, can be deduced from the constructed database. Additionally, a first approach to the evaluation of the radioactive cleaning processes in the estuary can be found in Ref. [8], were the case of ^{226}Ra was studied.

In this paper, we present the activity concentration of natural radionuclides in water and sediment samples collected in three campaigns performed in the Huelva estuary after 1998. The objective was to analyse the temporal evolution of the contamination after the change in the management of the phosphogypsum wastes and to analyse the effectiveness of the natural radioactive cleaning processes in the area.

For the evaluation of the degree of radioactive contamination in the estuary and the time-evolution of the cleaning, quite precise values for the natural radioactive background need to be established. To that effect a broad definition of contaminant was recently published [9]. According to Ref. [9], a contaminant is a component added to a sedimentary reservoir at concentration levels higher than the defined natural background. However, it should be borne in mind that the values of the natural background may be non-homogenous in the analysed area because several factors determine the distribution pattern of minerals and elements in an estuary (e.g. the sediment grain size and the physical-chemical conditions of waters and hydrology) [10]. For that reason, an accurate determination of the natural background levels could be achieved by taking deep sediment distributed across the estuary as a reference [9]. Alternatively, it may only be possible to estimate the natural background from onshore sediments.

2. EXPERIMENTAL

Three sampling campaigns were performed — in 1999, 2001 and 2002. Samples of surface water and surface sediment were taken at every sampling station at low tide. Water samples were filtered and acidified for better preservation. Sediment samples were dried and homogenized before analyses. The sampling stations can be classified into three different geographical zones (Fig. 1): the Odiel River, where direct waste discharges were carried out before 1998; the Tinto River, close to the phosphogypsum piles; and the common Odiel-Tinto mouth, where tidal effects are clearly observed.

Different radiochemical treatment processes were applied to determine the activity concentration of each radionuclide. The concentration of ^{226}Ra in water was determined using a liquid scintillation counter, using the radiochemical separation and measurement methods described in Ref. [11] or using a Berthold LB 770 gas-proportional counter [12], while ^{226}Ra in sediment samples was determined by liquid scintillation counting using a Quantulus Wallac 1220, following the radiochemical procedure described in Ref. [8]. In both cases, the radiochemical procedure was based on co-precipitation of the Ra isotopes with $BaSO_4$. Other alpha-emitting radionuclides, such as uranium isotopes and ^{210}Po, were measured by alpha spectrometry using PIPS detectors. After the application of a sequential solvent extraction technique, the ^{210}Po was self-deposited in a silver disc [6], while the uranium isotopes were electroplated onto stainless steel planchets according to Ref. [13]. Finally ^{210}Pb was determined by liquid scintillation counting, applying a radiochemical method based on the precipitation of ^{210}Pb through precipitation of $PbSO_4$ (a slight modification of the radiochemical procedure described in Ref. [14]).

The procedures and techniques described above were validated through participation in several intercomparison exercises, and/or by their application to reference material.

3. RESULTS AND DISCUSSION

3.1. Natural radionuclides in river water

The time pattern of the activity concentrations of ^{226}Ra, ^{238}U and ^{210}Po in the Odiel River water close to the fertilizer factories is shown in Fig. 2. The radiological effect of direct discharges into the zone can be clearly observed in the samples collected before 1998. In the case of ^{226}Ra, the activity concentration in 1990 reached levels higher than 600 mBq/L, whereas the levels were lower than 14 mBq/L after 1998. Moreover, the ^{226}Ra activity concentration was 5 mBq/L in 2002, which can be considered as the natural background value of the estuary. The natural background activity concentrations are listed in Table 1. These values were determined in samples collected far from the waste pipes and the phosphogypsum piles. In this sense, if we define an index called the ‘enhancement factor’ as the ratio (in the same compartment) of the activity concentration before 1998 to that in 2002 as a way to quantify the different levels of contamination existing before and after the change in the phosphogypsum waste management policy, we can indicate that in the Odiel river waters the ^{226}Ra enhancement factor is about 11.

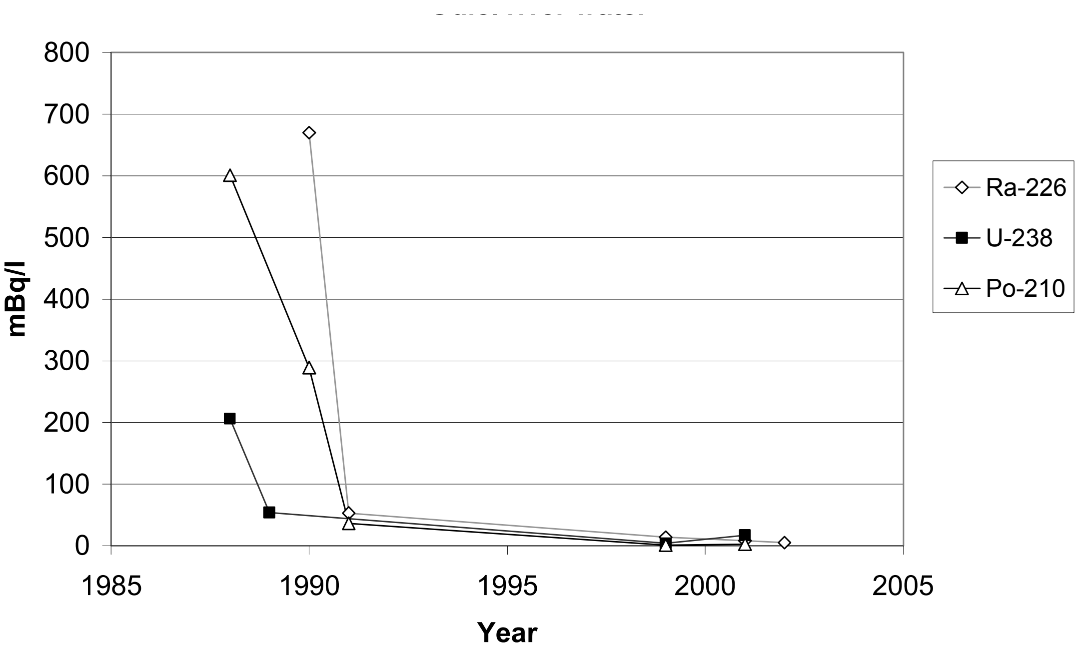

FIG. 2. Natural radioactivity in Odiel River water close to the phosphate factories

TABLE I. LOWEST ACTIVITY CONCENTRATIONS IN THE ODIEL RIVER ESTUARY FAR FROM PHOSPHORIC ACID PLANTS (Indicative of natural background for the purpose of evaluating the radiological impact of the plants)

Radionuclide	Activity concentration		
	Seawater (mBq/L)	River water (mBq/L)	Sediment (Bq/kg)
^{226}Ra	4.7 ± 0.5	7.0 ± 0.6	19 ± 1
^{238}U	43.0 ± 1.6	1.7 ± 0.2	4.4 ± 0.2
^{234}U	49.2 ± 1.8	1.9 ± 0.2	4.9 ± 0.2
^{210}Po	1.0 ± 0.1	1.0 ± 0.1	14.8 ± 0.7
^{210}Pb	—	—	24 ± 2

The decrease with time was also observed for the ^{238}U activity concentration in the Odiel River water collected close to the fertilizer factory — the enhancement factor was 12. These results correspond to samples collected at low tide. If we were to compare the results obtained after 1998 to those obtained before 1998 in samples collected at high tide, the decrease would be higher because the direct phosphogypsum discharges to the Odiel River were regularly done during periods of high tide.

Fig. 3 shows the activity concentrations of ^{226}Ra and ^{238}U in the Tinto River. This water was collected in the neighbourhood of the phosphogypsum piles and was affected by them in the past because some of the radionuclides in the phosphogypsum piles were transported into the Tinto River by river water that interacted with the piles due to tidal action or rainfall. The activity concentrations have also decreased in this zone because of the environmental protection measures implemented in the new phosphogypsum piles. However, a continuous decrease, such as the one observed in the Odiel River, was not observed — large quantities of radionuclides from the phosphogypsum entered the Tinto river in 1998 as a result of an accident.

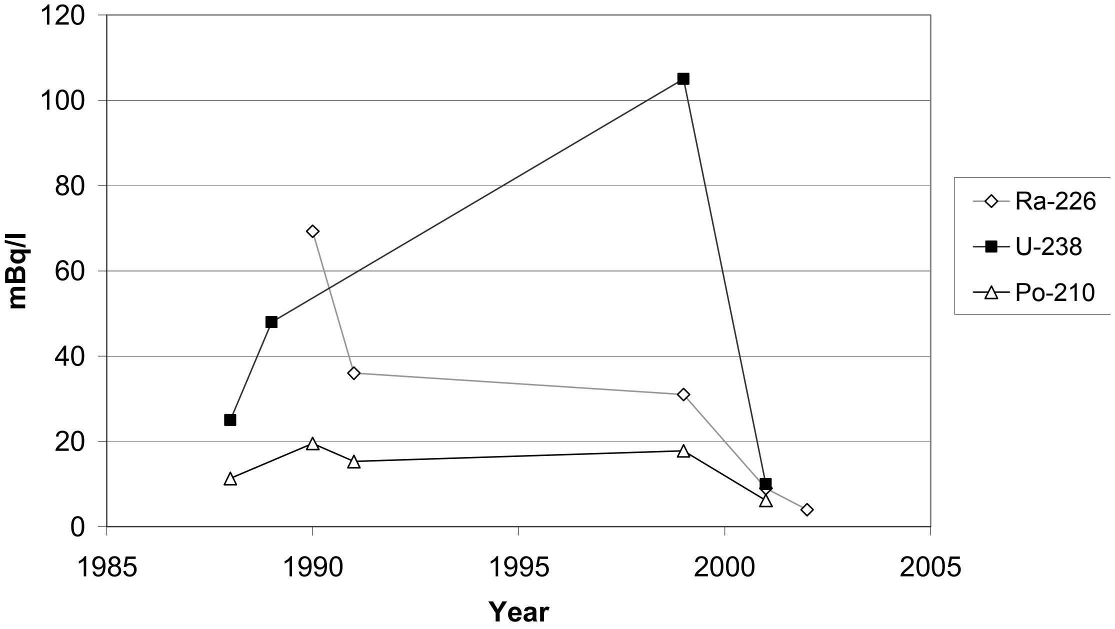

FIG. 3. Natural radioactivity in Tinto River water close to the phosphogypsum piles

The activity concentrations of natural radionuclides in samples collected in 2001 and 2002 might be considered as representative of the natural background in that area. An accurate level of background cannot be determined because of the dependence of activity concentration in water on the seawater and river water mixture. For instance, the background level of ^{226}Ra in seawater is 4.7 ± 0.5 mBq/L but is 7.0 ± 0.6 mBq/L in river water (Table I).

3.2. Natural radionuclides in river sediments

The activity concentrations of natural radionuclides (^{226}Ra, ^{238}U, ^{210}Pb and ^{210}Po) in Odiel River sediment samples collected close to the fertilizer factories are shown in Fig. 4. For each radionuclide, the activity concentrations show a clear time-dependence, decreasing with time after 1998 when the direct discharges of phosphogypsum in the Odiel River was stopped. This behaviour has also been observed in a zone of the Cumbrian coast affected by releases of phosphogypsum, although in that case the activity concentration decrease was related to the dilution and dispersion of the anthropogenic enhancement by tidal flows [15].

In the Odiel River sediments, the activity concentrations of natural radionuclides were in the range 800–1200 Bq/kg in samples collected before 1998, whereas the range decreased to 200–600 Bq/kg in samples collected after 1998. However, these levels remain significantly higher than the background levels in the area (Table I). That means that the dissolution of radionuclides from the sediments and/or the addition of inert material on the surface sediments is slow, and a fraction of those radionuclides released into the river and deposited in sediments remains stored for years.

The activity concentrations of natural radionuclides (^{226}Ra, ^{238}U, ^{210}Pb and ^{210}Po) in sediment samples collected in the Tinto River are shown in Fig. 5. These samples were also collected close to the uncovered phosphogypsum piles. The activity concentrations have decreased with time in these superficial sediments and a typical natural background level was obtained for each radionuclide analysed in the most recent sample. For instance, the ^{226}Ra activity concentration was 28 Bq/kg in 2002, being within the range of activity concentrations in the Spanish Tagus River (13–100 Bq/kg) [16].

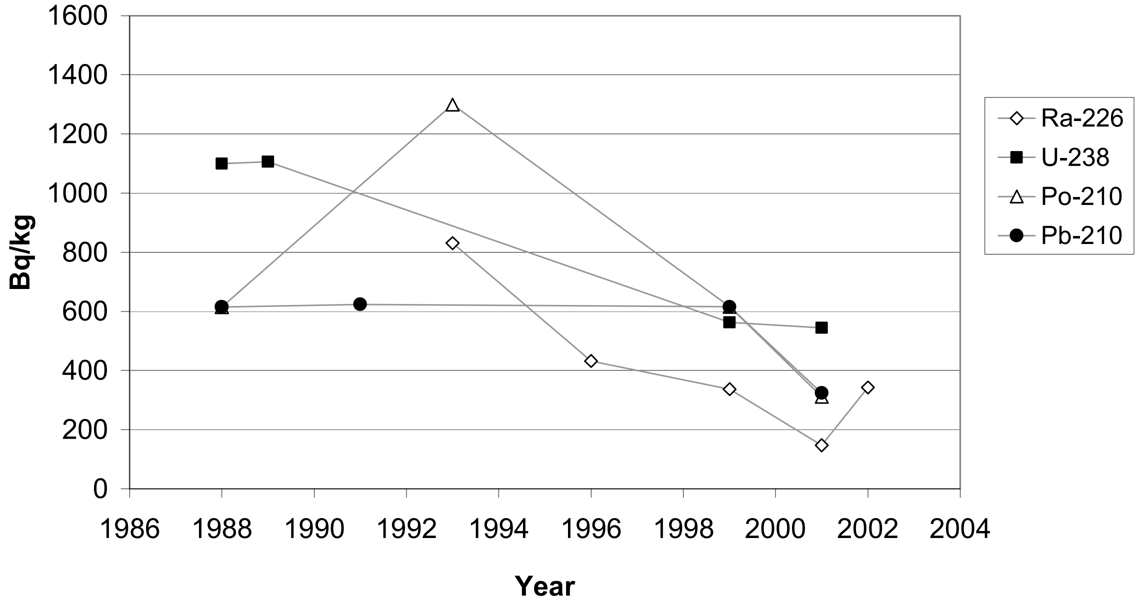

FIG. 4. Natural radioactivity in Odiel River sediments close to the phosphate factories.

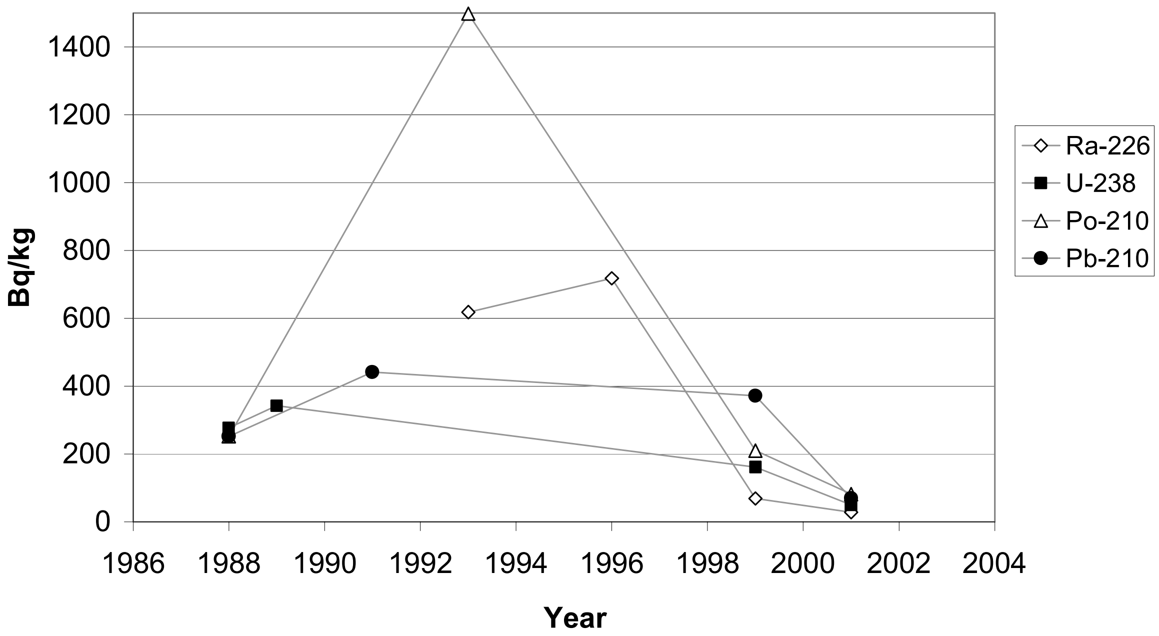

FIG. 5. Natural radioactivity in Tinto River sediments close to the phosphogypsum piles

3.3. Activity ratios ^{234}U/^{238}U after 1998

3.3.1. Water samples

The ^{234}U/^{238}U activity ratios calculated in all river water samples located in the three areas into we have divided the Huelva estuary (Fig. 1) are shown in Fig. 6, and are presented separately. Significant differences were found, depending on the area analysed. In the Odiel River samples, the range of U isotope ratios is quite large: 1.0–1.5, with the higher values corresponding to samples with lower concentrations of these radionuclides and to waters transporting this element from the mining area and not affected by the phosphogypsum releases. In contrast, the samples from the Odiel river with the lower values of the U isotope ratio showed a wide range of activity concentrations of this nuclide, indicating different simultaneous sources of uranium (seawater, former wastes stored in sediments and lixiviation in the mining area).

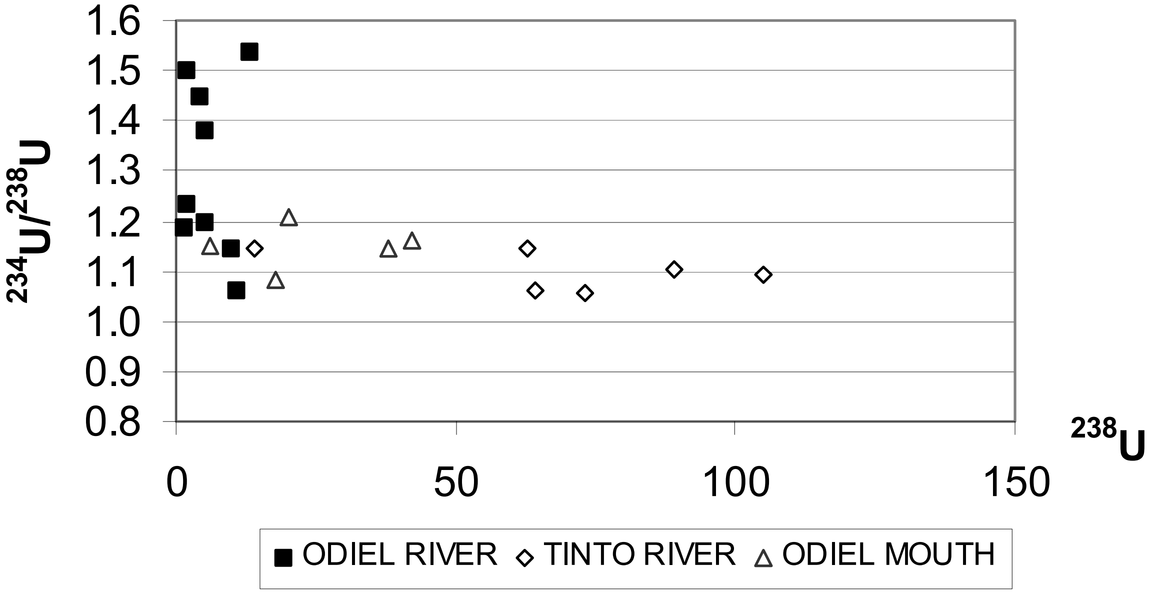

FIG. 6. Activity ratio $^{234}U/^{238}U$ versus ^{238}U activity concentration (mBq/L) in river water, 1999

The U isotope ratio in the Tinto River water shows a slight decrease with activity concentration. The activity ratio range was 1.0–1.2. An activity ratio of about 1.2 indicates uranium of natural origin (seawater or sediments of the mining area), whereas the activity ratio in phosphogypsum is about 1. This indicates that the uranium in these samples had dissolved or leached from the uncovered phosphogypsum piles, especially after the accident happened in 1998, depending on the activity ratio. The final ^{234}U/^{238}U activity ratio in the water samples collected in the Odiel mouth was about 1.2 (a typical non-perturbed activity ratio in marine waters). The vast majority of the water in this area of the estuary is of marine origin.

3.3.2. Sediment samples

The ^{234}U/^{238}U activity ratios versus ^{238}U activity concentration in sediment samples collected along the Huelva estuary are shown in Fig. 7, from which it can be seen that in the Odiel River the ratio is close to unity, indicating possible contamination by uranium associated with wastes discharged by factories. In the Tinto River, the activity ratio decreases with activity concentration, indicating possible contamination with uranium associated with the phosphogypsum deposits. Finally, in the Odiel mouth the activity ratios are close to unity, indicating also the presence of uranium associated with phosphogypsum wastes. Thus, the impact of the fertilizer factories can be observed in sediments covering the majority of the estuary bed — this demonstrates the importance of the tidal activities in the redistribution of the contamination through the estuary.

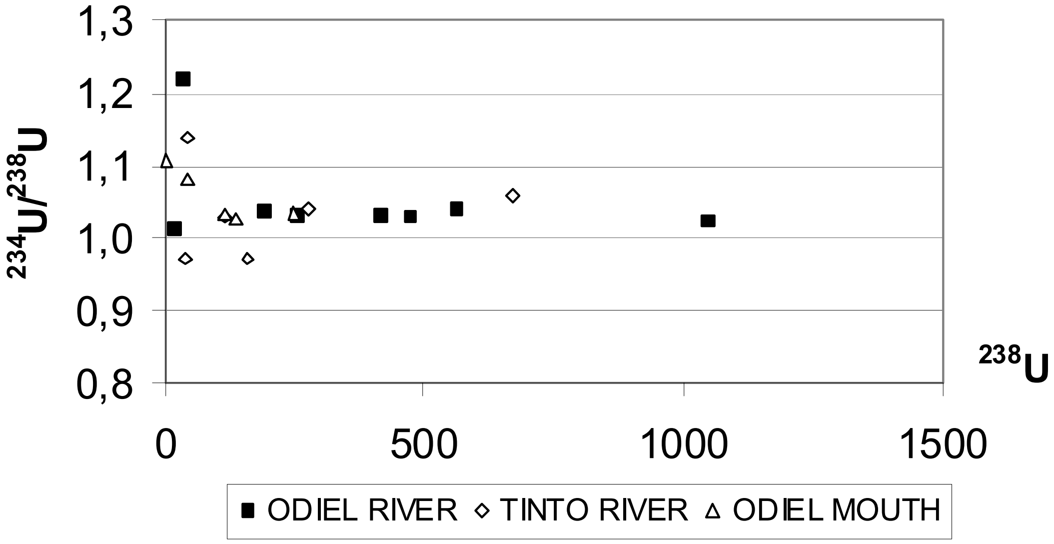

FIG. 7. Activity ratio $^{234}U/^{238}U$ versus ^{238}U activity concentration (mBq/L) in sediment, 1999

3.4. Activity concentration of ^{238}U in water, and conductivity

The conductivity of water is related to the salinity. Thus, high conductivities in seawater and low conductivities in river water are expected. The presence of seawater in the Huelva estuary causes typical high conductivity levels in the river waters. Thus, the conductivity can be used to characterize the mixture of seawater and river water in estuarine water. The activity concentration of ^{238}U versus conductivity in river water samples collected in 1999 and 2001 is shown in Figs 8 and 9 respectively.

In the Odiel River and the Odiel mouth, the activity concentration increases with conductivity, meaning that the presence of seawater in the river is related to higher activity concentrations. Similar results have been reported for the Domingo Rubio rivulet [17]. Only one sample showed a high activity concentration and a low conductivity. In this case, the origin of uranium was due to lixiviation in the mining area and transport to the estuary.

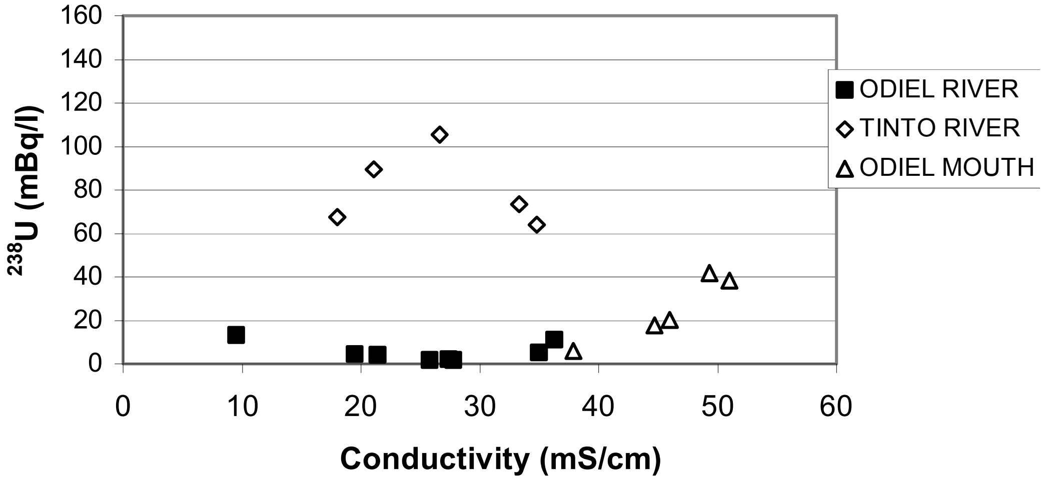

FIG. 8. Activity concentration of ^{238}U versus conductivity in river water, 1999

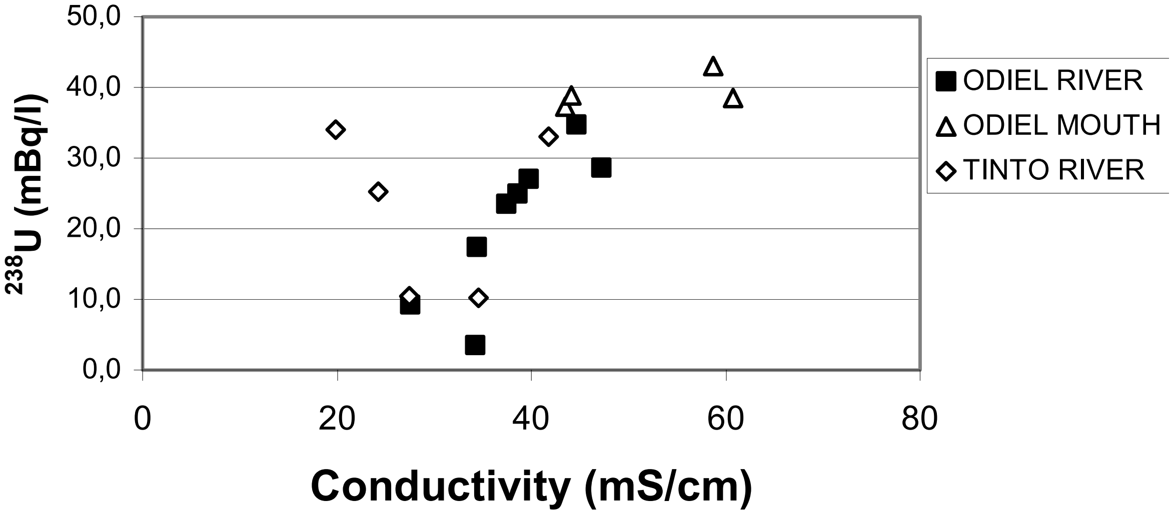

FIG. 9. Activity concentration of ^{238}U versus conductivity in river water, 2001

In the Tinto River, the activity concentration versus conductivity in samples collected in 1999 showed a maximum. In this case, the uranium content was affected by the accident involving the phosphogypsum piles, and activity concentration cannot be related to conductivity. The maximum activity concentration corresponds to Estero del Rincón, a rivulet located close to the phosphogypsum piles. Estero del Rincón (Fig. 1) could be the main radionuclide migration route from the phosphogypsum piles into the Tinto River. However, the correlation between ^{238}U activity concentration and conductivity is not clearly observed in the samples collected in 2001. In this case the origin of uranium might be the lixiviation of sediments in the mining area and transport to the estuary.

3.5. Activity ratio ^{210}Pb/^{210}Po

The ^{210}Pb/^{210}Po activity ratios calculated in sediment samples in 1999 and 2001 are shown in Fig. 10. Most samples show activity ratios around unity, regardless of the activity and the sampling area. The average ^{210}Pb/^{210}Po activity ratio for the whole estuary in both years was 1.0 ± 0.3 for 1999 and 1.2 ± 0.3 for 2001. These data show the existence of secular equilibrium between ^{210}Pb and ^{210}Po in riverbed sediments from the estuary. The values are significantly higher than the expected value in a non-contaminated area or a harbour area affected by phosphate mineral loading [18]. The data also indicate that the cleaning process of the sediments from the estuary is taking place equally for ^{210}Pb and ^{210}Po.

3.6. Activity ratio ^{210}Pb/^{226}Ra

The ^{210}Pb/^{226}Ra activity ratio calculated in sediment samples collected after 1998 is shown in Fig. 11. The activity ratio generally remains between 1 and 2, although sometimes higher. Most ratios are greater than 1. The average value was 2 in 1999, and 3 in 2001. These results are similar to those obtained before 1998, when the average activity ratio was 2.6 [17]. In the samples collected before and after 1998, there was an excess of ^{210}Pb that could not be attributed exclusively to unsupported ^{210}Pb, given that the ^{210}Pb activity is 100 Bq/kg higher than the ^{226}Ra activity in some cases.

The disequilibrium is attributed to the differing geochemical behaviour of the two radionuclides. Generally speaking, ^{226}Ra is more soluble than ^{210}Pb. Furthermore, the desorption/dissolution of ^{226}Ra in water increases with increasing salinity [19, 20]. When the phosphogypsum containing ^{226}Ra and ^{210}Pb was released to the river, ^{210}Pb was associated with the suspended matter and part of it was precipitated to the river bed. Because ^{226}Ra remained longer in the soluble phase, the content of ^{226}Ra in the river bed sediments was lower and the ^{210}Pb/^{226}Ra activity ratio was greater than 1.

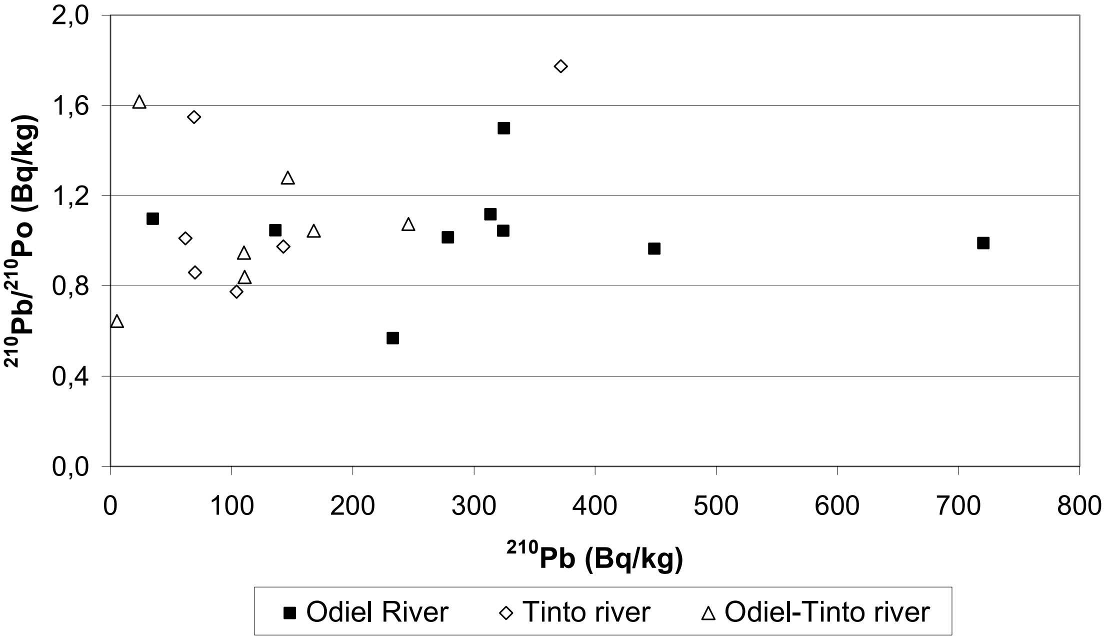

FIG. 10. Activity ratio ^{210}Pb/^{226}Ra in river water, 1999

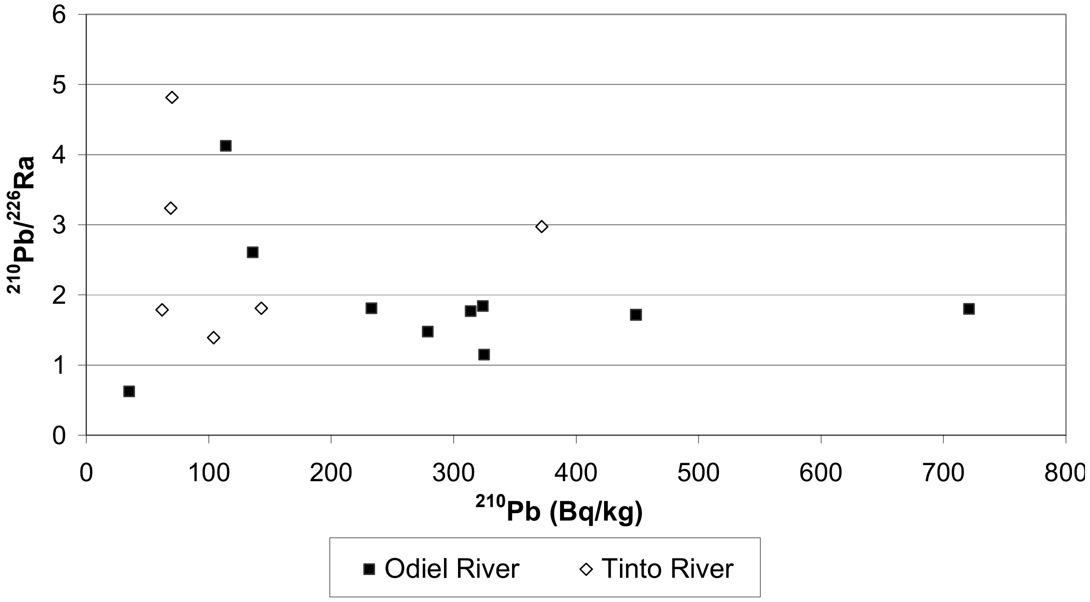

FIG 11. Activity ratio ^{210}Pb/^{226}Ra in sediments, 1999

4. CONCLUSIONS

The activity concentrations of natural radionuclides in the Odiel River estuary have decreased in recent years due to the discontinuation of direct waste releases and a well-designed protection system for new phosphogypsum piles. Activity concentration levels in sediment samples have decreased but they remain two orders of magnitude above the natural background of the area. The radiological impact of an accident that occurred in a new phosphogypsum pile was evaluated through the increase of activity concentration in Tinto River water samples collected in 1999.

ACKNOWLEDGEMENTS

This work was partially supported by ENRESA, EU-contract 1FD97-0900-C02-01 (AMB) and UE-contract REMOTRANS. The help of Junta de Andalucía (Regional Government of Andalusie) in the sampling campaigns is acknowledged.

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EXAMINING THE NATURAL RADIOACTIVITY OF WATER SOURCES TO EVALUATE THE IMPACT ON SURROUNDING COMMUNITIES

A. Faanhof[1], **P. Kempster**[2]

[1]South African Nuclear Energy Corporation, Pretoria, South Africa
[2]Institute for Water Quality Studies, Pretoria, South Africa

Abstract

Naturally occurring radioactive material (NORM) is quite common in the South African mining and mineral processing industry, to the extent that uranium is even produced as a by-product at certain gold and copper mining sites. Other major industries associated with NORM are the coal, copper and heavy minerals sectors. Legislation in South Africa addresses the maximum allowable annual radiation dose received by workers and the general public, and adheres to the internationally accepted standards of 20 mSv/a and 1 mSv/a respectively for these categories. The annual dose is obviously the sum of the contributions from every individual radionuclide from all possible sources. Accordingly, for members of the public, individual sources have to be evaluated at the (South African) guideline level of 25 μSv/a. This imposes severe constraints on the ability of the radioanalytical laboratory to offer an affordable routine service, due to the sensitivity required to analyse these NORMs and the variety of matrices involved. Determination of all required parameters to evaluate the annual dose is possible, although costly. Correlations of annual dose with one or two chemical/radionuclide components will allow an affordable monitoring strategy. According to the evaluation of a survey performed in one of the gold mining catchment areas in South Africa, this seems indeed possible.

1. INTRODUCTION

In South Africa, artificial radioactivity is associated with the generation of nuclear power and operation of smaller research facilities. There exists only one power plant situated at Koeberg and an accelerator facility at Faure, both near Cape Town in the south, and a small nuclear research reactor at the South African Nuclear Energy Corporation (NECSA) at Pelindaba, near Pretoria in the north. NECSA formerly enriched its own uranium and manufactured fuel elements for the Koeberg and Pelindaba sites. The research reactor is used mainly for production of medical and industrial isotopes, silicon irradiation, colour modification of gemstones, neutron diffraction for industrial applications and neutron activation analysis.

Natural radioactivity is associated with the vast mineral resources in such concentrations that the radionuclides from the natural uranium, thorium and actinium decay series are sources of concern for occupational exposure at certain mining and minerals processing industries and for public exposure in communities living around these areas. The main industries concerned are the gold, copper, heavy mineral sands and coal mining and processing operations.

The radiological impact of all operations is monitored as part of the authorization obligations imposed by the South African Nuclear Energy Act [1]. The National Nuclear Regulator is mainly concerned about the impact on workers and the release of effluents and dust to the environment, while the Department of Water Affairs and Forestry is intensively studying the concentration of radionuclides in identified catchment areas around the mining and minerals processing sites to assess the impact on the public using these water sources as part of their dietary intake.

Occupational exposure at the Koeberg nuclear power station resulted in an average annual effective dose of about 0.9 mSv for the years 1994 and 1995 [2]. Liquid and gaseous effluents discharged from this plant in 1995 resulted in an estimated radiation dose received by members of the public of about 0.45 mSv/a. Data for the operation of the NECSA site showed an average effective dose of 0.59 mSv for the year 1995, while public exposure due to airborne effluent discharges was calculated at a maximum of 12 μSv/a during 1995.

Compared with the nuclear industry, the occupational and public exposure arising from the mining and mineral processing industries is more difficult to assess due to the numerous potential transport mechanisms and pathways of the natural radioactivity. Preliminary data show that occupational exposure due to inhalation of respirable dust could be substantial if suitable measures are not taken. Annual doses could be as high as 40 mSv in certain areas of the uranium, copper and heavy mineral processing industries. Recent monitoring of surface and borehole water in catchment areas around the major gold mining activities revealed that public exposure could result in effective doses of up to 0.5 mSv/a if these water sources were to be used as the main sources of drinking water available to the communities living in and around this area.

Assessment of the annual dose from the natural radionuclides of the uranium, thorium and actinium series poses a major challenge to NECSA's radioanalytical laboratories. Up to 25 individual radionuclides may need to be assessed, each of which has its own dose conversion factor [3]. In practice, after assuming radioactivity equilibrium between short-lived daughters with their respective parents, one has to determine about 12 long-lived radionuclides. The concentration levels to be determined differ vastly from one radionuclide to another, and also depend on the annual intake through ingestion and/or inhalation. The first order dose assessment is based on certain default intake values and a dose screening level of 25 μSv/a per individual source [4].

Some of the radionuclides in NORM, specifically ^{238}U, ^{235}U and ^{232}Th, can be determined conveniently with instrumental neutron activation analysis (INAA) or inductively coupled plasma mass spectrometry (ICP-MS). However, the majority require (radio)chemical separation procedures followed by mass spectrometry or radiation detection. The original matrix may vary between drinking water, foodstuffs and respirable airborne dust, each of which requires an individual approach to analyse its natural radionuclides. For drinking water one should be able to analyse radionuclides like ^{227}Ac, ^{231}Pa, ^{228}Ra, ^{210}Po, ^{210}Pb and ^{232}Th at typically a lower limit of determination (LLD) of about 1 mBq/L. For certain foodstuffs one is faced with an LLD of around 1 mBq/kg, which again poses problems with dissolution to allow radiochemical separations, as direct measurements by gamma spectrometry are not adequately sensitive for all radionuclides of interest to assess the annual dose. With respirable airborne dust one faces the problem of limited sample quantities. This requires a specific analysis protocol, which again places severe constraints on the turnaround time of the analyses. All these factors, together with the economic requirement to produce large quantities of data at low cost challenge the capabilities of our radioanalytical laboratories (at present 31 staff members).

2. RADIOANALYTICAL INFRASTRUCTURE

Most national and commercial nuclear centres throughout the world have access to a variety of nuclear and related analytical techniques. The basic requirements for analysis of NORM at high sensitivity are INAA, ICP-MS, high- and low-energy gamma spectrometry

(HEGS and LEGS), alpha particle spectrometry (APS), liquid scintillation counting (LSC) and radiochemical separation techniques for the elements Po, Pb, Ra, Ac, Pa, Th and U. In addition to these, the laboratory should cater for sample conservation, representative sub-sample preparation and sample dissolution/destruction. An adequate QA/QC system is mandatory. This last aspect is vital to avoid disputes between possible polluters and the national regulatory authorities on the reliability of the data produced.

3. MATRICES INVOLVED

The major pathways of NORM intake by the public are via inhalation of respirable airborne dust and ingestion of foods and liquids. The annual intake of NORM via inhalation depends on the breathing rate (related to age and profession [5]), the concentration of the airborne dust and the concentration of individual radionuclides in the respirable fraction of the dust. This aspect is important, as large differences in radionuclide concentrations have been observed as a function of particle size. Intake via ingestion depends on the dietary habits of the affected groups and/or individuals (which are also age-related), and the concentration of the radionuclides concerned. To allow a first order assessment of the radiological impact, default values for consumption may be assumed. Typical values for the South African environment are shown in Tables I and II. Other aspects to be dealt with are the fresh/dry ratio and specific mass of the dried food matrices. The variable volatility of the elements concerned, and even isotopes of the same element, prevent pre-concentration by ashing at elevated temperatures. The specific mass of dried products allows the estimation of the sensitivity of instrumental techniques like gamma spectrometry. Some typical values observed in our laboratories are provided in Table III.

TABLE I. SOUTH AFRICAN DEFAULT VALUES FOR INHALATION INTAKES [4, 5]

Parameter		Value
Breathing rate (m^3/h)		
Members of the public — age (years):	<1	0.21
	1–2	0.21
	2–7	0.34
	7–12	0.64
	12–17	0.96
	>17	0.95
Workers		1.2
Dust concentration (μg/m^3)		
Environmental		50
Workplace		150

TABLE II. SOUTH AFRICAN DEFAULT VALUES FOR INGESTION INTAKES [4]

Foodstuff	Annual consumption (kg fresh weight)					
Age (years)	<1	1–2	2–7	7–12	12–17	>17
Freshwater fish	0.5	1	5	10	10	25
Meat	10	20	50	75	100	100
Poultry	7.5	15	35	60	75	75
Eggs	3	6	15	25	30	30
Cereals and grains	45	60	75	90	128	150
Root crops	51	68	85	102	145	170
Other vegetables, fruit, nuts	39	52	65	78	111	130
Water (L)	200	260	300	350	600	730
Milk (L)	300	300	300	300	300	250

TABLE III. TYPICAL VALUES FOR FRESH/DRY RATIO AND SPECIFIC MASS OF VARIOUS FOODSTUFFS

Foodstuff	Fresh/dry ratio	Specific mass (g/mL)
Fish		
- Meat	4.4	0.50
- Bone	3.1	0.59
- Intestine	4.0	0.57
Milk	23.5	0.66
Meat		
- Bacon	4.5	0.67
- Bone	1.9	0.65
Cereals and grains	1.2	0.77
Root crops	4.6	0.37

4. DOSE CONVERSION FACTORS

Dose conversion factors (DCFs) can be obtained from the literature [3]. It should be emphasized that the DCFs are age-related and dependent on particle size.

5. A CASE STUDY: EVALUATION OF THE MOOI RIVER CATCHMENT

5.1. Introduction

During 1997, the Department of Water Affairs and Forestry performed a survey of one of the major catchment areas influenced by the gold mining industry on the West Rand. During phase 1 of the study, some 1000 samples collected from about 40 monitoring points were analysed for their gross alpha–beta activity and uranium, thorium and radium content. During phase 2, some 100 samples were collected at about 20 monitoring sites and analysed for a comprehensive suite of natural radionuclides. The average annual dose associated with the individual monitoring points was calculated from the natural radionuclide data, the age-dependent dose conversion factors [3] and the default consumption rates [4]. To obtain a first order estimation of the annual dose throughout the catchment area an average lifetime dose weighted according to age group was calculated assuming a life span of 70 years, although the most sensitive groups are <1 year and 12–17 years. The radionuclide data showed a dominance of the uranium activity, and accordingly the correlation between the annual dose and the uranium concentration was evaluated. This would provide a practical solution to monitor this specific catchment, although care should be taken to use the correlations obtained for all catchments in South Africa. The impact on the various age groups was evaluated, and it was anticipated that application of the lifetime average dose would provide a fair tool to establish the annual dose received by potentially affected communities and/or individuals.

5.2. Database

Due to budgetary constraints, not all radionuclides of the natural uranium, thorium and actinium decay series were determined. Phase 1 provided data for ^{238}U, ^{235}U, ^{232}Th, ^{226}Ra, ^{224}Ra and ^{223}Ra, while sampling was performed weekly during the first 6 months of 1997. Phase 2, during the latter half of 1997, provided results for most of the longer-lived nuclides (^{238}U, ^{235}U, ^{234}U, ^{232}Th, ^{230}Th, ^{228}Th, ^{227}Th, ^{228}Ra, ^{226}Ra, ^{224}Ra, ^{223}Ra, ^{210}Pb and ^{210}Po) on 18 of the original 41 monitoring points. ^{231}Pa and ^{227}Ac were only measured on 3 of these 18 sampling sites showing elevated uranium concentrations.

5.3. Quality assurance

In addition to an intercomparison of uranium, thorium and radium analyses between two national laboratories and one overseas laboratory, the quality assurance programme included the application of independent radiochemical and ICP-MS techniques for the determination of ^{238}U, ^{235}U and ^{232}Th in phase 2 of the survey. The correlation between the two techniques could be evaluated from the ^{238}U and ^{235}U data obtained (^{232}Th was frequently detected at the lower limit of determination by ICP-MS and accordingly not reliable for correlation evaluations). For the 98 samples surveyed in phase 2, the following correlation was obtained:

$$[\mathrm{U}]_{\mathrm{ICP\text{-}MS}} = 0.993 \times [\mathrm{U}]_{\mathrm{radiochem}} - 0.563 \qquad (R^2 = 0.906)$$

where [U] is the uranium concentration in μg/L. In natural uranium, the ratio between the ^{238}U activity concentration ($A_{\mathrm{U\text{-}238}}$) and that of ^{235}U ($A_{\mathrm{U\text{-}235}}$) is 21.719. The following relationships were obtained from linear regression between the relevant data obtained by both radioanalytical and ICP-MS analyses:

- Radioanalytical (phase 2, 98 data points): $A_{\mathrm{U\text{-}238}} / A_{\mathrm{U\text{-}235}} = 21.341 \pm 0.115$ $(R^2 = 0.996)$
- ICP-MS (phase 2; 63 data points): $A_{\mathrm{U\text{-}238}} / A_{\mathrm{U\text{-}235}} = 22.171 \pm 0.571$ $(R^2 = 0.860)$
- ICP-MS (phase 1; 570 data points): $A_{\mathrm{U\text{-}238}} / A_{\mathrm{U\text{-}235}} = 20.785 \pm 0.030$ $(R^2 = 0.999)$

Accordingly, it can be concluded that both sets of data as well as the radiochemical determination of all other radionuclides can be accepted as providing a fair representation of the radionuclide composition of the sites surveyed in the complete 1997 study of the Mooi River catchment.

5.4. Assumptions in the dose calculations

To enable an 'all-radionuclide' dose calculation to be performed, the following equilibrium assumptions were made, considering the half-lives of all members of the decay series and the individual radionuclides measured during the survey:

- ^{234}Th and ^{234m}Pa in equilibrium with ^{238}U;
- ^{222}Rn, ^{218}Po, ^{214}, Pb, ^{214}Bi and ^{214}Po in equilibrium with ^{226}Ra;
- ^{210}Bi in equilibrium with ^{210}Pb;
- ^{231}Th in equilibrium with ^{235}U;
- ^{219}Rn, ^{215}Po, ^{211}Pb, ^{211}Bi and ^{207}Tl in equilibrium with ^{223}Ra;
- ^{228}Ac in equilibrium with ^{228}Ra;
- ^{220}Rn, ^{216}Po, ^{212}Pb, ^{212}Bi, ^{212}Po and ^{208}Tl in equilibrium with ^{224}Ra.

The concentration of ^{227}Ac at the time of sampling was calculated from two consecutive determinations of ^{227}Th. The results for the three monitoring points surveyed for actinium (18 data) showed a good correlation between these mother–daughter radionuclides (with a Th/Ac ratio of 6.12 ± 1.69). Accordingly, the activity for the remainder of the samples in the second phase of the survey was estimated from the ^{227}Th data obtained.

There was no evidence of any direct correlation between the ^{231}Pa concentrations at the sampling points surveyed for this radionuclide and the average concentration observed (0.2 ± 0.9 mBq/L) was taken as the default value for the global mean of phase 2.

5.5. Dose calculations and correlations

According to the outline in Section 5.4, the evaluation was performed for the most sensitive age groups (i.e. <1 year followed by 12–17 years) and the calculated lifetime average dose. The calculations were done to allow proper evaluation of the dose received during the one year period and to evaluate the possibility of using a single monitoring parameter for the Mooi River catchment to estimate the annual dose (instead of doing a full radionuclide-specific analysis). From the two sets of data (i.e. the 'all radionuclide' dose for the first and the second halves of 1997 for the 18 corresponding sites, with the omission of one point at which the stream dried up during the second phase) the average 'all radionuclide' dose was calculated. The average uranium concentration was calculated from the phase 1 and phase 2 data. The linear regression between the average 'all radionuclide' dose (in mSv/a) and the average uranium concentration (in µg/L) was calculated, using all monitoring sites in the evaluation. The following correlations were obtained:

- Age < 1 year: 'All radionuclide' dose = 0.00409 × [U] + 0.063 ($R^2 = 0.932$)
- Age 12–17 years: 'All radionuclide' dose = 0.00275 × [U] + 0.020 ($R^2 = 0.901$)
- Lifetime average: 'All radionuclide' dose = 0.00124 × [U] + 0.017 ($R^2 = 0,970$)

The good correlation obtained between uranium concentration and dose is due to the higher solubility of uranium compared to the other radionuclides of the natural decay series. In addition, it was found that good correlations existed between ^{238}U and ^{226}Ra and between ^{226}Ra and ^{223}Ra, with other radionuclides at either very low concentrations or relatively constant over the entire catchment (e.g. ^{210}Pb).

5.6. Uncertainties

Uncertainties in the estimation of the annual dose received through drinking environmental (untreated) water arise from analytical uncertainties, environmental variations, the correlation between uranium concentration and dose, the default age-dependant intake values, and the sampling frequency.

5.6.1. Analytical uncertainty

This was examined by comparing the uranium results obtained in phase 2 by radiochemical and ICP-MS analysis techniques. The correlations between the uranium concentration and the 'all radionuclide' dose described in Section 5.5 were determined using the radiochemical uranium database. The same evaluation based on the ICP-MS uranium data showed the following correlations:

- Age < 1 year: 'All radionuclide' dose = 0.00415 × [U] + 0.065 ($R^2 = 0.922$)
- Age 12–17 years: 'All radionuclide' dose = 0.00273 × [U] + 0.024 ($R^2 = 0.889$)
- Lifetime average: 'All radionuclide' dose = 0.00124 × [U] + 0.017 ($R^2 = 0{,}964$)

These correlations compare well with those obtained from the radiochemical uranium determination. The difference in the calculated dose based on radiochemical and ICP-MS analysis at a dose of 75 µSv/a is about 2%, 4% and 1.5% for the age groups < 1 year, 12–17 years and lifetime average evaluations, respectively.

5.6.2. Environmental variations

These were estimated from the standard deviation observed for the individual radionuclide analyses in phases 1 and 2. Again the total annual dose correlation was calculated, now using the 'upper' and 'lower' bound regions of the analytical data (i.e. the average concentrations plus and minus one standard deviation respectively). The correlations were determined using the radiochemical and ICP-MS uranium data sets obtained in phase 2 of the study. Once more, the sets did not differ substantially from each other and accordingly the mean values were taken to evaluate the annual fluctuation in the dose. It was found that at an estimated average annual dose of around 100 µSv/a, the variations in the 'upper' limits of the evaluated dose were not more than 50%, 30% and 20% for the age groups <1 year, 12–17 years and lifetime average evaluations, respectively. This showed that the calculated annual dose based on the average annual radionuclide concentrations would provide a fair estimation of the radiological impact on the public.

5.6.3. Correlation between uranium concentration and dose

The derived correlation between uranium concentration and annual dose would show a slight variation if sampling sites were to be randomly omitted from the regression calculations. For an annual dose of about 100 µSv/a, the omission of one sampling site that exhibited high radionuclide concentrations during phase 1 but dried up during phase 2 would have caused a difference of +6% in the calculated dose levels, while the omission of the sampling site exhibiting the highest average uranium concentration during the monitoring period would have caused a –3% deviation. The expected uncertainty in the correlation obtained between the annual dose and the uranium concentration for the Mooi River catchment was less than 10%, provided statistically reliable average uranium data were obtained (e.g. through monthly monitoring).

5.6.4. Default age-dependent intake values

These values could give rise to large uncertainties in the dose calculations, since it was assumed that the daily intake was always from the same source, this being the only source of drinking water available to the individuals concerned. Accordingly, at sites showing potentially elevated dose levels corresponding to the default water intake (e.g. above 100 μSv/a) one should determine the actual annual consumption from the source by the communities and/or individuals concerned.

5.6.5. Sampling frequency

The influence of the sampling frequency on the calculated annual dose was estimated from the uranium data obtained in phase 1. The average concentrations were calculated for the individual sites together with the four-weekly average, shifting the intervals by one week respectively. The average concentrations for uranium were thus obtained at the following four sets of intervals:

- Weeks 1, 5, 9, 13, 17, 21;
- Weeks 2, 6, 10, 14, 18, 22;
- Weeks 3, 7, 11, 15, 19, 23;
- Weeks 4, 8, 12, 16, 20, 24;

A comparison of the minimum and maximum differences between these individual data and the average concentration observed over the entire sampling period provided an estimate of the possible over- or underestimation of the uranium concentration. In this model the sites not sampled at a particular date were regarded as not being accessible, although for dose calculations one should regard ‘dry’ sites as having zero uranium concentration as they would not contribute to the annual dose at that specific time. The following observations are made:

- Four-weekly sampling compared with weekly sampling could over- or underestimate the annual dose by a factor of up to 3. (In deriving this result, one site was discarded due to infrequent sampling).
- The data obtained in phase 2 could not be clearly related to seasonal influences. Two sites showed increased levels of uranium during phase 2 that were not readily explained by sampling frequency variations. One site showed a decreased uranium content in phase 2; this site dried up due to decreased/ceased input of waste water directly related to gold mining activities.

5.7. Suspended solids

The suspended solids from the 15 sites sampled in the final month of the study (December 1997) were analysed semi-quantitatively for their alpha-emitting natural radionuclides. The annual dose was calculated for both the suspended solids and the residual water fractions. A comparison of the dose contribution from the suspended solids with that from the residual water is shown in Table IV. Contributions from the suspended solids came mainly from ^{210}Pb/^{210}Po, ^{227}Ac, ^{230}Th, ^{231}Pa and ^{232}Th, while ^{238}U/^{234}U and ^{226}Ra governed the contribution from the residual water. This clearly indicates the distinction between the solubility of the various radionuclides in the environmental ecosystems of the catchment.

TABLE IV. DOSE CONTRIBUTION FROM SUSPENDED SOLIDS

Age group	Dose contribution from suspended solids compared with that from residual water (%)			
	Average	Median	Maximum	Minimum
<1 year	1.3 ± 1.2	1.2	5.0	0.0
12–17 years	2.5 ±2.4	2.0	8.3	0.1
Lifetime average	2.3 ± 2.1	1.9	7.6	0.1

5.8. Measurement of gross alpha–beta activity

The use of gross alpha–beta activity data was restricted to primary screening surveys. The data should not be used to assess non-identified radionuclides from limited radionuclide-specific information to estimate annual doses. Evaluation of the data of phase 1 (922 data) showed that the gross alpha–beta activity, measured directly on the filtered water by LSC generally agreed well with the calculated activities. The following linear regressions were observed:

- Measured alpha activity [LSC] = 1.19 × calculated alpha activity ($R^2 = 0.71$)
- Measured beta activity [LSC] = 1.01 × calculated beta activity ($R^2 = -0.04$)

This indicated that the gross alpha activity measurement could be used as a screening tool, but that the beta activity measurements through direct LSC provide highly scattered data. In phase 2, NECSA evaluated the validity of the LSC data by applying an alternative technique involving evaporation of the filtered water followed by gross alpha–beta activity measurement on a gas-flow counting system. The correlation through linear regression between the LSC and evaporation (Evap) techniques (98 data points) gave the following relationships:

- Alpha activity [LSC] = 0.82 × alpha activity [Evap] + 0.10 ($R^2 = 0.30$)
- Beta activity [LSC] = 1.07 × beta activity [Evap] + 1.24 ($R^2 = 0.20$)

This indicated a fair correlation between the alpha–beta activities measured by each technique, although the data were strongly scattered. Evaluation of the average gross activity concentration data, according to the same outline provided in Section 5.5 for the correlation between annual dose and uranium concentration, gave the following results for lifetime average exposure:

- ‘All radionuclide’ dose (mSv/a) = 0.02835 × gross alpha (Bq/L) + 0.021 ($R^2 = 0.856$)
- ‘All radionuclide’ dose (mSv/a) = 0.02059 × gross beta (Bq/L) + 0.017 ($R^2 = 0.779$)

Also here an environmental blank contribution of about 0.02 mSv/a is observed.

5.9. Contribution of radium

Examination of the data suggested a possible twin correlation between the measured uranium concentration and the calculated dose. Evaluation of the ‘upper’ and ‘lower’ correlations revealed that one could make a distinction between sampling sites correlated with mainly uranium contamination and those affected by both uranium and radium, as follows:

- Upper correlation:

  'All radionuclide' dose (mSv/a) = 0.001431 × [U] (μg/L) + 0.01853 ($R^2 = 0.995$)

- Lower correlation:

  'All radionuclide' dose (mSv/a) = 0.001025 × [U] (μg/L) + 0.01856 ($R^2 = 0.994$)

The upper correlation contained all 'background' sites with uranium concentrations less than about 5 μg/L together with sites exhibiting relatively high radium concentrations. The lower correlation contained all background sites together with sites exhibiting relatively low radium concentrations. The nature of the increased/decreased mobility of radium at specific sites is not clearly understood yet. Future work is envisaged to find a correlation between the chemical constituents also measured during the survey and the observed radium mobility differences, although previous work performed by the Institute of Water Quality Studies did not show any direct correlation between chemical constituents and radioactivity. Furthermore a fair correlation has been found between ^{226}Ra and ^{227}Ac (^{223}Ra). This indicates that the mobility of actinium, which has relatively high radiotoxicity, should not be underestimated.

5.10. Ratio of ^{234}U to ^{238}U

The literature often refers to the ^{234}U/^{238}U ratio as a parameter that can be used for evaluating the origin of the source [6]. A high ratio (>2) and low concentration may indicate incongruent weathering from silicate rocks, while a low ratio (~1) and high concentration indicates congruent weathering from carbonate and sulphate sedimentary rock. Other studies indicate that a low ^{234}U/^{238}U ratio in mining-related areas suggests contamination of the water sources due to the mining and mineral processing activities [7]. From the results obtained in the 1997 and 1998 surveys, a possible indication can be found that a high concentration and a low ratio may indicate leaching from recently disturbed minerals, while a high concentration and a high ratio could indicate leaching from old tailings dams and dumps. This preliminary observation should be explored further to gain insight into the possible origins when elevated uranium concentrations are observed in South African water sources.

5.11. Conclusions

(a) Based on the data obtained from this study, Table V shows a ranking of the number of sampling locations according to proposed guideline dose values. At sites showing potentially significant dose levels, the extent to which the water is actually used as a drinking water source should be determined, and the possibilities for reducing the radionuclide concentrations should be investigated.

(b) The observed correlation between the uranium concentration (in μg/L) or the gross activity (in Bq/L) and the 'all radionuclide' annual dose (in mSv/a) can be used for routine monitoring purposes of the Mooi River catchment area. The uncertainty is estimated to be less than 20%. The proposed monitoring frequency is monthly for uranium and every 6 months for the full range of radionuclides to evaluate whether the correlation is sustainable.

(c) The contribution of radium to the annual dose estimate is considerable and should be monitored along with the uranium determination for those points were more precise data are required to calculate the annual dose. The positive correlation between ^{226}Ra and ^{227}Ac indicates that monitoring of ^{227}Ac, which has the highest dose conversion factor for ingestion (i.e. the highest radiotoxicity), should be performed on a wider scale.

TABLE V. RANKING OF SAMPLING LOCATIONS ACCORDING TO DOSE

Potential ingestion dose (µSv/a)		Number of sampling locations		
	Age (years):	<1	12–17	Lifetime average
<100		19	28	34
100–250		13	7	6
250–1000		8	6	1
1000–5000		1	0	0
>5000		0	0	0

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URANIUM ISOTOPES IN PUBLIC DRINKING WATER IN POLAND

Z. Pietrzak-Flis[*], **I. Kamińska, E. Chrzanowski**

Central Laboratory for Radiological Protection, Warsaw, Poland

Abstract

^{238}U, ^{234}U and ^{235}U were determined in tap water from municipal water pipes supplied with water from rivers or lakes (surface water) and from wells (groundwater), in various locations in Poland. Average activity concentrations of ^{238}U, ^{234}U and ^{235}U in tap water from surface waters were 9.94, 13.2 and 0.43 mBq/L, respectively, whereas from groundwater they were 4.53, 5.68 and 0.18 mBq/L, respectively. Activity concentrations of ^{234}U were higher than ^{238}U. (^{234}U/^{238}U ratios ranged from 1.7 to 2.6), indicating the lack of equilibrium between these isotopes. The ^{234}U/^{238}U ratios for the surface and groundwater were similar. The average ^{235}U/^{238}U ratio was 0.044 being close to 0.046 for natural uranium. Average annual intake with water and food was 7.48 Bq for ^{238}U and 9.45 Bq for ^{234}U. The annual committed effective doses calculated from these intakes for adults were 0.34 and 0.46 μSv, respectively.

1. INTRODUCTION

Uranium enters the human body mainly through ingestion, and to a considerably lesser degree by inhalation [1, 2]. The contribution of drinking water to the total intake of uranium isotopes varies over wide ranges [3]. In the United States, the intake of water-derived uranium is on average 5–10 times greater than that of food-derived uranium [4], although in New York City the contribution of water-derived uranium is much lower, being about 8% [2].

In Poland, the intake of uranium isotopes through ingestion was determined for the regions of central Poland [5], Wałbrzych [6] and the Świetokrzyskie Mountains [7]. It was found that in these regions the contribution of water-derived ^{238}U and ^{234}U was 66–91% and 76–93%, respectively.

The aim of the present work was to determine the activity concentrations of uranium isotopes in tap water at various sites in Poland. The total ingestion of ^{238}U and ^{234}U was calculated using the data for drinking water obtained in this work, and data for the intake with foodstuffs from Refs [5–7].

2. MATERIALS AND METHODS

Samples of tap water were collected in 2002 and 2003 from water supply systems located in various parts of Poland. The systems were supplied with surface water from rivers or lakes (15 water pipes) and from deep underground wells (16 water pipes). The sites of tap water collection are presented in Fig. 1.

Determinations of uranium isotopes were performed in 5 L samples of water. ^{232}U was used as an internal tracer for counting alpha activity and chemical recovery. After evaporation of water, uranium was chemically separated by anion exchange and extraction. Finally,

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[*] E-mail: pietrzak_flis@clor.waw.pl

uranium was electrodeposited on a stainless steel disc. The activity of the deposited uranium was measured with an alpha spectrometry system. PIPS detectors for alpha spectrometry were placed in a vacuum chamber and connected to a multichannel analyser Multiport II MCA (Canberra MP2-GE) with GENIE 2000 spectroscopy software. Details of the analytical procedure are described elsewhere [6].

The average uranium tracer recovery was approximately 77%. The lower limit of detection (LLD) with a counting time of 82 000 s was 0.22 mBq per sample for ^{234}U and 0.29 mBq per sample for ^{238}U and ^{235}U.

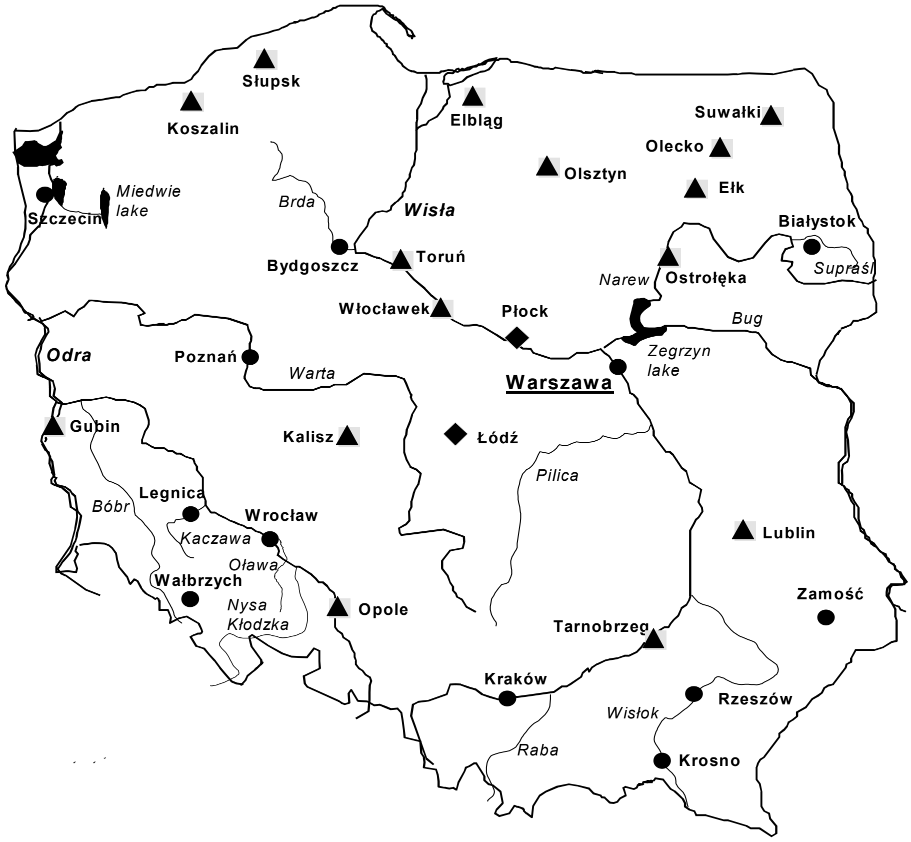

FIG.1. Sites of tap water collection
● *surface water,* ▲ *ground water,* ♦ *surface and ground water.*

3. RESULTS

The activity concentrations of ^{238}U, ^{234}U and ^{235}U in drinking water supplied from surface water are presented in Table I. The activity concentration of ^{238}U ranged from 1.79 mBq/L in Kraków to 23.9 mBq/L in Legnica. The concentrations of ^{234}U ranged from 2.47 mBq/L in Bydgoszcz to 34.1 mBq/L in Legnica. The concentrations of ^{235}U were lowest in Kraków (0.10 mBq/L) and highest in tap water collected in Wrocław from a water pipe supplied from the Oława river (19.9 mBq/L). The mean activity concentrations of ^{238}U, ^{234}U and ^{235}U were 9.94, 13.2 and 0.43 mBq/L, respectively. In all samples the activity concentration of ^{234}U was higher than that of ^{238}U. The activity concentration ratio was in the range 1.07–2.60, with a mean value 1.37.

TABLE I. URANIUM ACTIVITY CONCENTRATIONS IN DRINKING WATER SUPPLIED FROM SURFACE WATER

Location	River or lake	Activity concentration (mBq/L)[1]			^{234}U/^{238}U activity ratio
		^{238}U	^{234}U	^{235}U	
Szczecin	Miedwie Lake	14.5 ± 0.93	15.5 ± 1.02	0.56 ± 0.07	1.07
Białystok	Supraśl River	6.91 ± 0.58	8.35 ± 0.69	0.29 ± 0.07	1.21
Bydgoszcz	Brda River	2.00 ± 0.23	2.47 ± 0.27	0.11 ± 0.04	1.24
Płock	Vistula River + groundwater[2]	4.56 ± 0.40	5.87 ± 0.50	0.19 ± 0.05	1.29
Poznań	Warta River	13.6 ± 0.93	16.11 ± 1.09	0.48 ± 0.08	1.19
Warszawa	Zegrzyn Lake	6.43 ± 0.81	7.86 ± 0.99	0.28 ± 0.08	1.22
Łódź	Pilica River, Tomaszów[3]	2.59 ± 0.23	3.32 ± 0.23	0.15 ± 0.04	1.28
Legnica	Kaczawa River (infiltration)	23.9 ± 1.66	34.1 ± 2.33	0.96 ± 0.09	1.43
Wrocław	Oława River (infiltration)	19.9 ± 1.36	26.4 ± 1.78	0.98 ± 0.12	1.32
Wrocław	Nyska Kłodzka River	10.9 ± 0.59	13.5 ± 0.73	0.48 ± 0.05	1.24
Wałbrzych	Bóbr River (infiltration)	5.07 ± 0.42	13.2 ± 0.98	0.24 ± 0.08	2.60
Zamość	Łabuńka River (infiltration)	20.7 ± 1.34	29.4 ± 1.88	0.90 ± 0.11	1.42
Kraków	Raba River	1.79 ± 0.21	2.97 ± 0.30	0.10 ± 0.04	1.66
Rzeszów	Wisłok River, Zwięczyca[3]	11.4 ± 0.81	13.5 ± 0.95	0.52 ± 0.07	1.18
Krosno	Wisłok River, Iskrzynia[3]	4.85 ± 0.39	5.94 ± 0.46	0.14 ± 0.04	1.22
Mean ± SD		9.94 ± 7.22	13.2 ± 9.87	0.43 ± 0.31	1.37 ± 0.37

Activity concentrations of ^{238}U, ^{234}U and ^{235}U in drinking water supplied from groundwater are given in Table II. In the majority of tap waters the activity concentrations of uranium isotopes were much lower than those supplied from surface water. The lowest concentration of ^{238}U was found in Ostrołęka and Gubin (0.36 mBq/L) and the highest in Suwałki (23.2 mBq/L). As was the case with tap water supplied from surface water, the activity concentrations of ^{234}U were higher than those of ^{238}U. They ranged from 0.46 mBq/L in Ostrołęka to 25.7 mBq/L in Suwałki. In 6 out of 16 water pipes, the concentrations of ^{235}U were below the LLD (0.06 mBq/L); the highest value was noted in Suwałki (1.04 mBq/L). The mean activity concentrations of ^{238}U, ^{234}U and ^{235}U were 4.53, 5.68 and 0.18 mBq/L, respectively.

An assessment of uranium intakes in food and water performed in three regions of Poland showed that the variability of food-derived ^{238}U and ^{234}U activity was smaller than that of water-derived activity [5–7]; the results of these investigations are summarized in Table III. In these regions the annual intake of ^{238}U was 8.08–22.2 Bq with an average of 12.8 Bq, whereas the annual intake of ^{234}U was 9.69–31.8 Bq with an average 18.7 Bq. The average ^{238}U and ^{234}U activity intakes from food ingestion were 2.27 and 2.66 Bq, respectively. These values were obtained for the regions with a wide variety of natural radionuclides [8], hence it can be postulated that they also represent other regions of Poland. Therefore, in the present work it has been assumed that food-derived intakes in the sites studied are equal to the

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[1] Value ± counting error at the 95% confidence level.

[2] 1:1 mixture.

[3] Site of the water intake.

average food-derived intakes given in Table III. Annual intakes of ^{238}U and ^{234}U with water were evaluated from the concentrations of these radionuclides in tap water (Tables I and II). The annual consumption of water for adults was taken as 730 L [9]. Intakes with food were assumed to be 2.27 and 2.66 Bq for ^{238}U and ^{234}U, respectively. The estimated total intakes with water and food are given in Table IV.

TABLE II. URANIUM ACTIVITY CONCENTRATIONS IN DRINKING WATER SUPPLIED FROM GROUND WATER

Location	Activity concentration (mBq/L)[4]			^{234}U/^{238}U activity ratio
	^{238}U	^{234}U	^{235}U	
Słupsk	10.5 ± 0.73	12.3 ± 0.84	0.58 ± 0.08	1.17
Koszalin	0.80 ± 0.07	1.36 ± 0.11	<0.06	1.70
Elbląg	2.07 ± 0.15	2.44 ± 0.17	0.09 ± 0.02	1.18
Suwałki	23.2 ± 1.34	25.7 ± 1.48	1.04 ± 0.04	1.11
Olecko	1.90 ± 0.22	2.92 ± 0.30	0.10 ± 0.04	1.54
Ełk	10.3 ± 0.86	12.2 ± 1.00	0.40 ± 0.08	1.18
Olsztyn	4.71 ± 0.41	5.76 ± 0.48	0.12 ± 0.04	1.22
Ostrołęka	0.36 ± 0.08	0.46 ± 0.09	<0.06	1.28
Toruń	6.90 ± 0.55	8.63 ± 0.67	0.28 ± 0.06	1.25
Włocławek	0.89 ± 0.12	0.99 ± 0.13	<0.06	1.11
Łódź	1.34 ± 0.11	1.56 ± 0.13	0.06 ± 0.02	1.16
Gubin	0.36 ± 0.06	0.52 ± 0.07	<0.06	1.44
Kalisz	0.61 ± 0.06	0.67 ± 0.07	<0.06	1.10
Lublin	2.07 ± 0.18	2.28 ± 0.19	0.08 ± 0.03	1.10
Opole	5.19 ± 0.41	11.4 ± 0.82	0.16 ± 0.04	2.19
Tarnobrzeg	1.35 ± 0.11	1.63 ± 0.12	<0.06	1.21
Mean ± SD	4.53 ± 6.00	5.68 ± 6.89	0.18 ± 0.27[5]	1.31 ± 0.29

TABLE III. ANNUAL INTAKES OF URANIUM WITH FOOD AND WATER IN THREE REGIONS OF POLAND (PREVIOUS STUDIES [5–7])

Region	Activity intake (Bq)			
	^{238}U		^{234}U	
	Total	Food-derived	Total	Food-derived
Central Poland	8.08 ± 1.57	2.01 ± 0.19	9.69 ± 1.56	2.24 ± 0.18
Wałbrzych	8.13 ± 0.38	2.81 ± 0.20	14.5 ± 0.70	3.52 ± 0.24
Świętokrzyskie Mountains	22.2 ± 0.97	2.00 ± 0.17	31.8 ± 1.48	2.21 ± 0.20
Average ± SD	12.8 ± 8.14	2.27 ± 0.46	18.7 ± 11.6	2.66 ± 0.74

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[4] Value ± counting error at the 95% confidence level.

[5] Where ^{235}U concentration was below the LLD, a concentration of 0.5 × LLD, i.e. 0.03 mBq/L was assumed.

TABLE IV. INTAKES OF URANIUM WITH FOOD AND WATER (PRESENT STUDY)

Location	^{238}U annual activity intake		^{234}U annual actibity intake	
	Total (Bq)	Drinking water contribution (%)	Total (Bq)	Drinking water contribution (%)
Szczecin	12.9 ± 0.82	82.3	14.0 ± 1.05	81.0
Białystok	7.32 ± 0.63	68.9	8.75 ± 0.90	70.0
Bydgoszcz	3.73 ± 0.49	39.1	4.46 ± 0.77	40.5
Płock	5.60 ± 0.55	59.4	6.94 ± 0.83	61.7
Poznań	12.2 ± 0.82	81.4	14.4 ± 2.09	81.6
Warszawa	6.97 ± 0.75	67.4	8.39 ± 1.09	68.4
Łódź[6]	3.65 ± 0.48	37.7	4.44 ± 0.76	40.3
Legnica	19.7 ± 1.30	88.5	27.6 ± 1.86	90.4
Wrocław	16.8 ± 1.09	86.5	21.9 ± 1.50	87.9
Wrocław	10.2 ± 0.63	77.8	12.5 ± 0.92	78.8
Wałbrzych	5.97 ± 0.56	61.9	12.3 ± 1.03	78.4
Zamość	17.4 ± 1.08	86.9	24.1 ± 1.56	89.0
Kraków	3.58 ± 0.49	36.5	4.82 ± 0.78	45.0
Rzeszów	10.6 ± 0.75	78.6	12.5 ± 1.02	78.8
Krosno	5.81 ± 0.55	60.9	6.99 ± 0.82	62.0
Słupsk	9.94 ± 0.71	77.1	11.6 ± 0.97	77.2
Koszalin	2.86 ± 0.47	20.4	3.65 ± 0.75	27.2
Elbląg	3.78 ± 0.48	39.9	4.44 ± 0.76	40.2
Suwałki	19.2 ± 1.08	88.2	21.4 ± 1.31	87.6
Olecko	3.66 ± 0.49	37.9	4.79 ± 0.78	44.5
Ełk	9.79 ± 0.78	76.8	11.6 ± 1.04	77.0
Olsztyn	5.71 ± 0.55	60.2	6.86 ± 0.83	61.3
Ostrołęka	2.54 ± 0.47	10.4	2.99 ± 0.75	11.2
Toruń	7.31 ± 0.61	68.9	8.95 ± 0.89	70.4
Włocławek	2.92 ± 0.47	22.2	3.38 ± 0.75	21.4
Gubin	2.54 ± 0.48	10.4	3.03 ± 0.75	12.5
Kalisz	2.72±0.47	16.4	3.14 ± 0.75	15.6
Lublin	3.78 ± 0.48	39.9	4.32 ± 0.76	38.5
Opole	6.06 ± 0.55	62.5	11.0 ± 0.96	75.8
Tarnobrzeg	3.26 ± 0.47	30.2	3.84 ± 0.75	30.9

The total intakes varied over wide ranges: 2.54–19.7 Bq for ^{238}U and 2.99–27.6 Bq for ^{234}U. The contributions from water were similar for both radionuclides, ranging from about 10 to 90%.

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[6] Calculated for mixed water used for consumption by the Łódź inhabitants.

The annual committed effective doses resulting from 1 year of ingestion were calculated from the annual intake of ^{238}U and ^{234}U (Table IV) and from the dose coefficients given in Ref. [10]. Table V gives values calculated for the average intake and for locations supplied with surface and groundwater. Average annual intakes for inhabitants of all studied locations were 7.48 and 9.45 Bq for ^{238}U and ^{234}U respectively. The annual doses were 0.34 and 0.46 μSv, respectively, amounting to 0.8 μSv in total.

TABLE V. AVERAGE ANNUAL INTAKES OF URANIUM WITH FOOD AND WATER AND ASSOCIATED EFFECTIVE DOSES

Location	^{238}U		^{234}U	
	Intake (Bq)	Dose[7] (μSv)	Intake (Bq)	Dose[7] (μSv)
Average, for all locations	7.48 ± 3.96	0.34 ± 0.18	9.45 ± 0.46	0.46 ± 0.22
Locations supplied from surface water	9.49 ± 5.37	0.43 ± 0.24	12.3 ± 7.28	0.60 ± 0.36
Locations supplied from groundwater	5.58 ± 4.38	0.24 ± 0.20	6.80 ± 5.03	0.32 ± 0.25

4. DISCUSSION

The results of this work show that activity concentrations of uranium isotopes in tap water in various locations in Poland can vary over wide ranges. Tap water supplied from groundwater contain ^{238}U in concentrations of 0.36–23.2 mBq/L and ^{234}U in concentrations of 0.52–27.7 mBq/L. Tap water supplied from surface water contains ^{238}U in concentrations of 1.79–23.9 mBq/L and ^{234}U in concentrations of 2.47–34.1 mBq/L. The activity concentrations reported in Ref. [11] for the Gdańsk agglomeration fall within these ranges. The lowest concentrations measured in the present study were almost the same as those given in Ref. [12] for the USA. However, the highest concentrations in Poland were about ⅓ of those in the USA (77 and 117 mBq/L for ^{238}U and ^{234}U respectively). Concentrations similar to those in Poland were found for New York City tap water (0.87 and 1.04 mBq/L for ^{238}U and ^{234}U respectively) [2] and in Salt Lake City (17.8 and 29.6 mBq/L for ^{238}U and ^{234}U respectively) [13].

Despite the variations observed in the present work, activity concentrations for groundwater are, on average, lower than those for surface water. This is in contrast to the situation in the USA, where concentrations in groundwater were in some States up to 4 times higher than in surface water. However, in many States the uranium concentrations in tap water taken from ground and surface water were identical [4].

This variability of uranium concentrations is understandable, because uranium concentration in water depends on many factors, such as the uranium concentration in the aquifer rock and chemical composition of water, including pH, redox potential, content of oxygen, CO_2, and complexing agents [4, 12].

In all the water samples analysed, the activity concentration of ^{234}U was higher than that of ^{238}U. The activity ratios of ^{234}U/^{238}U were similar for tap water supplied from surface and groundwaters, being on average 1.37 and 1.31, respectively (Tables I and II). Numerous

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[7] The dose coefficients for ^{238}U and ^{234}U are 0.045 and 0.049 μSv/Bq respectively [10].

studies on ^{238}U and ^{234}U in water indicate that these isotopes occur in disequilibrium and that, with a few exceptions, the water contains more ^{234}U than ^{238}U [4, 11, 12, 14–16]. The higher activity of ^{234}U in water results from the ^{234}U atom displacement from the crystal lattice of uranium minerals. The ^{234}U atom is liable to be oxidized to the hexavalent stage and can be leached into the water phase more easily than its parent nuclide ^{238}U [1].

The average activity ratio of ^{235}U to ^{238}U for water samples was 0.044, which is very close to the value 0.046 for natural uranium.

The annual committed effective dose from the intake of ^{238}U and ^{234}U was 0.80 μSv. In locations where tap water was taken from surface water, this dose was about 1 μSv, whereas in locations in which tap water was taken from groundwater the dose was lower — 0.56 μSv. The annual dose from uranium isotopes constitutes only a small fraction of that from natural radionuclides of the uranium and thorium series ingested with food and water, which was estimated to be about 90 μSv [17].

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CONCENTRATIONS OF ^{222}Rn IN GROUNDWATERS FLOWING THROUGH DIFFERENT CRYSTALLINE ROCKS: AN EXAMPLE FROM ŚLĘŻA MASSIF (SW POLAND)

T.A. Przylibski*

Wrocław University of Technology, Faculty of Geoengineering, Mining and Geology
Institute of Mining Division of Geology and Mineral Waters, Wrocław, Poland

Abstract

Ślęża Massif is situated in the south-western part of Poland, about 30 km SW of Wrocław, the capital city of Lower Silesia. The geological setting of the research area is typical of the Sudety Mountains. Different types of crystalline rocks, of both igneous and metamorphic origin, occur over an area of 25 km^2. On the surface of this relatively small area, Lower Carboniferous to Lower Permian Strzegom–Sobótka Granite and Devonian Ślęża Ophiolite are uncovered. The result is the occurrence of granites, gabbros, amphibolites and serpentinites, directly neighbouring on each other. The author selected this area for determining the influence of rock type on the concentration of ^{222}Rn dissolved in groundwater flowing through crystalline rocks. The first stage of the research consisted of determining typical values of ^{222}Rn concentration in groundwater flowing through different types of rocks and describing the scale of seasonal changes in ^{222}Rn concentration. In the next stage of the research, an attempt to apply ^{222}Rn as one of the isotopic hydrogeochemical tracers of the flow pathway of fissure groundwater will be undertaken. The results show that the highest values of ^{222}Rn concentration (reaching 229 Bq/L) were observed in groundwater flowing out of springs located within granite, whereas the lowest one (1.1 Bq/L) was noted in a spring located within serpentinite. The average ^{222}Rn concentrations obtained in groundwater flowing out of two springs within granite were 170 and 103 Bq/L, whereas the average values in two springs located within amphibolites reached 7.3 and 8.2 Bq/L. The average ^{222}Rn concentrations in the springs flowing out of gabbro and serpentinite amounted to 7.6 and 1.2 Bq/L respectively. The ^{222}Rn concentration in the groundwater flowing out of the spring located within serpentinites was stable during the whole year — likewise for the discharge of the spring. ^{222}Rn concentrations between 1.1 ± 0.2 and 1.4 ± 0.2 Bq/L were measured. On the other hand, ^{222}Rn concentrations in waters flowing out of springs located within granite were characterized by distinct changes. The highest values (164 and 229 Bq/L) were noted in winter and summer respectively, whereas the lowest (70 and 127 Bq/L) were recorded in spring. There is no distinct correlation between radon concentration and the discharge of the springs. In the remaining springs, radon concentration changes were on a low scale but also of irregular character. The results obtained prove the necessity of precise location of groundwater intakes in the areas with complicated geological structure due to the need to ensure radiation protection of local people. They also point to a possibility to employ radon (^{222}Rn) as a natural radioactive tracer of flow pathways and mixing zones of different components of underground and surface waters.

1. INTRODUCTION

The concentration of radon (^{222}Rn) in groundwater depends on numerous factors, the most important of which are the emanation coefficient of reservoir rocks and the content of ^{226}Ra, the parent isotope of radon, in these rocks. The concentration of ^{226}Ra in rocks is strictly related to the geochemical environment of their formation, hence also with the petrological type of the rock. In the study of radon hydrogeochemistry, it is important to become familiar with the relationship between the concentration of radon dissolved in

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* E-mail: tadeusz.przylibski@pwr.wroc.pl

groundwater and the type (lithology) of their reservoir rocks. This is especially significant in areas built of crystalline rocks (magmatic and metamorphic), which usually contain higher ^{226}Ra concentrations than sedimentary rocks and more frequently undergo brittle deformations, producing favourable conditions for fast migration of radon and groundwater. The greatest diversity of radon concentrations in groundwater can be expected in areas with a complicated geological set-up and a large proportion of crystalline rocks. Conducting research in such an area may enable significant hydrogeochemical observations related to the occurrence of radon dissolved in groundwater to be made. This information could be later applied both for radiological protection and isotopic hydrogeological studies employing radon as a natural radioactive tracer of processes occurring in groundwater reservoirs. The best area for conducting this kind of investigations in Poland, due to the geological structure, is the Sudetes. They contain rather small zones characterized by a very complicated geological set-up in a relatively small area, and which could be treated as natural proving grounds. One of such zones is the Ślęża Massif, which had the additional advantage to the author of being close to Wrocław, the capital of Lower Silesia.

2. GEOLOGICAL SETTING

Ślęża Massif lies in SW Poland, within the geological structures of the Sudetes, in their part lowered tectonically in the Tertiary, on so-called Fore-Sudetic block (Fig. 1). Ślęża Massif is composed of rocks belonging to two tectonic units of the western Sudetes. These are Lower-Carboniferous/Lower-Permian granites intruding into the epimetamorphic rocks of the Kaczawa metamorphic unit, forming the granite massif of Strzegom–Sobótka. In the SE, these granites come in contact with the largest Devonian ophiolite complex in Poland, the so-called Ślęża ophiolite, built chiefly of gabbros and serpentinites.

On the selected proving ground, acidic igneous rocks (granites) and basic gabbros, metamorphic serpentinites and metadiabases, as well as metabasalts, formerly referred to as amphibolites, occur on the surface or under a relatively thin cover (Fig. 1). Measurements of radon concentrations were conducted in spring water flowing out of all the above-mentioned rock types. These are fissure and rubble springs, which can all be counted among slope springs. Their location is shown in Fig. 1.

3. MEASUREMENTS

The measurements of radon concentration in the spring water of the Ślęża Massif started in late autumn 2002, and are still proceeding. Together with every measurement of radon concentration, the temperature of water, its electrolytic conductivity (ECW), pH value, the total dissolved solids (TDS), and the spring discharge were measured. All these measurements were conducted directly in the field, with the use of a conductometer and a pH meter manufactured by SLANDI™. Only ^{222}Rn concentration was determined in a laboratory — from each spring, four 0.33 L water samples were collected in glass bottles secured tightly with plastic caps. After being transported to the laboratory, the water was transferred with a 0.1 L syringe to an AquaKIT™ measurement set, which was connected to an AlphaGUARD™ portable radon monitor. As a result of forced air movement in the measurement set, using a gas-tight AlphaPUMP™, radon was released from the water in the AquaKIT™ system and transported to the ionization chamber of the AlphaGUARD™ meter, where the proper measurement took place. The values of radon concentration in the air obtained in this way were then converted into concentrations in the relevant water samples by means of the computer programme AlphaEXPERT™, as well as with algorithms allowing concentration conversion at the moment of sample-taking. A more detailed description of this measurement method can be found in numerous publications, including Refs [2–4].

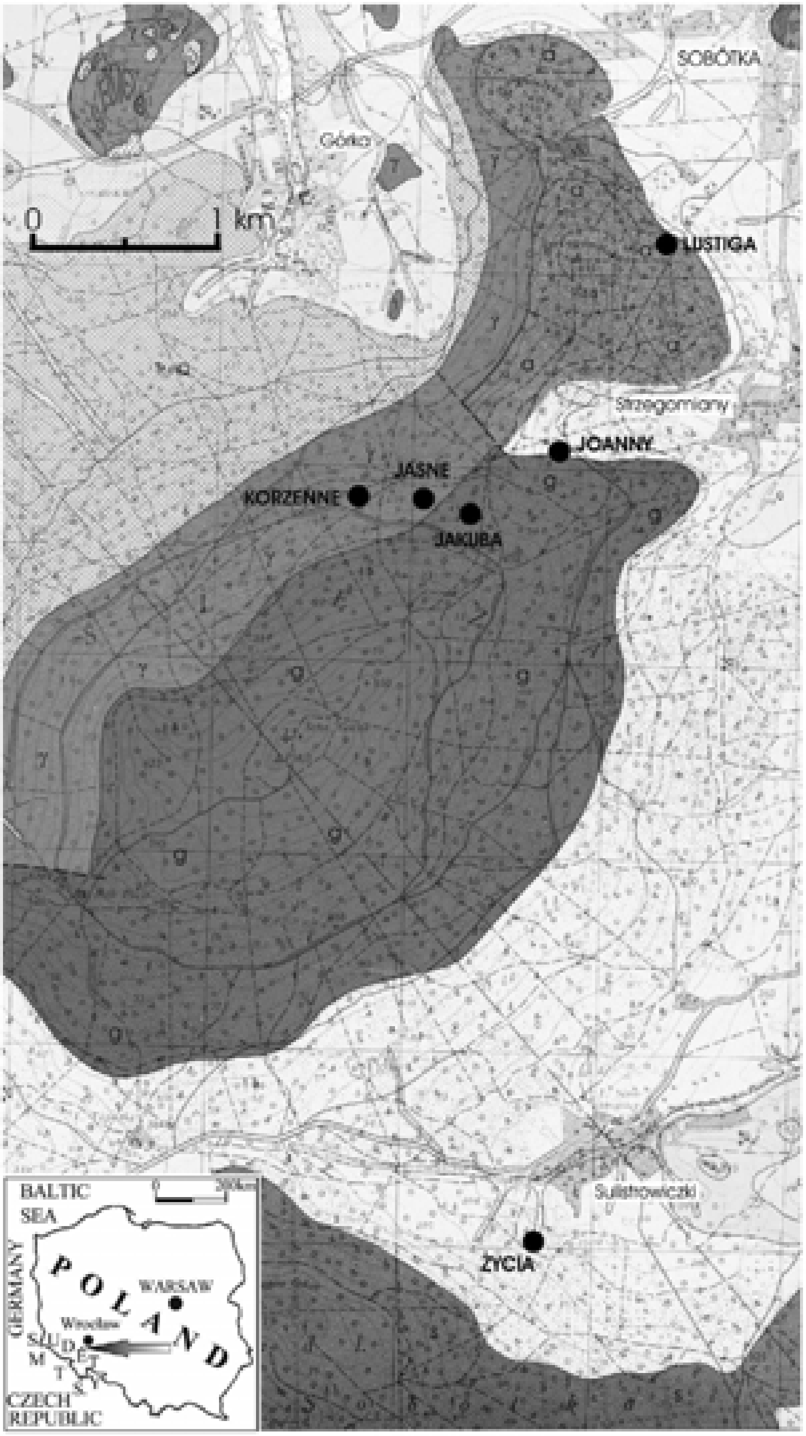

FIG. 1. Geological sketch of the Ślęża Massif (according to Ref. [1]) showing the springs in which radon concentrations were determined

Key: s = serpentinites (Devonian); a = amphibolites (now referred to as metadiabases and metabasalts) (Devonian); g = gabbros (Devonian); γ = granites (Upper Carboniferous); Tr+Q = granite waste rock (Tertiary and Quaternary); Q = clays, sands and gravels of the Quaternary; black circles show spring location; the arrow on the map of Poland shows the location of the Ślęża Massif.

4. RESULTS AND DISCUSSION

The measurement results are shown in Table I. The relatively small number of data collected so far does not allow a full analysis of the variability of radon concentration in the water of particular springs. Therefore, it is not possible to determine potential correlations between the changes of the measured parameters. To do so, measurements are being continued in all springs. Nevertheless, the number of results obtained so far enables the drawing of first conclusions about the range of value changes in the radon concentrations registered in the groundwater flowing out of particular types of reservoir rocks. Unquestionably, the lowest values are characteristic of the water flowing out of serpentinites (‘źródło Życia’, or ‘life spring’). What is also very distinct is the absence of seasonal variations in the measured radon concentrations, which remain almost within the measurement error limits 1.1–1.4 Bq/L. Another characteristic of this spring is the constant discharge value (Table I).

As expected, the highest values of radon concentrations were measured in the water flowing out of granites (Jasne and Korzenne springs). They vary from 127 to 229 Bq/L in Jasne spring and from 70 to 164 Bq/L in Korzenne spring (Table I). Radon concentration changes are high, although there are no regularities in their character. The maximum in Jasne spring was recorded in summer at low spring discharge while, in Korzenne spring, it was in winter at high discharge.

Similarly, irregular variability of radon concentration was observed in the water flowing out of gabbros and amphibolites (metadiabases and metabasalts), but the values were much lower in comparison with those in the water flowing out of granites and higher than those in the water flowing out of serpentinites (Table I). Radon concentrations in the water of Jakub spring (flowing out of gabbros), as well as Lustig and Joanna springs (flowing out of metadiabases and metabasalts), oscillated between 6.5 and 10.5 Bq/L. Variations in the radon concentration in the water from these springs are much smaller than those in the water flowing out of granites in Jasne and Korzenne springs.

Table II presents the extreme and mean concentration values of radon dissolved in the groundwater flowing out of different types of crystalline reservoir rocks of the Ślęża Massif. In spite of the yet-incomplete analytical material, distinct differences in the recorded values are observable between water flowing out of granites and serpentinites, in relation to all the remaining rock types. At the same time, radon concentrations recorded in the water flowing out of metadiabases, metabasalts and gabbros do not differ from each other, although they are different from those in the water flowing out of granites and serpentinites (Table II). Lack of differences between radon concentrations recorded in the water flowing through gabbros and those flowing through metadiabases and metabasalts results from the geochemical similarity of the environments in which these rocks were formed (especially with reference to U and Ra content). A similar geotectonic position — the zone of the midocean rift — also did not help to diversify these rocks regarding their geochemical composition, as they were probably formed in the same magmatic reservoir.

Based on these results, it can be said that even in a small area, e.g. within about 200 m of Jakub and Jasne springs (Fig. 1), in regions with complicated and diversified geological set-up one can expect considerable differences in the concentration of radon dissolved in groundwater. It is essential to recognize such a situation accurately while making plans for supplying water to the residents of such areas. From a radiation protection aspect, the location of intakes should be planned very carefully in such cases. Knowledge of the range of radon concentrations in the water flowing out of (and through) different types of reservoir rocks is also of great importance for the possible use of radon as a natural tracer of flow pathways and the mixing zones of different components of underground and surface water. The results of the ongoing research in the Ślęża Massif and other parts of the Sudetes, [3] will form a basis for the use, in such an application, of radon occurring in groundwater in different concentrations, depending on the type of the reservoir rock.

TABLE I. CHARACTERISTICS OF SPRING WATER OF THE ŚLĘŻA MASSIF FLOWING OUT OF DIFFERENT TYPES OF CRYSTALLINE RESERVOIR ROCKS

Spring	Date of sampling	Radon concentration (Bq/L)	Discharge		Temp. (°C)	ECW (μS/m)	TDS (ppm)	pH	Type of reservoir rock
			(L/min)	(m^3/h)					
Życia	26/11/2002	1.3 ± 0.3	13.3	0.80	10.0	375	—	—	Serpentinite
	23/1/2003	1.1 ± 0.3	13.8	0.83	9.9	412	—	—	
	19/3/2003	1.2 ± 0.3	13.6	0.81	9.9	394	276	—	
	20/5/2003	1.2 ± 0.3	13.6	0.81	10.0	394	276	7.81	
	16/7/2003	1.1 ± 0.3	13.3	0.80	10.1	394	276	7.65	
	11/9/2003	1.1 ± 0.2	12.4	0.74	10.0	393	275	7.75	
	18/11/2003	1.3 ± 0.2	12.0	0.72	9.9	397	279	7.95	
	28/1/2004	1.4 ± 0.2	12.2	0.73	9.6	392	276	7.95	
Jakuba	19/1/2003	7.3 ± 0.9	4.6	0.28	6.6	292	—	—	Gabbro
	19/3/2003	8.0 ± 1.1	3.8	0.23	5.4	276	193	6.50	
	25/5/2003	7.8 ± 1.2	5.7	0.34	7.1	275	193	6.30	
	22/7/2003	7.2 ± 0.9	1.3	0.08	9.8	272	190	6.38	
	7/9/2003	6.7 ± 0.5	0.7	0.04	10.6	287	201	6.32	
	23/11/2003	7.1 ± 0.5	0.4	0.02	8.1	288	201	6.35	
	06/2/2004	9.3 ± 0.8	1.5	0.09	6.5	277	194	6.55	
Lustiga	25/5/2003	7.0 ± 1.0	4.2	0.25	8.7	293	205	6.05	Amphibolite
	16/7/2003	10.5 ± 1.2	2.3	0.14	10.8	304	213	5.95	
	11/9/2003	8.6 ± 0.6	0.7	0.04	12.4	293	205	5.95	
	18/11/2003	7.8 ± 0.5	0.3	0.02	8.0	263	184	6.25	
	28/1/2004	7.3 ± 0.5	0.2	0.01	3.6	276	193	6.75	
Joanny	22/7/2003	8.1 ± 1.0	0.6	0.04	13.8	259	—	6.47	
	7/9/2003	6.5 ± 0.5	0.1	0.01	13.7	264	185	6.49	
Jasne	19/1/2003	149 ± 9	66	3.96	8.0	208	—	—	Granite
	19/3/2003	154 ± 10	80	4.80	7.4	187	131	6.36	
	25/5/2003	127 ± 9	74	4.43	7.4	192	135	5.95	
	22/7/2003	229 ± 14	1.1	0.06	8.4	210	147	6.24	
	7/9/2003	209 ± 6	1.1	0.06	9.3	212	150	6.32	
	23/11/2003	166 ± 6	3.6	0.21	7.5	215	154	6.25	
	16/2/2004	155 ± 5	3.0	0.18	6.0	277	194	6.55	
Korzenne	6/8/2003	101 ± 7	1.7	0.10	11.4	210	147	—	
	7/9/2003	70 ± 3	0.5	0.03	11.5	220	—	6.60	
	23/11/2003	76 ± 4	1.0	0.06	8.3	224	157	6.25	
	6/2/2004	164 ± 5	14.7	0.88	7.2	195	137	6.35	

TABLE II. RADON CONCENTRATIONS IN SPRING WATER OF THE ŚLĘŻA MASSIF FLOWING OUT OF DIFFERENT TYPES OF CRYSTALLINE RESERVOIR ROCKS

Spring	Reservoir rock	Radon concentration (Bq/L)		
		Minimum	Mean	Maximum
Życia	Serpentinite	1.1	1.2	1.4
Jakuba	Gabbro	6.7	7.6	9.3
Joanny	Amphibolite	6.5	7.3	8.1
Lustiga	Amphibolite	7.0	8.2	10.5
Jasne	Granite	127	170	229
Korzenne	Granite	70	103	164

5. CONCLUSIONS

Investigations into the concentration changes of radon dissolved in the groundwater flowing out of springs in the Ślęża Massif confirmed their dependence on the type of reservoir rock. The highest and simultaneously the most changeable values were recorded in the water flowing out of granites, while the lowest values, exhibiting no significant variations in time, are characteristic of the water flowing out of serpentinites. The measurement of radon concentrations dissolved in the groundwater of this region make it possible to distinguish the water flowing through granites and serpentinites from those flowing through the other rock types. On the other hand, groundwater flowing through gabbros, metadiabases and metabasalts do not differ with regard to the concentration of radon dissolved in them.

The investigation results obtained so far point to the necessity of careful location of groundwater intakes in the areas with complicated (mosaic-like) geological setup, like the Sudetes, in order to ensure the radiation protection of the local residents.

The results, presented here, of the research carried out in the Ślęża Massif, as well as in other parts of the Sudetes, suggest the possibility of employing radon as a natural radioactive tracer of flow pathways and mixing zones of different components of underground and surface water.

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RADIUM LEACHING FROM MINE DEPOSITS AND OTHER MATERIALS

S. Chałupnik[1*], J. Aguado[2]

[1]Laboratory of Radiometry, Central Mining Institute, Katowice, Poland
[2]Huelva University, Spain

Abstract

Saline waters occurring in underground coal mines in Poland often contain natural radioactive isotopes, mainly ^{226}Ra from the uranium series and ^{228}Ra from the thorium series. Approximately 40% of the total amount of radium remains underground in the form of radioactive deposits, but 225 MBq of ^{226}Ra and 400 MBq of ^{228}Ra are released daily to the rivers with mine effluents through surface settling ponds. A very peculiar situation is observed in coal mines where, as a result of precipitation of radium from radium-bearing waters, radioactive deposits are formed. Sometimes the natural radioactivity of such materials is very high. In the case of scaling from coal mines, the radium concentration may reach 400 000 Bq/kg — similar to that in a 3% uranium ore. Usually such deposits can be found underground, but sometimes co-precipitation of radium and barium takes place on the surface, in settling ponds and in rivers. Therefore, maintenance of solid and liquid waste with technologically enhanced natural radioactivity (TENORM) is a very important subject. Lately, another problem appeared — due to a decrease in production from the Polish coal industry and the dismantling of several coal mines, the ground reclamation also needs to be done in the vicinity of such mines. But in several cases, deposits in the ponds contain enhanced concentrations of radium. Therefore, laboratory tests were done to investigate the possibility of re-entry of radium into groundwater or river waters from such deposits. Results show that in the case of insoluble barium and radium sulphates co-precipitated out from type A water, the re-entry ratio is very small. A different situation can be observed in the case of radium adsorbed on bottom sediments from type B waters, because the re-entry ratio is much higher. This phenomenon seems to be important and significant for the prediction of pollution of the adjacent areas of the settling ponds in future. A similar situation can be observed for other materials with enhanced radium content, for instance phosphogypsum. Therefore, further study of radium leaching from different solid materials is necessary.

1. INTRODUCTION

Saline waters from underground coal mines in Poland often contain naturally occurring radioactive isotopes, mainly ^{226}Ra from the uranium decay series and ^{228}Ra from the thorium series. Approximately 40% of the total amount of radium remains underground as radioactive deposits, but significant quantities of radium isotopes are released daily into the settling ponds and rivers along with the other mine effluents from all Polish coal mines. Technical measures such as inducing the precipitation of radium in gobs and decreasing the amount of meteoric inflow water into underground workings have been undertaken in several coal mines, and as a result of these measures the total amount of radium released to the surface waters has diminished by about 60% during the last 5–6 years.

Previous investigation has shown that the concentration of radium in water is correlated with its salinity [1]. As the salinity of mine waters usually increases with depth, waters with higher radium concentration occur in the deeper levels. Two different types of radium-bearing

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[*] E-mail: s.chalupnik.@gig.katowice.pl

water were found in coal mines [2]. One type (type A) contains high concentrations of radium and barium, but no sulphate ions, whilst the other (type B) has very low barium but high radium and sulphate concentrations. From type A waters, radium is easily co-precipitated with barium sulphate when mixed with other natural waters containing sulphate ions. For radium-bearing type B waters, there is no co-precipitant for radium, therefore precipitation does not occur. Further investigation showed that radium-bearing waters released from coal mines sometimes cause widespread contamination of both small and larger rivers in the vicinity [3]. This contamination is caused by radium being present in ionic form in water as well as in suspended matter. Highly radioactive deposits are formed by co-precipitation of barium and radium as sulphates from radium-bearing type A water [1]. This process results in the reduction of the total activity released into rivers because part of the radium remains in the underground mine workings. Precipitation of barium and radium sulphates in underground mine workings takes place either spontaneously or as a result of applied treatment procedures which aim to reduce the radium concentration in waste waters below the permitted level.

The presence of barium in waters is the most important factor influencing the future behaviour of radium isotopes in mine galleries or on the surface. From type A waters, radium and barium always co-precipitate as sulphates when such waters are mixed with any water containing sulphate ions. As a result of the precipitation of barium sulphate, deposits with highly enhanced radium concentrations, which may sometimes reach 400 000 Bq/kg, are formed [4]. By comparison, the average radium content in soil is 25 Bq/kg [5]. In the case of type B radium-bearing water, no precipitation occurs due to the absence of the barium carrier. Radium is removed from such waters in a slow process of sorption on bottom sediments in gautons in underground galleries or on the surface in the settling ponds and rivers. In this case, the increase of radium content in sediments is much lower than that for type A water; but we can observe enhanced concentrations of radium isotopes in river water or in bottom sediments for a long distance downstream from the discharge points [6].

Nowadays a new problem arises — as a result of the decrease of the coal production in Poland, several collieries were closed. Thousands of tonnes of bottom sediments with enhanced natural radioactivity remain in their settling ponds. Radium from such deposits may be leached as a result of groundwater impact and may cause the contamination of the natural environment in the vicinity of abandoned mines. The study of that problem needs to be performed carefully.

2. THE SCOPE OF INVESTIGATIONS

The scope of the investigation was focused on radium leaching from different types of mine deposits, but additionally experiments with phosphogypsum were carried out to compare the results with those of other investigations.

A technique for radium leaching from solid materials was developed during previous experiments [7]. Appropriate methods were chosen to determine the concentration of radium isotopes in the solid phase (gamma spectrometry) and in solutions (liquid scintillation counting (LSC)). The analysis of the results enabled the possibility of groundwater contamination in the vicinity of abandoned settling ponds to be predicted. Additionally, a study of radium leaching from Spanish phosphogypsum was performed to compare the results of the experiments with the results of Spanish investigations. One of the reasons was to check whether the results were dependent on leaching technique.

3. RESULTS OF RADIUM LEACHING

3.1. Measurements of radium concentration in solid phase

Solid samples were analysed for the presence of radioisotopes from the uranium and thorium decay series and ^{40}K. For these measurements, a gamma spectrometry system was used — it comprised an HPGe detector (45%, PGT), a multi channel analyser built into a computer and the Genie-2000 software for spectra analyses (Canberra). This instrumentation could measure concentrations of ^{226}Ra as low as 1 Bq/kg and of ^{228}Ra, ^{210}Pb, ^{40}K and other natural and artificial isotopes [8] down to similar levels.

Different types of bottom sediments were used in the leaching experiments, as well as phosphogypsum samples. The results of the gamma spectrometric measurements are shown in Table I.

TABLE I. NATURAL RADIONUCLIDES IN SOLID SAMPLES

Type of the sample	Activity concentration (Bq/kg)		
	^{226}Ra	^{228}Ra	^{210}Pb
Type B bottom sediment from abandoned pond:			
Mine R	1810 ± 90	980 ± 50	140 ± 30
Mine P	5900 ± 300	9950 ± 500	—
Spanish phosphogypsum	680 ± 40	18 ± 3	980 ± 90

3.2. Leaching technique and measurements of radium in solution

For the leaching experiment, 50 g of dried solid sample was used. This was mixed with 0.5 L of the solution (deionized water or other solvent). Firstly, the mixture was continuously stirred with a magnetic stirrer for 1 h and then left in contact for a given time (from 1 h up to 7 days). Finally, after the filtration of the sample, the radium isotopes were analysed and measured using LSC.

Radioactivity in water from coal mines is mostly from radium isotopes — ^{226}Ra from the uranium series and ^{228}Ra from the thorium series. An existing method of chemical separation of radium [9] was modified for LSC [10]. In this method, radium was co-precipitated with barium in the form of sulphates, and this precipitate was then mixed with a liquid gelling scintillator. The prepared samples were measured by a low background liquid scintillation spectrometer (Quantulus, Wallac Oy, Finland). This counter has alpha–beta separation with an anti-coincidence shield, which enables measurements of ^{226}Ra concentration above 3 Bq/m^3 with simultaneous measurement of ^{228}Ra at a lower limit of detection (LLD) of 30 Bq/m^3.

Deionized water was applied as the basic solvent due to its very low ionic strength. Therefore this solvent should leach only the fraction of radium atom that is loosely bound to the surface of sediment grains. It simulates leaching caused by rainwater. We predict elevated salinity of groundwater near settling ponds, therefore in some cases the solvent was prepared from deionized water and sodium chloride NaCl (10 g/L) with admixtures of potassium sulphate or carbonate (K_2SO_4 or K_2CO_3 at 2 g/L), barium or strontium chlorides ($BaCl_2$, $SrCl_2$ at 1 g/L). We wanted to simulate leaching of radium by solutions with elevated mineralization and different chemical compositions. Different admixtures were used:

- Potassium sulphate was used to simulate the presence of sulphate ions, which should decrease the radium leaching;
- Potassium carbonate was used to simulate the presence of carbonates in water, as radium carbonate is soluble;
- Barium chloride was added to increase radium leaching and the further possibility of co-precipitation of radium;
- Strontium chloride was used to check its influence on the rate of radium leaching from deposits.

One of the important conclusions from the measurements of radium content in deposits is the following. Water with very low radium content has been discharged to the settling pond of mine R. The maximum concentration of ^{226}Ra never exceeded 150 Bq/m^3 [11]. Despite this fact, the ^{226}Ra concentration in the bottom sediments was 1700–2500 Bq/kg, while the ^{228}Ra concentration was up to 1500 Bq/kg. This confirms the importance of radium adsorption on bottom sediments and other solid materials in settling ponds. After a certain time, the radium content in the solid phase may be high, even when the radium concentration in the water is low. Such a phenomenon seems to be crucial in waterworks [12], especially in cases where underground water is treated.

3.3. Leaching of radium from deposits in the settling pond of mine R

Samples of bottom sediments were taken from the settling pond during preparations for the ground reclamation of the area. The settling pond was located on an old pile of waste rocks, constructed from concrete blocks, and connected and sealed against leakage. The thickness of the sediment layer was about 40 cm, while the surface of the pond was about 2000 m^2. The ground reclamation technique entailed covering the sediments by a 5–7 m thick layer of waste rock. On the flat surface of the waste rock, soil was brought in from elsewhere and finally trees and grass were planted. Such a method of ground reclamation was proposed by experts from the Central Mining Institute.

In the sediment sample from the pond, the ^{226}Ra concentration was 1800 Bq/kg, while the concentration of ^{228}Ra was close to 1000 Bq/kg. These sediments were relatively young (less than 2 years), as the ^{210}Pb concentration was only 140 Bq/kg.

After drying of the sediments, 50 g samples were mixed with different solvents to calculate the leaching coefficients from solid to liquid phase. Different solvents were used, not only deionized water but also solutions of sodium chloride with admixtures of potassium carbonates or sulphates, barium chloride or strontium chloride.

The results of the radium measurements in the liquid phase after leaching are shown in Fig. 1. The concentrations of ^{226}Ra are plotted as a function of contact time. The 50 g sediment samples contained approximately 90 Bq of ^{226}Ra and 50 Bq of ^{228}Ra. It can be seen from Fig. 1 that the amount of leached-out radium activity was about 0.6 Bq for ^{226}Ra and 0.4 Bq for ^{228}Ra when barium chloride solvent was used. In the case of potassium carbonate solvent, only 0.2 Bq of ^{226}Ra and 0.2 Bq of ^{228}Ra activity were transferred from the solid to liquid phase. The calculation of leaching coefficients gave the following results — 0.6% of the ^{226}Ra activity and 0.8% of the ^{228}Ra activity were leached into the barium chloride solvent, while 0.2% of the ^{226}Ra activity and 0.4% of the ^{228}Ra activity were leached into the carbonate solvent. For deionized water, the values of leaching coefficients were lower — 0.15% for ^{226}Ra and 0.3% for ^{228}Ra. It should be noted that the uncertainties for the ^{228}Ra coefficients were rather high (at least 25%), even for the maximum value. In the case of ^{226}Ra, the uncertainties were lower —approximately 10%.

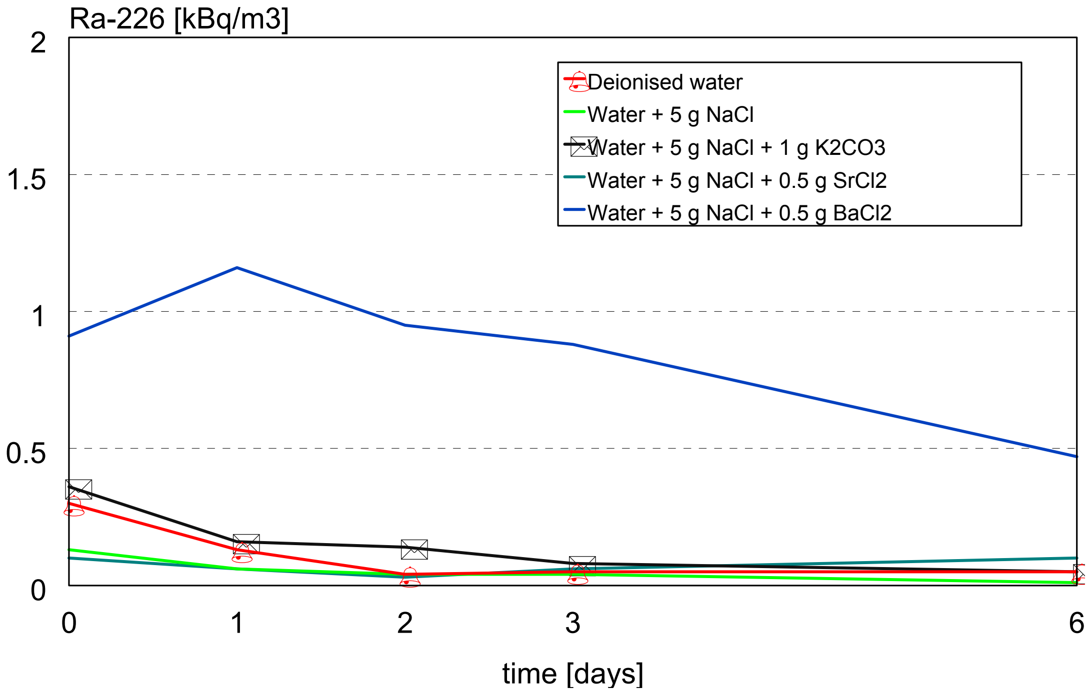

FIG.1. Results of radium leaching experiments on settling pond sediment at mine R

One important conclusion is that strontium, unlike barium, does not influence the leaching of radium from deposits. The chemical properties of strontium seem to be closer to the properties of calcium. Therefore, there should be no correlation between strontium concentrations and radium concentrations in mine water.

3.4. Leaching of radium from deposits in the settling pond of mine P

In another series of experiments, the bottom sediment from mine P was used. A sediment sample was taken from the abandoned settling pond 1½ years after the release of water from the pond. The bottom sediments were exposed to atmospheric precipitation during this time, and one of the aims of our investigations was to check whether any changes of leaching coefficient could be seen. The sample was taken at the location where the highest radon exhalation factor had been measured. Moreover, in the same place, samples of bottom sediments had been taken a year ago. It gave us the opportunity to check the changes of radium availability in the upper layer of sediment. In this part of the pond, the total thickness of the deposit was about 1 m. Even though the deposit was almost entirely saturated with water, the radon exhalation was extremely high — up to 350 $mBq{\cdot}m^{2}{\cdot}s^{-1}$. Radon exhalation may be an important source of radiation hazard in such areas. Therefore, reclamation technique of abandoned settling ponds musts be chosen properly. The results of radium leaching from the bottom sediments of mine P settling pond are shown in Fig. 2.

Sediments from settling pond P contained 29 Bq of ^{226}Ra and 50 Bq of ^{228}Ra in the 50g sample. Fig. 2 shows the results of experiments performed with different solvents. The maximum radium activity in the solutions after the leaching tests was 0.1 Bq for ^{226}Ra and 0.15 Bq for ^{228}Ra. The leaching coefficient was calculated, and the maximum value was 0.3% for each radium isotope. No significant differences were observed between particular solvents, except for slightly higher concentrations in the barium chloride solvent. A similar effect was found for this type of deposit during earlier investigations [7].

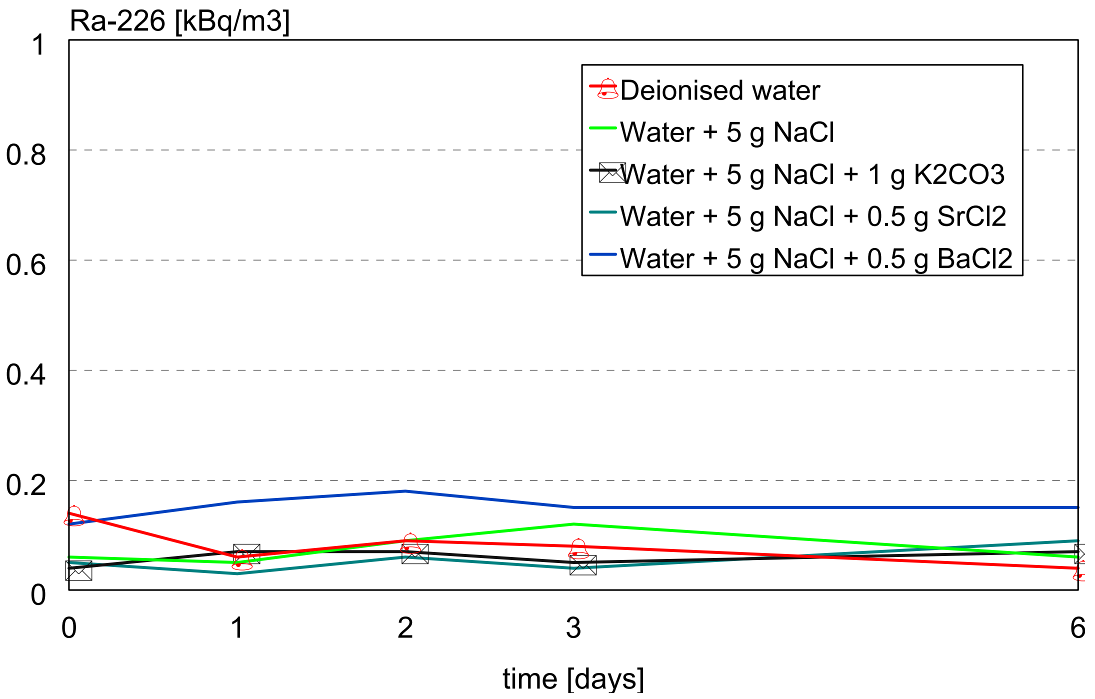

FIG. 2. Results of radium leaching experiments on settling pond sediment at mine P

These results were surprisingly low in comparison with previous results of radium leaching from sediments taken from the same pond and site two years earlier. The previous investigations showed leaching factors up to 10%. A comparison of these results is shown in Fig. 3.

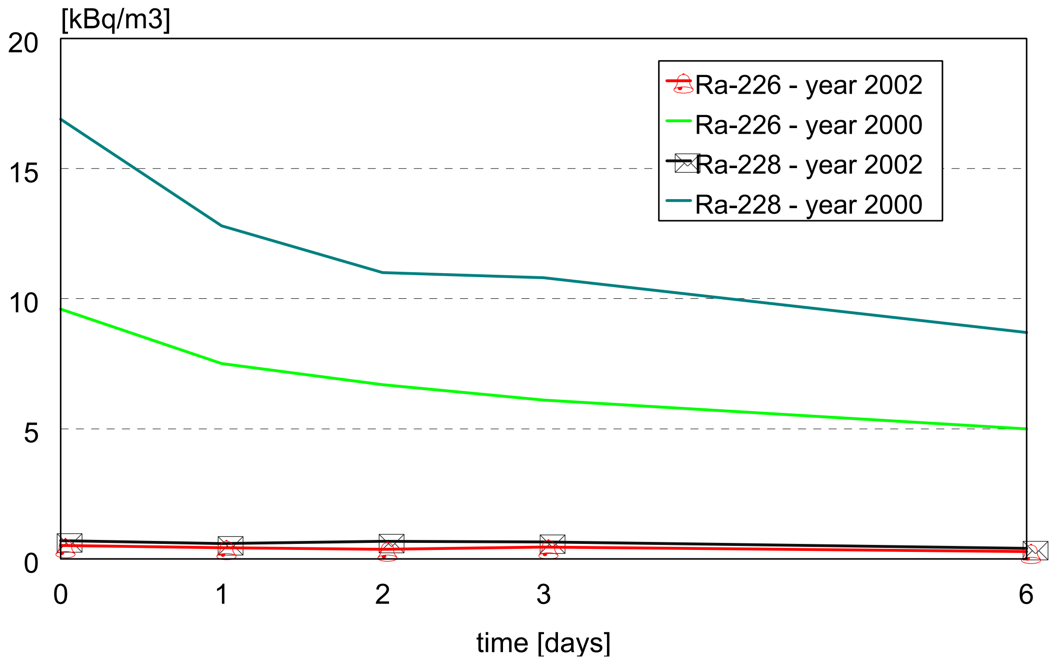

FIG. 3. Comparison of 2000 and 2002 results of radium leaching experiments on settling pond sediment at mine P

Such significant differences may be due to two possible reasons. One reason could be the drying-out of the sediments and the effect of this on the chemical processes in which radium may have been involved for a relatively long time. Another reason could be that most of the radium had already been leached by rainwater into deeper layers of sediment, whereas samples had been taken from the surface. Two conclusions can be drawn from this comparison. Firstly, bottom sediments in settling ponds must be isolated from groundwater and meteoric waters. The transfer of radium into the liquid phase from dry deposits is very low; therefore the possibility of groundwater contamination is also low. In such cases, the contamination of adjacent areas should be negligible.

On the other hand, radium leaching by meteoric waters is sometimes significant, especially in the case where deposits are left uncovered for a long time. Therefore, deposits with enhanced radium concentrations should not be disposed of in surface waste piles where seepage of rainwater might be an important source of surface water contamination.

4. COMPARISON OF THE TECHNIQUE WITH THOSE OF OTHER INSTITUTES

In recent years, investigations of radium leaching from different materials have become increasingly important. Various institutions have identified this phenomenon as a significant source of pollution in the vicinity of settling pond and waste disposal tips. For instance, several presentations were focused on this subject during the Natural Radiation Environment Conference held in Rhodes, Greece in 2002 (NRE VII). However, the results of different experiments vary significantly for similar samples, probably due to different leaching techniques. To check such a possibility, a comparison of measurements has been started at the Central Mining Institute.

In the first instance, a comparison was proposed with the results obtained by a team from Huelva University, Spain [13]. During investigations made at this centre, it was found that leaching factors for phosphogypsum into the water phase were about 1%. The leaching time was 7–14 days. The concentration of radium was measured using the LSC technique.

A small sample of phosphogypsum (200 g) was analysed at the Central Mining Institute. Firstly, gamma spectrometric analysis was done (see Table I). Later, leaching experiments were performed in accordance with the technique used routinely at that laboratory. The only difference was the smaller amount of the solid sample (25 g instead of 50 g) mixed with the solvent. The results of the experiments are shown in Fig. 4. Calculations of the leaching coefficients gave a wide range of values, depending on the solution. For instance, the coefficient was only 0.04 % in the case of barium chloride solution (the lowest) and 0.19 % for deionized water. The highest values were found for the sulphate solvent (0.29 %) and for the solution with enhanced salinity (0.35 %). The results were in good agreement with results of the Spanish investigators. The most significant difference between leaching processes from mine sediments and from phosphogypsum seems to be the different influence of barium in the solvent. In the case of bottom sediments from settling ponds, the presence of barium ions in the solution leads to an increase in radium leaching. For phosphogypsum, the opposite situation is observed. This can be explained rather easily — phosphogypsum is partly soluble and, in water, sulphate ions appear as a result of this process. It leads to the co-precipitation of barium and radium as sulphates, i.e. the secondary removal of radium from the liquid phase and a decrease in the effective leaching coefficient. On the other hand, the admixture of potassium sulphate has no effect, as sulphate ions are already in the solution. To compare results for different types of phosphogypsum, further experiments with phosphogypsum samples from Greece, Czech Republic and Poland have been started.

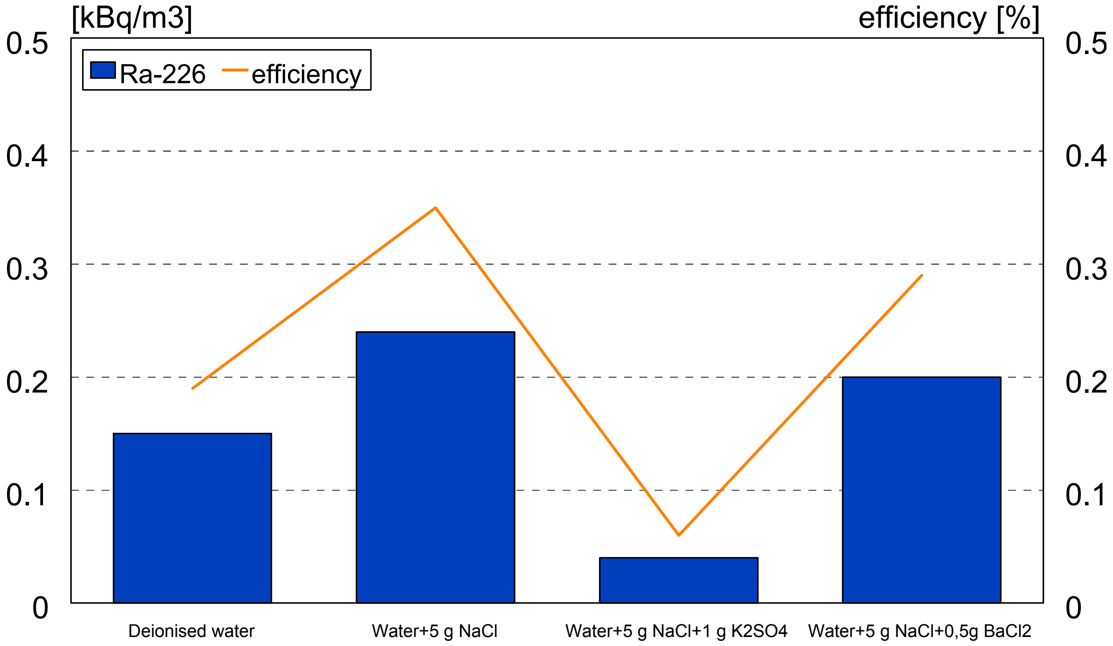

FIG. 4. Results of radium leaching experiments on Spanish phosphogypsum

5. CONCLUSIONS

The results of the investigations are consistent with those of preliminary assessments — they show that the leaching of radium from mine sediments formed from type B water may be an important source of groundwater contamination in the vicinity of settling ponds. Therefore, special methods of ground reclamation should be applied in such areas to decrease the potential for pollution of the natural environment. The main issues are the mitigation of groundwater flow through sediments and the design of an appropriate monitoring system. It will increase the costs of ground reclamation.

In contrast, the radium concentrations in type A water sediments are often much higher but the leaching effects are extremely low. Ground reclamation of settling ponds with such sediments should be cheaper and safer for the environment and population of adjacent lands. Unfortunately, scarce data are available, concerning the long-term fate of radionuclides in such deposits. Therefore further investigations are necessary.

Sediments with enhanced radium content can be formed as a result of the long-term release of water with low radium content or the treatment of groundwater in waterworks. All sediments from such settling ponds or filters should be examined for the presence of radionuclides. Appropriate methods of disposal must be applied to avoid contamination of the natural environment.

A comparison of results of leaching experiments shows that some form of standard method should be developed for this purpose, despite the fact that different techniques in different laboratories have given comparable results. Further comparisons and unification of the methods are necessary.

Our investigations show that the process of radium leaching from mine deposits into groundwater or surface waters in not an insignificant problem for environmental protection and requires more attention in the future.

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RADIUM BALANCE IN DISCHARGE WATERS FROM COAL MINES IN UPPER SILESIA REGION

S. Chałupnik*, M. Wysocka, A. Mielnikow, B. Michalik, J. Skowronek

Laboratory of Radiometry, Central Mining Institute, Katowice, Poland

Abstract

Saline waters from underground coal mines in Poland often contain natural radioactive isotopes, mainly ^{226}Ra from the uranium decay series and ^{228}Ra from the thorium series. Approximately 60% of the radium remains underground as radioactive deposits, but 120 MBq of ^{226}Ra and 200 MBq of ^{228}Ra are released daily into the rivers along with the other mine effluents from all Polish coal mines. Technical measures such as inducing the precipitation of radium in gobs and decreasing the amount of meteoric water flowing into underground workings have been undertaken in several coal mines, and as a result of these measures the total amount of radium released to the surface waters has diminished by about 60% during the last 5–6 years. Mine water can have a severe impact on the natural environment, mainly due to its salinity. However associated high levels of radium concentration in river waters, bottom sediments and vegetation have also been observed. Sometimes radium concentrations in rivers exceed 0.7 Bq/L, which is the permitted level for waste waters under Polish law. The extensive investigations described here were carried out for all coal mines and on this basis the total radium balance in effluents was calculated. Measurements in the vicinity of mine settling ponds and in rivers have given us an opportunity to study radium behaviour in river waters and to assess the degree of contamination.

1. INTRODUCTION

Very often, human activity connected with the exploitation of mineral resources leads to the contamination of the natural environment. Sometimes natural radionuclides are released or concentrated as waste material. In Poland, the main source of waste and by-products with enhanced concentration of natural radionuclides is the power industry, based on coal exploitation and combustion. In the hard coal mining industry, 50 million t of different waste materials are produced annually. As a result of coal combustion in power plants, the area of fly ash and sludge piles is increased by several square kilometres per year [1].

The Upper Silesian Coal Basin (USCB) is located in the south-western part of Poland. Presently there are 66 underground coal mines there extracting approximately 150 million t/a of coal. The depth of the mine workings is 350–1050 m. Upper Silesia is characterized by a very complicated and differentiated geological structure with numerous faults and other tectonic dislocations [2]. Additionally, the area is very affected by mining.

Two hydrological regions of the USCB have been distinguished. The first region is located in southern and western Silesia with thick strata of sediments covering the carboniferous formation. This overlay is composed mainly of Miocene clays and silts. The thickness of these rocks is up to 700 m. Such strata make the migration of water and gases almost impossible. In the second region, Miocene clays do not occur. Carboniferous strata are covered by Quaternary sediments, slightly compacted.

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* E-mail: s.chalupnik.@gig.katowice.pl

The oldest formations in this area form isolated sediments of Permian or Triassic limestone, strongly fissured. There are numerous outcrops of coal seams. These formations enable very easy migration of water and gases.

An additional and unexpected component of the radioactive contamination of the natural environment, and different from that usually associated with this kind of industry, is caused by underground coal exploitation. In many coal mines located in the USCB, water with an enhanced radium content occurs [3]. Sometimes, barium ions are also present in radium-bearing brines in concentrations up to 2 g/L. Such water has been classified as radium-bearing type A water. On the other hand, in the second kind of water, which has been called type B, no barium can be found but radium and sulphate ions are present.

About 40 underground coal mines operate in the USCB. The total water outflow from these mines is about 800 000 m^3/day. The salinity of these brines is far higher than that of ocean water. The total amount of salt (total dissolved solids (TDS)) carried with mine water to the rivers is about 10 000 t/day. The commonest ions in these brines are Cl^- and Na^+ with concentrations up to 70 and 40 g/L respectively. Additionally, brines usually contain several grams per litre of Ca^{2+} and Mg^{2+} and significant amounts of other ions [4]. Water with high radium concentration occurs mainly in the southern and central part of the coal basin where coal seams are overlaid by a thick layer of impermeable clays [5]. This saline water causes severe damage to the natural environment, mainly because of its high salinity (sometimes >200 g/L), but also because of its high radium concentration, reaching 390 Bq/L [6].

The presence of barium in water is the most important factor for the future behaviour of radium isotopes in mine galleries or on the surface. Radium and barium always co-precipitate as sulphates from type A water when mixed with any water containing sulphate ions. As a result of the precipitation, barium sulphate is deposited along with the formation of highly enhanced radium concentrations [3, 7]. The total activity of radium isotopes in these sediments may sometimes reach 400 000 Bq/kg. In comparison, the average radium content in soil is 25 Bq/kg [8]. In case of radium-bearing type B water, no precipitation occurs due to the lack of the barium carrier, and that is why the increase of radium content in sediments is much lower than those originating from type A water.

2. APPLIED METHODS AND INSTRUMENTATION

Radioactivity in water from coal mines is mostly from ^{226}Ra from the uranium series and ^{228}Ra from the thorium series. An existing method of chemical separation of radium [9], has been modified for liquid scintillation counting [10]. Radium is co-precipitated with barium in the form of sulphates and this precipitate is mixed with liquid gelling scintillator. The prepared samples were measured by a low background liquid scintillation spectrometer (Quantulus, Wallac Oy, Finland). This counter is equipped with alpha–beta separation and anti-coincidence shield, which enables measurements of ^{226}Ra concentration above 0.003 Bq/L with simultaneous measurements of ^{228}Ra (LLD = 0.03 Bq/L) and ^{224}Ra (LLD = 0.05 Bq/L). In addition, the procedure enables the simultaneous preparation of ^{210}Pb, which can be separated from radium isotopes at the last stage of analysis and also measured in the LS spectrometer with a detection limit of 0.02 Bq/L.

3. SYSTEM OF MONITORING IN THE VICINITY OF COAL MINES

In the mining industry in Poland, the monitoring of radioactivity in mine waters and precipitates, as well as gamma doses has been obligatory since 1989. The monitoring of radioactive contamination caused by effluents and tailings from coal mines has been a requirement since 1986 [11]. In terms of these regulations, the following measurements must be done in the vicinity of the mine:

- The concentration of ^{226}Ra and ^{228}Ra in effluent from the settlement pond, in the river above and below the discharge point, and in water supplies near the discharge point;
- The concentrations of natural radionuclides in solid material dumped onto the piles.

Such a complex monitoring system gives an opportunity to obtain a complete picture of the radiological impact of a certain mine on the underground and surface employees as well as on inhabitants of adjoining areas.

The concentration of radium isotopes in original water samples from different coal mines varies in a very wide range — from 0 to 0.11 Bq/L for ^{226}Ra and from 0 to 0.07 Bq/L for ^{228}Ra [12]. In the 1980s, water with a radium concentration above 1 Bq/L was found in 43 out of 65 coal mines in the USCB. The highest concentrations of radium were measured in highly mineralized water from deeper levels in type A radium-bearing water. The ratio of ^{226}Ra to ^{228}Ra in type A radium-bearing water was on average about 2:1. In contrast, in type B radium-bearing water there was more ^{228}Ra than ^{226}Ra, the ratio ^{226}Ra to ^{228}Ra being from 1:2 up to 1:3. The concentration of ^{226}Ra in this water reached 20 Bq/L, while the maximum concentration of ^{228}Ra was as high as 32 Bq/L. These values justify the statement that Upper Silesian radium-bearing water has some of the highest known radium concentrations.

The monitoring requirements for mine water are shown in Table I.

TABLE I. MONITORING FREQUENCY FOR DISCHARGE WATER IN POLAND

Sampling site	Frequency of monitoring	
	All mines	If concentration of ^{226}Ra + ^{228}Ra in discharge waters exceeds 700 Bq/m^3
Discharge water from underground workings at the inflows and outflows of surface settling ponds	Once a year	At least once per quarter
Discharge points into rivers	Once a year	At least once per quarter
River water upstream and downstream from discharge points	Once a year	At least once per quarter
Underground water for drinking or utilization	Once per 6 months	—
Surface wells possibly influenced by discharge of brines	—	At least once per quarter

Original water flowing from different aquifers into the mine workings through the rock is collected in gutters in underground galleries, brought together from different parts of the mine, clarified and pumped out to the surface. The radium concentration in this mixed water was found to be lower than in the original water and did not exceed 25 Bq/L of ^{226}Ra and 14 Bq/L of ^{228}Ra [12].

Based on the results of measurements of radium concentration in the original water inflows into the mine workings and on data on the flow rates of water provided by the mine hydrologists, the total activities of both radioisotopes of radium flowing with water to different parts of the mines and to different mines were calculated. These results were compared with the radium concentrations in mixed water taken from the drainage system (from gutters) from different parts of mines and the corresponding flow rates obtained from the mines. The difference indicates the activity of radium remaining in the underground mine workings due to spontaneous precipitation of radium and barium sulphates or due to water purification. The activity of radium remaining in the underground mine workings as deposits in all Upper Silesian coal mines was calculated to be 525 MBq/day of ^{226}Ra and 480 MBq/day of ^{228}Ra. These values cannot be considered as very accurate, since the uncertainty of the flow rate measurements of small inflows is rather large. The approximate amount of ^{226}Ra in water inflows in coal mines in the USCB have been calculated to be as high as 650 MBq/day (i.e. 230 GBq per year) while for ^{228}Ra this value is about 700 MBq/day or 255 GBq per year. Although radium concentrations in type B water are usually lower than in type A water, the total inflows to mines where type B radium-bearing waters occur are much higher. As a result, the total activity of radium carried with type B water is higher. The highest values for a single mine (with type B water) are 78 MBq per day of ^{226}Ra and 145 MBq per day of ^{228}Ra.

In comparison, the corresponding inflows of radium with saline waters in 4 copper mines in Poland are 31 MBq of ^{226}Ra and 3 MBq of ^{228}Ra per day.

4. ASSESSMENT OF RADIUM BALANCE IN DISCHARGE WATERS

One of the biggest advantages of the monitoring system in the Upper Silesia region is the possibility of making an assessment of the radium balance in discharge water periodically. Such assessments were conducted in 2002 and 2003. For the calculations, about 300 mine waters results were taken as well as 40 analyses of river water. The term ‘mine water’ means not only mine water but also river waters close to the discharge points. The term ‘river water’ is used for the samples taken at the sampling points of the regional water quality monitoring system. All the data were included in the mine waters database in the Laboratory of Radiometry as inputs to radiation hazard monitoring and environmental monitoring. A comparison of the assessment results in the periods of investigation is shown in Table II.

The assessment of the total activity of radium released from coal mines in Upper Silesia with waste water is based on:

- Results of the determination of radium isotopes in waters released by collieries;
- Data on the amount of water released by individual mines.

We have also estimated the total activity of radium remaining in underground workings in the form of deposits precipitated out of radium-bearing water either due to unintended mixing of natural water of differing chemical composition or due to the purification of radium-bearing water. This estimation was based on:

- Results of the determination of radium isotopes in the original water flowing into the underground mine workings through the rock;
- A rough estimation of the amounts of water inflows from different sources or parts of mines;
- The calculated value of the total activity of radium pumped out from underground mine workings with waste waters by individual mines.

The results of the calculations of the total activities of radium present in water pumped out from individual mines are much more accurate. These values were calculated based on the radium concentration determined in this water and on water quantity data provided by mines.

Samples of discharged water were taken from settling ponds. In outflows from these ponds, the ^{226}Ra concentration exceeded 0.008 Bq/L in 87 % of mines, exceeded 0.1 Bq/L in 25% of mines, and exceeded the permissible level (0.7 Bq/L) in 8 % of mines [12].

TABLE II. COMPARISON OF RADIUM BALANCE ASSESSMENTS IN RIVERS IN THE UPPER SILESIA REGION

Catchment area	No. of mines	Total activity (MBq/day)				
		1987	1995		2003	
		^{226}Ra	^{226}Ra	^{228}Ra	^{226}Ra	^{228}Ra
Inflows into Olza pipeline	11	261.8	9.8	6.7	6.8	6.8
Olza river: discharge of Olza pipeline	11	35.4	1.6	1.4	2.5	1.8
Ruda–Nacyna rivers	3	4.8	2.2	1.4	0.7	0.7
Bierawka river	5	7.4	1.6	1.2	2.7	3.2
Bytomka river	5	0.6	0.4	0.5	1.5	3.0
Kłodnica river	7	7.3	2.6	2.9	2.6	3.7
Rawa river	4	0.7	0.2	0.2	1.2	2.7
Brynica river	4	1.1	0.0	0.0	1.4	2.4
Przemsza river	2	7.8	0.4	0.8	2.3	5.6
Bobrek river	3	4.0	0.2	0.2	0.3	1.2
Black Przemza river	4	1.2	1.6	3.1	1.3	2.3
Gostynka river	3	224.6	133.9	248.1	61.1	146.7
Mleczna river	2	0.7	1.3	2.4	1.5	3.3
Upper Vistula river	4	191.8	73.0	117.2	42.9	84.2
Total	35 active 30 abandoned	397.7	219.1	380.1	120.1	258.2

In rivers, enhanced concentrations of radium can be observed many kilometres below the discharge points. This is mainly true for type B radium-bearing waters, because radium is not easily precipitated out of these waters. The highest value of ^{226}Ra concentration was 1.3 Bq/L — it was found in a small stream near its conjunction with the Vistula river.

The significant decrease of daily discharge of radium can be seen in the period 1987–1995. There were two reasons for this effect. Firstly, the purification of type A mine waters was started in several coal mines in the catchment areas of the Olza river and Upper Vistula. Another reason was due to economic changes in the mining industry — dewatering of deep mines became increasingly expensive and hydro-technical solutions were applied in numerous mines to reduce water inflows into underground galleries, with special emphasis on brines.

The decrease of radium activity in discharge waters during the most recent period was due mainly to the purification of type B brines in Piast colliery. The implementation of treatment technology in the deeper levels of the mine caused a decrease in the radium release from the mine to 150 MBq/day (60 MBq/day of ^{226}Ra and 90 MBq/day of ^{228}Ra). The application of purification technology in another mine should further reduce the discharge of radium. Construction of the system has been already started. Additionally, a purification system for a second level of Piast mine is being designed, which will solve most of the problems with radium contamination of river waters in the Upper Silesia region.

Enhanced radium concentrations are observed mainly in the Vistula river, into which most of the radium is discharged with type B waters — approximately 110 MBq of ^{226}Ra and 250 MBq of ^{228}Ra per day. A ^{226}Ra concentration of 0.035 Bq/L was observed in the Vistula river in Krakow, 70 km downstream from Upper Silesia. Some of these waters are not discharged directly into the Vistula river, but into its tributaries. The influences of individual inflows can be seen very clearly. Moreover, the water from the first mine is type A and the difference in radium behaviour (fast precipitation) in comparison with the other 3 mines (type B water) is very evident. A different situation was observed in the vicinity of the Oder river, where the water in the coal mines is mainly type A. The amount of radium discharged into this river is much lower — 10 MBq of ^{226}Ra and 5 MBg of ^{228}Ra per day. As a result, concentrations of radium in the Oder *are below 0.1 Bq/L.*

The concentrations of radium isotopes in some rivers in Upper Silesia are clearly enhanced compared with natural levels. In comparison with data from other locations, the concentrations of radium isotopes in the rivers in the USCB are significantly higher. Enhanced concentrations of radium in river water in Upper Silesia are caused solely by the influence of mine water.

Due to the release of radium-bearing mine waters from coal mines, there is contamination of river water. As a result, the radium concentration in some small rivers exceeds the permissible level for radioactive wastes. Therefore, the development and application of purification methods is justified and further efforts should be done to reduce the contamination of rivers, particularly the Vistula river and its tributaries.

On the other hand, we must take into account that the exploitation of deeper coal seams will cause more problems with inflows of radium-bearing brines into underground workings, even in mines where no radium problems exist now. Therefore, periodic monitoring of discharge waters is necessary. Another legal problem must be also solved — responsibility for the monitoring of waters released from abandoned mines.

5. SUMMARY

- Coal mining may cause significant pollution of the natural environment due to the release of waste water with enhanced concentrations of natural radionuclides (mainly radium isotopes). This phenomenon is well known not only in the USCB but also in other regions of underground exploitation of coal (the Ruhr Basin), oil and gas, or other resources.
- Due to mitigation measures undertaken by mines, a significant improvement can be observed during the last two decades. In most cases, radium concentrations in discharge water are low and surface water is not contaminated. Moreover, a further decrease of radium release is predicted as a result of underground mine water purification in two collieries.
- A monitoring system for natural radionuclides in waste water and river water is an important element of the prevention of pollution of the natural environment. Moreover, it is a source of data for optimization of ground reclamation of previously contaminated areas (mainly settling ponds) of abandoned coal mines.

Of course, further improvement of the system is required, as well as a solution to important legal problems related to the closure of coal mines, harmonization with EU regulations etc.

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TEST THRESHOLDS FOR ASSESSMENT OF POSSIBLE GROUNDWATER CONTAMINATION AT SITES CONTAMINATED WITH RADIOACTIVE MATERIALS

R. Gellermann[1*], M. Hahn[2], U. Haberlau[2], J. Beetz[2]**

[1]HGN Hydrogeologie GmbH, Magdeburg, Germany

[2]Landesamt für Verbraucherschutz und Landwirtschaft Brandenburg, Frankfurt (Oder), Germany

Abstract

At several sites in Brandenburg the ground is contaminated with natural radionuclides, especially thorium from former industrial processes. Such type of contamination is regulated neither in the Federal Ordinance on Soil Protection and Contaminated Sites (BBodSchV) nor in the German Radiation Protection Ordinance (StrlSchV). However, the European Basic Safety Standards Directive specifies that areas of a former practice or work that are a source of permanent risk to people have to be demarcated and controlled. If necessary, intervention measures need to be carried out and access must be restricted. Therefore treatment of such cases requires technical regulations and supporting instructions to facilitate correct decisions by the relevant authorities. Such regulations must conform to the existing regulations, especially the BBodSchV and guidelines of urban land-use planning. When assessing existing situations, the groundwater exposure pathway is of particular significance for any decision-making. Suitable criteria and instructions were derived in order to identify for this special pathway those areas that can be considered uncontaminated and therefore exempt from further radiological investigations and from any restrictions concerning land-use planning. The methodical approach corresponds to the leachate forecast according to BBodSchV. The results obtained are presented in the paper.

1. INTRODUCTION

Several sites in Brandenburg are contaminated with residues from former thorium and uranium production or use. Such type of contamination is regulated neither in the Federal Ordinance on Soil Protection and Contaminated Sites (BBodSchV) nor in the German Radiation Protection Ordinance (StrlSchV). Nevertheless, the risks resulting from such contamination must be assessed for any decisions concerning the planning and use of the land. Therefore, the Environmental Protection Agency of Brandenburg initiated a study [1] with the following aims:

- Derive test thresholds for assessment of sites with radioactive contaminants for potential groundwater contamination by radionuclides,
- Develop a guideline for application of these test thresholds in a stepwise investigation of suspicious sites.

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[*] E-mail: r.gellermann@hgn-online.de
[**] E-mail: michael.hahn@lvl.brandenburg.de

It was required that the test thresholds should differentiate between soils that can be classified as uncontaminated and those that must be investigated in greater detail, and that the test thresholds should be based on measurable values related to soil, leachate or groundwater.

2. RADIONUCLIDES — HARMFUL SUBSTANCES OF A SPECIAL KIND?

Thorium and uranium are natural radioactive elements. If their concentrations cause a significant increase in exposure, they cannot be disregarded from the radiation protection point of view (EU Directive 96/29 Title VII).

Due to their special status in environmental legislation and a sensitive awareness of the public, radionuclides are often seen as a special kind of harmful substances different from 'common' contaminants. However, the comparison between natural radionuclides, organic contaminants (e.g. PAH) and heavy metals given in Table I reveals some general similarities of these contaminant groups. All of them are mixtures of components with different constituents. In soils contaminated with thorium or uranium these radionuclides are isotopes of U, Th, Ra, Pb, Po.

TABLE I: COMPARISON OF SOME BASIC ATTRIBUTES OF RADIONUCLIDES, ORGANIC CONTAMINANTS (PAH), AND HEAVY METALS

	Natural radionuclides	PAH	Heavy metals
No. of substances	36 radionuclides	16 compounds (EPA)	~ 20 elements
Relevant no. of substances in water	5–7 (^{238}U, ^{226}Ra, ^{210}Pb, ^{210}Po, ^{228}Ra, ^{228}Th)	6–8	6–8
Temporal changes of total amounts	Physically exact calculation, not influenced by other factors	Depending on many factors	No change
Toxicology	Carcinogenic	Carcinogenic	Various
Toxicological evaluation	Described by dose coefficients	Described by different toxicological factors	Described by different toxicological factors

Chemically, most of the natural radionuclides are heavy metals and their migration in soil and groundwater proceeds in a way similar to heavy metals. As the radionuclides belong to different chemical elements, their concentration in water reflects the different mobility of these elements under the specific geochemical conditions. Therefore, radionuclides generally can be considered similar to other contaminants and the concepts of soil protection can be applied to them, too. However, a few peculiarities have to be considered. Firstly, the radionuclides are members of the uranium or thorium decay series; this means that the decay and increase of radionuclides proceed in a physically exact way (parameter: half-life $T_{1/2}$ or decay constant $\lambda = \ln(2)/T_{1/2}$) and are not influenced by any physical, chemical or biological factors. Secondly, a radiological risk assessment can be made according to a well established system of consumption rates, dose coefficients and dose limits ('dose concept'). This makes it somewhat easier to assess certain situations than in the case of many common contaminants.

3. DERIVATION OF TEST THRESHOLDS — METHODOLOGICAL ASPECTS

As to the principles of soil protection, the 'risk threshold in the worst case' was used as a general criterion to derive threshold values. A two-step approach was used for transfer of this principle to an applicable concept. The general scheme of the approach is shown in Fig. 1.

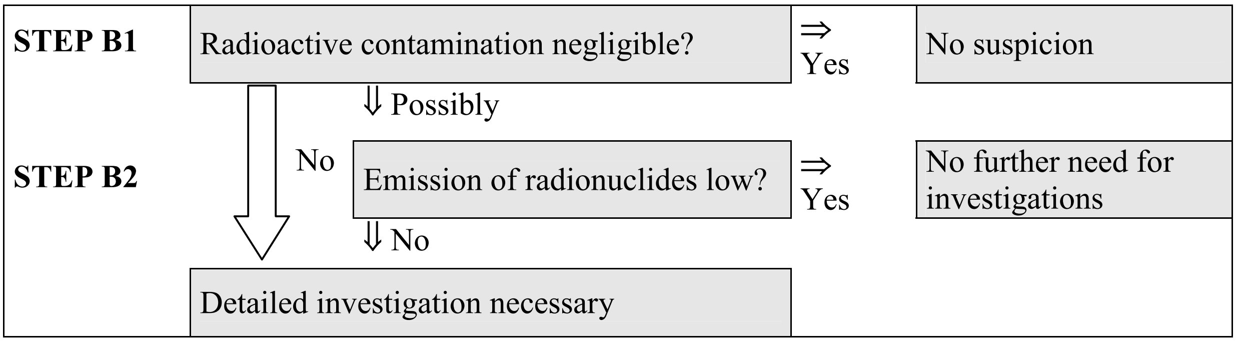

FIG. 1. General scheme for assessment of radioactive soil contamination with regard to groundwater

In step B1, the soil is assessed for significant radioactivity that may affect the groundwater. If the activity concentration is sufficiently low, any suspicion can be excluded and the soil is declared uncontaminated. On the other hand, if the activity concentration is enhanced above test threshold values, the contamination will be classified as significant with a need for detailed investigation.

This, however, oversimplifies the matter of differentiating only between ‘no suspicion’ and ‘significant contamination’. Therefore, step B2 is included in the scheme to be used for cases that are characterized by slightly enhanced soil activities. According to the aims of this approach, the possible transfer of radionuclides by seepage water into the groundwater is checked in step B2.

The test thresholds are derived as activity concentration in soil (Bq/g) or in seepage water (Bq/L), which yield a defined ingestion dose when drinking groundwater. The values were derived according to the rules of leachate forecast, using the following steps:

- Estimation of radionuclide concentration within the contaminated soil layer in the vadose zone (‘source term’);
- Calculation of radionuclide concentrations at the soil–groundwater interface by a transport prognosis;
- Risk assessment by calculating ingestion doses for persons as a measure of exposure;
- Derivation of test thresholds by relating the doses to the limits.

This approach was applied to an area with:

- Sandy soils and an unconfined aquifer;
- Water table about 2–4 m below the surface;
- Various types of radioactive soil contamination, mainly thorium ores (monazite), residues from previous thorium extraction from the ores and partly thorium compounds; residues from processing uranium ores occur in some places, too [2].

Different distributions of contamination in soil were reduced to two case scenarios:

- Contamination close to or in contact with groundwater; the thickness of the uncontaminated horizon is negligible ($x = 0$);

- Contamination significantly higher than groundwater; assumed thickness of uncontaminated horizon: $x = 2$ m.

Other contaminants from previous industrial production were factored out; that means any possible cross-effects were not considered in the risk assessment. Due to the very low level of radiological doses used in this study, such an approach is acceptable.

It should be pointed out that the approach described above is focused on the assessment of potential groundwater contamination originating from soil. Therefore, the values derived are not applicable to the assessment of risks from ground-borne gamma radiation, inhalation of dust or ingestion of soil particles. If necessary, these exposure paths must be assessed separately. They also cannot be used without the specific scenarios given above.

4. DETERMINATION OF SOURCE TERM

The first process to be described is the transfer of radionuclides from the solid to the liquid phase, i.e. from soil material into water. This source term was determined from measurements of the radionuclide concentration C (Bq/m³) in distilled-water extraction (DIN 38 414-4, S4) of soil samples of specific activity a (Bq/g). A transfer factor:

$$TF(i) = \frac{C_i}{a_i \times 1000} \qquad (1)$$

for the relevant radionuclides was estimated from the measurement results obtained. The values derived by summarizing the results are shown in Table II.

TABLE II. PARAMETERS OF RADIONUCLIDE MOBILIZATION AND TRANSPORT USED IN THE MODEL CALCULATIONS

Radionuclide	$T_{1/2}$ (a)	TF (g/m^3)	k_d (m^3/g)	R	Λ_{migr} (m)	Type of migration
^{232}Th	1.4×10^{10}	100	10^{-3}	4500	>> 1000	Isolated
^{228}Ra	5.8	250	10^{-5}	45	0.19	Isolated
^{228}Th	1.9	100	10^{-3}	4500	<0.01	Coupled
^{238}U	4.4×10^{9}	500	10^{-5}	45	>> 1000	Isolated
^{234}U	2.5×10^{5}					
^{226}Ra	1600	250	10^{-5}	45	52	Isolated
^{210}Pb	22.3	200	10^{-4}	450	0.07	Coupled
^{210}Po	0.38	100	10^{-4}	439	0.001	Coupled

The transfer factor can be used to calculate the radionuclide concentration in seepage water within a contaminated soil layer according to:

$$C_i = TF(i) \times a_i \times 1000 \qquad (2)$$

It is important to note that the transfer factor does not correspond with the inverse of the distribution coefficient k_d used in the transport model (see below). The transfer factor is a phenomenological figure characterizing the transfer of radionuclides from bulk soil into seepage water, while the k_d value characterizes the sorption at the surface of minerals.

As in radionuclide analysis, at least 1–2 L of water are required to obtain sufficiently low detection limits — the leachate experiments could not be carried out with the 'BSE' method (DIN V 19735).

5. TRANSPORT PROGNOSIS

The second process to be described is the transport of radionuclides dissolved in seepage water. The fundamental value of this process is the seepage velocity v_a. In the area studied, v_a was estimated to be about 1.6 m/a.

Two mechanisms influence the travel velocity of a real migration front: dispersion increases the velocity but retardation decreases it. Under steady-state conditions, only retardation takes effect. Assuming a linear equilibrium approach with a distribution coefficient k_d, the retardation factor R is:

$$R = 1 + \rho \frac{n-1}{n} k_\mathrm{d} \tag{3}$$

where ρ = grain density and n = porosity. The k_d values used for calculating R (see Table II) were adopted from the literature [3].

Two different models must be used to determine the transport of decay-series radionuclides in seepage or groundwater. In **Model 1 ('isolated migration')**, radionuclide i is assumed to migrate in an 'isolated manner', i.e. transport proceeds without any significant radiogenic production from a precursor. The concentration $C_{i,0}$ of such a radionuclide in water decreases due to radioactive decay exponentially with the distance x according to:

$$C_i = C_{i,0} \times \mathrm{e}^{-x / \Lambda(i)_\mathrm{migr}} \tag{4}$$

The parameter $\Lambda(i)_\mathrm{migr}$, given by

$$\Lambda(i)_\mathrm{migr} = \frac{v_a}{R_i \times \lambda_i} \tag{5}$$

characterizes the length of migration, i.e. the distance that reduces the concentration by a factor 1/e due to radioactive decay (λ = decay constant = $\ln(2)/T_{1/2}$, see Table II) and retardation R. This model is applicable to long-lived radionuclides without dissolved precursors. Typical examples of such nuclides are ^{238}U, ^{234}U, ^{232}Th and ^{226}Ra.

The parameters compiled in Table II show very low migration lengths (^{210}Pb, ^{210}Po, ^{228}Th). These nuclides will not arrive at the groundwater table if the distance between contaminated horizon and groundwater is more than 1 m. However, due to radiogenic production, the short-lived daughter radionuclides are generated so fast that an activity equilibrium exists in the entire water–rock system. Consequently, the short-lived nuclides must be taken into account when a long-lived precursor reaches the groundwater table. In such case the concentration of dissolved radionuclides results from the different sorption–desorption behaviour of the type of radionuclide involved. This effect is described by **Model 2 ('coupled migration')** [4]. The concentration of daughter radionuclide j, which migrates coupled to the precursor i, can be calculated from:

$$C_j = \frac{R_i}{R_j} \times C_i \tag{6}$$

For application of both models a distinction must be made between radionuclides that migrate in an isolated manner and those that are regarded as 'coupled'. In the case under review, two migration groups were considered:

- Migration group 1: ^{226}Ra as a long-lived precursor with isolated migration; ^{210}Pb, ^{210}Po as coupled daughter radionuclides.
- Migration group 2: ^{228}Ra as a long-lived precursor with isolated migration; ^{228}Th, ^{224}Ra as coupled daughter radionuclides. ^{228}Ra was stated as the precursor because its precursor ^{232}Th is not usually dissolved and the radiological relevance of ^{228}Ra is very high.

The long-lived nuclides ^{238}U, ^{234}U, ^{232}Th were involved, too. The concentration C_i of an 'isolated' radionuclide i in the zone of transition into the groundwater ('site of assessment') resulting from the soil contamination a_i is calculated according to:

$$C_i = TF(i) \times a_i \times e^{-x / \Lambda(i)_{\mathrm{migr}}} \quad (7)$$

The corresponding concentrations of the 'coupled' radionuclides are obtained from equation (6).

6. CALCULATION OF DOSES

As mentioned in Table I, radionuclides are classified as carcinogenic substances. The radiation effects are quantified using a linear non-threshold dose-effect relationship. The risk resulting from ingestion of radionuclides with concentration C (Bq/L) can be evaluated by calculation an ingestion dose H_{ing} (Sv):

$$H_{\mathrm{ing}} = VR \times \sum_i DK_i \times C_i \quad (8)$$

where VR = consumption rate (L/a) and DK = dose coefficient (Sv/Bq). Consumption rates and dose coefficients depend on the age of the persons concerned. They are defined in the German Radiation Protection Ordinance (StrlSchV). For a simple comparison, dose factors ($VR \times DK_i$) for drinking water consumption of the most sensitive age group (0–1 years) are given in Table III. It is obvious that ^{228}Ra, ^{210}Pb and ^{210}Po are the major potential contributors to the dose.

TABLE III: DOSE FACTORS FOR DRINKING WATER (AGE GROUP 0–1 YEARS)

Radionuclide	$VR \times DK_i$ (mSv/a per Bq/L)
^{238}U	0.058
^{234}U	0.063
^{226}Ra	0.80
^{210}Pb	1.43
^{210}Po	4.42
^{232}Th	0.78
^{228}Ra	5.10
^{228}Th	0.63

7. REFERENCE LIMITS

Using the models described above, a relationship can be established between a specific soil activity and the potential dose resulting from drinking the water. For derivation of the threshold values it is necessary to relate these doses to reference limits.

In Germany there exists one general concept for deriving threshold values in seepage water. It was developed by the 'Länderarbeitsgemeinschaft Wasser' (LAWA) and defines soil contamination as harmless in relation to groundwater if the contaminant concentration in the seepage water is below the limits of the German Drinking Water Directive (TrinkwV) and ecological effects can be excluded. If this concept is used, the primary reference dose is 0.1 mSv/a.

The German Radiation Protection Ordinance defines 1 mSv/a as the general protection level for members of the public. This level refers to all types of exposure caused by special situations with enhanced concentrations of natural radionuclides. As drinking of water covers only one exposure pathway, the German Radiation Protection Commission (SSK) already used 0.5 mSv/a as a reference value in terms of a former recommendation [6].

Both dose values (0.1 mSv/a and 0.5 mSv/a) were used to assess soil contamination. This resulted in a two-level concept of threshold values. Specific activities or radionuclide concentrations corresponding to the level of 0.1 mSv/a are termed Lower Assessment Values (Untere Beurteilungswerte, 'UBW'), those of level 0.5 mSv/a are termed Upper Assessment Values (Obere Beurteilungswerte, 'OBW').

8. RESULTS

Threshold values were derived for each radionuclide, starting out from the general concept (Fig. 1), the data (Table II), models, and reference limits. For practical use, these values were rounded and adjusted to the figures compiled in Tables IV and V. The index "max" indicates that the radionuclide with the maximum activity measured in the relevant decay series (^{232}Th or ^{238}U) has to be used for comparison.

The values given correspond to the specific activity (soil) or activity concentration (water) of every single type of radionuclide, which (under the model assumptions) lead to doses of 0.1 mSv/a or 0.5 mSv/a, respectively. Because decay-series radionuclides occur always as a mixture, the threshold values can be applied only in connection with the summation formula:

$$\sum \frac{\textit{Measured values}}{\textit{Threshold values}} < 1 \qquad (9)$$

As the summation formula is not common practice in soil protection, a simplified assessment was found to be appropriate. Based on the knowledge of the radiological relevance and the typical radionuclide patterns, especially in water, new threshold values were derived which roughly conform to the summation formula (Tables VI and VII).

TABLE IV. TEST THRESHOLDS FOR SOIL MATERIAL IN ASSESSMENT STEP B1 (IN CONNECTION WITH SUMMATION FORMULA)

Scenario	Radionuclide	Test threshold (Bq/kg)	
		UBW	OBW
Contamination close to or in contact with groundwater	$^{232}Th_{max}$	70	350
	$^{238}U_{max}$	90	450
Contamination significantly higher than groundwater	$^{232}Th_{max}$	15 000	75 000
	^{238}U	800	4000
	^{226}Ra	300	1500

TABLE V. TEST THRESHOLDS FOR LEACHATE IN ASSESSMENT STEP B2 (IN CONNECTION WITH SUMMATION FORMULA)

Scenario	Radionuclide	Test threshold (mBq/L)	
		UBW	OBW
Contamination close to or in contact with groundwater	^{228}Ra	20	90
	^{228}Th	150	600
	^{238}U	400	2000
	^{226}Ra	120	600
	^{210}Pb	70	350
Contamination significantly higher than groundwater	^{228}Ra	1000	5000
	^{228}Th	100	500
	^{238}U	400	2000
	^{226}Ra	120	600
	^{210}Pb	Not relevant	Not relevant

TABLE VI. TEST THRESHOLDS FOR SOIL MATERIAL IN ASSESSMENT STEP B1 (SIMPLIFIED ASSESSMENT)

Scenario	Radionuclide	Test threshold (Bq/kg)	
		UBW	OBW
Contamination close to or in contact with groundwater	$^{232}Th_{max}$	40	200
	$^{238}U_{max}$	40	200
Contamination significantly higher than groundwater	$^{232}Th_{max}$	1000	5000
	$^{238}U_{max}$	200	1000

TABLE VII. TEST THRESHOLDS FOR LEACHATE IN ASSESSMENT STEP B2 (SIMPLIFIED ASSESSMENT)

Scenario	Radionuclide	Test threshold (mBq/L)	
		UBW	OBW
Contamination close to or in contact with groundwater	^{228}Ra	20	60
	^{228}Th	10	50
	^{238}U	80	400
	^{226}Ra	20	100
	^{210}Pb	20	100
Contamination significantly higher than groundwater	^{228}Ra	200	1000
	^{228}Th	20	100
	^{238}U	80	400
	^{226}Ra	20	100
	^{210}Pb	Not relevant	Not relevant

Soils can be declared uncontaminated as to potential groundwater contamination if the measured specific activities in soil are lower than the UBW values in Table 6 *for all nuclides* of the corresponding decay series. There will be a risk of groundwater contamination if the value *of at least one nuclide* is higher than the OBW value. Contamination between UBW and OBW can be assessed by measuring leached samples (method DIN 38414-4, 'S4') and applying Table VII in the same manner as described before. This enables a first assessment by a simple comparison of measuring results and threshold values.

A more detailed user guideline for the threshold values can be found in Ref. [5].

9. BACKGROUND CONCENTRATIONS

Any use of threshold values would become absurd if the values were too close to background concentrations. In the case presented here, background values are compared with the UBW values in Table VIII, which shows that the differences are sufficient for distinguishing between contaminated situations and background.

TABLE VIII. COMPARISON OF BACKGROUND VALUES WITH UBW VALUES OBTAINED FOR CONTAMINATION CLOSE TO GROUNDWATER

Radionuclide	Values for soil (sand) (Bq/kg)		Values for water (mBq/L)	
	Background	UBW (simplified assessment)	Background	UBW (simplified assessment)
^{228}Ra	15	40	5	20
^{228}Th			1	10
^{238}U			5	80
^{226}Ra			8	20
^{210}Pb			5	20

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RADIUM IN GROUNDWATER CLOSE TO BUENA LAGOON IN COASTAL ZONE OF RIO DE JANEIRO STATE, BRAZIL

D.C. Lauria[1*], R.M.R. Almeida[2], O. Sracek[3]

[1]Instituto de Radioproteção e Dosimetria (IRD), Rio de Janeiro, RJ, Brazil
[2]Department of Civil Engineering, Universidade Federal Fluminense (UFF),
Rio de Janeiro, RJ, Brazil
[3] Institute of Geological Sciences, Faculty of Science, Masaryk University,
Brno, Czech Republic

Abstract

Groundwater close to the head of Buena Lagoon has a high salinity and low pH values. Radium is present predominantly as ^{228}Ra. Factors responsible for the high radium mobility in groundwater seem to be the high salinity with the resulting competition for adsorption sites, and low pH values with the resulting limited adsorption of Ra^{2+} on positively charged surfaces of adsorbents. The behaviour of uranium and thorium is also influenced by their speciation and low pH conditions. Uranium is present as the positively charged uranyl ion UO_2^{2+} in low pH samples and is very mobile. Similarly, the presence of positively charged Th^{4+} and thorium complexes with sulphate result in relatively high thorium concentrations at a low pH range. On the other hand, the mobility of the phosphate released from the dissolution of monazite is probably reduced due to its adsorption and precipitation close to its source.

1. INTRODUCTION

Several natural radioactive elements are present in groundwater and surface water at the coastal zone close to Buena Lagoon in Brazil, but only the long-lived radium isotopes ^{226}Ra and ^{228}Ra are found in concentrations that are significant from the point of view of potential effect on human health [1, 2]. The behaviour of radium and actinide elements in the environment is of interest not only from the point of view of their environmental impact, but also because the environmental behaviour of radium can be considered analogous to that of ^{90}Sr, and the thorium behaviour is considered to be similar to that of ^{239}Pu [3]. Both radionuclides are present in nuclear wastes.

The behaviour of radium in the environment is controlled by adsorption and co-precipitation. In freshwater systems, radium tends to be rapidly adsorbed from the aqueous phase, and its mobility is quite limited. Among water chemical parameters, increased salinity and/or low pH have been observed as important parameters responsible for a high dissolved radium concentration [1, 4]. Of its aqueous species, Ra^{2+} is likely to be the most important in the environment, but complexes like $RaOH^+$, $RaCl^+$, $RaCO_3^0$ and $RaSO_4^0$ may influence radium mobility in water [5–7]. The behaviour of uranium depends on redox conditions. Dominant forms are U(VI) under oxidizing conditions and U(IV) under reducing conditions. Concentrations of U(IV) are quite low because they are controlled by precipitation of low solubility minerals such as UO_2(am). In contrast, U(VI) may be present in high concentrations as the positively charged uranyl ion UO_2^{2+} under low pH conditions and becomes increasingly

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[*] E-mail: dejanira@ird.gov.br

adsorbed when the pH increases. In the neutral and alkaline pH range, carbonate complexes such as $(UO_2)_2(CO_3)_2^{2-}$ predominate, and dissolved uranium concentrations become high again. Thorium is present only as Th(IV) and the solubility of Th minerals like ThO_2 is low. Adsorption of Th^{4+} becomes more important with increasing pH values. There is the formation of complexes such as $Th(HPO_4)_3^{2-}$, $Th(SO_4)_2^0$, and $Th(OH)_4^0$ [8], and some thorium complexes like $Th(OH)_4^0$ have high affinity for adsorption.

In waters of the Buena Lagoon in the north of Rio de Janeiro state-Brazil (Fig. 1), in a region rich in monazite, high concentrations of dissolved ^{226}Ra and ^{228}Ra have been found. These findings resulted in a survey aiming to investigate the origin of the high radium concentrations observed. During this investigation, several springs with high concentrations of radium were discovered close to the Buena Lagoon [9]. The objectives of this paper are to report on the characterization of groundwater and spring water, the identification of the causes of high concentrations of radium and other radionuclides in water, and the contribution to a better understanding of the behaviour of radium and other radionuclides in a coastal tropical environment.

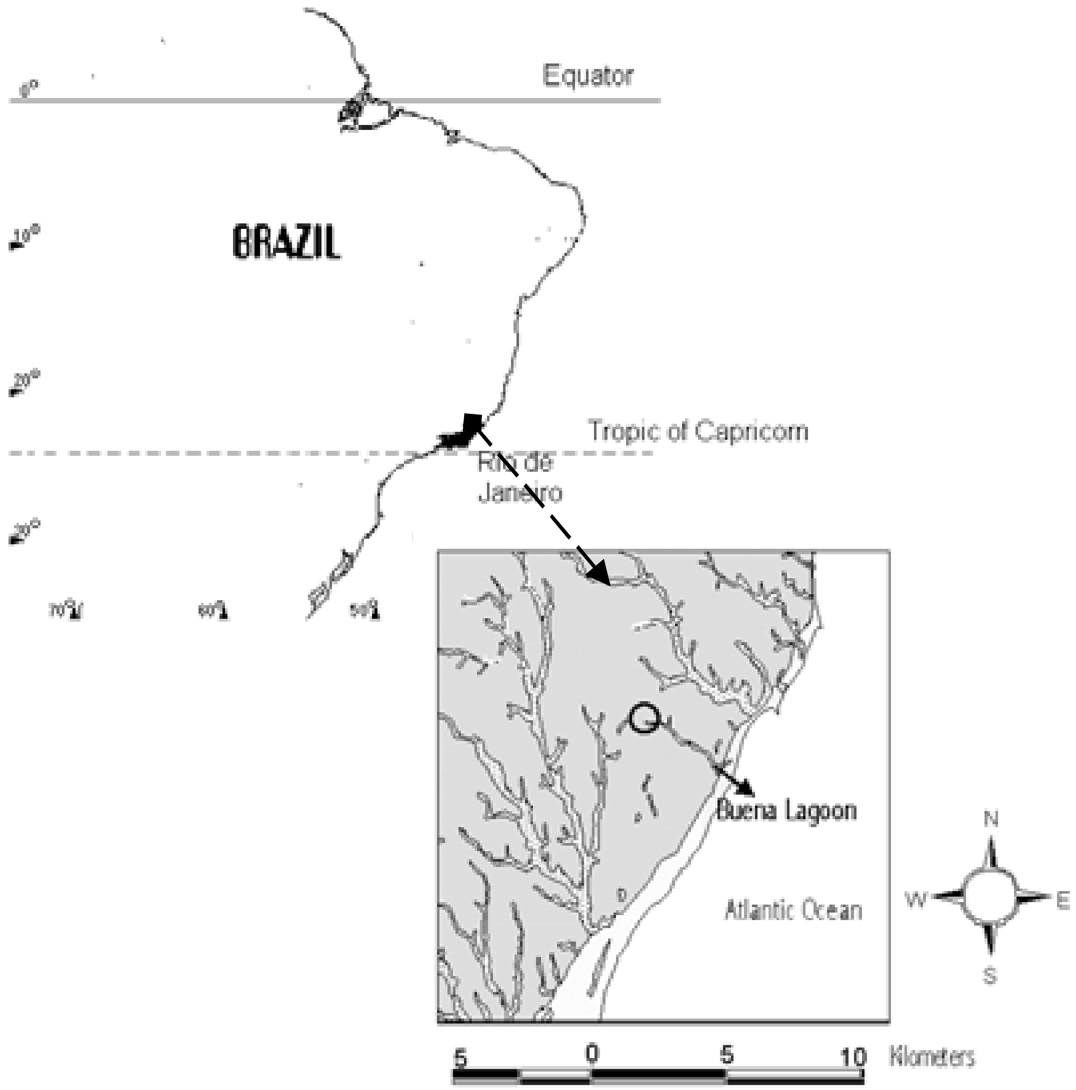

FIG. 1. Location of Buena Lagoon

2. MATERIALS AND METHODS

Water from 4 springs (S), 3 private wells (PW) and 6 new wells (W) located close to the Buena Lagoon head was sampled. Additionally, the solid phase from the boreholes surrounding the springs was sampled. The geographic location of the sampling points was determined by a satellite navigation system, GPS (Garmin, model 45 XL). The sampling point locations are shown in Fig. 2.

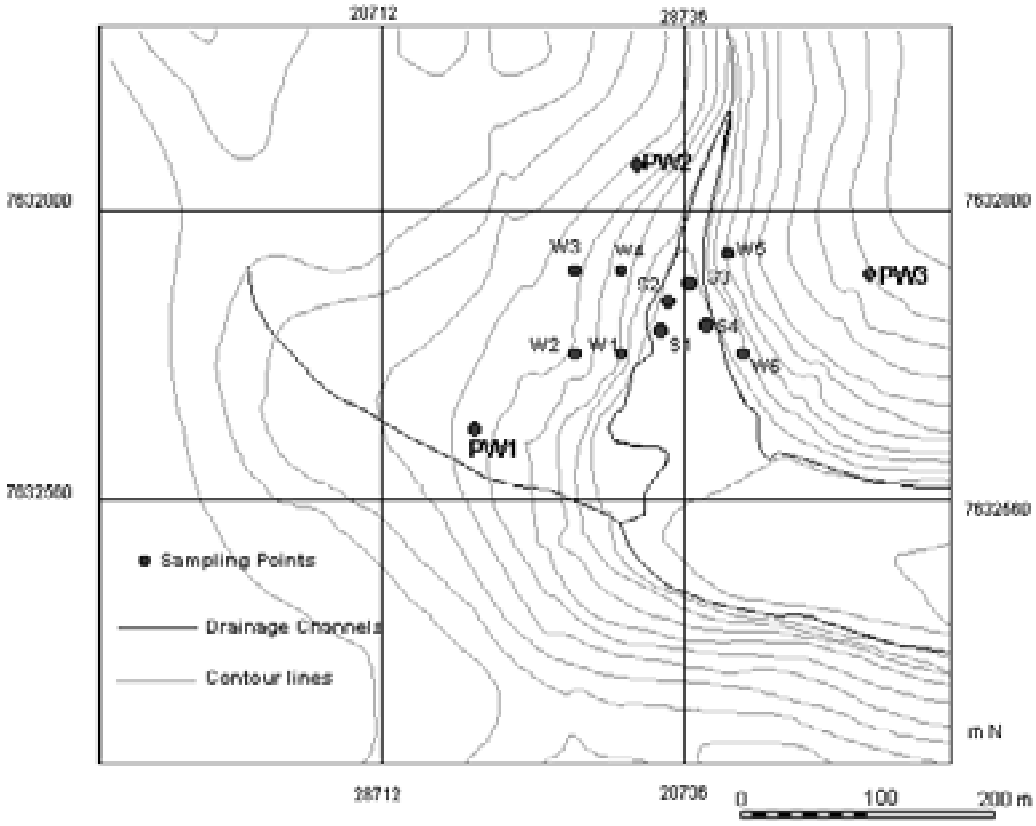

FIG. 2. Location of sampling points: springs (S), private wells (PW), and drilled wells (W) at the head of the Buena Lagoon

Approximately 3 L of sample were collected. The physical-chemical parameters (pH, Eh, temperature, and electrical conductivity) were measured in the field. Alkalinity was determined in the field by titration with H_2SO_4. For thorium, uranium, rare earth element, major cation, metal and radium isotope determinations, 2 L of each sample were filtered by a Millipore membrane (0.45 µm), and samples were acidified with ultra-pure HNO_3.

The activities of ^{226}Ra and ^{228}Ra in the water were determined by gross alpha and beta counting using a proportional counter of small area. Radium was concentrated by co-precipitation with $BaSO_4$. H_2SO_4 and $BaCl_2$ were added to a 1 L sample and Ba(Ra)SO_4 was co-precipitated. The sulphate was washed and dissolved with nitrilotriacetic acid (NTA). Barium (radium) sulphate was reprecipitated by adding acetic acid until the pH reached 4.5–5.0. The aqueous and solid phases were separated and the Ba(Ra)SO_4 was purified by dissolution in an ethylene diamine tetra-acetic acid (EDTA) solution at pH 10. Then the sulphate mixture was reprecipitated by acetic acid (pH 4.5–5.0). The precipitate was filtrated and after one month of growth, ^{226}Ra was determined by gross alpha counting. ^{228}Ra was determined by beta counting, whereas the alpha particles of ^{226}Ra were stopped by a filter paper. Corrections were made if there was any contribution from the daughter products of

^{226}Ra. Alpha and beta activities were counted in a low-background anticoincidence proportional detector (Bertold, model: LB770-1) [10].

Th, U, light rare earth elements (La–Sm), major cations Ca, Mg, Na, K, and metals Mn, Al and Fe were determined by inductively coupled plasma mass spectrometry, ICP-MS, (Perkin-Elmer SCIEX ELAN 6000) after diluting 1:20 with water quality Milli-Q, applying the so-called TotalQuant® method and In and Tl internal standards [1].

About 0.5 L of the sample was filtered through a Millipore membrane (0.45 μm) for the determination of chloride (Volhard's argentometric method), sulphate (turbidimetry) and fluorine (by selective electrode). Approximately 0.25 L of the sample was filtered by a glass fibre filter, and stored in dark glass flasks. These samples were analysed for nitrate spectrophotometrically after reduction to nitrite in a cadmium/copper column, and for phosphate by the ammonium molybdate/ascorbic acid method [11].

Soil samples were collected from the soil–water interface in the bore well bottoms (1.5–3.3 m depth). The soils were transferred to plastic bags and pH and Eh measurements were performed immediately. At the laboratory, the samples were air dried and passed through a 2 mm sieve. Then, about 300 g of sample was transferred to a polyethylene bottle and after 20 days the samples were analysed by gamma spectrometry for ^{226}Ra (^{214}Pb 614 keV) and ^{228}Ra (^{228}Ac 911 keV) determinations [12]. The other soil analysis were performed in the National Soil Research Centre-CNPS (Embrapa): particle-size by pipette method, cation exchange capacity (CEC) by ammonium acetate and potassium chloride methods, iron oxides by sulphuric acid extraction and titration with EDTA and organic carbon by reduction of dichromate by organic matter [13].

2. RESULTS AND DISCUSSION

2.1. General hydrogeochemistry

The results of water analyses are presented in Tables I–III. The presumed groundwater flow direction follows the topographic gradient, e.g. from the slopes towards the springs S1–S4 in the flat swampy area close to the Buena Lagoon head (Fig. 2). Thus, the swamp close to the Buena Lagoon head is the discharge zone for groundwater recharged on the surrounding slopes.

Groundwater is of the Na–Cl type, with elevated concentrations of sulphate in some samples. This is consistent with the expected strong impact of marine aerosols on groundwater chemistry in the coastal zone. Only a few samples with pH values >5.5 exhibited significant values of alkalinity. Most samples had much lower alkalinity, less than 2 mg/L as HCO_3^-. In all samples, the concentrations of phosphate were less than the detection limit of 0.03 mg/L. The values of redox potential Eh_{H2} were very positive (from 315 to 582 mV). Concentrations of F^- were significant in some samples (S1, W4, and W6). They may be related to the dissolution of minerals like apatite caused by generally low dissolved calcium concentrations. Low pH values have been observed at other regions of the coastal zone of Rio de Janeiro State [2] and they are probably related to several factors, including evaporation and a lack of carbonate buffers in the soil.

Saturation indices (SIs) for selected minerals calculated with the program PHREEQC [14] are shown in Table IV. All samples were under-saturated with respect to gypsum, and amorphous silica, and most samples were under-saturated with respect to amorphous $Fe(OH)_3(a)$. In contrast, all samples were supersaturated with respect to goethite, which is a more stable mineral of ferric iron in aged sediments. All samples were under-saturated with respect to $Al(OH)_3(a)$ and samples with pH >4.5 were supersaturated with respect to gibbsite.

The samples were generally close to equilibrium with kaolinite (SIs not shown), which is consistent with the presence of minerals of the kaolinite group like nacrite in soil (see solid phase discussion).

TABLE I. CONCENTRATIONS OF RARE EARTH ELEMENTS AND RADIOACTIVITY IN GROUNDWATER SAMPLED NEAR THE HEAD OF BUENA LAGOON

Site	Rare earth concentrations (µg/L)					Radioactivity content			
	La	Ce	Pr	Nd	Sm	Th (µg/L)	U (µg/L)	^{226}Ra (Bq/L)	^{228}Ra (Bq/L)
S1	51.61	115.40	15.25	59.03	11.48	0.22	3.72	0.43	1.81
S2	52.33	118.60	16.23	67.66	12.36	0.15	2.79	0.49	1.68
S3	52.65	118.50	15.09	62.48	10.36	0.09	2.44	0.52	2.18
S4	45.70	101.60	13.00	52.73	9.72	0.22	1.79	0.53	2.50
PW 1	30.74	66.49	8.20	29.36	5.26	0.05	0.73	0.58	3.17
PW 2	8.67	14.75	1.72	7.07	1.13	0.05	<0.01	0.56	1.83
PW 3	0.12	0.27	0.03	0.41	0.16	<0.04	0.07	0.17	0.38
W1	6.96	13.01	1.46	6.46	1.31	0.13	0.26	0.11	<0.05
W2	29.14	54.42	6.52	23.99	3.92	0.25	0.78	0.27	1.87
W3	0.88	1.43	0.18	0.95	0.24	0.02	<0.01	0.01	2.00
W4	27.42	48.18	5.40	19.58	2.97	0.03	0.17	0.37	1.43
W5	3.12	11.10	0.92	3.22	0.57	0.25	0.17	0.01	0.01
W6	45.01	98.01	8.57	29.37	4.56	0.08	0.38	0.35	0.97

TABLE II. CONCENTRATIONS OF MAJOR CATIONS AND METALS IN GROUNDWATER SAMPLED NEAR THE HEAD OF BUENA LAGOON

Site	Concentration (mg/L)							
	Na	Mg	K	Ca	Al	Si	Mn	Fe
S1	564	64.18	22	10.8	4.76	2.25	0.06	0.26
S 2	229	71.36	23	12.7	5.47	2.38	0.08	0.24
S 3	240	71.19	23	13.3	5.28	2.48	0.09	0.38
S 4	400	74.65	25	13.0	4.85	2.47	0.08	0.23
PW1	528	60.50	19	11.6	3.16	1.92	0.06	0.31
PW2	456	33.91	28	15.9	0.26	0.50	0.04	0.10
PW3	501	39.43	24	9.6	0.06	1.55	0.03	0.13
W1	305	36.12	11	14.0	0.38	1.36	0.04	0.21
W2	567	76.65	29	43.8	0.03	1.79	0.08	1.30
W3	337	42.94	23	23.6	0.09	1.41	0.07	0.16
W4	527	66.16	23	38.0	1.48	2.59	0.20	1.92
W5	441	56.20	23	34.1	0.05	1.69	0.28	0.44
W6	528	61.78	26	24.6	1.23	2.81	0.18	1.44

TABLE III. MAJOR ANION CONCENTRATIONS, pH AND ELECTRICAL CONDUCTIVITY IN GROUNDWATER SAMPLED NEAR THE HEAD OF BUENA LAGOON

Site	Nitrate (mg/L)	Sulphate (mg/L)	Cl (mg/L)	Alkalinity (mg/L HCO_3)	F (mg/L)	pH	Eh_{H2} (mV)	Conductivity (mS/cm)
S 1	3.14	78.26	962	<2	0.23	3.70	496	4.01
S 2	1.09	20.43	327	<2	0.11	3.70	517	4.37
S 3	0.79	32.95	416	<2	0.11	3.74	447	4.53
S 4	2.17	7.13	655	<2	0.10	3.80	415	4.16
PW1	5.99	6.26	744	<2	<0.01	3.78	468	4.11
PW2	4.26	7.65	466	<2	0.09	4.66	513	2.24
PW3	7.06	5.47	337	916	0.04	6.79	492	1.70
W1	3.13	66.95	476	<2	0.08	4.60	462	2.05
W2	23.2	85.21	903	405	0.02	5.86	607	3.94
W3	10.22	70.43	536	208	0.02	5.63	569	2.24
W4	0.91	91.30	883	<2	0.20	4.39	406	3.59
W5	0.07	121.73	734	173	0.05	5.86	315	3.04
W6	0.18	99.13	734	<2	0.32	4.59	367	3.27

TABLE IV. SIs FOR SELECTED MINERALS (Figures in bold indicate supersaturation)

Sample / mineral	$Fe(OH)_3(a)$	Goethite	$Al(OH)_3(a)$	Gibbsite	Gypsum	$SiO_2(a)$
S1	-3.94	**1.95**	-4.14	-1.45	-2.75	-1.71
S2	-3.90	**1.99**	-3.83	-1.26	-3.20	-1.69
S3	-3.59	**2.30**	-2.98	-1.13	-2.98	-1.67
S4	-5.18	**0.70**	-3.81	-1.10	-3.71	-1.67
PW1	-3.59	**2.30**	-3.89	-1.25	-3.80	-1.78
PW2	-1.45	**4.44**	-3.47	**0.25**	-3.47	-2.36
PW3	**1.65**	**7.54**	-3.83	**1.98**	-3.83	-1.87
W1	-1.98	**3.89**	-2.71	**0.00**	-3.03	-1.91
W2	**1.95**	**7.85**	-1.18	**1.53**	-2.64	-1.79
W3	**0.86**	**6.73**	-0.97	**1.73**	-3.84	-1.90
W4	-2.66	**3.22**	-2.75	-0.05	-2.62	-1.63
W5	-0.48	**5.39**	-1.06	**1.65**	-2.51	-1.82
W6	-3.15	**2.73**	-6.26	-3.55	-3.83	-1.59

Concentrations of dissolved aluminum were relatively high as a consequence of the low pH. A stability diagram for a K_2O-Al_2O_3-SiO_2-H_2O system is shown in Fig. 3. There is a scatter of points in the kaolinite field, suggesting formation of kaolinite at well-drained sites. At some sites, there may be transformation of kaolinite to gibbsite as suggested by a point close to the gibbsite field. However, gibbsite becomes unstable at a pH of about 4.2 [15, 16] and releases dissolved aluminum. There were increased sulphate concentrations in some samples from drilled wells and springs (1–3), but dissolution of gypsum can be excluded because the concentrations of dissolved calcium are low. Thus, the most probable sources of sulphate are marine aerosols and oxidation of pyrite.

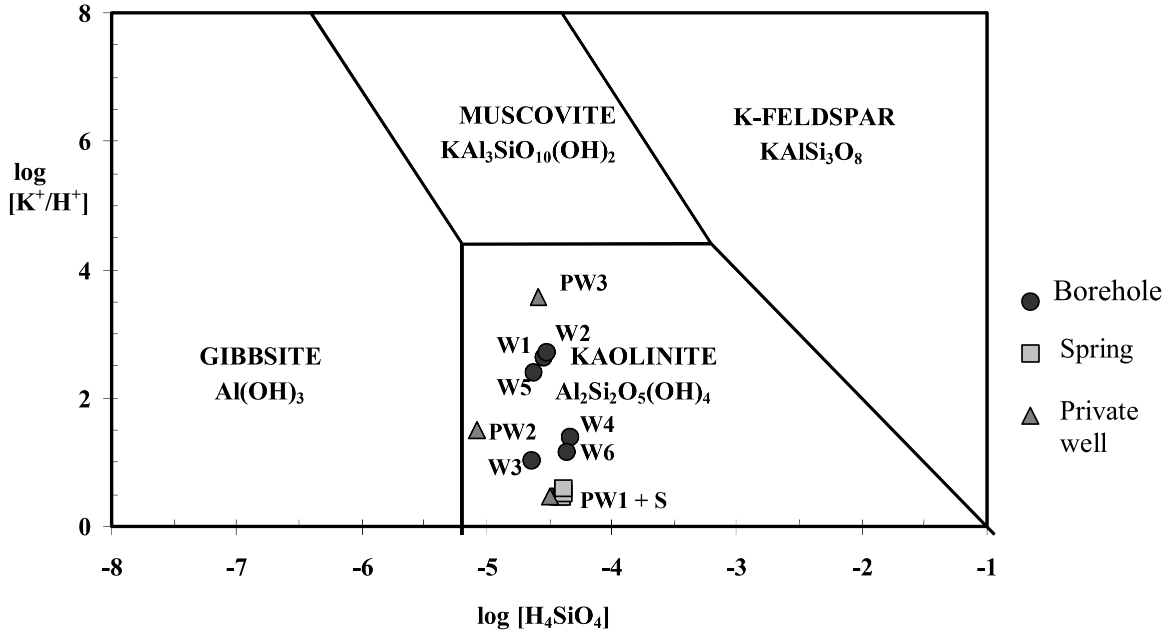

FIG. 3. Stability diagram for a K_2O-Al_2O_3-SiO_2-H_2O system with groundwater samples

2.2. Behaviour of radionuclides

2.2.1. Speciation of uranium, thorium and radium

Concentrations of uranium were in the range <0.01–3.72 μg/L (Table I). High Eh_{H2} values suggest that uranium is present predominantly as U(VI). Thorium concentrations were in the range 0.02–0.25 μg/L. Activities of ^{226}Ra were in the range 0.01–0.58 Bq/L and activities of ^{228}Ra were in the range from <0.05–3.17 Bq/L. The highest radium activities were found in groundwater from PW1.

Hydrogeochemical speciation of radionuclides was performed using the PHREEQC program [14] and data from the Lawrence Livermore National Laboratories database implemented in PHREEQC-2 [17]. Equilibrium constants for radium were taken from Ref. [18]. The total uranium concentrations were split on the basis of field Eh_{H2} values.

The results of radium speciation indicate that in all samples the predominant species of radium is the free ion Ra^{2+}. The role of the $RaSO_4^0$ complex is not significant even in samples with a relatively high sulphate concentration (Samples S1 and W5) The complex comprises about 3 % of total radium in sample S1 and about 5 % in sample W5 with a high sulphate concentration and a low concentration of dissolved radium.

Thorium is present in low pH samples mostly as Th^{4+} or forms complexes with sulphate and fluorine. Complex $Th(SO_4)_2$ plays an important role in samples with a high sulphate concentration (39 % of total thorium in sample S1). Other important complexes are

$Th(OH)_2^{2+}$ and ThF_3^+. In samples with high pH values, the complex $Th(OH)_4^0$ comprises most of the dissolved thorium (97 and 95 % in samples W2 and W3, respectively) and other complexes are relatively insignificant.

Uranium is present as the positively charged uranyl ion UO_2^{2+} in samples with low pH values (93 % of total U(VI) in sample S1). However, complexation with sulphate, chloride, and fluorine also plays a significant role. Complexes with carbonates such as $UO_2CO_3^0$ and $UO_2(CO_3)_2^{2-}$ are important only in samples with a relatively high pH and alkalinity (56 % and 43 % in sample W3, respectively).

The light rare earth elements are predominantly in the form of free ions (La^{3+} and Ce^{3+}). In sample PW3 with the highest pH value (6.79), besides the free ionic species (~70%), the light rare earth elements form complexes with carbonates.

2.2.2. Solid phase composition and adsorption of radium

Solid phase data, based on samples collected from the bottom of boreholes, are shown in Table V. Relatively complete analyses are available only for boreholes W3 and W4. The soils have a significant fraction of clay, reaching values of about 40 %. Values of CEC are between 2.6 and 9.7 meq/100 g. The organic matter content is low, less than 1.0 wt. %. Thus, the contribution of organic matter to adsorption is negligible. On the other hand, concentrations of Fe(III) expressed as goethite are higher, between 1.3 and 2.57 wt. %. Thus, ferric oxides and hydroxides probably play a significant role in the adsorption of radionuclides. The value of pH_{ZPC} for goethite is about 7.3, and this means that the surface charge is positive at the observed pH range surface [16, 19].

TABLE V. SOLID PHASE DATA

Site	$^{226}Ra_w$ (Bq/L)	$^{228}Ra_w$ (Bq/L)	$^{226}Ra_s$ (Bq/kg)	$^{228}Ra_s$ (Bq/kg)	K_d (L/kg)	Clay (%)	CEC (meq/100 g)	Goethite (wt %)	C_{org} (wt %)	pH_{water}
W1	0.109	0.05	35	112	923	n.a.[1]	n.a.	n.a.	n.a.	4.60
W2	0.271	1.9	26	112	65	n.a.	n.a.	n.a.	n.a.	5.86
W3	0.014	2.0	17	66	41.2	38	2.6	1.80	0.07	5.63
W4	0.367	1.4	<2	<2	2.0	38	9.7	1.57	0.85	4.39
W5	0.006	0.01	34	100	8400	n.a.	n.a.	n.a.	n.a.	5.86
W6	0.351	0.97	40	116	118	n.a.	n.a.	n.a.	n.a.	4.59

The principal clay mineral was identified as nacrite, a member of the kaolinite group. Minerals of this group have relatively low CEC values, in the range 1–10 meq/100 g [15]. Thus, relatively high values of CEC, e.g. 9.7 meq/100 g at sample W4, may correspond to a contribution of ferric minerals. Activities of adsorbed radium isotopes are much higher than their dissolved concentrations and ^{228}Ra predominates (Table V), just as in groundwater. The maximum calculated K_d values are high, reaching 8400 L/kg for a soil sample from the bottom of borehole W5. Values of K_d as a function of pH are shown in Fig. 4. There is a trend of increasing K_d values for radium with increasing pH. This is consistent with a positive charge of dissolved radium and a more negative surface charge with increasing pH. The

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[1] Not available

considerable scatter in the graph is probably caused by the impact of complexation and by variability in the solid phase composition.

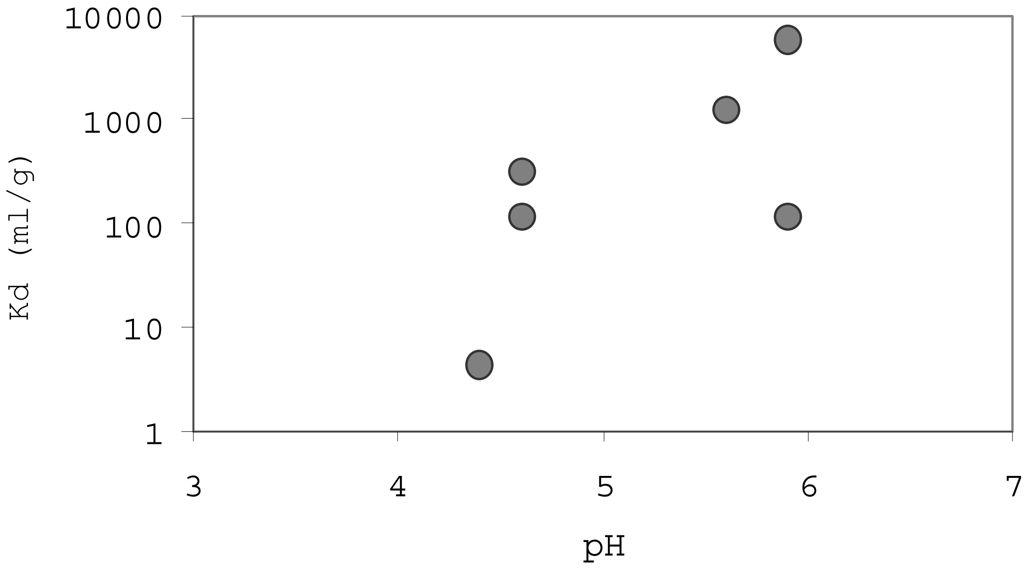

FIG. 4. Relationship between groundwater pH and K_d value

The adsorption of Ra^{2+} on hydrous ferric oxide (HFO) with a composition of goethite was modelled by PHREEQC using the following parameters in a diffuse double layer (DDL) model: HFO concentration 1.0 wt. %, porosity 0.3, bulk density of soil 2 kg/L, and a specific surface of HFO 100 m^2/g. This last value corresponds to the reduced specific surface of goethite [16] present in soils at the site. Strong adsorption sites (density 0.005 mol sites/mol HFO) and weak adsorption sites (density 0.2 mol sites/mol HFO) used in Ref. [20] were scaled down to maintain a constant site density per nm^2. Intrinsic adsorption constants for barium were used as a proxy for modelling radium adsorption because intrinsic adsorption constants for radium were not available and adsorption behaviours of both elements are similar [16]. The dissolved Ra concentration in water with pH 3.70 was used as the starting concentration because it was assumed that the adsorption of Ra was limited at this pH. There was increasing adsorption, and thus decreasing dissolved Ra concentration, with increasing pH (Fig. 5). This behaviour was consistent with field observations. This is typical for ferric oxides and hydroxides and supports the hypothesis about their significant role in the adsorption of radium. If minerals of the kaolinite group were the only adsorbents, there would not have been a significant change in K_d values with pH because their bulk surface charge and adsorption properties do not change very much over the observed pH range.

2.2.3. Origin of groundwater chemistry and radionuclide behaviour

In order to verify the hydrogeochemical similarities between water samples, the data were analysed using multivariate statistics implemented in the program PAST [21]. Only principal ions, trace metals, and radionuclides were included, and rare earth elements were omitted. The results of the Principal Component Analysis (PCA) are in Fig. 6, where the loadings of Principal Component 1 (PC1) and Principal Component 2 (PC2) are plotted for all samples.

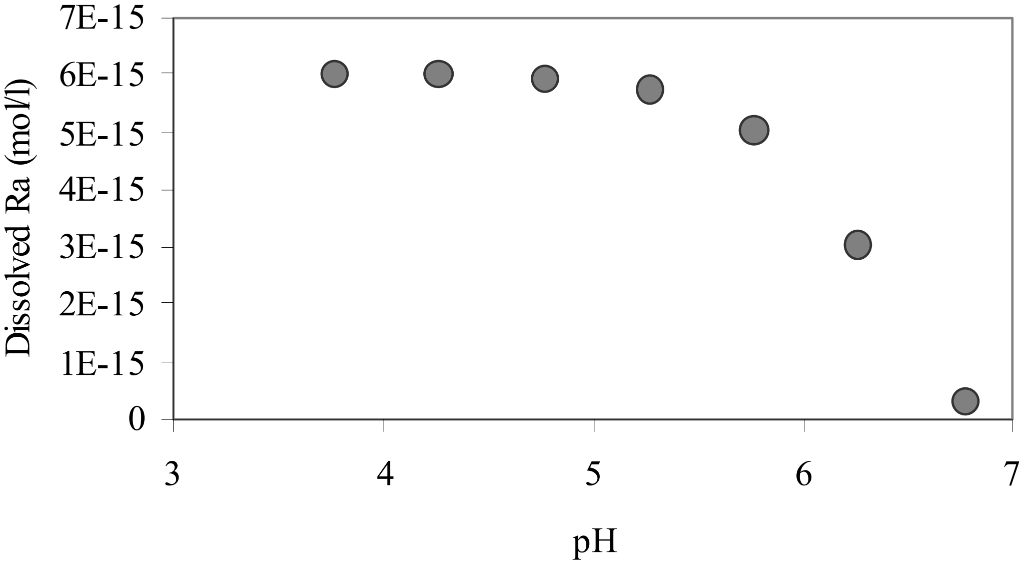

FIG. 5. Modelled concentration of Ra^{2+} *in groundwater as a function of pH*

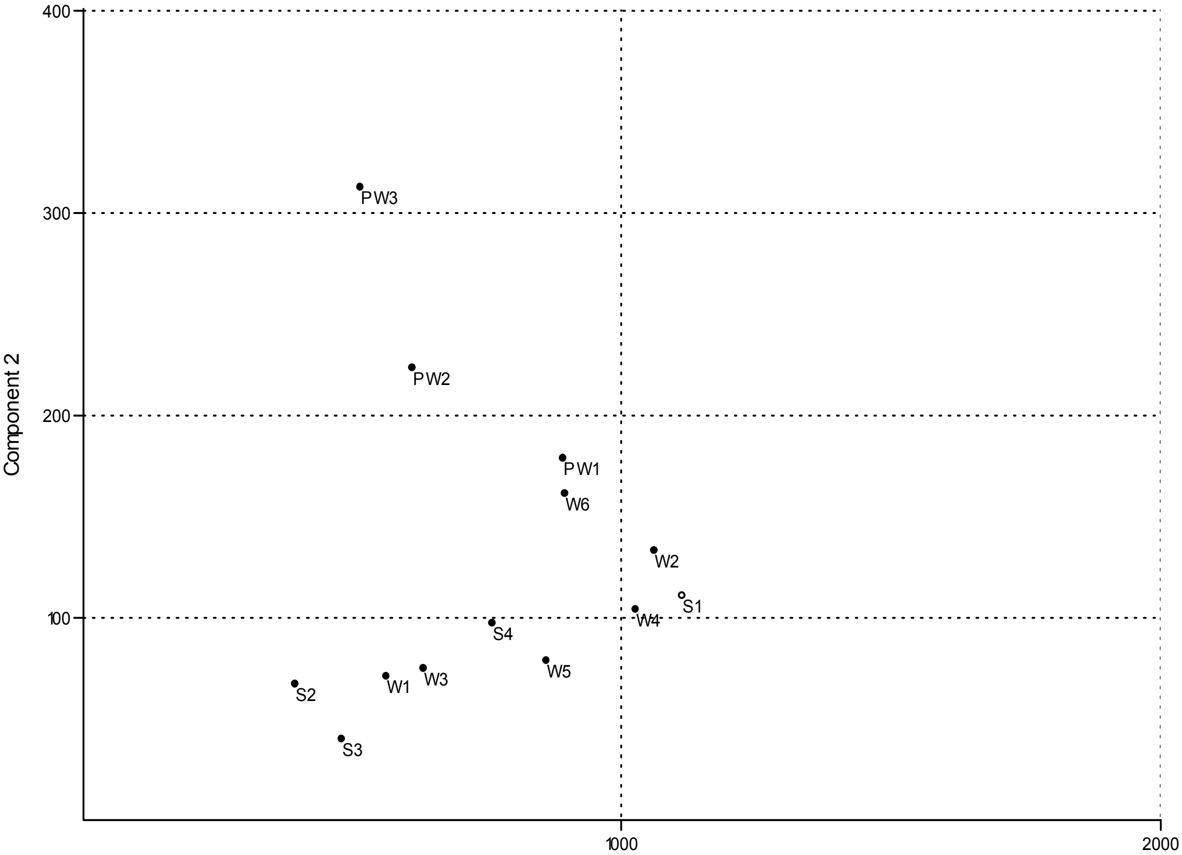

FIG. 6. Results of Principal Components Analysis (PCA.)

PC1 explains 89 % of the total variability and is related to Na, Cl, Mg, and SO_4, e.g. to typical seawater ions. PC2 explains only 9 % of the variability and is not well characterized, comprising Na and K and exhibits relatively low sulphate and chloride concentrations. Samples S1, W2, and W4 are together, representing samples with strong seawater impact. There is evolution towards this end-member from two groups of outsiders: a group comprising samples S2 and S3, and a group comprising PW2 and PW3. The gradual evolution from samples S2 and S3 towards samples S1, W2, and W4 probably represents the increasing influence of marine aerosols. Outsiders PW2 and PW3 may represent groundwater of lithogenic origin with limited seawater influence. This is consistent with their high elevation above the Buena Lagoon head.

The Pearson correlation coefficient of PW1 and springs variables (Table VI) indicate a strong correlation between light rare earth elements, radium isotopes and Th. The concentrations of ^{226}Ra, ^{228}Ra, and Th were negatively correlated with pH values. Although the concentrations of ^{228}Ra, and U showed good correlation with electrical conductivity (EC), the correlation for ^{226}Ra was weaker (R = 0.717).

TABLE VI. CORRELATION BETWEEN RADIONUCLIDES AND STABLE ELEMENTS IN GROUNDWATER SAMPLES

Radionuclide	Correlation coefficient (Pearson), significance level >95%							
	Ce	La	Nd	Pr	Sm	H^+	^{228}Ra	EC
^{226}Ra	0.879	0.898	0.830	0.873	0.770	0.900	0.967	0.717
^{228}Ra	0.903	0.913	0.861	0.897	0.816	0.926	0.967	0.800
U			0.757		0.820			0.868
Th	0.835	0.826	0.861	0.840	0.879	0.803		0.784

The existing relationships between radium concentrations and light rare earth element concentrations suggest their common origin in groundwater, presumably from the leaching of monazite. The positive correlation with H^+ and electrical conductivity (e.g. with mineralization) may indicate an important role of these factors in the leaching and mobility of radium in the aqueous phase. A comparison of the chondrite-normalized rare earth element pattern found in the local monazite with the pattern observed in PW1 sample is shown in Fig. 7. The patterns are quite similar, without a negative cerium anomaly but with a negative europium anomaly. According to Ref. [22], very low pH values in spring waters result in the presence of cerium as Ce^{+3} under oxidizing conditions. Therefore, the data suggest disturbance of the chemical stability of monazite by high salinity and low pH of groundwater.

3. GENERAL DISCUSSION

Two principal factors, high salinity and low pH values, seem to be responsible for the high dissolved radium concentrations. The high cation concentrations in groundwater (predominantly Na^+) can result in competition for available exchange sites on the solid phase with a resulting release of Ra. The low pH values can also increase the dissolution rate of monazite, releasing Ra from the solid phase. Furthermore, the surfaces of natural adsorbents of Ra, such as ferric oxide and hydroxides, have a positive charge under low pH conditions. There is limited adsorption of radium present as Ra^{2+} at low pH values, and the adsorption of radium increases with increasing pH (adsorption edge) [18]. The behaviour of uranium and thorium is also related to the presence of their positively charged species such as UO_2^{2+} and Th^{4+} under low pH conditions. When pH values increase, the mobility of uranium and thorium is reduced due to adsorption. However, the trend is reversed for uranium at close to neutral pH values due to the formation of carbonate complexes [23, 24]. Furthermore, there is inhibition of thorium adsorption by the formation of complexes with the sulphate [25]. On the other hand, the formation of relatively strongly adsorbed thorium hydroxy complexes like $Th(OH)_4^0$ is limited in low pH samples.

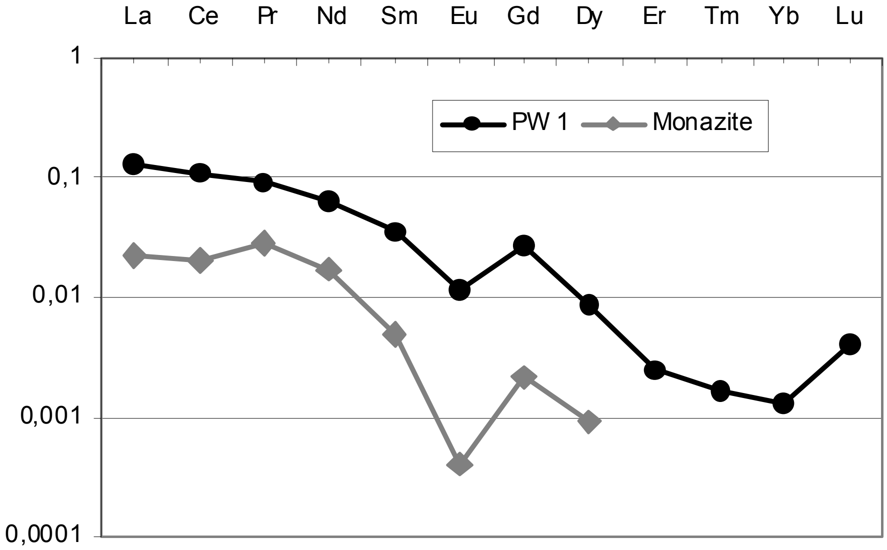

FIG. 7. Chondrite-normalized rare-earth element pattern found in the local monazite and that observed in Private Well I

Phosphate released by monazite dissolution is in anionic form and is adsorbed on positively charged surfaces in the low pH range. There also is a possibility of precipitation of phosphate minerals like strengite ($FePO_4.2H_2O$) and variscite ($AlPO_4.2H_2O$), [26] in the proximity of dissolving monazite because the concentrations of Fe^{3+} and Al^{3+} in the groundwater are relatively high.

4. CONCLUSIONS

Groundwater close to the head of Buena Lagoon in the coastal zone of Rio de Janeiro State exhibits high salinity and generally low pH values. Probably the most significant factor playing a role in the formation of the groundwater chemistry is the influence of marine aerosols, resulting in high concentrations of Na and Cl in the groundwater. The strong correlation between concentrations of radium and light rare earth elements suggests the leaching of monazite as a common source. The factors responsible for the high radium mobility in the groundwater seem to be the high salinity with resulting competition for adsorption sites, and low pH values with resulting limited adsorption of Ra^{2+} on the surface of adsorbents like ferric oxide and hydroxides. The behaviour of uranium and thorium is also influenced by their speciation and generally low pH conditions. Uranium is present as the positively charged uranyl ion UO_2^{2+} under low pH conditions and is very mobile. Carbonate uranium complexes predominate in some samples with close to neutral pH and the mobility of uranium increases again. Positively charged Th^{4+} and thorium complexes with sulphate predominate in low pH samples with a relatively high concentration of thorium. Further study should be focused on the aquifer delimitation, as well as on the causes of the low pH values.

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MEASUREMENT TECHNIQUES

IMPORTANCE OF SAMPLING IN RELATION TO THE GAMMA SPECTROSCOPIC ANALYSIS OF NORM AND TENORM MATERIAL

L.P.M. van Velzen[1*]**, C.W.M. Timmermans**[2**]

N.R.G. vof, Arnhem, Netherlands

Abstract

This paper describes the developments over the past 25 years of low background gamma-spectroscopic analysis of NORM and TENORM materials to a state-of-the-art semi-automatic gamma analysis system. The developments were initiated in the early 1980s in order to be able to measure low specific activities in fly ash samples. The developments involved modifications and improvements of commercially available hardware, auxiliary equipment, improvement and development of analyzing software, correction software and processing software to a semi-automatic reporting of the analysis results. The effort summarized above has led to detection limits of ^{238}U: 3 Bq/kg, ^{235}U: 0.3 Bq/kg, ^{226}Ra: 5 Bq/kg, ^{210}Pb: 30 Bq/kg, ^{40}K: 60 Bq/kg, with a measuring time of 70 000s using a specially tuned gamma spectroscopy system for NORM and TENORM materials. These low detection limits show the need to set up representative sampling procedures for NORM and TENORM materials. It is not possible to define a sampling procedure that would be valid for all types of sampling. Therefore it is advised that, where sampling is expected to be performed at regular times, a sampling procedure for the materials being dealt with should be set-up and validated. The procedure has to be based on an existing national or international standard.

1. INTRODUCTION

In the Netherlands, problems arose with naturally occurring radioactive materials (NORM) and technologically enhanced concentrations of NORM (TENORM) in the early 1980s. This was due to discussions about the reuse of fly ash in building and road construction materials [1]. Gamma spectroscopic analysis of NORM and TENORM samples was at that time still in its infancy. Nowadays, different gamma spectroscopic analysis techniques exist, each with its particular accuracy. Today's state-of-the-art techniques are able to assess the activity concentration of uranium and thorium chains present in a variety of NORM and TENORM materials with an accuracy of about 3%. This means in practice that the error due to sampling of NORM material has become and will continue to be increasingly important in the radiological characterization of NORM and TENORM samples. This importance has been also increased by the implementation of the EC Directive L159 in the national legislation of the European Community Member States.

The main aim of this paper is to give an overview of the improvements achieved in the last decades — technical as well as procedural — that have led to the state-of-the-art gamma spectroscopy analysis techniques for NORM and TENORM. The second aim is to provide information about how to set up representative sampling of NORM and TENORM in practice, in order to increase the sampling accuracy and thus increase the overall accuracy.

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[*] E-mail: vanvelzen@nrg-nl.com

[**] E-mail: timmermans@nrg-nl.com

2. GAMMA SPECTROSCOPIC ANALYSIS

The development of gamma spectroscopy as a tool for the non-destructive analysis of materials started in the early days of the nuclear industry and was further developed for the analysis of activated materials. Due to the relative simplicity of the technique, it has become one of the most widespread analysis tools used for the assessment of activity concentrations in materials.

A distinction has to be made between ‘low-resolution’ and ‘high-resolution’ gamma spectroscopy systems. Generally low-resolution gamma spectroscopy systems are equipped with a NaI(Tl) detector — the applied detector has a full-width-at-half-maximum (FWHM) of more than 6% at 661 keV. These low-resolution systems are suitable for the analysis of radioactive materials emitting a single or a few well-separated gamma energies. In the case of NORM and TENORM, due to the high number of gamma energies, NaI(Tl) detectors are less suitable and will therefore not be taken into account further. High-resolution gamma spectroscopy systems are in general equipped with a semiconductor detector.

The first wide scale commercially available semiconductor detectors for high energy gamma photons were Ge(Li) detectors (see Fig. 1). Detectors were soon commercially available with active volumes of about 45 cm^3 and an FWHM of 5–10 keV for ^{60}Co [2].

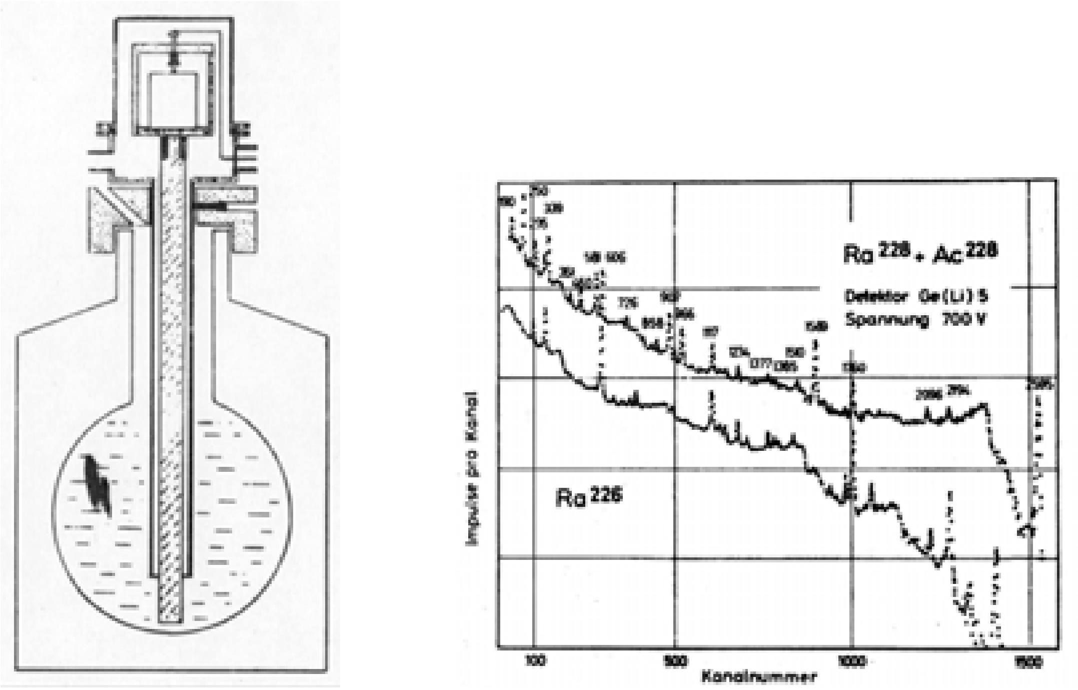

FIG. 1. Schematic diagrams of a semiconductor detector fabricated in the year 1967 and recorded gamma spectra of ^{226}Ra and ^{228}Ra including daughters [2]

As stated before, problems arose in the early 1980s with NORM and TENORM in the Netherlands, and this was mainly due to the reuse of fly ash in building and road construction materials. At the nuclear department of KEMA, the predecessor of NRG, knowledge and experience existed at that time [3] to start the development of very low background semiconductor gamma spectroscopy systems [4] in order to be able to measure accurately the specific radioactivity of flyash. In the following years, a large number of possible improvements were investigated and the most beneficial implemented, some of which are nowadays generally accepted and applied. The improvements concerned:

- Construction materials used for the manufacture of the detector,
- Construction of the detector,
- Shielding of the measuring cavity,
- Flushing of the measuring cavity with gases,
- Calibration,
- Sample geometry,
- Software.

(a) Construction materials used for the manufacture of the detector

To decrease the intrinsic background of the system, a programme was started to measure the activity concentration of all used construction materials [5]. The method followed is described in Ref. [6]. As an outcome of this programme, it was decided to start a selection procedure to obtain construction materials with little or no radioactivity content — especially the replacement of aluminum by other materials such as magnesium and stainless steel to decrease the total activity concentration of the detector.

(b) Construction of the detector

The standard end cap of the detector was replaced by an extended cap so that the pre-amplifier could be placed outside the measuring cavity and shielded. From the above-mentioned measuring programme it was found that the molecular sieve exhibited a relatively high activity concentration. This activity was shielded from the detector by placing a cylindrical block of aged lead around or into the cold finger.

(c) Shielding of the measuring cavity

To decrease the measuring time and to be able to reach the very low detection limits required, the special lead shielding had to enclose a cavity large enough for a 4 L Marinelli beaker. This meant that the cavity had to have at least a cylindrical shaped space with a height of 320 mm and a diameter of 550 mm. The shielding of the measuring cavity had to be multi-layered and, as a minimum, consisting on all sides of — starting from the outside — 100 mm common lead but selected for low activity concentration, 10 mm of aged lead manufactured at least 300 years ago, 2 mm of cadmium, and 10 mm of low activity copper.

(d) Flushing of the measuring cavity

The radionuclides ^{222}Rn and ^{220}Rn are present naturally in air. Both radon isotopes are continuously emanated from the soil and building construction materials. The concentration in the air is low and equilibrium will be established due to radioactive decay. The contribution to the background by ^{222}Rn and ^{220}Rn and daughters is substantial because of the small source-to-detector distance. However, this equilibrium strongly depends on local meteorological and geological circumstances. This means that the equilibrium can quickly change in time and thus the background can also change quickly. To establish a stable background in the first instance, filtered air was pumped into the measuring cavity preventing environmental air entering the cavity by the small overpressure (Fig. 2). However, this method did not fulfill all expectations, especially in the long term. Therefore, the measuring cavity is now flushed with nitrogen and cleaned with alcohol at regular intervals. All plastics are removed from the cavity (plastics become electrostatic in the long term and accumulate short-lived radon decay products). By adopting the above-mentioned measures, the background can be substantially reduced, as shown in Table II.

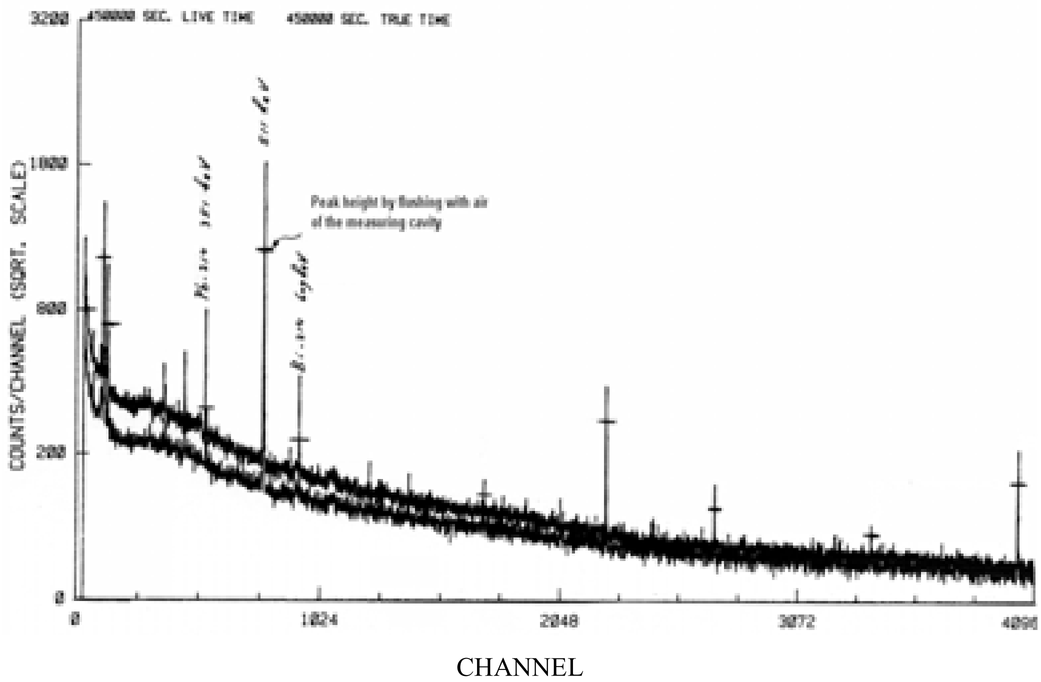

FIG. 2. Influence on the background of flushing the inner space with filtered air

TABLE II. OVERVIEW OF BACKGROUNDS ACHIEVED FOR SOME PHOTON ENERGIES REPORTED IN THE LITERATURE

Photon energy (keV)	No. of systems	Background count per 1000 s		
		Maximum	Minimum	Median
185	9	15	<0.006	0.3
239	16	8.9	<0.005	0.77
352	12	17	<0.1	2.2
511	9	19	0.25	10
583	14	6	<0.002	0.62
609	16	5.8	<0.003	0.77
911	12	1.1	<0.001	0.18
1461	18	4.4	0.008	1.05
2615	14	2.5	<0.001	0.51

(e) Calibration

Because gamma spectroscopy analysis had its origin in the nuclear industry and activation research with a wide variety of radionuclides, the calibration of these systems is mainly ‘energy’ instead of ‘radionuclide’ orientated. Energy-dependent calibrations have therefore become the most widespread and are described in national and international standards [7, 8]. The advantage of an energy- over a radionuclide-dependent calibration is that identification of an unknown photon peak is relatively easy, but the disadvantage is that corrections for coincidence and summing are difficult. Samples coming from the nuclear industry such as from cooling systems or environmental monitoring programmes are well defined and will not vary much in density or in composition in time. For this reason it is rather easy to manufacture a calibration source that matches these samples (see Table II), so that no actions have to be performed to correct for the self-absorption of photons in the sample. This is not valid for NORM and TENORM samples. These samples can of course be chemically and/or physically treated in such a way that they match a standard calibration source. However, the disadvantage is that those samples will no longer be in their original state and cannot be used for follow-up analyses. Furthermore, it is evident that each step of a chemical or physical treatment has to be verified and that these treatments will decrease the overall accuracy and will increase the routine analysis costs.

TABLE II. RECOMMENDED RADIONUCLIDES TO BE USED IN AN ENERGY DEPENDENT CALIBRATION OF HIGH-RESOLUTION GAMMA SPECTROSCOPY SYSTEMS

(For NORM and TENORM analysis, the list has to be extended by the addition of ^{210}Pb)

Nuclide	Photon energy (keV)
^{241}Am	59.5
^{133}Ba	81.0
^{109}Cd	88.0
^{57}Co	122.0
^{203}Hg	279.2
^{133}Ba	356.0
^{137}Cs	661.6
^{54}Mn	834.8
^{88}Y	898.0
^{60}Co	1173.2
^{60}Co	1332.5
^{40}K	1460.8
^{88}Y	1836.0
^{210}Pb	46.5

In the case of NORM or TENORM samples, coincidence and summing corrections can be performed provided that the exact absolute efficiency for the entire energy range is known. For instance, without coincidence corrections it is not possible to calculate the contribution of ^{235}U in the 186 keV photon peak. Therefore it is advisable to perform a new calibration as soon as a sample differs from the applied calibration source. At NRG as a rule of thumb “a new calibration has to be performed when the analyst assesses that the density and/or chemical composition of the sample differs more then 5% from the calibration source”. It is obvious that there are so many combinations of density and chemical composition possible that fulfil this rule of thumb that it will become an impossible job to create physically all the calibration sources needed. Therefore NRG has set up research and development projects to develop experimental methods to routinely assess the self-absorption behaviour of samples for different photon energies [9, 10] and software to calculate the absolute efficiency curves for every unique sample [11–14]. The software code developed is a semi-empirical Monte Carlo program able to calculate the relative differences between a unique sample and the applied calibration source. The software needs as input a geometry description of the detector crystal and sample. Both inputs can be sufficiently determined from the manufacturers' specifications. The code has been validated extensively in house [15] and by participation in an international comparison exercise [16]. Through the developments described above, an accuracy of better then 4% could be achieved for the ^{226}Ra and ^{228}Ra chain, and better then 8% for ^{210}Pb. However, the accuracy for ^{238}U and ^{235}U was still dependent on and influenced by the physical properties of the unique sample, and varied from 5% to 10%. This accuracy could not be reduced further, mainly due to the fact that, by taking into account coincidence and summing corrections, not only the accuracy of the absolute value of the specific activity but also the uncertainty of the value increased [17].

To overcome this problem, investigations were performed with 'radionuclide-dependent' calibrated gamma spectroscopic systems, because this type of calibration has in principle less problems with coincidence corrections. Radionuclide-dependent calibrations were performed for each of the natural radionuclides of interest. Calibration samples were prepared directly form certified materials or indirectly by application of known amounts of certified tracer solutions onto aluminum oxide powder [18]. By applying the developed technique for calculating calibration factors per unique sample, an accuracy of better then 5% could also be achieved for ^{238}U and ^{235}U.

(f) Software

The analysis software has to be capable of combining the different radionuclide-dependent calibrations. At present, no commercially available software package can achieve this adequately. Therefore, the final calculations are performed in a specially-developed Excel spreadsheet in which the results of the gamma spectroscopy analysis are used as input. In this spreadsheet, the results of different energies belonging to a single radionuclide are statistically weighted and outliers are removed. This approach improves the accuracy of the measurement result and decreases the uncertainty at the same time.

(g) Sample geometry

It is evident that the sample geometry has a direct influence on the absolute efficiency and the minimum detection limit. In the case of samples taken from low specific activity NORM that can be expected to be in secular equilibrium, large volume samples can be measured e.g. in Marinelli beakers on P-type high-purity germanium detectors. However in the case of TENORM samples it is advisable to measure smaller samples, up to 100 cm^3, that can be placed directly on top of an N-type high-purity germanium detector (N-type HpGe detectors are more suited for measuring photons below 60 keV then P-type HpGe detectors). This is due to the fact that, in TENORM samples, ^{210}Pb is not expected to be in secular equilibrium with the remainder of the natural uranium decay series and its emitted photon has an energy of 46.5 keV. Photons of 46.5 keV are not able to pass through the construction materials of the sidewall of the HpGe-detector end cap.

3. REPRESENTATIVE SAMPLING

The results of gamma spectroscopic analysis of NORM and TENORM samples often define the follow-up actions for all the material that the samples represent. The current national legislation of European Member States are based on the EC Directive L159 [19] and is in general more stringent than any former legislation with regard to NORM — as a direct consequence, the financial costs of follow-up actions will increase.

Existing state-of-the-art gamma spectroscopic systems can provide some compensation. However, due to the fact that sampling is at present mostly not performed according to national or international standards, the accuracy determined by a gamma spectroscopic analysis will be and often *has to be* decreased by an assessed accuracy based on the performed sampling. This assessed accuracy will be in general (much) larger then the determined accuracy of the gamma spectroscopic analysis. This means (see also Table I) that at this moment, when analyses are performed with a state-of-the-art system, the most benefit with regard to the overall accuracy of the results can be gained by improving the sampling procedures.

It is not possible to define a general procedure valid for all types of sampling. This can be concluded directly from the large number of different sampling procedures described in the various national and international standards. The list of available standards is extensive and it looks like there is a standard for every topic. Besides this, defining such a procedure will not give you any guarantee that governmental agencies and inspectorates will accept the developed sampling procedure. Therefore the approach to establish a representative sampling according to a validated procedure has to be pragmatic, meaning:

- Select the two or three most appropriate standards from those available. The search for applicable standards should not be limited to national standards or to standards applied normally in your industrial activities, e.g. select out of national standards and ISO-standards;
- Compare these standards and make a (draft) note. In this note the following has to be unambiguous — which standard is the most applicable, which has to be accompanied by an in-depth motivation;
- Test the selected standard e.g. validate the standard for your NORM or TENORM material(s);
- Finalize the note, including results of the performed validation;
- Send an official request with the final report to involved governmental agencies and inspectorates to agree that the selected standard is applicable for your NORM or TENORM material(s).

It is evident that such an approach will have the largest benefit as soon as it becomes clear that sampling has to be performed on a regular basis. The sampling can deal of course with raw bulk materials, scales of tubes, sludges, liquids, etc. It is also evident that informing involved governmental agencies at an early stage and during the different stages will facilitate the decision-making.

4. DISCUSSION AND CONCLUSION

Gamma spectroscopy is an efficient and powerful tool for measuring the activity concentration in NORM and TENORM samples. A schematic overview of parameters is given in Table III, indicating their influence on three important properties of a gamma spectroscopy system: background, detection limit and accuracy.

TABLE III. OVERVIEW OF PARAMETERS INFLUENCING THE BACKGROUND, DETECTION LIMIT AND ACCURACY OF GAMMA SPECTROSCOPY ANALYSIS

Parameter	Background of the system	Detection limit	Accuracy
Applied materials in the detector	+	+	
Construction of the detector	+	+	
Efficiency of the detector		+	+
Shielding of the measuring cavity	+	+	
Flushing of the measuring cavity with gases	+	+	
Calibration			+
Sample geometry		+	+
Specific activity of the sample		+	+
Measuring time		+	+
Software			+
Sampling			+

When setting up such a specialized tool for analyses of NORM and TENORM samples, the following aspects have to be taken into account:

- Selection of HpGe-detector. Samples taken from NORM that can be expected to be in secular equilibrium can be measured with a P-type detector. However this type of detector is not suited for measuring TENORM. Therefore it is advised to perform such measurements with a low background N-type detector.
- Measuring cavity. The shielding surrounding this cavity has to be made of materials selected on their activity concentration and has to be multi-layered as described above to optimize its background reduction. The cavity always has to be flushed with nitrogen, and no plastics are allowed.
- Calibration. The best analysis results will be obtained by radionuclide-dependent calibrations of the system in combination with software that is able to calculate the unique self-absorption correction per sample. The accuracy of this software has to be better then 7 % for photons from 40 keV up to 100 keV and better then 4% above 100 keV.
- Analyzing software. This software has to be able to combine the different radionuclide-dependent calibrations.
- Sample geometry. There are no volume restrictions for samples of NORM that are in secular equilibrium. In principle, this is also valid for samples of TENORM but, because ^{210}Pb is the restricting radionuclide, samples with a volume of 100 cm^3 will generally be sufficient.
- Accuracy. For obtaining the most accurate results from NORM and TENORM samples, samples have to be maintained in a gas-tight enclosure for a period long enough to establish the radioactive equilibrium between ^{226}Ra and its daughters (e.g. 3 weeks). During the preparation of the samples, attention has to given to the lock-up procedure, because free space is not allowed above the samples — otherwise, ^{222}Rn will not stay homogenously distributed inside the sample.

With a gamma spectroscopy system equipped with an N-type HpGe-detector having a relative efficiency of 25% that incorporates also the above-mentioned innovations, the following detection limits can be obtained — ^{238}U: 3 Bq/kg, ^{235}U: 0.3 Bq/kg, ^{226}Ra: 5 Bq/kg, ^{210}Pb: 30 Bq/kg, ^{40}K: 60 Bq/kg using a measuring time of 70 000s. It is evident that detection limits depend on the total activity of the sample.

These low detection limits show also the need to set up representative sampling procedures for NORM and TENORM. It will not be possible to define a sampling procedure valid for all types of sampling. Therefore, when it is expected that sampling is to be performed at regular intervals, it is advisable to base the set-up and sampling procedure validation for your materials on an existing national or international standard.

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APPLICATION OF LIQUID SCINTILLATION COUNTING TECHNIQUES TO GROSS ALPHA, GROSS BETA, RADON AND RADIUM MEASUREMENT IN PORTUGUESE WATERS

I. Lopes[*], M.J. Madruga, F.P. Carvalho

Nuclear and Technological Institute,
Department of Radiological Protection and Nuclear Safety,
Sacavém, Portugal

Abstract

Natural waters may contain a number of alpha and beta emitters and the routine control of the drinking water quality requires measuring mixtures of naturally occurring and artificial alpha and beta emitters. Portuguese law has adopted radioactivity limit values of 0.1 and 1 Bq/L for gross alpha and gross beta activities, respectively. The main goal of this work was to develop, test and optimize new radiometric techniques for measuring mixtures of alpha and beta emitters in drinking waters. The liquid scintillation counting technique has been optimized for the determination of these radiological parameters. A low background liquid scintillation system with the ability to discriminate between alpha and beta particles by pulse shape analysis was used. High counting efficiencies and very low limits of detection were obtained by optimizing the pulse shape discrimination and careful selection of scintillation cocktails. The first studies on the radioactivity content of some bottled waters and drinking water from public supplies showed that the limits were not exceeded in general. Radon concentrations in water could also be determined through direct measurement of ^{222}Rn short-lived daughter products using the liquid scintillation counting technique. The counting efficiency was closer to the theoretical maximum expected, i.e. 500%. The lower limit of detection for radon measurements in water was 0.195 Bq/L using a counting time of 60 min. The technique was also tested for the determination of ^{226}Ra in natural waters, and results are shown for gross alpha, gross beta, ^{222}Rn and ^{226}Ra measurements in drinking waters and pond waters in old open-pit uranium mines.

1. INTRODUCTION

Portuguese law [1] on the quality of water for human consumption adopted limit values of 0.1 and 1 Bq/L for gross alpha and gross beta activities, respectively. Radon (^{222}Rn) concentration in drinking water is not regulated in Portugal. However, a European recommendation on the radiological quality of drinking water [2] sets guidelines on radon and long-lived radon decay products. For water supplied as part of a commercial or public activity, if the concentration of radon exceeds 100 Bq/L, the Member State should set a reference level for radon, to be used for consideration whether remedial action is needed to protect human health. A level higher than 100 Bq/L may be adopted if national surveys show that this is necessary for implementing a practical radon programme.

The gross alpha and beta activities measured in drinking water from public water supplies during the previous years were, in general, lower than the limits recently adopted in Portuguese Law [3, 4]. However, some water samples collected in granite regions did show activity values higher than the recommended limits [5]. Therefore the periodic analysis of

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[*] E-mail: ilopes@itn.mces.pt

radioactivity in water for human consumption is of great importance to ensure the radiological quality of water to the population.

One of the most practical methods for determination of gross alpha, gross beta and ^{222}Rn in water is based on liquid scintillation counting (LSC). LSC has been widely used in the area of radiological analyses of environmental samples. This method has several advantages over the more conventional counting methods [6, 7]. The LSC technique combines the advantages of minimal sample preparation time, small sample size, reduced counting time, high sensitivity and detection efficiency closer to 100%. For the determination of gross alpha/beta activities by the LSC technique, there is no self-absorption problem like the one observed in the conventional analytical method where the sample is evaporated to dryness on a planchet and the radiation emitted by the residue measured in a counter [8, 9].

The LSC technique also became widely used for measuring radon [10–13]. Radon is highly soluble in toluene and in other organic solvents frequently used in the preparation of scintillation cocktails. In a closed vial, the ^{222}Rn is extracted from the water phase into the organic phase of the scintillation cocktail.

This work investigated the use of a very low background LSC system with pulse shape analysis to determine gross alpha, gross beta and radon, as well as dissolved radium in drinking water at low concentration levels.

2. MATERIALS AND METHODS

2.1. Equipment and radioactive standards

For gross alpha, gross beta and radon measurements in water samples, a low-level Tri-Carb 3170 TR/SL (Packard) measurement system was used. The counter has a bismuth germanium oxide (BGO) guard detector that completely surrounds the sample vial and delivers a background lower than in common counters. Typically, background counts in the 0–1000 keV region are 2–4 count/min for alpha particles and 11–16 count/min for beta emitters. This counter has the ability to discriminate between alpha and beta particles by pulse-shape discrimination (PSD) based on pulse-shape analysis (PSA). To optimize the discriminator setting, two standard sealed vial sources of ^{241}Am and ^{36}Cl (Packard), each with 50 000 disintegrations per minute (dpm), were counted. The efficiency counting for gross alpha/beta and radon measurements was determined with standard source solutions of ^{241}Am, ^{90}Sr and ^{226}Ra purchased from Amersham. Sets of standards with various radionuclide concentrations were prepared from these solutions, diluting a few microlitres of the source solution with 10 mL of distilled water and mixing with 10 mL of cocktail in 22 mL glass scintillation vials (Packard). The Ultima Gold AB cocktail (Packard) was used in the preparation of ^{241}Am and ^{90}Sr sources and the Opti-Fluor-O (Packard) in the preparation of ^{226}Ra standards. The background vials were prepared with distilled water using the same 10:10 volume ratio.

2.2. Determination of gross alpha/beta

Water samples (1000 mL) were acidified with 1 mL HCl[1] to avoid losses due to salt precipitation in the glass beakers with heating. Samples were pre-concentrated by slow evaporation on a hotplate to improve the detection limits. Usually, in acidified water the reduction of sample volume by a factor of 10 was sufficient to obtain samples with

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[1] Nitric acid was avoided because it reacts with the cocktail Ultima Gold AB [14].

measurable activities without the formation of precipitates and without losses of volatile activity [8]. One aliquot of 10 mL of this aqueous concentrate was withdrawn and added to 10 mL of cocktail (Ultima Gold AB, Packard) in a 22 mL glass scintillation vial (Packard). With this cocktail and with this sample-to-scintillator volume ratio at 20ºC, the sample was entirely soluble in the LSC cocktail and did not exceed the holding capacity of the cocktail. According to the manufacturer, Ultima Gold AB cocktail is a safe cocktail designed specifically to hold large volumes of acid aqueous solutions with excellent alpha/beta separation performance [15]. The counting time for each sample was 240 min. The detection efficiency was evaluated by measuring ^{241}Am and ^{90}Sr/^{90}Y standards prepared in laboratory.

2.3. Determination of radon and radium

Prior to sample collection, 10 mL of a non-aqueous liquid scintillation solution, Opti-Fluor-O (Packard) was added to a 22 mL glass scintillation vial[2] and tightly closed with a poly-cone cap. The vials containing scintillation fluid were weighed. In the field, 10 mL[3] water samples were taken with a plastic syringe and the water gently injected below the surface of the cocktail to avoid degassing of ^{222}Rn from the sample to the atmosphere. The vial was tightly closed again and the time of sample collection recorded. The vials were taken to the laboratory for counting ^{222}Rn activity as soon as possible. The sample vials were reweighed to determine more accurately the mass of the sample and hence the volume, assuming unit density for water. Radon background vials were prepared using the same method as for drinking water samples. A waiting period of at least 3 h was always allowed between the collection and the measurement of the sample radioactivity, in order to ensure the formation of radioactive equilibrium between ^{222}Rn and its short-lived decay products. Measurements were carried out at 20ºC using a counting time for each sample of 60 min. The net count rate of every sample vial was corrected for the radioactive decay of radon between the time of sample collection and radioactivity counting. The same sample was measured again 30 d later. At this time, the original radon in the water had decayed away and the radon then measured was ^{222}Rn in equilibrium with ^{226}Ra dissolved in the water sample. This second measurement allowed for the easy determination of radium concentration in water.

3. EXPERIMENTAL RESULTS

3.1. PSA optimization

The new liquid scintillation counters have the ability to discriminate between alpha and beta particles by PSD based on PSA. The discrimination of alpha and beta pulses is based on the well-known difference between the delay component of their decay [18]. Typically, alpha-produced events have longer decay lifetimes than beta events. This is due to the fact that it takes a longer time for the cocktail to release its excitation energy as light when the excitation is caused by an alpha particle in comparison with a beta particle. However, with alpha and beta emitters simultaneously present in the sample there is no absolute separation of the counts. Some counts due to alpha particles may be recorded in the beta counting window and vice versa, giving rise to a partial crossover.

In order to select the best PSD parameter value, the optimization of PSA was made by measuring separately an alpha emitter (^{241}Am) and a beta emitter (^{36}Cl). ^{241}Am is an alpha

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[2] Radon diffuses through polyethylene and losses may occur [16].

[3] Better performance was obtained with the 10:10 sample-to-cocktail ratio than with other volume configurations [17].

emitter (E_α = 5.54 MeV) with a weak emission of gamma rays (E_γ = 59 keV). ^{36}Cl is a pure beta emitter ($E_{\beta max}$ = 709.55 keV) with no alpha particle emission. After counting the pure alpha emitter source, the percent of alpha events that were counted as beta events was plotted on the discriminator setting. Similarly, the events recorded as alpha emissions in the counting of the pure beta emitter source were plotted also on the same graph as a percentage of total counts, against the discriminator setting. Fig. 1 shows the spillover curve obtained with ^{241}Am and ^{36}Cl standards.

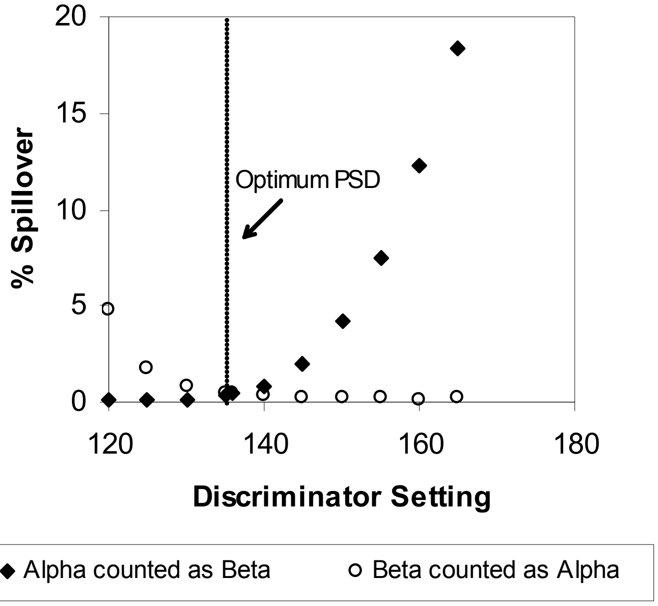

FIG. 1. Crossover plot using ^{241}Am and ^{36}Cl standard sources

The pulse decay discriminator setting chart (% spillover vs. time) was a typical alpha/beta crossover plot for ^{241}Am/^{36}Cl radionuclides [19]. The optimum PSD level was obtained by setting the discriminator at 136. For this PSD value the percent spillover for alpha and beta events was kept at a minimum, 0.41% and 0.40% for alpha and beta particles, respectively. Using this PSD value, the counting efficiency for each standard source was 98.25% and 99.74 % for the ^{36}Cl and ^{241}Am, respectively. This discriminator setting was used later in the counting of alpha/beta activities in real water samples.

3.2. Method validation for gross alpha/beta measurements

Validation of the method required pure alpha and beta reference sources matching the chemical and physical characteristics of the environmental samples to be measured. For this purpose, as a first stage, pure alpha (^{241}Am) and pure beta (^{90}Sr/^{90}Y) reference sources were prepared with activities in the range 1–25 Bq/L. With these sources, the efficiency for alpha and beta emitters was determined to be 97.1% for the ^{241}Am standard and 91.7% for the ^{90}Sr/^{90}Y standard, with the PSD set at 136 (Tables I and II).

As a second stage, in order to validate the proposed method for determination of gross alpha and gross beta measurements, tap water samples spiked with ^{241}Am and ^{90}Sr were prepared. Tap water samples without added radioactivity were used as background. The counting time for the background and the samples was 240 min and the pulse shape discriminator was set at PSA = 136. The nominal activities of spiked samples and results obtained by measurements are shown in Table III. There is excellent agreement between the two sets of values.

TABLE I. COUNTING EFFICIENCY AT DIFFERENT ^{241}Am CONCENTRATIONS

^{241}Am standard activity (Bq/L)	Counting efficiency and standard deviation (%)
24.25	101.72 ± 0.35
12.13	98.79 ± 0.47
4.85	98.28 ± 0.75
1.21	89.53 ± 1.41
Average	97.08 ± 0.42

TABLE II. COUNTING EFFICIENCY AT DIFFERENT ^{90}Sr CONCENTRATIONS

^{90}Sr standard activity (Bq/L)	Counting efficiency and standard deviation (%)
23.90	91.74 ± 0.23
11.95	92.75 ± 0.32
5.97	91.29 ± 0.45
1.19	91.04 ± 0.98
Average	91.70 ± 0.38

TABLE III. ALPHA AND BETA MEASUREMENTS FOR WATER SAMPLES SPIKED WITH KNOWN ACTIVITIES OF ^{241}Am AND ^{90}Sr

Known activity (Bq/L)[4]	Measured activity (Bq/L)[5]
Alpha activity (^{241}Am)	
48.5	45.98 ± 1.70
24.25	23.47 ± 1.56
11.64	10.90 ± 1.48
5.82	5.65 ± 0.05
1.16	1.03 ± 0.06
Beta activity (^{90}Sr)	
23.90	24.76 ± 0.05
11.95	12.38 ± 0.12
5.17	5.35 ± 0.02
1.19	1.21 ± 0.01

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[4] The uncertainties of the nominal values of activity were 0.47% and 0.88% for ^{241}Am and ^{90}Sr, respectively.

[5] The average of the measurement of three replicate samples with the same nominal activity.

3.3. Calibration tests for ^{222}Rn and ^{226}Ra measurements

In order to determine the counting efficiency for ^{222}Rn and ^{226}Ra measurements and to check the linear response of the counter to different ^{226}Ra concentrations, a set of ^{226}Ra standards were prepared with Opti-Fluor-O (Packard) cocktail as described in Section 2. This cocktail, based on the high flash-point solvent linear alkyl benzene, was chosen to obtain two immiscible phases when we added the water sample to the organic cocktail in the scintillation vial. With this cocktail, ^{226}Ra is not extracted into the organic phase, remaining dissolved in the aqueous phase, and does not contribute to the counts recorded. The activity measured is due to ^{222}Rn only, which diffuses into the organic phase. Thirty eight days after closing the vial, ^{222}Rn is in equilibrium with ^{226}Ra. For the counting, a wide-open window was applied in order to integrate the contributions of all alpha and beta particles emitted in the decay chain of ^{222}Rn through to ^{214}Po. At equilibrium, for every radon alpha decay there are three alpha particles (from ^{222}Rn, ^{218}Po and ^{214}Po) and two beta particles (from ^{214}Pb and ^{214}Bi) emitted in a rapid sequence of nuclear disintegrations. Each individual particle is counted with an efficiency close to 100% [20]. In the case of our ^{226}Ra sources, the counting efficiency for ^{226}Ra in equilibrium with the daughters was 481.86% due to the cumulative contribution of the radioactive emitters by the short-lived progeny of radon (Table IV). Similar values were reported by other authors [21].

TABLE IV. COUNTING EFFICIENCY FOR ^{226}Ra STANDARDS

^{226}Ra standard activity (Bq/L)	Counting efficiency and standard deviation (%)
22.13	477.03 ± 2.41
11.10	472.28 ±. 3.38
4.44	490.09 ± 5.39
1.11	500.23 ± 10.58
0.44	469.70 ± 15.48
Average	481.86 ± 5.78

Fig. 2 shows the linear response of the counter to different ^{226}Ra concentrations, measured in the conditions of a closed system in radioactive equilibrium between ^{226}Ra and ^{226}Ra decay products. This linear response demonstrates also that no ^{222}Rn leaks occurred from vials during the storage time.

To follow the ingrowth of ^{222}Rn with time until the formation of radioactive equilibrium, two sets of three replicate ^{226}Ra standard solutions of 31 and 15.5 Bq/L, respectively, were measured for up to nearly 40 days following the preparation of the samples. Thirty days after sealing the vials and thereafter, the counts recorded became nearly constant. At this point, ^{222} Rn is in near radioactive equilibrium with ^{226}Ra (Fig. 3). Using this method, water samples with unknown concentrations of ^{226}Ra can be measured and the ^{226}Ra concentration present in water can easily be determined using the efficiencies reported above.

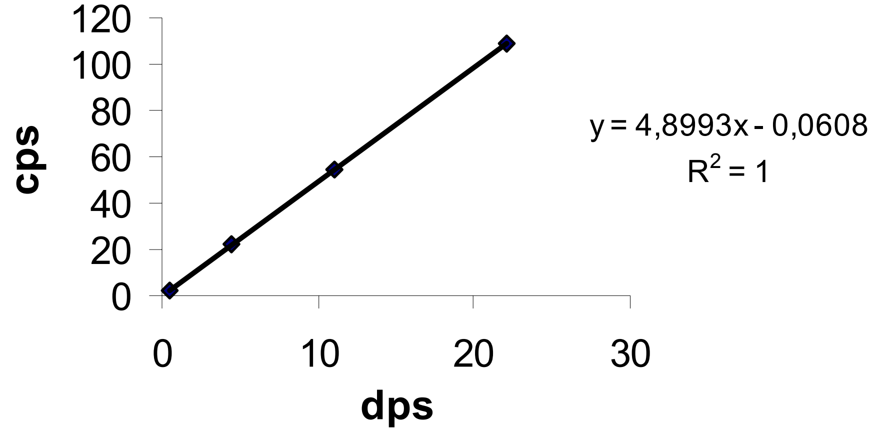

FIG. 2. Plot of cps (counts per second) vs dps (disintegrations per second) for a set of ^{226}*Ra standard solutions*

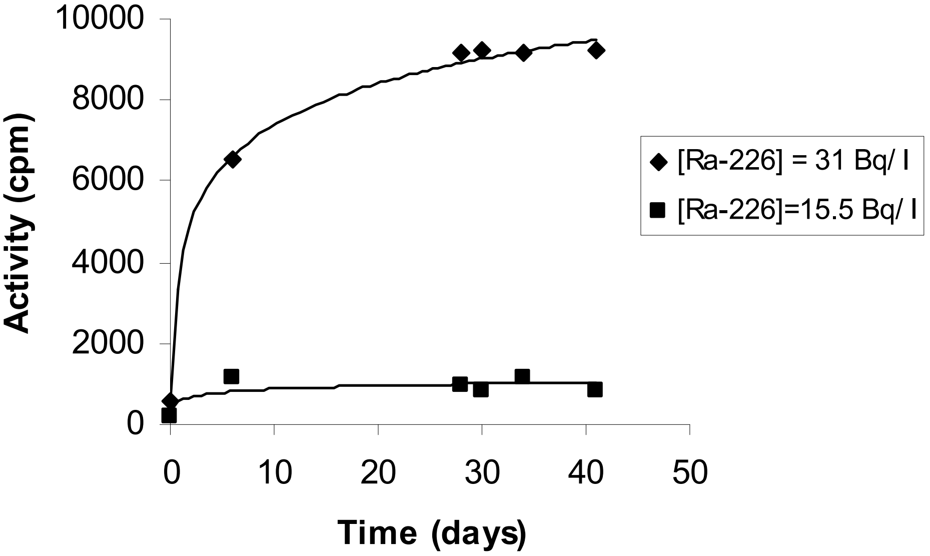

FIG. 3. Temporal evolution of the average activity of two different ^{226}*Ra solutions*

Fig. 4 shows the decay of ^{222}Rn activity in three natural water samples measured shortly after collection and containing an excess of ^{222}Rn compared with ^{226}Ra activity. After 30 days, no excess ^{222}Rn is present in the samples. The radon activity remains constant and it is supported by the decay of ^{226}Ra present in the aqueous phase. The computed half-time for the decay observed during the initial 15 days is close to 4 days, confirming that the decrease of the activity is due to radon decay only ($T_{1/2}$ = 3.8 days).

Analysis of the spectra obtained using these two-phase sample vials corroborates that, in the spectrum, only ^{222}Rn and its short-lived progeny contribute to the counts. A typical pulse-height spectrum for radon and its daughters is shown in Fig. 5.

4. APPLICATION OF THE LSC TECHNIQUE TO ENVIRONMENTAL SAMPLES

After validation as described in Section 3, the LSC technique was applied to radioactivity measurements of drinking water and surface waters. The results for gross alpha and gross beta activities are presented in Table V. Gross beta activities ranged from 0.052 Bq/L, the lower limit of detection (LLD), to 6.54 Bq/L; gross alpha activities ranged from 0.022 Bq/L (LLD) to 7.27 Bq/L. The values are within the limits approved by law for radioactivity in water for human consumption with the exception of sample 5. However, this sample is a mineral water, which is not covered in the EU recommendation.

The LSC technique has been used for radon measurements in drinking water samples from municipal supplies, drinking water from local supplies in small villages and non-drinking water from ponds, including artificial ponds and in old open-pit mines in granite rock. Values presented in Table VI illustrate the concentration levels found in the central and northern regions of the country. Radon measurements range from the LLD (0.195 Bq/L) to 349.15 Bq/L.

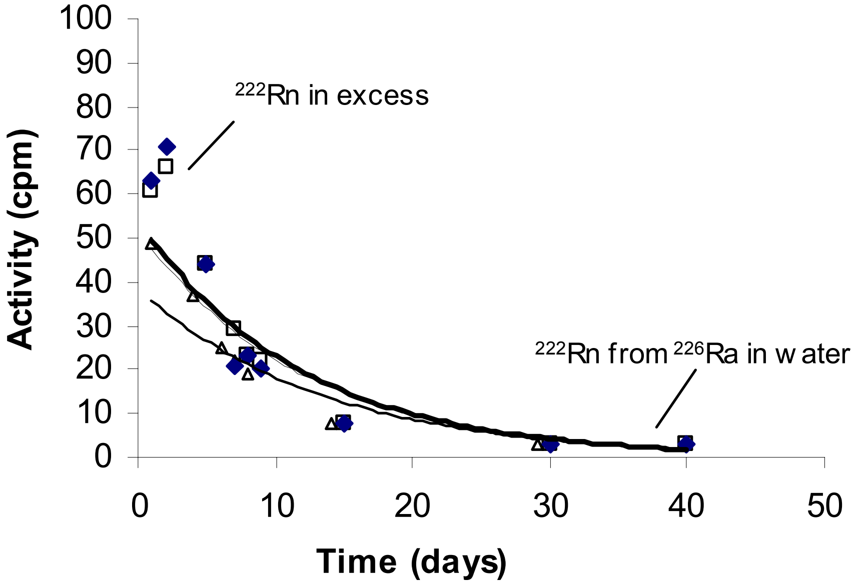

FIG. 4. Decrease of activity of ^{222}Rn in natural water samples with time

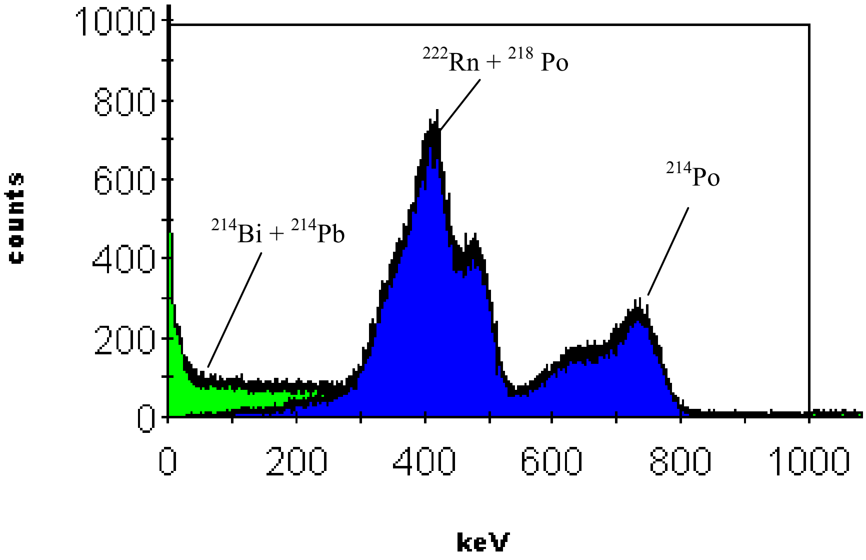

FIG. 5. A pulse-height spectrum obtained for a ^{226}Ra standard (22.3 Bq) recorded 30 days after capping the liquid scintillation vial

TABLE V. GROSS ALPHA AND BETA MEASUREMENTS IN DRINKING WATER

Sample		Activity concentration (Bq/L)	
		Gross beta	Gross alpha
1.	Tap water	0.190 ± 0.034	< 0.022
2.	Tap water	0.127 ± 0.044	0.120 ± 0.017
3.	Tap water	0.101 ± 0.051	< 0.022
4.	Tap water	< 0.052	< 0.022
5.	Bottled mineral water	6.54 ± 0.105	7.27 ± 0.084
6.	Bottled water	< 0.052	< 0.022
7.	Bottled water	0.224 ± 0.041	0.107 ± 0.018
8.	Tap water	0.100 ± 0.036	< 0.022
9.	Tap water	0.189 ± 0.034	< 0.022
10.	Tap water	0.269 ± 0.033	< 0.022
11.	Tap water	0.179 ± 0.033	< 0.022
12.	Tap water	0.162 ± 0.030	< 0.022

TABLE VI. RADON MEASUREMENTS IN WATER FROM MUNICIPAL SUPPLIES AND OPEN PONDS

Type of water source	Site	Radon activity (Bq/L)
Tap water from the municipal distribution supply system	Guarda	35.24 ± 1.60
	Lamegal	48.58 ± 2.03
	Sobral da Serra	< 0.195
	Ázere	< 0.195
	V. N. Tázem	1.90 ± 0.19
	Trancoso	112.77 ± 3.23
	Aguiar da Beira	61.29 ± 2.29
Drinking water from the village local water supply (spring source or aquifer)	Vila Fernando	349.15 ± 6.39
	Freixeda	166.52 ± 4.30
	Esmolfe	198.09 ± 4.41
Pond water, either natural or in an old open pit of a former uranium mine	Mondego Sul	34.89 ± 1.88
	Fontinha	14.02 ± 0.95
	Maria Dónis	24.28 ± 1.27
	Corga do Valbom	33.01 ± 1.55

5. CONCLUSIONS

The use of a low background LSC system with PSA enables the simultaneous determination of alpha and beta activities in water samples with counting efficiencies of up to near 100% for both alpha and beta particles. The LSC technique is a good alternative to the conventional radiochemical method used for monitoring gross alpha and beta activities, based on counting a thin layer source containing the salt residue. Measurement of spiked water samples showed that the LSC method is suitable for the routine determination of gross alpha and beta activities in drinking water using counting times of 240 min. Detection limits are 0.022 and 0.052 Bq/L, respectively, for gross alpha and gross beta at a 95% confidence level. The LSC method is also very convenient for ^{222}Rn and ^{226}Ra measurement in drinking water samples. This method requires minimal sample pre-treatment and its low detection limit makes it ideal for environmental monitoring of radioactivity in water. A lower limit of 0.195 Bq/L using counting times of 60 min is sufficient for control of the radiological quality of water for human consumption. Furthermore, this technique has been also successfully applied to monitor radioactivity, including dissolved radon, in mine waters from old uranium mines.

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IN SITU GAMMA RAY SPECTROMETRY IN COMMON ROCK RAW MATERIALS MINED IN KRAKOW VICINITY, POLAND

D. Malczewski[1], **L. Teper**[1], **G. Lizurek**[1*], **J. Dorda**[2]

[1]Faculty of Earth Sciences, University of Silesia, Sosnowiec, Poland
[2]Institute of Physics, University of Silesia, Katowice, Poland

Abstract

The natural radioactivity of ^{40}K, ^{208}Tl, ^{212}Pb, ^{212}Bi, ^{214}Pb, ^{214}Bi, ^{228}Ac and the fallout of ^{137}Cs in common rock raw materials mined in the vicinity of Krakow were measured in situ using a portable gamma-ray spectrometry workstation. The measurement points were chosen for different regional rocks in: Devonian and Jurassic limestones, dolomite, trachyandesite, porphyry, porphyry tuff, diabase and melaphyre. The ^{40}K activity varied from about 82 Bq/kg (Jurassic limestone) to 3150 Bq/kg (porphyry tuff). The activity concentrations associated with ^{228}Ac (^{232}Th series) varied from 9 Bq/kg (Jurassic limestone) to 56 Bq/kg (porphyry tuff), whereas the activity of ^{226}Ra (^{238}U series) ranged from about 13 Bq/kg (Jurassic limestone) to 43 Bq/kg (Devonian limestone). The highest deposition of ^{137}Cs (20 kBq/m^2) was recorded in Devonian limestone.

1. INTRODUCTION

The Krakow surroundings are one of the places where human settlement started in the central part of Europe. This region has been ranked among the most densely populated areas in Poland for centuries. Favourable geological features have enabled local communities to mine a great variety of rocks and use them as raw materials for building purposes since the early Middle Ages. Presently, some of the local rocks are exploited on a commercial scale and the output supplies the home industry serving as mineral raw materials for many fields of production. In the current study, the natural radioactivity of ^{40}K, ^{208}Tl, ^{212}Pb, ^{212}Bi, ^{214}Pb, ^{214}Bi, ^{228}Ac and the fallout of ^{137}Cs were measured in situ in common rock raw materials mined in the vicinity of Krakow using a portable gamma-ray spectrometry workstation.

2. GEOLOGICAL SETTING AND MEASUREMENT LOCATIONS

The study area occupies the south-east edge of the regional geological unit called the Silesian-Krakowian Monocline (SKM). The SKM forms a layered plate whose upper complex consists of Permian-to-Cretaceous rocks inclined towards the northeast. Aside from the regional direction of dip, the southern part of the monocline subsides in a step-like manner, being partially overthrusted by the Carpathians, which emerged in the south, and partially included in the vast tectonic depression of the Carpathian Foredeep (Fig. 1). The older formation, which underlies the Mesozoic complex of the SKM, was folded and faulted during Carboniferous-to-Permian tectonic episode. Elevations of that time were subsequently flattened out and the plain was covered consecutively by Permian, Triassic, Jurassic and Cretaceous deposits. Monoclinal features of the rock mass originated at the end of the Cretaceous period when both lower and upper complexes were tilted to the north-east

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[*] E-mail: glizurek@us.edu.pl

direction. In the Palaeogene when the SKM area remained a land, its southern part, as the most uplifted, was subjected to extensive denudation. Long-lasting erosion resulted in removal of a thick series of rock cover and exposed older formations in the Krakow neighbourhood (see Fig. 1). Tectonic activity in the Neogene was expressed as folding within collisional orogeny of the Carpathians south of Krakow area. Large scale northwards overthrusts of orogenic units resulted in the concurrent faulting of the overloaded foreland where a number of horst and grabens formed. The marine transgression onto newborn tectonic depressions in front of the Carpathian belt took place in the Miocene. One of such down-dropped blocks crosses the outskirts of Krakow town. This narrow west–east elongated depression called the Krzeszowice graben (Fig. 1) is limited by roughly parallel normal faults. Footwalls of the faults are typical places where the formations belonging to both lower and upper complexes of the SKM crop out. Most exposed rocks are considered as highly valued raw materials. Their outcrops were selected as sites for conducting the field measurement of radioactivity levels in rocks with gamma-ray spectroscopy. The sites are described below in stratigraphical order starting from the oldest rocks.

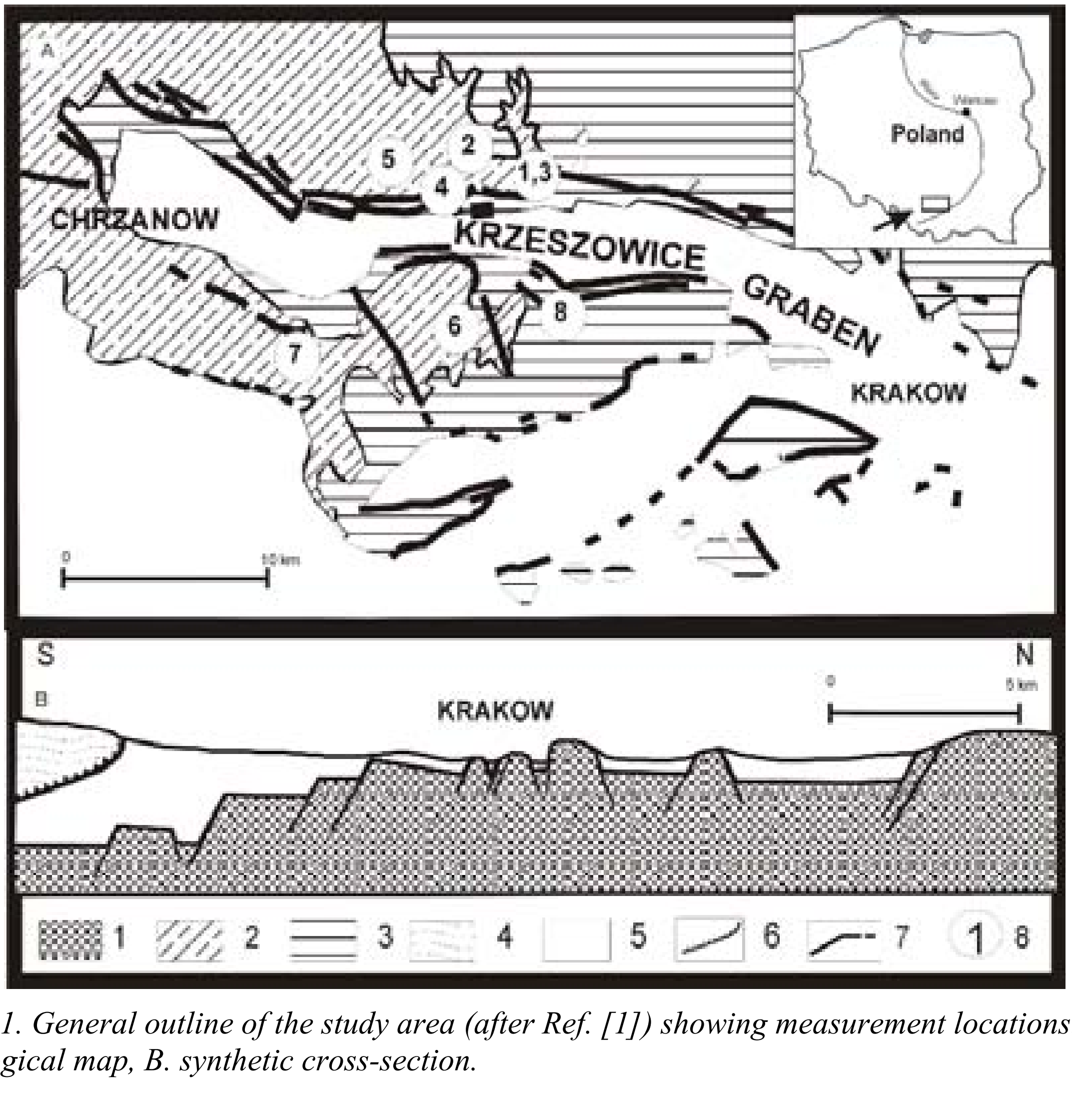

FIG. 1. General outline of the study area (after Ref. [1]) showing measurement locations. A. geological map, B. synthetic cross-section.

1: Palaeozoic and Mesozoic formations (not distinguished), 2: Palaeozoic rocks, 3: Mesozoic complex, 4: the Carpathian folded units, 5: Miocene marine sediments of the Carpathian Foredeep, 6: the Carpathian orogeny front, 7: main faults, 8: locations of field measurements

Point 1 (see Fig. 1) was established in the Dubie quarry. Dolomites, which are mined there, resulted from Variscan dolomitization of coral and stromatoporoid limestones deposited during the Lower Givetian period. They make up the oldest of the formations that surface in the SKM. Building aggregates produced by the Dubie quarry are mainly used as crushed stones for road pavements. Measurement in the Debnik quarry (see Fig. 1, point 2) was done for bituminous limestone of Upper Givetian age. This site is the only black limestone occurrence in Poland, which has been exploited since 1415. Raw blocks of this attractive high-quality 'marble' are in great demand on the domestic market.

Felsic subvolcanic rocks here and there intrude Devonian carbonates (points 1 and 2) during the Upper Carboniferous and Lower Permian periods. Site 3 (see Fig. 1) was located on the trachyandesite dyke, which cuts the vertically dolomite complex in the Dubie quarry. This rock, according to its chemical properties, was used as a ceramic material. Where the volcanites approached ground surface, felsic lava flows of Variscan age formed. Now they are exposed in both the southern and northern edges of the Krzeszowice graben. One of those outcrops is the Miekinia quarry where porphyry mined since 1852 (see Fig. 1, point 4) lies on Lower Permian continental deposits. The main Miekinia products were building and paving stones as well as porphyry elements of small architecture. Porphyry tuff, which is common loose material coming from felsic volcanic eruptions, occurs near Filipowice. This tuff has for ages served as an important local building stone. The Kowalska Gora closed quarry of the Filipowice tuff was another place chosen for present measurement (see Fig. 1, site 5).

Apart from the felsic one there is also mafic igneous formation, originating during Variscan folding of the SKM lower complex. Point 6 (see Fig. 1) was established where diabase crops out near the Niedzwiedzia Gora quarry. There, a syntectonic sill of hypersthene-quartz diabase intruded the Upper Carboniferous clastic sediments. The diabase, exploited since 1910, is regarded as a very good raw material for aggregates used in the road construction industry. A volume of mafic lava-flows remained from the same episode of magma genesis. From among them an outcrop of Lower Permian melaphyre at the Regulice closed road-stone quarry (see Fig. 1, site 7) was selected to perform the present measurement. Point 8 (see Fig. 1) was localized in the Nielepice quarry, which mines the most common raw material belonging to the upper complex of the SKM. This is Upper Jurassic platy limestone; formerly traditional building stone used to construct most of medieval monuments in southern Poland, currently used mainly for cement and lime production. For more detailed information on the geology and rock raw materials of the Krakow area, Refs [2–5] can be recommended.

3. METHODS

The system (EG&G ORTEC) consists of an HPGe detector (30% efficiency, crystal length: 59 mm, diameter: 58.6 mm) with cryostat PGM-5 (liquid nitrogen) mounted on a tripod, a multichannel buffer DART, and a laptop. The manufacturer's quoted resolutions of the detector are 0.67 keV at 122 keV and 1.73 keV at 1.33 MeV. The software used for determination of the radionuclides — M-1-B32 (EG&G ORTEC) — implements the 1 m geometry in situ analysis methods developed by the U.S. DOE Environmental Measurements Laboratory [6]. The software is divided into two main parts: the supervisor program which uses the programs M-1 Setup and Gamma Vision-32, and the operator program M-1 for Windows. In field conditions, the detector was mounted 1 m above the rock and, in this case, the detector view for gamma emitters was approximately 10 m in radius to a depth of about 30 cm, depending on the ground and the energy source [7]. For the determination of the presence of discrete radionuclides and calculations of their activities, the following gamma-ray transitions (in keV) were chosen: ^{7}Be (477), ^{40}K (1460.8), ^{137}Cs (661.7), ^{208}Tl (510.8, 583.1 and 860.5), ^{212}Pb (238.6 and 300.1), ^{212}Bi (727.2 and 1620.6), ^{214}Pb (241.9, 295.2 and

351.9), ^{214}Bi (609.3, 1120.3, 1238.1 and 1764.5) and ^{228}Ac (338.3, 911.1 and 968.9) [8]. The energy tolerance for library file (1Meter.lib) was stated as 1.75 keV. The counting time was set for 3 h for each measured location. The energy calibration of the spectrometer was carried out using powdered mixture ^{40}K (840 Bq), ^{226}Ra (218 Bq) and ^{232}Th (127 Bq) calibration sources. The vertical distribution of particular radionuclides is described within the M-1 software by parameter α/ρ, where α is the reciprocal of the relaxation length (flux reduction by factor *e*) for the gamma energy line being observed (cm^{-1}) and ρ is the soil (rock) density (g/cm^{3}) [9]. Three cases represent the general source distribution: $\alpha/\rho < 0.1$, uniform source distribution (natural radionuclides), $\alpha/\rho > 0.5$, planar source distribution (fresh fallout) and $0.1 < \alpha/\rho < 0.5$, not uniform or planar. Values of α/ρ ranging from 0.1 to 0.5 have been found to describe realistic fallout distributions adequately; the more aged fallout will be represented by the smaller values. In our work we assumed $\alpha/\rho = 0$ for distributions of ^{40}K, ^{208}Tl, ^{212}Pb, ^{212}Bi, ^{214}Pb, ^{214}Bi and ^{228}Ac, whereas for ^{137}Cs, $\alpha/\rho = 0.21$ (the manufacturer's recommended values) [9, 10].

4. RESULTS AND DISCUSSION

The results of in situ γ-ray measurements of ^{40}K, ^{137}Cs, ^{208}Tl, ^{212}Pb, ^{212}Bi, ^{214}Pb, ^{214}Bi, ^{228}Ac and calculated activity concentration of ^{226}Ra at all measurement locations are given in Table I. The total uncertainty value given in the Table consists of the random and systematic errors in all of the factors involved in calculating the final radionuclide concentration result [10]. The error can be expressed as:

$$\sigma_{\mathrm{t}} = \sqrt{\sum \sigma_{\mathrm{ri}}^2 + \frac{1}{3}\sum \sigma_{\mathrm{si}}^2} \qquad (1)$$

where σ_{t} is the total uncertainty, σ_{ri} is the individual random error and σ_{si} is the individual systematic error. The random uncertainties are counting, random summing and absorption correction, whereas the systematic uncertainties are radionuclide uncertainty from the library, efficiency fitting uncertainty, calibration source uncertainty and geometry correction. The random summing uncertainty is estimated to be 10% of Equation 1 [10].

4.1. Potassium-40

The highest activity concentrations of ^{40}K were noted in porphyry tuff: 3154 Bq/kg (point 5), melaphyre 1215 Bq/kg (point 7) and porphyry 1032 Bq/kg (point 4). The lowest activity concentrations of ^{40}K were measured in Jurassic limestone: 82 Bq/kg (point 8), dolomite 85 Bq/kg (point 1) and trachyandesite 184 Bq/kg (point 3). Intermediate values refer to the Devonian limestone: 473 Bq/kg (point 2) and diabase: 530 Bq/kg (point 6). A comparison of the ^{40}K activity concentration in rocks of the area studied with the average concentrations in soil and continental crust is shown in Fig. 2. As can be seen from the Figure, an extremely high concentration of ^{40}K was measured in porphyry tuff, nearly 4 and 8 times higher than the average ^{40}K activity concentrations for continental crust and soil, i.e. 850 and 400 Bq/kg respectively [11]. Activity concentrations of ^{40}K that are distinctly higher than crustal and soil averages are visible in melaphyre and porphyry. The concentration levels of ^{40}K that are clearly below the continental crust and soil averages are characteristic for Jurassic limestone, dolomite and trachyandesite (Fig. 2).

TABLE I. IN SITU GAMMA MEASUREMENTS OF RADIONUCLIDES IN THE VICINITY OF KRAKOW

Radio-nuclide	Activity concentration and standard deviation σ_t at different measurement locations (Bq/kg)							
	1	2	3	4	5	6	7	8
^{137}Cs[1]	< 66	20165 ± 168	< 66	8830 ± 188	3499 ± 133	1037 ± 95	7878 ± 168	< 66
^{40}K	85 ± 4	473 ± 9	184 ± 3	1032 ± 6	3154 ± 15	531 ± 6	1215 ± 10	82 ± 3
^{208}Tl	2.4 ± 0.3	11.4 ± 0.9	3.3 ± 0.6	14.2 ± 0.9	17.3 ± 1.7	13.2 ± 2.1	20.6 ± 0.7	3.4 ± 0.5
^{212}Pb	< DL[2]	30.3 ± 0.8	6.9 ± 0.4	38.8 ± 0.8	37.2 ± 1	33.4 ± 0.7	49.2 ± 1	7.8 ± 0.3
^{212}Bi	< DL	< DL	< DL	29.4 ± 3.7	< DL	41.5 ± 8.7	< DL	4.6 ± 0.7
^{228}Ac	7.2 ± 1.3	30.9 ± 5.6	9.7 ± 1.7	38.6 ± 4.4	55.9 ± 6.9	35.2 ± 5.2	55.3 ± 7.2	9.5 ± 2
^{214}Pb	20.3 ± 2.6	42.2 ± 4.8	23.6 ± 4.8	23.8 ± 2.2	34 ± 3.2	28.3 ± 3.4	30.1 ± 3.2	13.7 ± 1.8
^{214}Bi	18.1 ± 3.3	44.3 ± 6.7	20.4 ± 5.7	23.2 ± 5	31.4 ± 5.7	30.2 ± 3.9	25.8 ± 4.5	11.9 ± 2.7
^{226}Ra[3]	19.2 ± 3.7	43.2 ± 6.8	22 ± 6.4	23.5 ± 4.5	32.7 ± 5.5	29.2 ± 4.4	27.9 ± 5.1	12.8 ± 2.8

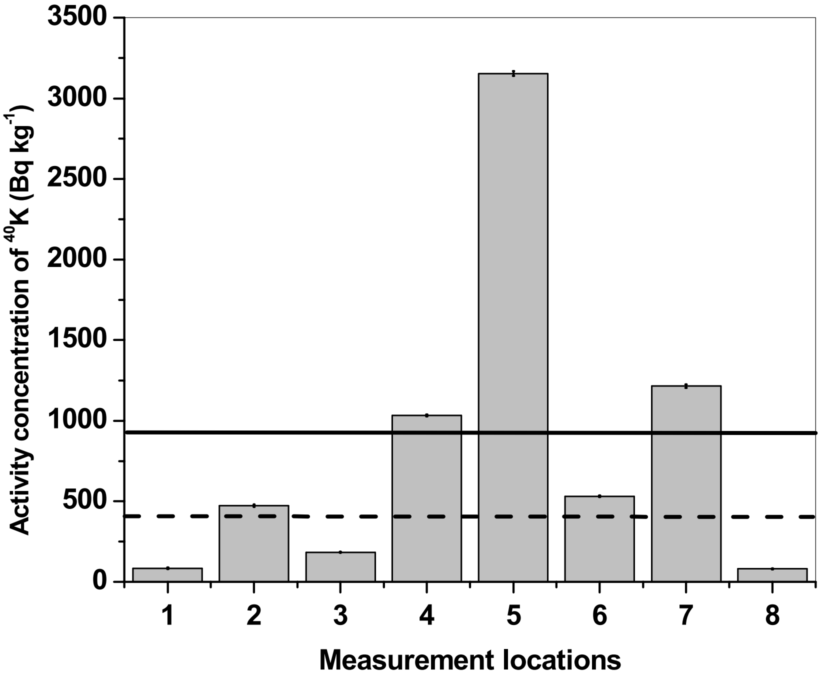

FIG. 2. Comparison of the ^{40}K activity concentrations (grey bars) with average activities reported for continental crust (solid line) and soil (dashed line) for each measurement location in the Krakow vicinity.

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[1] Bq/m^2.

[2] DL = detection limit.

[3] Based on ^{214}Bi and ^{214}Pb activities.

4.2. Caesium-137

The measurements in the Krakow vicinity have shown diverse levels of ^{137}Cs fallout activity after the Chernobyl accident and weapons tests, ranging from 20 165 Bq/m^2 in Devonian limestone (point 2) to less than 66 Bq/m^2 in dolomite (point 1), trachyandesite (point 3) and Jurassic limestone (point 8) (Table 1 and Fig. 3). Such low depositions of ^{137}Cs in these rocks are due to the removal of the superficial layer during exploitation of these quarries. As mentioned above, the highest depositions of ^{137}Cs were noted at point 2 (Fig. 3) in Devonian limestone, then at the following points: 4 (porphyry, 8829 Bq/m^2), 7 (melaphyre, 7877 Bq/m^2), 5 (porphyry tuff, 3498 Bq/m^2) and 6 (diabase, 1037 Bq/m^2). These depositions agree well with the deposition of ^{137}Cs for this part of Poland, ranging from 3000 to 20 000 Bq/m^2, as reported by the Polish Central Laboratory for Radiological Protection [12].

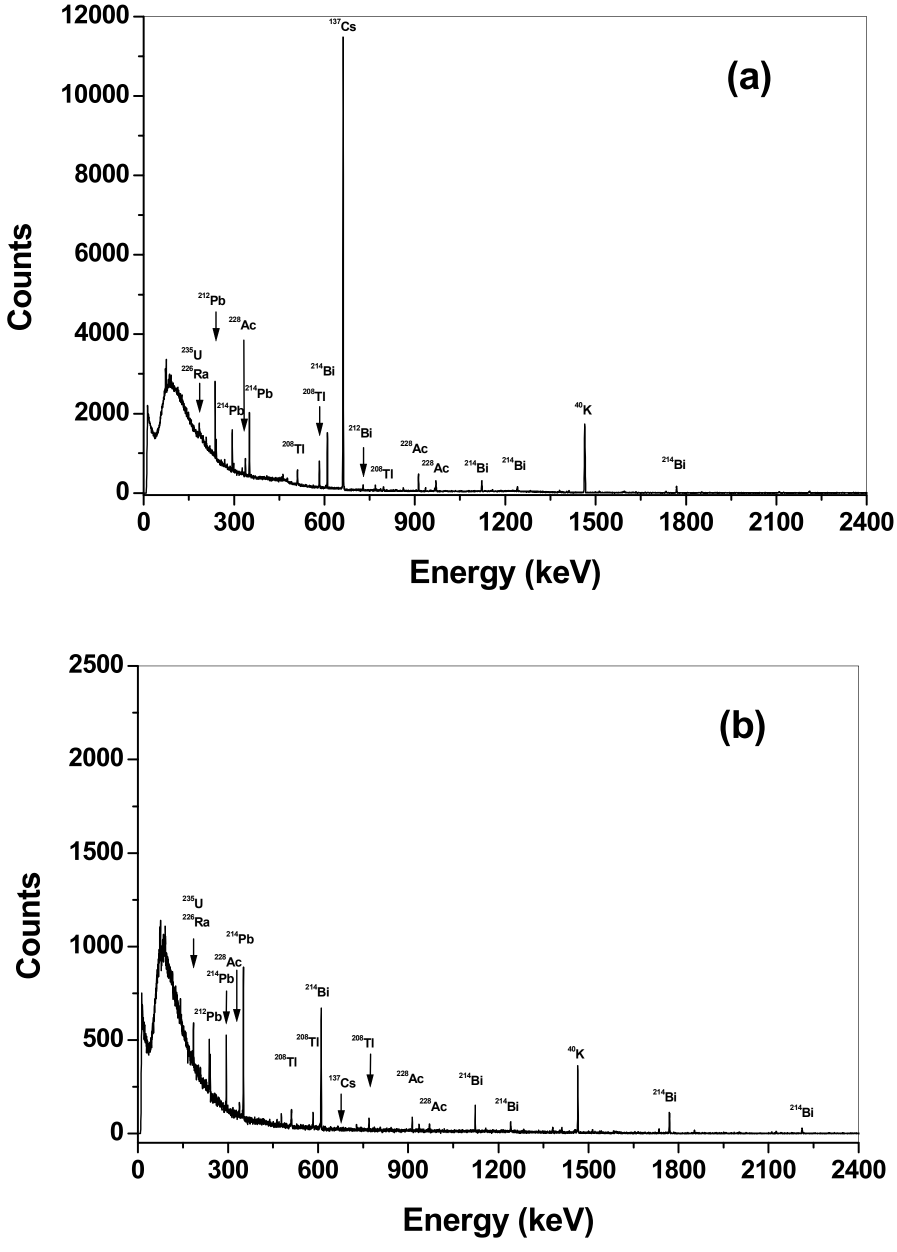

FIG. 3. In situ γ–ray spectra obtained with the portable gamma-ray spectrometry from: (a) Devonian limestone and (b) Jurassic limestone. The characteristic γ-ray emitters are marked above the corresponding peaks. The spectrum of Jurassic limestone does not show the characteristic 661.7 keV line from ^{137}Cs.

4.3. Thorium-232 series (^{228}Ac, ^{212}Pb, ^{212}Bi, ^{208}Tl)

As is shown in Table I, there is an excellent radioactive equilibrium between ^{228}Ac and ^{208}Tl in the ^{232}Th series at each measurement location. The activity concentrations associated with ^{228}Ac are the highest in porphyry tuff (point 5, Table I) and in melaphyre (point 7). Intermediate concentrations of ^{228}Ac: 38.6, 35.2 and 30.9 Bq/kg were noted in porphyry (point 4), diabase (point 6) and Devonian limestone (point 2), respectively. Activities of ^{228}Ac <10 Bq/kg were recorded in dolomite (point 1), trachyandesite (point 3) and Jurassic limestone (point 8).

4.4. Radium-226 (^{214}Pb, ^{214}Bi)

Activity concentrations of ^{226}Ra at locations 6, 7, 4, 3 and 1 (Fig. 1, Table I) vary in a relatively narrow range between 29.9 Bq/kg (diabase, point 6) and 19.2 Bq/kg (dolomite, point 1). The highest concentrations of ^{226}Ra (43.2 and 32.7 Bq/kg) were noted in Devonian limestone (point 2) and porphyry tuff (point 5) respectively, whereas the lowest value (12.8 Bq/kg) was recorded in Jurassic limestone.

4.5. Activity concentrations of ^{232}Th and ^{238}U

In this work we assumed radioactive equilibrium in the ^{232}Th → ^{228}Ac and ^{238}U →^{226}Ra →^{222}Rn → ^{214}Pb → ^{214}Bi decay chain segments. In relation to ^{214}Pb and ^{214}Bi, exhalation of ^{222}Rn from the soil (rock) can produce a 10–20% reduction in the gamma-emitting radionuclides ^{214}Pb and ^{214}Bi on the surface. However, in the field measurements the exhalation of ^{222}Rn was compensated in most part by the contribution of the flux from the same radionuclides in the ambient air [7]. Based on these assumptions, the activity concentrations of ^{232}Th and ^{238}U in rocks in the vicinity of Krakow are shown in Fig. 4. As can be seen in the Figure, at two points: 5 (porphyry tuff) and 7 (melaphyre), the concentrations of ^{232}Th exceeded the average concentration of this radionuclide in the continental crust, i.e. 44 Bq/kg [11, 13]. All other locations were characterized by concentrations lower than this value for thorium. In the case of ^{238}U, only Devonian limestone (point 2) clearly exceeded the average uranium concentration for the continental crust (36 Bq/kg). All the other rocks measured showed ^{238}U concentrations below the continental crust value (Fig. 4).

5. CONCLUSIONS

In situ gamma spectrometry appears to be a useful tool for obtaining actual concentrations of radionuclides in the environment. According to the results reported in this paper, some of the rocks from the Krakow vicinity are characterized by enhanced concentrations of ^{40}K (porphyry tuff, melaphyre and porphyry), ^{232}Th (porphyry tuff and melaphyre) and ^{238}U (Devonian limestone) in comparison with the continental crust averages for these radionuclides. The ^{137}Cs fallout measurements show that the deposition of this radionuclide varies widely, from less than 66 kBq/m^2 (dolomite, trachyandesite and Jurassic limestone) to more than 20 000 kBq/m^2 (Devonian limestone).

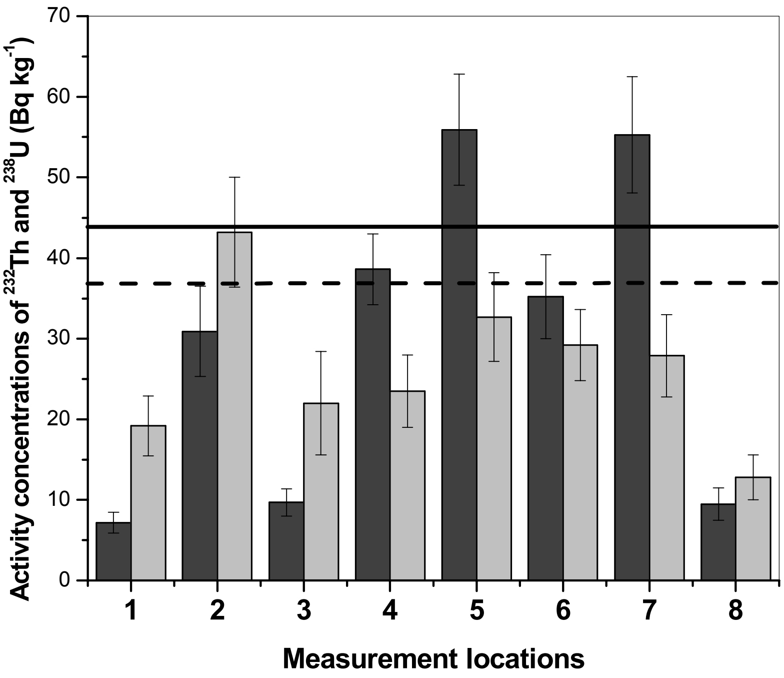

FIG. 4. Activity concentrations of ^{232}Th and ^{238}U obtained in situ in common rock raw materials in the Krakow vicinity (black and grey bars respectively) compared with average activity concentrations reported for ^{232}Th and ^{238}U in the continental crust (solid and dashed lines respectively)

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THE RAPID IDENTIFICATION OF NORM DISCHARGES REQUIRING REGULATORY CONTROL — A POSSIBLE SCREENING METHODOLOGY

E. Henrich[1*], A. Janssens[1], T.P. Ryan[1], J.-L. Daroussin[2], K.R. Smith[3], M.Y. Gerchikov[4], Z.K. Hillis[4], A. van Weers[5]

[1]European Commission, DG TREN, H4, Radiation Protection, Luxembourg
[2]IRSN/DEI/SARG/LERAR, Fontenay-aux-Roses Cedex, France
[3]NRPB, Chilton, Didcot, United Kingdom
[4]NNC Limited, Warrington, United Kingdom
[5]NRG, Petten, Netherlands

Abstract

The European Commission (EC) is mindful of the potential difficulties for national regulators in implementing a process of regulatory control as set out in Title VII of EU Council Directive 96/29/Euratom (Basic Safety Standards Directive) for NORM industries discharging into the environment. As a consequence, the EC commissioned a study to identify possible procedures for the rapid identification of such industries or work activities where members of the public are potentially exposed, with a view to producing guidelines. The results of the study are presented in this paper. It is well understood that there is no simple relationship between discharge rate from a NORM industry and dose to members of the public. However, with respect to regulatory control, a detailed site-specific analysis may not be warranted when, on the basis of a conservative approach, it can be concluded that the discharges are of no radiological significance. This introduces the idea of NORM discharge screening levels which may be defined as estimates of the amount of activity discharged to the environment, which, if not exceeded, mean that it is very unlikely that members of the public would receive an effective dose above a defined dose criterion. NORM discharge screening levels can be defined for each NORM release route and would be calculated using deliberately cautious assumptions. The derivation of such screening levels would comprise the following steps: definition of reference discharge situations; choices of models, exposure pathways and parameters; derived doses per unit discharge rate; dose criteria for screening levels and finally, discharge screening levels. In this paper, discharge-screening levels are derived and presented. It is unlikely that below these levels a more detailed site-specific radiological assessment of the discharges would be warranted. It is recommended that a dose criterion be chosen for the screening level that is below the dose constraint for the facility. If discharge-screening levels are exceeded it is recommended that regulatory bodies verify the actual level of discharge, re-examine discharge conditions such as stack height or river flow, re-examine the existence of assumed exposure pathways and decide on the need for site-specific assessment.

1. INTRODUCTION

1.1. Background

Aspects of radiation protection in the field of NORM are covered in Title VII of the European Basic Safety Standards [1]. A study on this topic, entitled *Effluent and dose control from European Union NORM industries — assessment of current situation and proposal for a harmonized community approach,* was completed in 2003 and a report published in the Radiation Protection Series of the European Commission's Radiation Protection Unit (DG TREN.H.4) [2]. The general aspects of EC NORM policy are covered in Ref. [3] and a review

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[*] E-mail: eberhardt.henrich@cec.eu.int

of NORM industries in the EU is given in Ref. [4]. This paper addresses a possible screening methodology.

1.2. NORM discharge screening levels

The discharges into air and water from NORM industries vary considerably with respect to the radionuclides discharged, the effective height of the stacks for aerial discharges and the characteristics of the receiving aquatic environment for liquid discharges. Radiation exposure of members of the public resulting from these discharges involves many exposure pathways and the level of exposure per unit discharge rate depends on quite a number of site-specific conditions. Consequently, no simple and general relationship exists between discharge rate and dose to members of the public. On the other hand, detailed site-specific analysis is not warranted when, on the basis of a generalized and conservative approach, it can be concluded that the discharges are of no radiological significance.

NORM discharge ‘screening levels’ are therefore defined as *estimates of the amount of activity discharged to the environment from a NORM plant, which, if not exceeded, mean that it is very unlikely that members of the public would receive an effective dose above a defined dose criterion*.

NORM discharge screening levels can be determined for each NORM release route, i.e. to atmosphere, rivers and the marine environment. Such screening levels are calculated using deliberately cautious assumptions such that compliance with them would ensure virtual certainty of compliance with a typical dose constraint. The derivation of the discharge screening levels comprises the following steps:

- Definition of reference discharge situations;
- Choice of models, exposure pathways and parameter values;
- Derived doses per unit discharge rate;
- Dose criteria for screening levels;
- Discharge screening levels.

It should be kept in mind that large uncertainties and variabilities may be involved in some of these steps.

The approach used in the study in deriving screening levels for discharges is similar to the methodology described in Ref. [5], although it uses more sophisticated models. The main features of the approach described in Ref. [5] are:

- The derived screening levels serve to assess compliance with environmental standards (limiting values);
- Doses estimated by screening are not intended to represent estimates of actual doses to individuals;
- Simple models should always be applied first;
- Models and parameters are chosen so as to produce conservative estimates of doses;
- Sophisticated models are not needed if compliance with environmental standards can be demonstrated on the basis of the screening models;
- Screening can be carried out for aerial discharges and for liquid discharges into fresh surface water and marine surface water;

- Screening can be carried out at two or three different levels of conservatism in the approach.

2. THE SYSTEMATIC APPROACH

2.1. Reference discharge situations

Reference discharge situations were defined for atmospheric releases (effective stack heights of 10 m, 50 m, 100 m and 200 m to cover a wide range of applications) and for discharges to rivers (large, medium and small rivers with flow rates from 500 down to 2.5 m^3/s). For releases to the marine environment a similarly straightforward method could not be applied. Therefore for both off-shore releases and on-shore releases, scenarios were chosen, and are presented here, that may not necessarily represent a conservative approach. Thus, for discharges to the marine environment a more detailed study of the actual situation is warranted.

2.2. Models, pathways and parameters

The screening levels were calculated for continuous, uniform discharges of radionuclides to the environment (annual discharges, assumed to continue for 50 years; ingrowth of radioactive progeny included).

2.2.1. Atmospheric releases

The following exposure pathways were taken into account: external exposure to the plume and to deposited activity; internal exposure due to inhalation of radionuclides from the plume and resuspended activity and ingestion of food produced on land contaminated by the plume. For release heights up to 100 m, a Gaussian dispersion model was used (part of PC CREAM [6]); for 200 m the more complex Atmospheric Dispersion Modelling System (ADMS) [7] was used. Doses were calculated assuming that the occupancy at 500 m from the release point was basically 100 % and that 50 % of the consumed food was grown locally.

2.2.2. River discharges

The exposure pathways considered were ingestion of untreated river water and of fish, and external gamma exposure to riverbank sediments. The model used (PC CREAM) assumed a discharge into a 1 km compartment of the river and complete mixing. Downstream transport of radionuclides in solution, with suspended sediment and in riverbed sediment was modelled as well as sedimentation itself.

2.2.3. Releases to the marine environment

The exposure pathways considered were consumption of fish, crustaceans and molluscs, and external exposure to beach sediment. The model (Poseidon [8]) used two of the boxes developed for the MARINA project [9], namely, the boxes ‘North Sea N’ and ‘Baie de la Seine’ as examples. They differ in volume by a factor of 200. Within the vertical compartments of the boxes homogeneity was assumed. The dispersion of radionuclides released into the box was described by water exchange with adjacent compartments, by exchange of radionuclides between dissolved and particulate state via sorption processes and by remobilization from the bottom sediments into the water layers due to bioturbation and diffusion. The prediction of the radionuclide concentration in marine biota was based on the steady-state approach, which assumed a constant equilibrium between the concentration of dissolved radioactivity in water and in marine organisms. For dose calculations, the habit data for critical groups were used rather than those for average adult consumers.

Due to the relatively small differences between the doses for adult and child age groups, only the adult age group was considered as reference group. The dose coefficients for ingestion and inhalation were taken from the European Basic Safety Standards Directive [1].

2.3. Dose per unit discharge rate

The determination of the dose per unit discharge rate (tabulated in the complete study report [2]) was based on the above-mentioned assumptions.

2.4. Screening levels of discharge rate

To define screening levels, one firstly has to choose a level of annual dose above which the discharge is regarded as potentially of radiological significance (and hence would require more detailed assessment). The choice of such a dose criterion is not straightforward. In the study, the screening levels were intended ultimately to identify NORM discharges that definitely should not be regulated or, conversely, to identify discharges that may be of potential radiological significance and would require a more detailed and possibly site-specific assessment. In this case it seems sensible to choose a dose criterion for the derivation of the screening levels that is below the dose constraint (which often is taken as 300 μSv/a), e.g. in the range 10–100 μSv/a. Therefore, the figures given in the study report, and presented below, show screening levels for 10, 100 and 300 μSv/a. For rough comparison, the figures include ‘typical’ discharges as estimated in the full report [2].

3. USE OF SCREENING LEVELS

(a) The screening levels are intended for screening purposes and have been calculated using a set of generic assumptions. For discharges below the screening levels there is unlikely to be a reason for a more detailed and site-specific radiological assessment of the discharge. Above the levels — although this does not necessarily imply that the dose criterion will be exceeded — such a detailed analysis is advised. In practice, discharges of more than one radionuclide will occur. Account must be taken of exposures from all radionuclides discharged. If the sum of the ratios for each nuclide discharged divided by the appropriate screening level is less than or equal to unity then the total discharge is below the screening level. For some sites it is possible that radionuclides will be discharged by more than one route, for example, discharges to atmosphere and to a local river may occur from the same location. In this case, the critical group for the different discharge routes is unlikely to be the same and so summing fractions of the screening level may be excessively cautious. If a site-specific dose assessment is required then a more realistic approach could be adopted where account is taken of exposure from all routes using a combination of critical group and average habits. In industrialized areas, several sources may discharge into the atmosphere or into the same river. The higher the chosen screening level dose criterion, the greater the chance that exposures of the same critical groups to the combined sources may approach or exceed the dose constraint or dose limit.

(b) The derived NORM discharge screening levels in TBq/a are estimates of the amount of activity discharged to the environment from a NORM plant, which, if not exceeded, mean that it is very unlikely that members of the public would receive an effective dose above a defined dose criterion. A dose criterion should be chosen for the screening levels that is below the dose constraint, e.g. in the range 10–100 μSv/a.

(c) The screening levels of discharge provided in Table I (for aerial discharges) and Table II (for river discharges) are based on a screening level dose criterion of 300 μSv/a. Such screening levels are calculated using deliberately cautious assumptions such that compliance with them would ensure virtual certainty of compliance with the dose constraint. For marine discharges, the figures given in Table III are only examples, rather than 'recommended' screening levels.

(d) Derived discharge screening levels are directly dependent on the selected dose criterion. This is illustrated in Figs 1–8 by comparing typical discharges from a number of NORM industries with derived screening levels of discharge based on dose criteria of 10, 100 and 300 μSv/a.

(e) If discharge screening levels are exceeded, the actual level of discharges should be verified, discharge conditions (e.g. stack height, river flow) and the existence of assumed exposure pathways should be checked, and a decision should be made on the need for a site-specific assessment.

TABLE I. SCREENING LEVELS FOR DISCHARGE INTO THE ATMOSPHERE

Radionuclide or chain segment	Screening level for different stack heights (TBq/a)[1]			
	10 m	50 m	100 m	200 m
^{238}U+	0.14	2.3	12	23
^{235}U+	0.12	2.2	9.3	20
^{234}U	0.11	2	10	20
^{232}Th	0.014	0.21	0.73[2]	1.9
^{230}Th	0.028	0.51	2.7	5
^{228}Th+	0.0093	0.17	0.94	1.7
^{231}Pa+	0.0028	0.48	0.22	0.460
^{228}Ra+	0.12	1.5[3]	0.41[3]	12[3]
^{226}Ra+	0.066	0.73[3]	0.16[2]	5.4[2]
^{227}Ac+	0.00071	0.013	0.073	0.13
^{222}Rn	150	2 700	16 000	28 000
^{220}Rn	2	37	210	370
^{210}Pb+	0.16[3]	1.6[3]	3.1[3]	11[3]
^{210}Po	0.07	0.8[3]	1.7[3]	5.8[3]

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[1] Based on a dose criterion of 300 μSv/a received by members of the critical group. The dominant exposure pathway is plume inhalation except where stated otherwise.

[2] The dominant exposure pathway is external radiation.

[3] The dominant exposure pathway is food consumption.

TABLE II. SCREENING LEVELS FOR DISCHARGE INTO A RIVER

Radionuclide or chain segment	Dominant exposure pathway	Screening level (TBq/a)[4]		
		Small river	Medium river	Large river
Average consumption and occupancy:				
^{238}U+	Water ingestion	**0.83**	33	160
^{235}U+	Water ingestion	0.77	31	155
^{234}U	Water ingestion	**0.77**	31	154
^{232}Th	External radiation	**4.8**	190	961
^{230}Th	External radiation	**4.3**	170	853
^{228}Th+	External radiation	**0.0049**	0.2	0.98
^{231}Pa+	Water ingestion	0.059	2.4	11.9
^{228}Ra+	Water ingestion	**0.042**	1.7	8.39
^{226}Ra+	Water ingestion	**0.075**	3	15.1
^{227}Ac+	Water ingestion	0.026	1.1	5.3
^{210}Pb+	Fish consumption	**0.032**	1.3	6.35
^{210}Po	Water ingestion	**0.037**	1.5	7.42
High consumption and occupancy:				
^{238}U+	Water ingestion	0.58	**23**	**120**
^{235}U+	Water ingestion	0.54	22	110
^{234}U	Water ingestion	0.54	**21**	**110**
^{232}Th	External radiation	4	**160**	**810**
^{230}Th	External radiation	3.7	**150**	**740**
^{228}Th+	External radiation	0.0049	**0.2**	**0.98**
^{231}Pa+	Water ingestion	0.042	1.7	8.5
^{228}Ra+	Fish consumption	0.016	**0.64**	**3.2**
^{226}Ra+	Fish consumption	0.034	**1.4**	**6.9**
^{227}Ac+	Fish consumption	0.015	0.62	3.1
^{210}Pb+	Fish consumption	0.005	**0.2**	**1**
^{210}Po	Fish consumption	0.013	**0.53**	**2.6**

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[4] Based on a dose criterion of 300 μSv/a received by members of the critical group. Results in bold used for comparison with doses from typical discharges.

TABLE III. EXAMPLES OF MARINE DISCHARGES RESULTING IN A DOSE OF 300 μSv/a RECEIVED BY MEMBERS OF THE CRITICAL GROUP

Radionuclide or chain segment	Small compartment (Baie de la Seine)		Large compartment (North Sea North)	
	Dominant exposure pathway	Discharge (TBq/a)	Dominant exposure pathway	Discharge (TBq/a)
Average consumption and occupancy:				
^{238}U+	Molluscs consumption	83 000	Fish consumption	780 000
^{234}U	Molluscs consumption	110 000	Molluscs consumption	4 500 000
^{232}Th	Fish consumption	83	Fish consumption	18 000
^{230}Th	Fish consumption	3 000	Fish consumption	210 000
^{228}Th+	Fish consumption	2 200	Fish consumption	490 000
^{228}Ra+	Fish consumption	100	Fish consumption	11 000
^{226}Ra+	Fish consumption	220	Fish consumption	10 000
^{210}Pb+	Fish consumption	330	Crustacea consumption	23 000
^{210}Po	Crustacea consumption	1 400	Crustacea consumption	74 000
High consumption and occupancy:				
^{238}U+	Crustacea consumption	9 200	Fish consumption	81 000
^{234}U	Crustacea consumption	16 000	Crustacea consumption	620 000
^{232}Th	External radiation	5.4	Fish consumption	660
^{230}Th	Fish consumption	240	Fish consumption	16 000
^{228}Th+	External radiation	93	External radiation	20 000
^{228}Ra+	Fish consumption	12	Fish consumption	1100
^{226}Ra+	Fish consumption	22	Fish consumption	1000
^{210}Pb+	Crustacea consumption	30	Crustacea consumption	1 500
^{210}Po	Crustacea consumption	89	Crustacea consumption	4 800

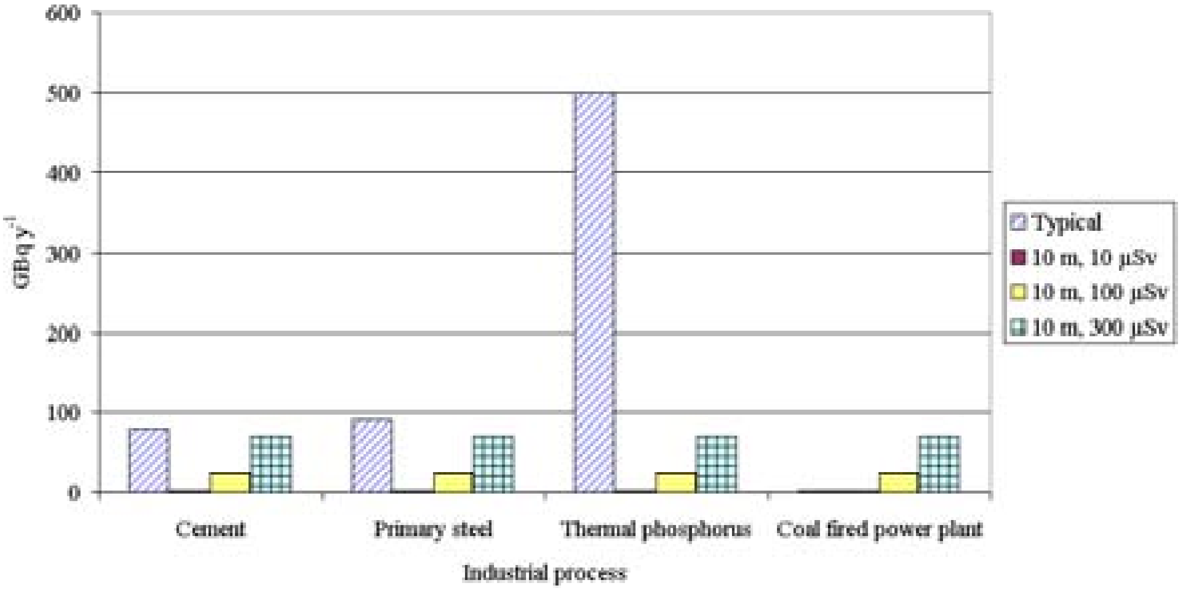

FIG. 1. Comparison of typical aerial discharges of ^{210}Po with derived screening levels for a 10 m stack height using three different dose criteria

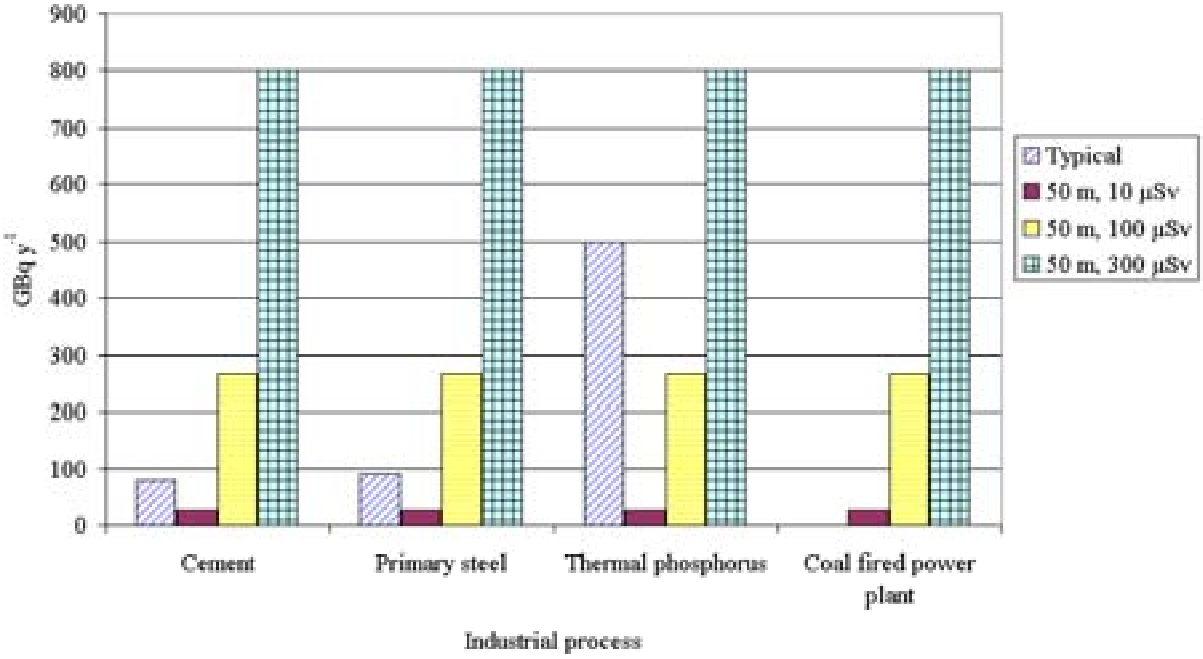

FIG. 2. Comparison of typical aerial discharges of ^{210}Po with derived screening levels for a 50 m stack height using three different dose criteria

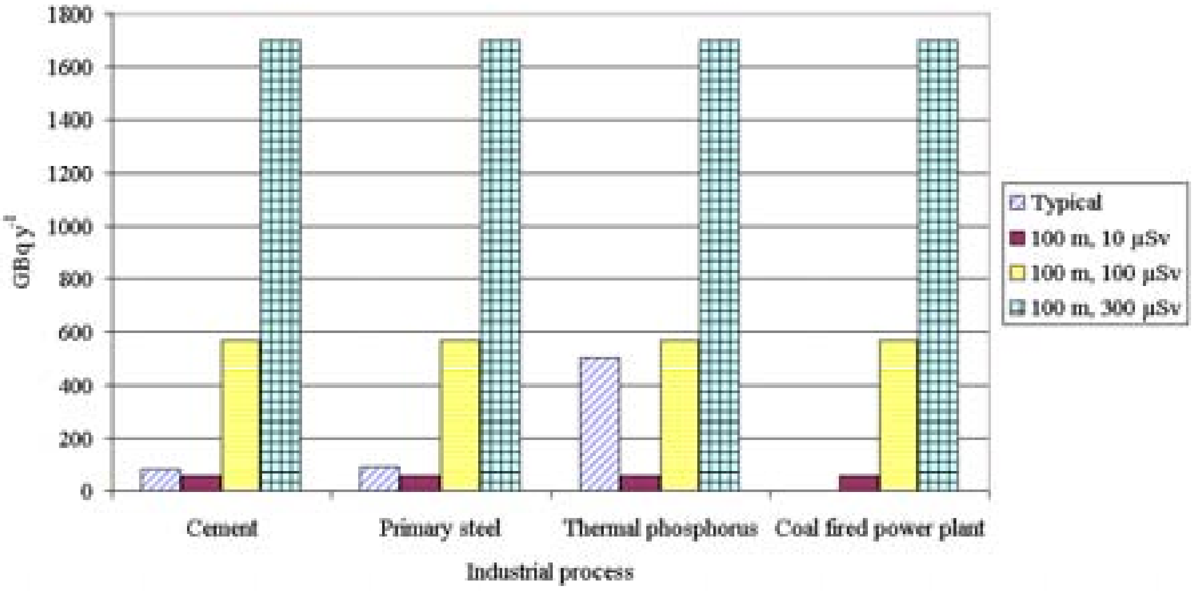

FIG. 3. Comparison of typical aerial discharges of ^{210}Po with derived screening levels for a 100 m stack height using three different dose criteria

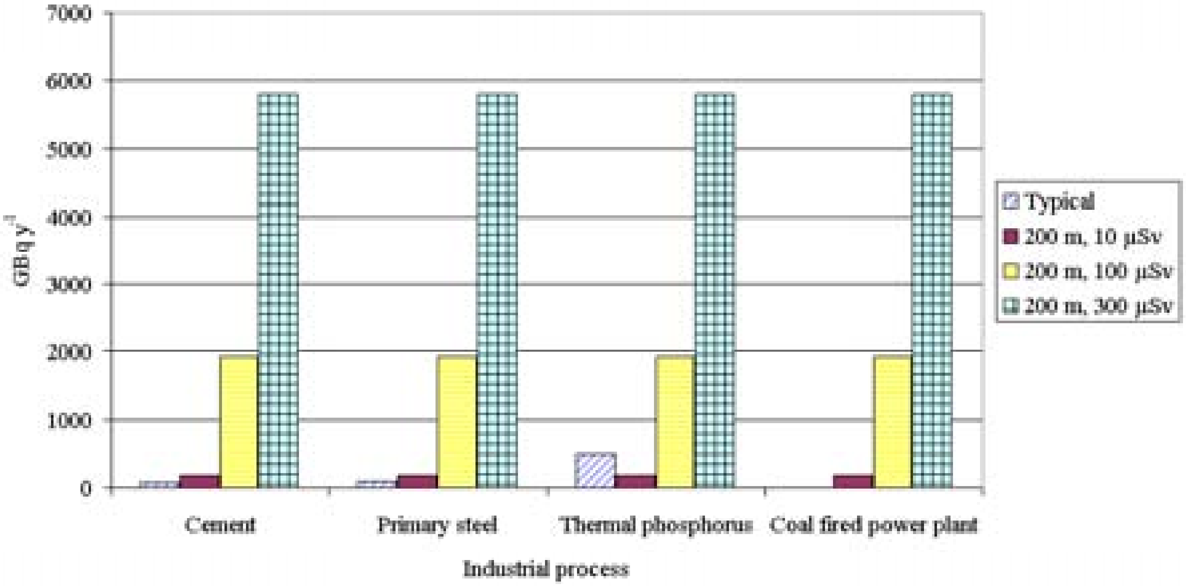

FIG. 4. Comparison of typical aerial discharges of ^{210}Po with derived screening levels for a 200 m stack height using three different dose criteria

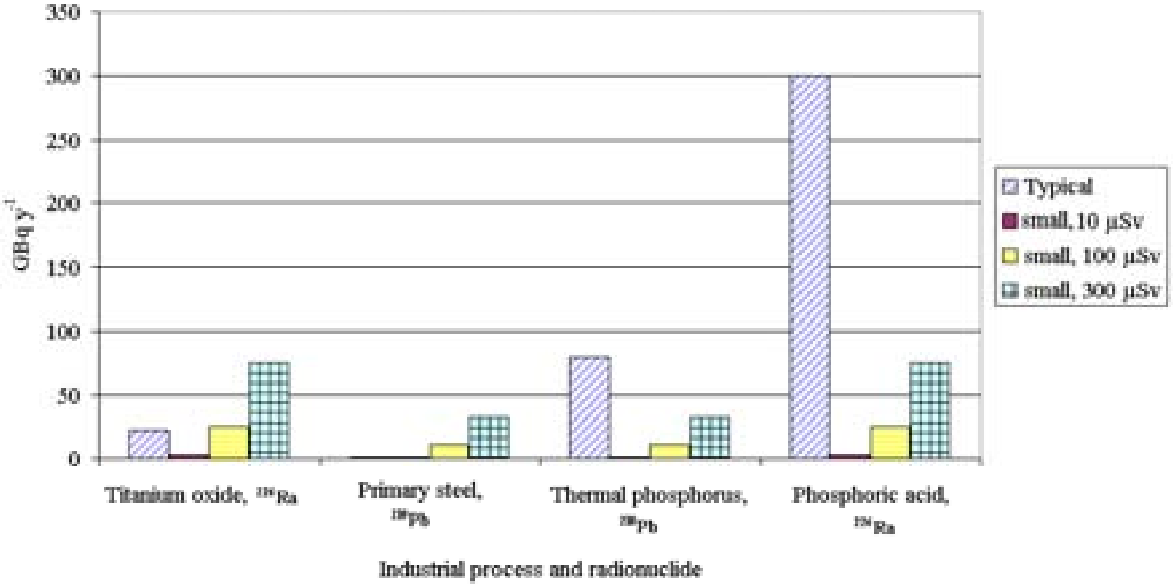

FIG. 5. *Comparison of typical discharges with derived screening levels for a small river using three different dose criteria*

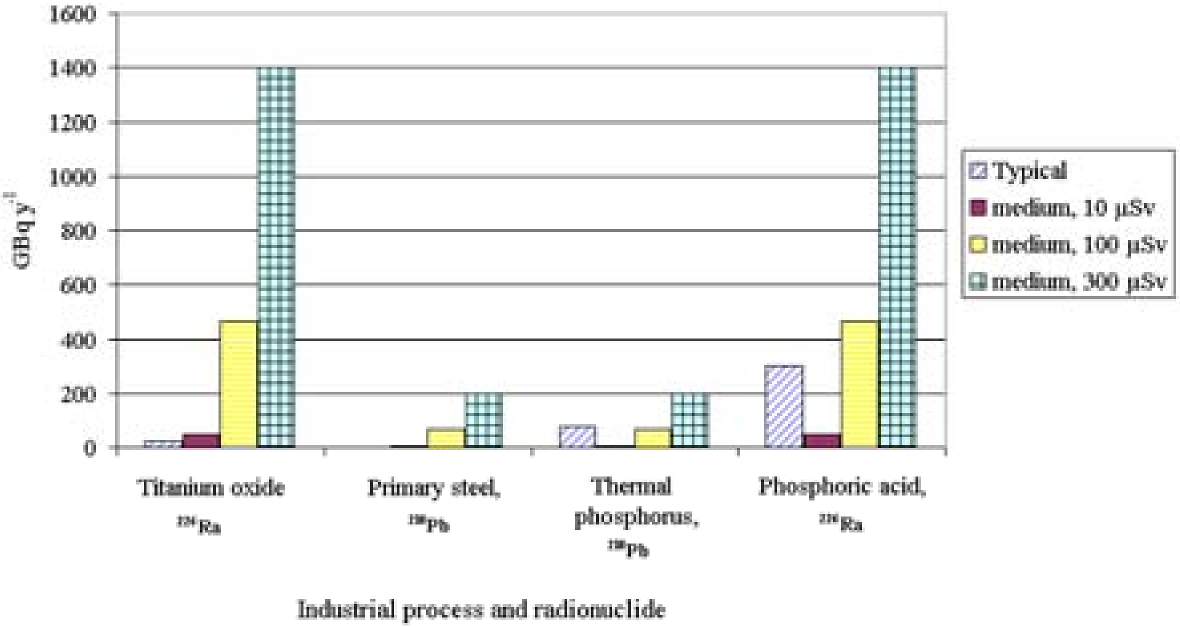

FIG. 6. *Comparison of typical discharges with derived screening levels for a medium river using three different dose criteria*

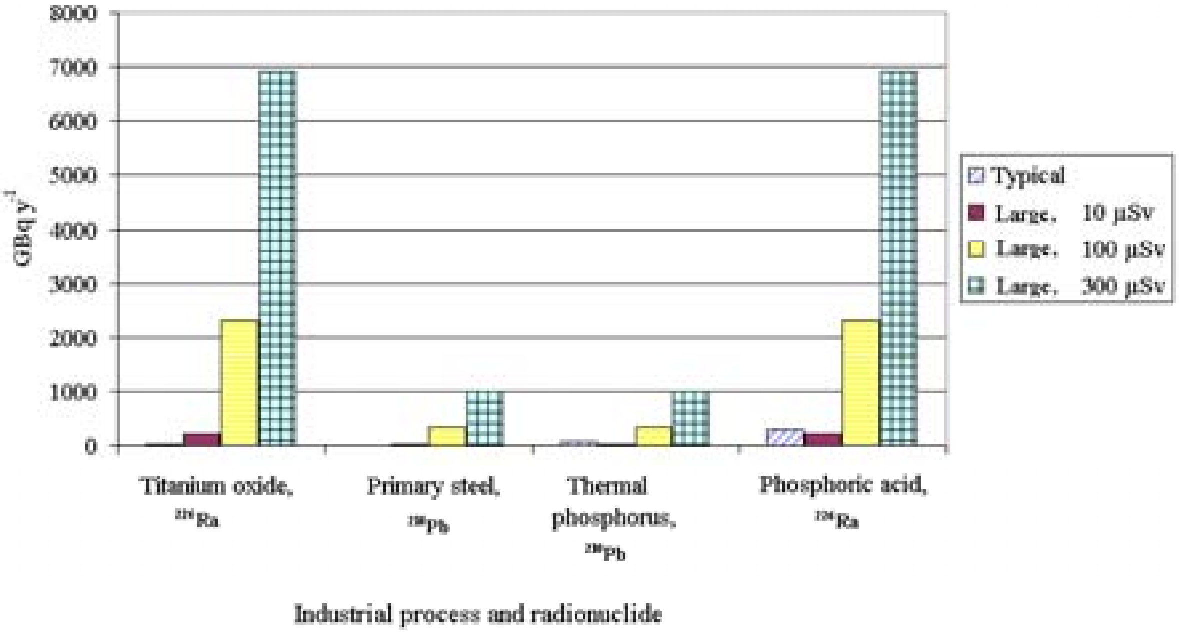

FIG. 7. Comparison of typical discharges with derived screening levels for a large river using three different dose criteria

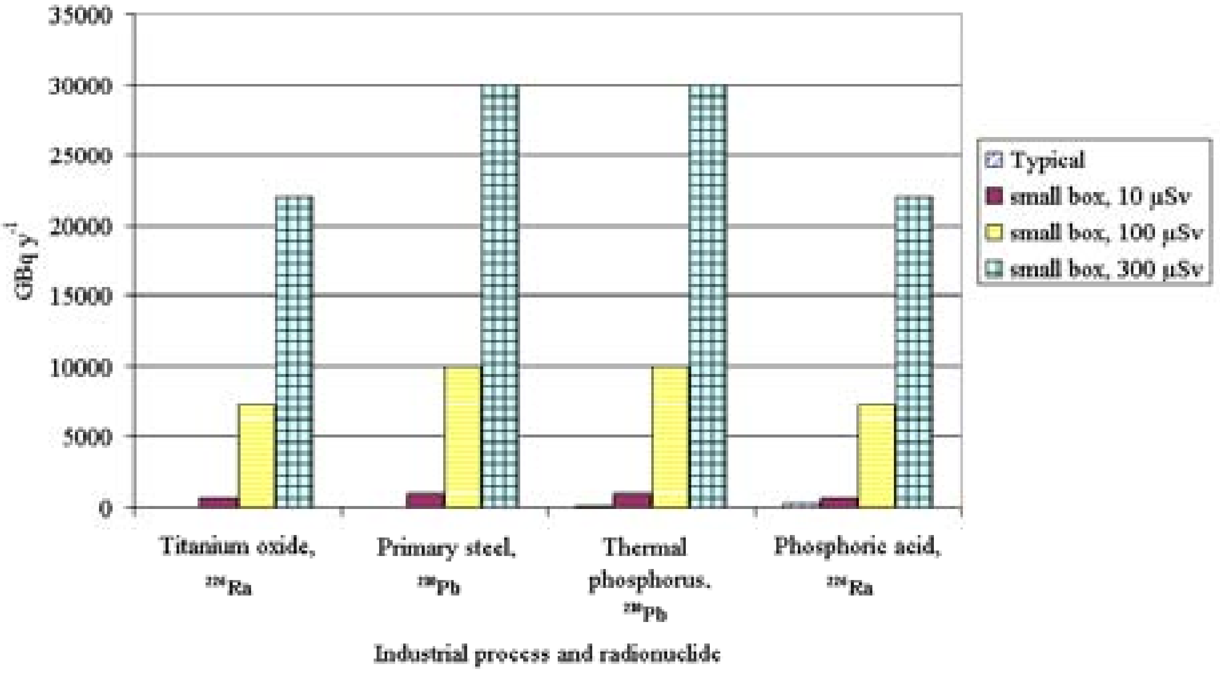

FIG. 8. Comparison of typical discharges with the calculated discharges in a small marine box resulting in three levels of dose being reached

ACKNOWLEDGEMENT

We would like to thank E.I.M. Meijne (NRG), Q. Chen (NRPB), J.-P. Degrange (CEPN) and S. Lepicard (CEPN) for the tremendous work they did in compiling the original study report without which this presentation would not have been possible.

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AEROSOL SAMPLING FOR RADIOLOGICAL PROTECTION: WHICH PARTICLE SIZE AEROSOL SAMPLER TO SELECT?

J.-P. Degrange[1]*, O. Witschger[2]

[1]Centre d'étude sur l'Evaluation de la Protection dans le domaine Nucléaire (CEPN), Fontenay-aux-Roses, France
[2]Institut National de Recherche et de Sécurité (INRS), Laboratoire de Métrologie des Aérosols, Vandoeuvre-les-Nancy Cedex, France

Abstract

Sampling of radioactive aerosols for the purpose of assessing or predicting occupational radiation doses has become an important issue in European countries. In particular, the 96/29/Euratom Council Directive specifies that aerosol sampling results can be used for assessing the individual dose when individual in vivo and/or bioassay methods are not possible or give insufficient results. This is precisely the case for exposures by inhalation to naturally occurring radioactive materials (NORM), for which bioassay methods may be associated with high detection limits while, in comparison, traditional aerosol sampling methods may lead to lower detection limits in terms of dose. A generic method has been developed to facilitate the identification of the particle size aerosol sampler to select (following the inhalable, thoracic or respirable convention) for minimizing the respective biases between the true and estimated exposure and the true and estimated effective dose associated with exposure by inhalation to any radioactive compound. Calculation based on this method has been applied to various radioactive compounds (of different absorption rates and particle size dispersion characteristics) of the ^{238}U and ^{232}Th natural chains. This paper presents the key elements of the method and the main results of its application to exposures by inhalation to NORM.

1. CONTEXT AND OBJECTIVE

Sampling of radioactive aerosols for the purpose of assessing or predicting occupational radiation doses has become an important issue in European countries. In particular, the 96/29/Euratom Council Directive [1] specifies that aerosol sampling results can be used for assessing the individual dose when individual in vivo and/or bioassay methods are not possible or give insufficient results. This is precisely the case for exposures by inhalation to naturally occurring radioactive materials (NORM), for which bioassay methods may be associated with high detection limits while, in comparison, traditional aerosol sampling methods may lead to lower detection limits in terms of dose.

The objective of this paper is to present the key elements of a generic method to facilitate the identification of the aerosol sampling techniques to use, in the radiological protection context of internal exposure by inhalation, for minimizing the respective biases between the true and estimated exposure and the true and estimated effective dose associated with exposure by inhalation to any radioactive compound, and to show the main results of its application to exposure by inhalation to various radioactive compounds of the ^{238}U and ^{232}Th natural chains.

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* E-mail: degrange@cepn.asso.fr

2. AEROSOL SAMPLING IN AN INDUSTRIAL HYGIENE CONTEXT

The aerosol sampling technique must be chosen as a function of the aims of the measurements. In the general context of industrial hygiene, aerosol sampling is most often accomplished in order to estimate the exposure of the concerned persons and to compare the measured concentrations to the permissible exposure limit to the considered air contaminant, expressed as time-averaged concentration values for a given conventional particle-size sampling fraction. Fig. 1 shows the three conventional sampling fractions (inhalable, thoracic and respirable) internationally agreed upon [2–4].

These fractions are commonly used in the industrial hygiene context and represent, respectively, the fraction of total suspended particles that enter the respiratory system via the nose or mouth, the portion of the particles that pass the larynx and penetrate into the conducting airways and the bronchial region of the lung, and the portion of the particles that enter the deepest part of the lung, i.e. the non-ciliated alveoli. The objective of these curves is to provide guidance on the measurement of individual exposure as realistically as possible, depending on the relative toxicity of the air contaminant deposited in each pulmonary region. These curves are also used as a reference for the development of aerosol sampling systems, as they constitute internationally agreed target sampling criteria.

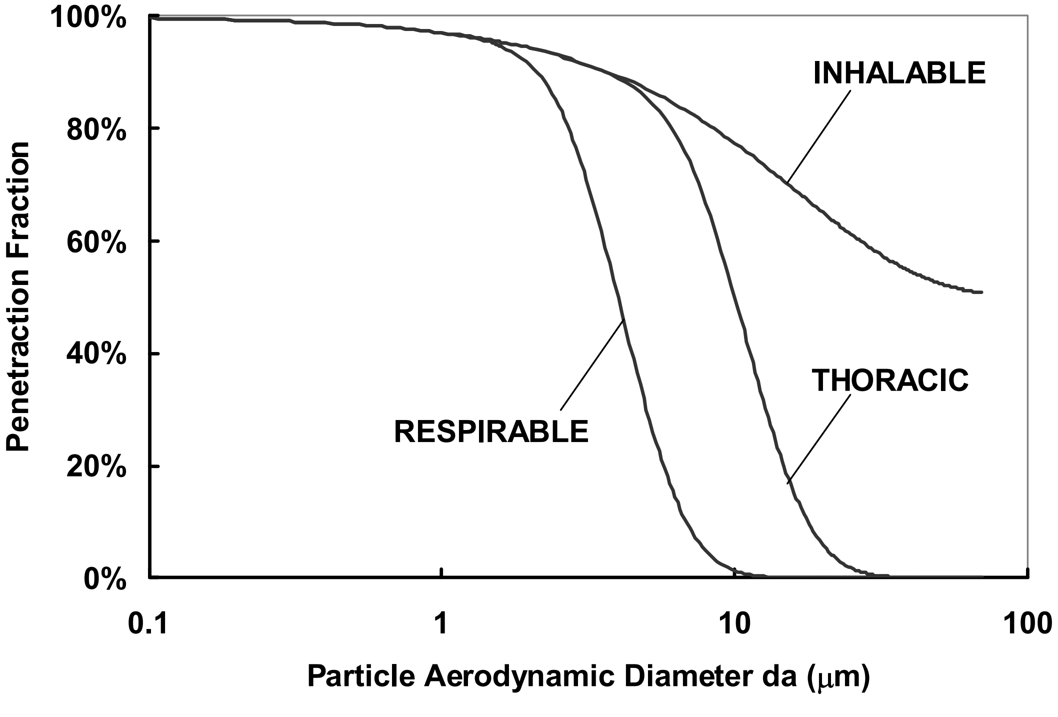

FIG. 1. Particle size fraction convention as a function of aerodynamic diameter [2–4]

3. AEROSOL SAMPLING IN A RADIOLOGICAL PROTECTION CONTEXT

In the particular radiological protection context of internal exposure by inhalation to a radioactive aerosol, the objective of such sampling measurements is quite different — beyond the mere assessment of the exposure (in Bq), these measurements may be aimed at evaluating the committed effective dose (Sv) received by the exposed person. This is notably stated in Ref. [1], where it is specified that workplace aerosol sampling results can be used for assessing the individual dose when individual in vivo and/or bioassay methods are not possible or give insufficient results. This is particularly the case with insoluble uranium particles [5], for which the detection limit of bioassay methods is very high (resulting in effective doses comparable to the annual radiation dose limit), while traditional aerosol sampling methods may lead to lower detection limits in terms of effective dose.

3.1. Assessment of the true activity concentration

For a polydisperse aerosol, whose aerodynamic diameter is supposed to follow a log-normal distribution characterized by its activity median aerodynamic diameter (AMAD) and geometric standard deviation (GSD), the true activity concentration of the ambient radioactive aerosol is given by:

$$C_{\mathrm{ambient}} = C_x(AMAD, GSD) \times R_x(AMAD, GSD)$$

where R_x is the correction factor which relates the activity concentration C_x (Bq/m^3) of the fraction measured by the sampler x (x = inhalable, thoracic or respirable) to the true (total) activity concentration of the ambient aerosol.

3.2. Assessment of the exposure

The exposure by inhalation of an individual is given by:

$$X_{\mathrm{true}} = C_x(AMAD, GSD) \times R_x(AMAD, GSD) \times B \times t_{\mathrm{E}}$$

where B and t_{E} represent, respectively, the ventilation rate of the worker (m^3/h) and the duration of the exposure (h).

One must note that the impact on the sampled activity (and derived exposure estimate) of the sampler particle-size fraction convention may be significant, as illustrated by Fig. 2, which compares the particle size distributions and activity concentrations of an example ambient aerosol ($AMAD = 10\,\mu\mathrm{m}, \quad GSD = 2, \quad C_{\mathrm{ambient}} = 1\,\mathrm{Bq/m^3}$) with those of the fractions sampled according to the three conventional fractions. One may see that the apparent activity concentrations measured according to the three conventions (inhalable, thoracic and respirable) for such an aerosol are respectively 1.3, 2.1 and 7.7 times lower than the true activity concentration of the ambient aerosol. These values correspond to the correction factors R_x that should be applied in that case to the measured activity concentrations in order to derive the true ambient aerosol activity concentration and associated exposure.

Moreover, the correction factors also depend strongly on the particle size characteristics (AMAD and GSD) of the ambient aerosol, as illustrated in Figs 3 and 4, which present the correction factors to be applied to the activity concentration measured according to the three conventional sampling fractions as a function of AMAD, and for two values of the ambient aerosol GSD.

3.3. Assessment of the effective dose

The true effective dose corresponding to the inhalation of a polydisperse aerosol of a specific radioactive compound is given by:

$$E_{\mathrm{true}} = e(AMAD, GSD, \quad) \times C_x(AMAD, GSD) \times R_x(AMAD, GSD) \times B \times t_{\mathrm{E}}$$

where e is the dose coefficient (Sv/Bq) for intake by inhalation of a given radioactive aerosol. The dose coefficient is calculated with the help of specific models (a human respiratory tract model (HRTM) describing the deposition, transport, and absorption into blood of the inhaled particles, and additional models describing the distribution, retention, excretion and irradiation of the organs by the incorporated radionuclides) that take into account not only the ambient aerosol particle size characteristics such as the AMAD and GSD, but also the physical and chemical characteristics of the compound that govern the rate of absorption into blood of the inhaled particles.

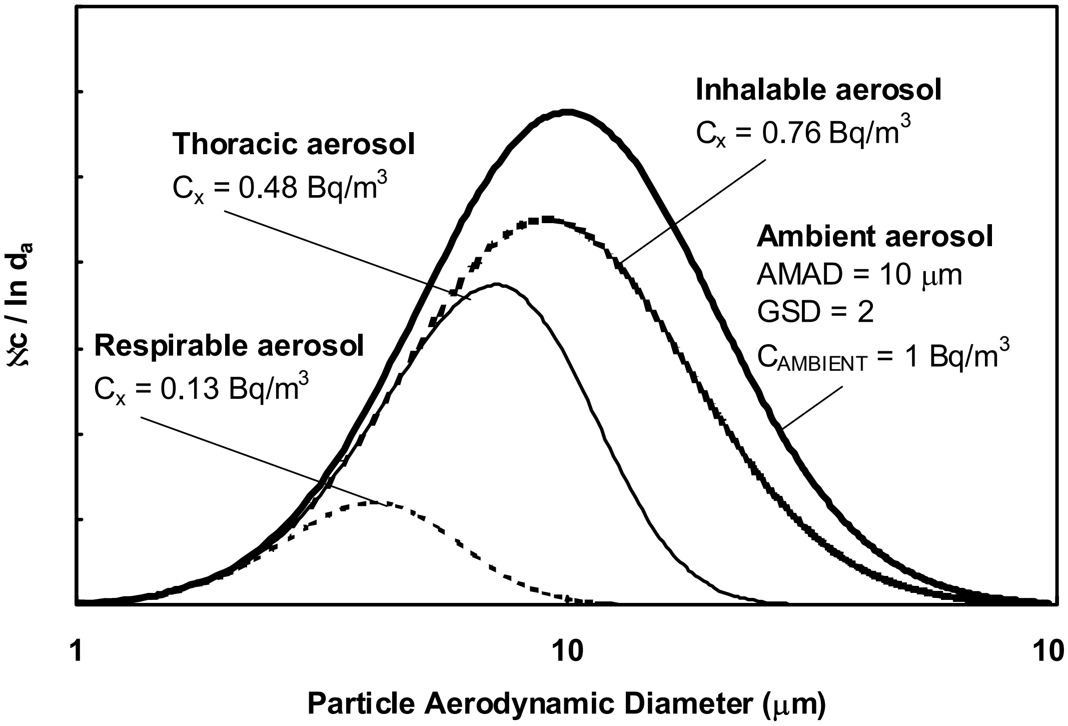

FIG. 2. Particle size distributions and concentrations for the ambient aerosol and the three conventional fractions

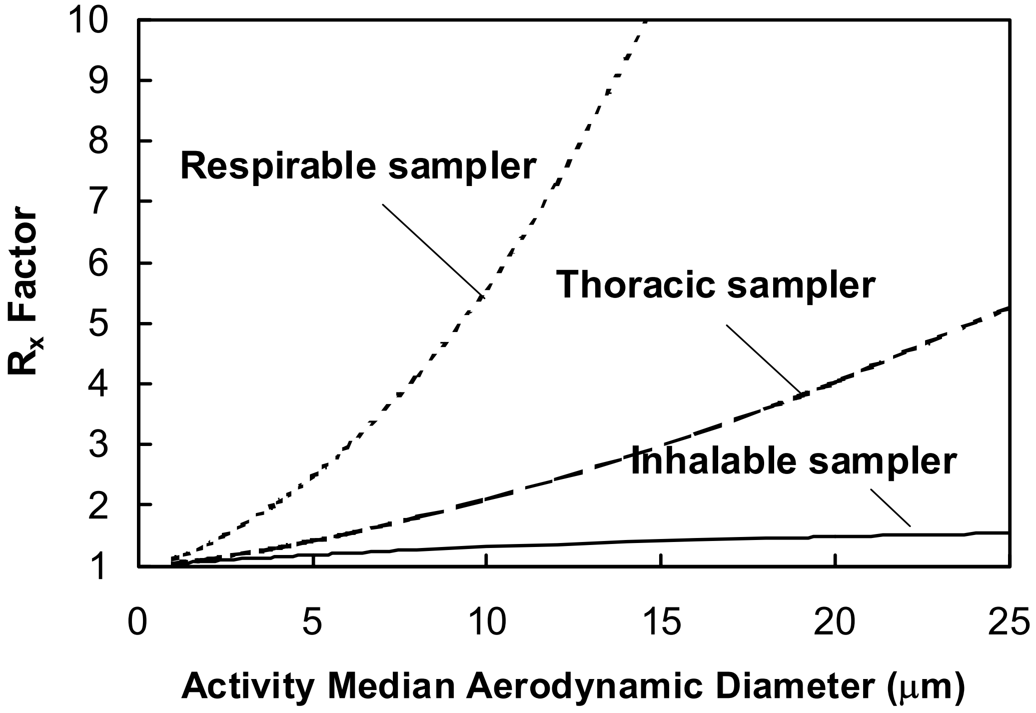

FIG. 3. Correction factors to be applied to the measured activity concentration for estimation of the true ambient aerosol activity concentration — GSD = 2.5

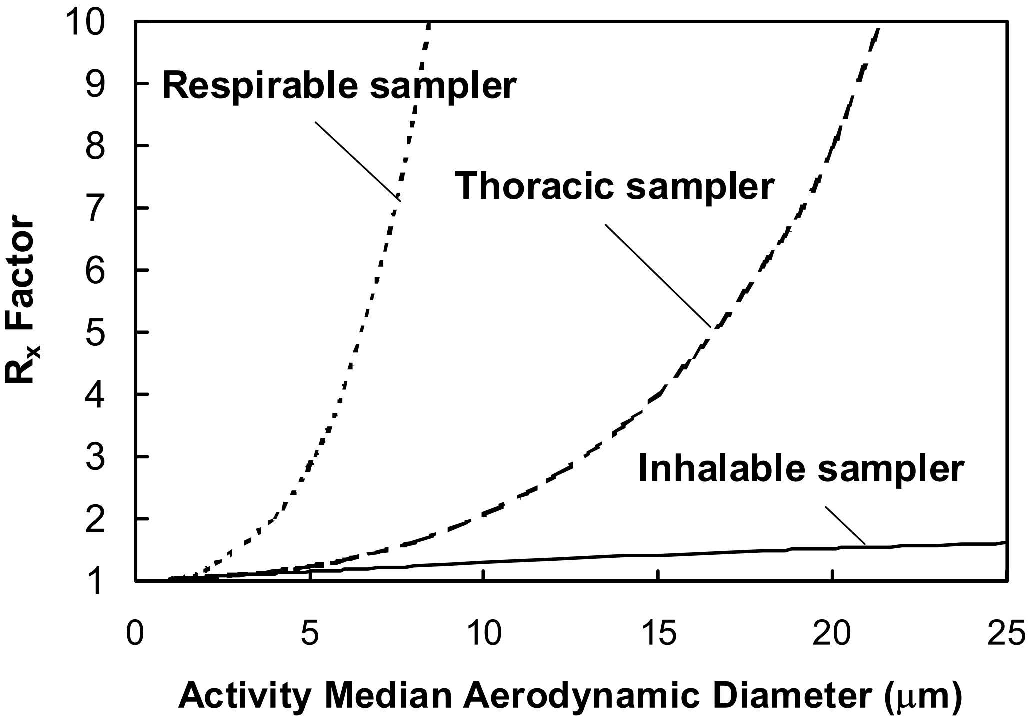

FIG. 4. Correction factors to be applied to the measured activity concentration for estimation of the true ambient aerosol activity concentration — GSD = 1.5

Dose coefficients for occupational exposure may be found in ICRP publications [6] and databases [7] for three default rates of absorption ('fast', 'moderate' and 'slow') and a limited set of AMADs and GSDs. Values for other rates and particle size characteristics may be calculated with dedicated software such as LUDEP [8].

One must note that while the dose coefficients based on the older HRTM of ICRP Publication 30 [9] had to be applied to the inhalable fraction of the ambient aerosol, the dose coefficients based on the most recent HRTM of ICRP Publication 60 [10] must be applied to the true (total) activity concentration of the aerosol, i.e. the measured activity concentration corrected by the correction factors presented above.

4. MINIMIZATION OF THE BIAS BETWEEN THE ESTIMATED AND TRUE EFFECTIVE DOSE

4.1. Situations considered

In this context, an important matter is to know which aerosol sampling technique is likely to minimize, for a given radioactive compound, the bias between the estimated effective dose and the true effective dose. The answer is complex, for it depends not only on the knowledge (and eventual correction) of the sampling performance of the chosen technique but also on the knowledge of the particle size characteristics (measured or considered as a default) of the aerosol (AMAD, GSD, etc.) and on the relationship between the dose coefficient and these latest data.

Fig. 5 presents a schematic of the four different situations that can occur, leading to different biases in the estimation of effective dose.

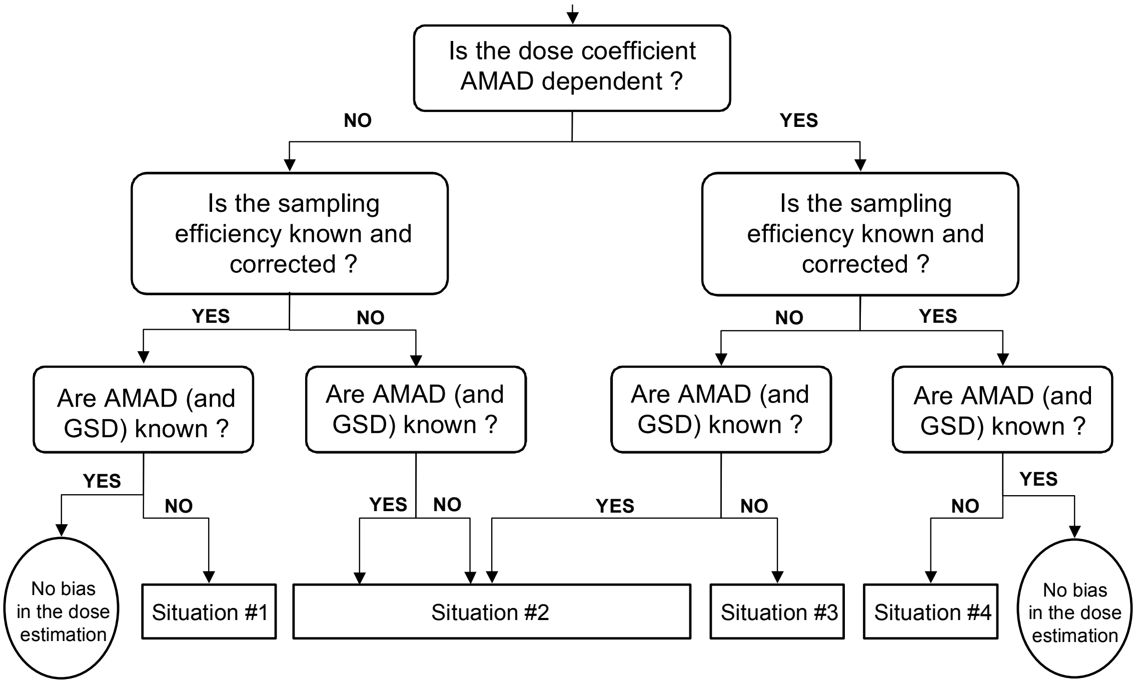

FIG. 3. Different situations to be taken into account in order to minimize the bias between the estimated and true effective dose.

Situations 2 and 3 correspond to situations in which the sampling performance is either not known or not corrected for — we have already seen above that such situations can lead to significant biases that can be easily corrected by the application of the relevant correction factor.

In the following, we will thus concentrate on situations 1 and 4 where the sampling efficiency is known and corrected for, and the bias is due only to the fact that the particle size characteristics (AMAD and/or GSD) of the ambient aerosol are not (perfectly) known.

4.2. Situation 1

In this situation, where the dose coefficient is not (or negligibly) dependent on AMAD (and GSD), the sampling efficiency is known and corrected for, but the AMAD (and GSD) is not (perfectly) known. The bias in this situation ($Bias_{\mathrm{sit1}}$) may be expressed as:

$$Bias_{\mathrm{sit1}} = \frac{R_x(AMAD_{\mathrm{D}}, GSD_{\mathrm{D}}) - R_x(AMAD, GSD)}{R_x(AMAD, GSD)} \times 100$$

where $AMAD_{\mathrm{D}}$ and GSD_{D} correspond, respectively, to the default AMAD and GSD values taken into account for the calculation when the particle size characteristics (i.e. the AMAD and the GSD) of the ambient aerosol are not (perfectly) known.

The above formula also corresponds exactly to the formulation of the bias (relative difference) between the estimated and true exposure (in Bq) of an exposed person, where no dose coefficients have to be applied.

Figs 6–9 show the bias between the estimated and true exposure for the three sampling conventions and four default aerosols $AMAD_{\mathrm{D}} = 1,\ 5,\ 10$ and $20\,\mu\mathrm{m}; GSD_{\mathrm{D}} = 2.5$.

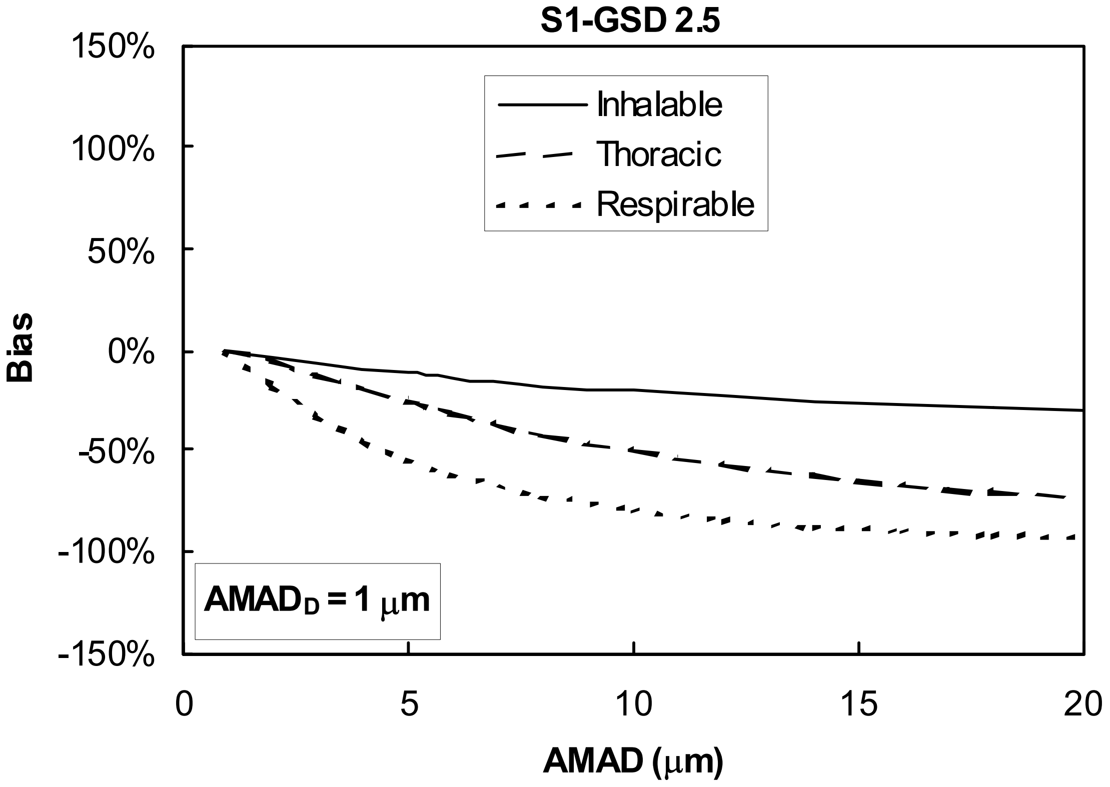

FIG. 6. Bias (relative difference) between the true and estimated exposure for the three sampling conventions — default AMAD = 1 µm

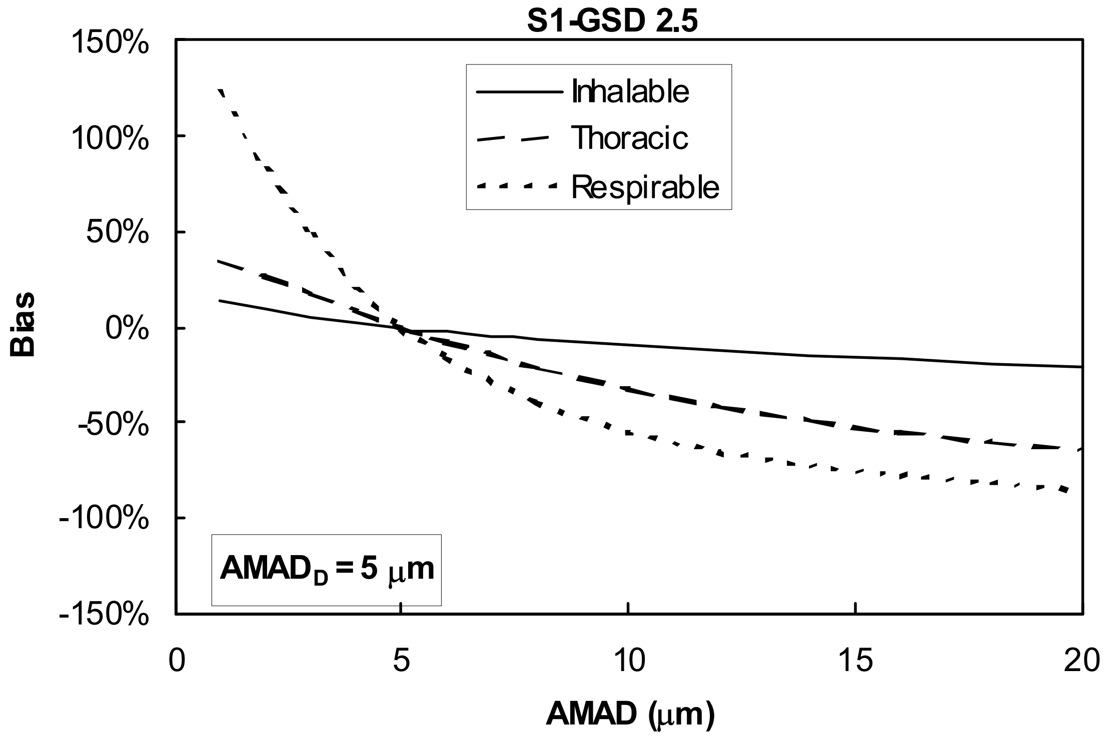

FIG. 7. Bias (relative difference) between the true and estimated exposure for the three sampling conventions — default AMAD = 5 µm

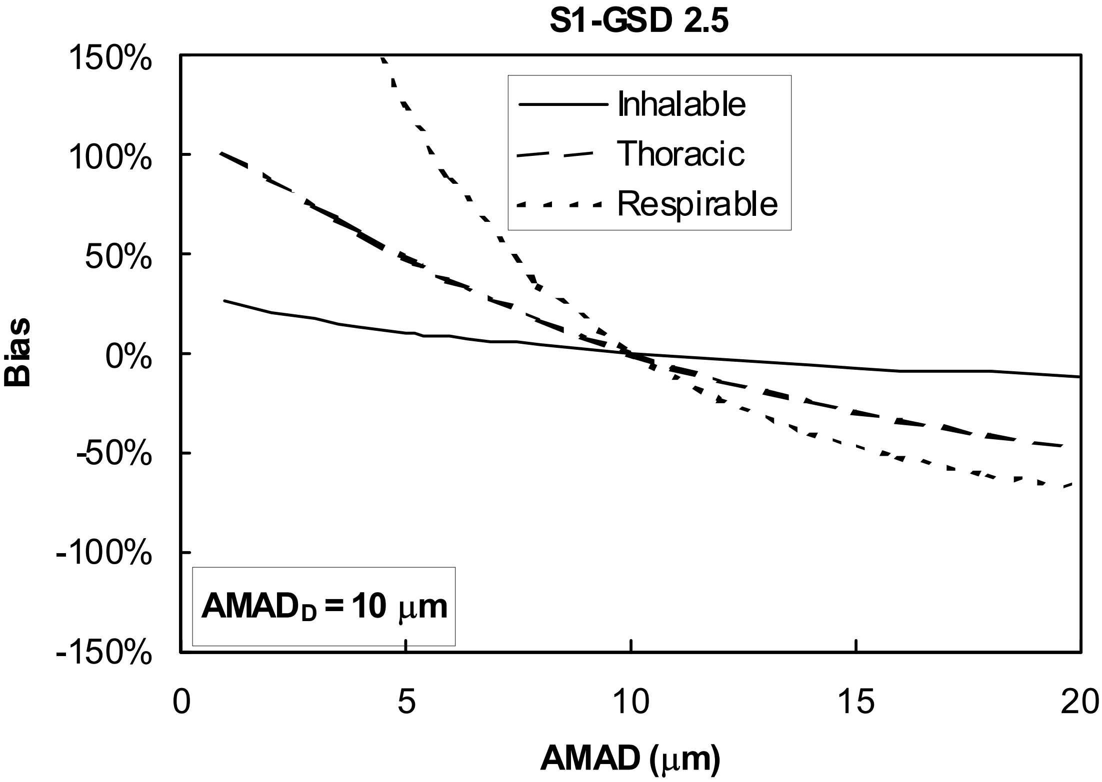

FIG. 8. Bias (relative difference) between the true and estimated exposure for the three sampling conventions — default AMAD = 10 μm

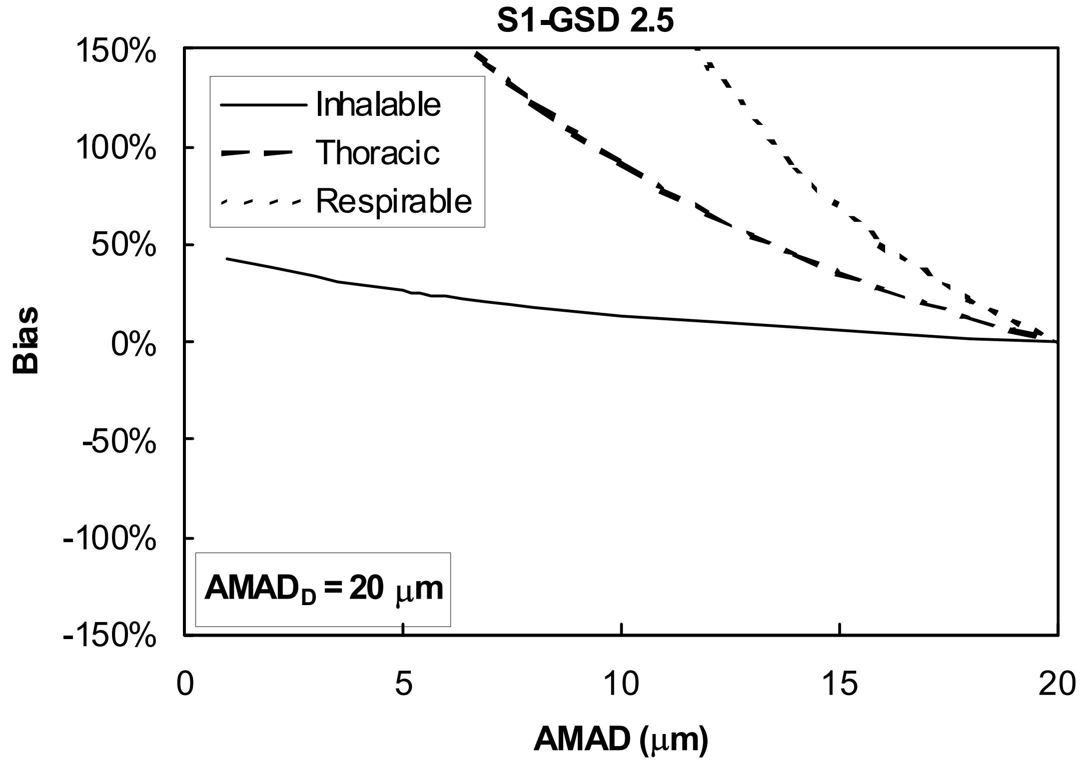

FIG. 9. Bias (relative difference) between the true and estimated exposure for the three sampling conventions — default AMAD = 20 μm.

As may be deduced from the above equation and shown in Figs 6–9, in this situation, if one wants to minimize the impact on the exposure of the uncertainty associated with the particle size distribution (AMAD) of the ambient aerosol, one has to choose a sampler for which the AMAD dependency of the sampling efficiency is as flat as possible (i.e. an inhalable sampler), whatever the true AMAD of the ambient aerosol and the value of AMAD considered as a default.

4.3. Situation 4

In this situation, where the dose coefficient is dependent on AMAD (and GSD), the sampling efficiency is known and corrected for, but the AMAD (and GSD) is not (perfectly) known, the bias in this situation ($Bias_{\mathrm{sit4}}$) may be expressed as:

$$Bias_{\mathrm{sit4}} = \frac{e\left(AMAD_{\mathrm{D}}, GSD_{\mathrm{D}}, \quad\right) \times R_x\left(AMAD_{\mathrm{D}}, GSD_{\mathrm{D}}\right) - e\left(AMAD, GSD, \quad\right) \times R_x\left(AMAD, GSD\right)}{e\left(AMAD, GSD, \quad\right) \times R_x\left(AMAD, GSD\right)} \times 100$$

As may be deduced from the above equation, the sampler that minimizes — for a given radioactive compound — the bias on the effective dose due to the fact that the particle size distribution (AMAD) of the ambient aerosol is not (perfectly) known, is the sampler for which the AMAD dependency of the sampling efficiency follows as closely as possible the AMAD dependency of the dose coefficients for the compound under consideration.

With the help of the IMBA (respiratory tract modelling) software [11, 12] and the PLEIADES (biokinetics and irradiation modelling) software [13], calculations have been performed of the effective dose associated with inhalation exposure to various radioactive compounds, for:

- Different blood absorption rates (fast, moderate and slow) and particle size dispersion characteristics (AMAD = 1–20 µm, GSD = 1.5 and 2.5[1]);
- The ^{238}U and ^{232}Th decay series radionuclides;

thus extending the existing ICRP occupational effective dose coefficient calculations, which are limited to more restrictive sets of absorption rates, AMADs and GSDs.

In Figs 10–13, the AMAD dependency of the sampling efficiency is compared with that of the effective dose coefficient. This is done for the three sampling conventions, for three ^{234}U compounds with slow, moderate and fast absorption rates, and for four default aerosols. These results suggest that, for uranium, the samplers for which the AMAD dependency of the sampling efficiency follows best the AMAD dependency of the considered compound dose coefficient are thoracic samplers for compounds of slow and moderate absorption rate and inhalable samplers for compounds of fast absorption rate.

As a consequence, and as suggested for uranium in Figs 14–25, if one wants to minimize the impact on the effective dose of the uncertainty associated with the particle size distribution (AMAD) of the ambient aerosol, whatever the true AMAD of the ambient aerosol and the value of AMAD considered as a default, one has to choose a thoracic sampler to sample an aerosol of a slow or moderate absorption rate compound, and an inhalable sampler to sample an aerosol of a fast absorption rate compound. Moreover, in the absence of (precise) information on the AMAD of the ambient aerosol, a 5 µm AMAD default value seems to reasonably minimize the bias, whatever the true value of the AMAD and GSD.

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[1] For an AMAD >1 µm, in the absence of specific knowledge a GSD of 2.5 is recommended by ICRP [10].

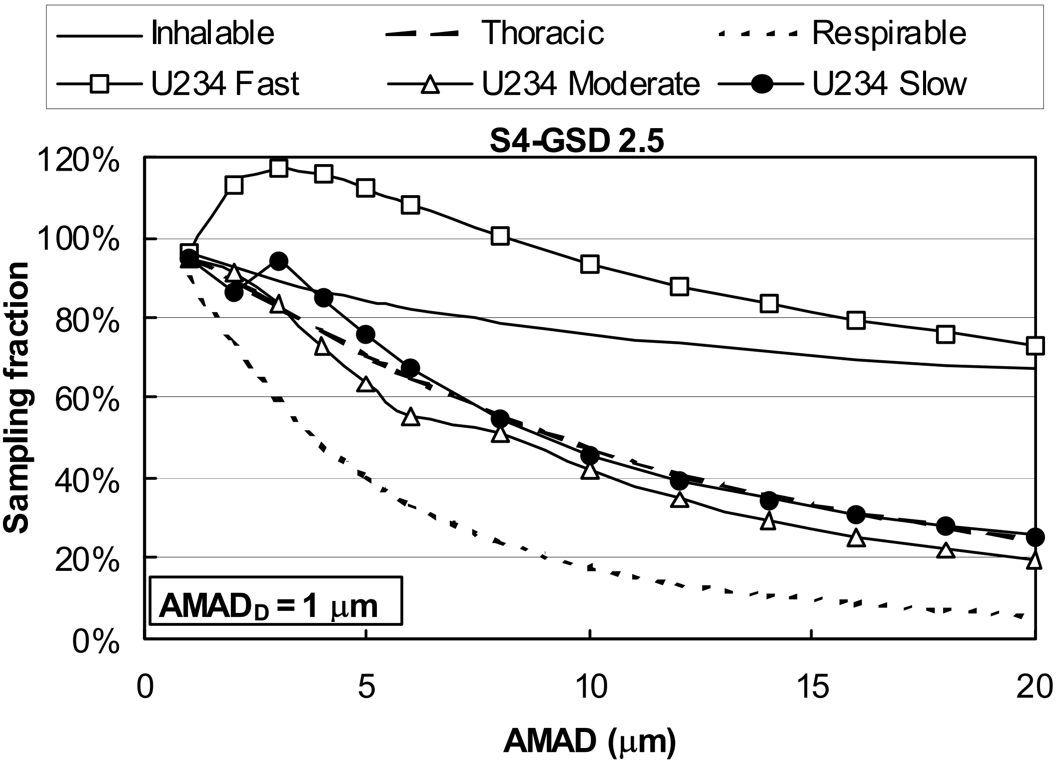

FIG. 10. Comparison of the AMAD dependency of the sampling efficiency, with that of the dose coefficients of uranium compounds of different solubility — default AMAD = 1 μm

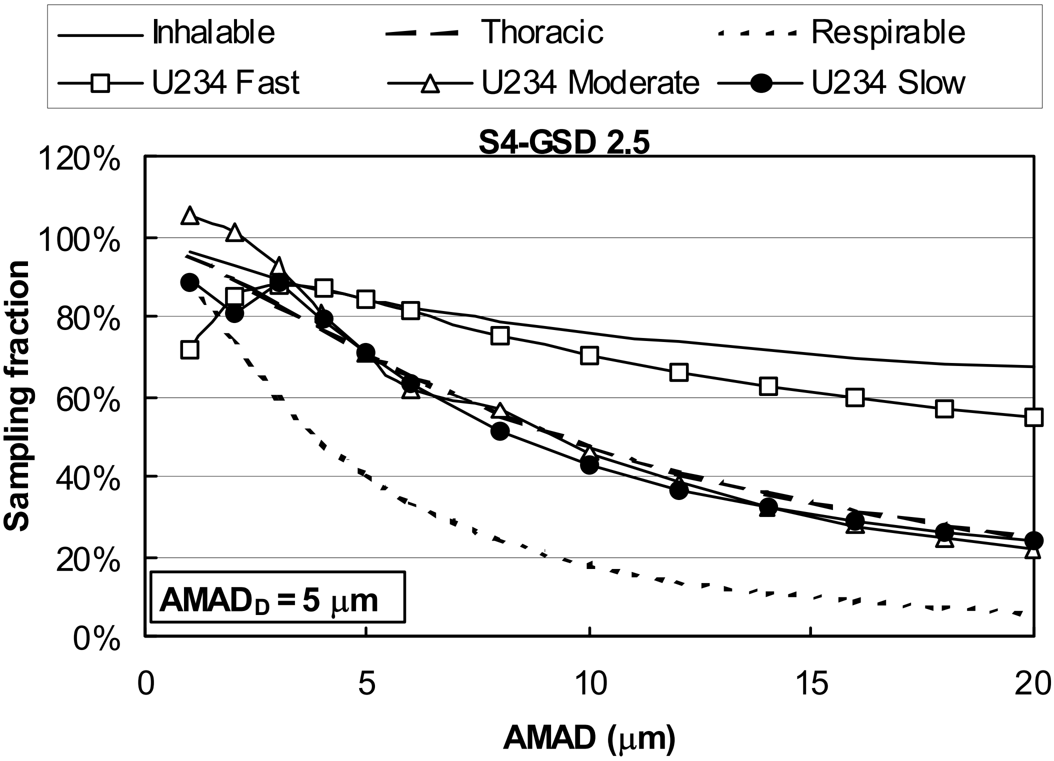

FIG. 11. Comparison of the AMAD dependency of the sampling efficiency with that of the dose coefficients for uranium compounds of different solubility — default AMAD = 5 μm

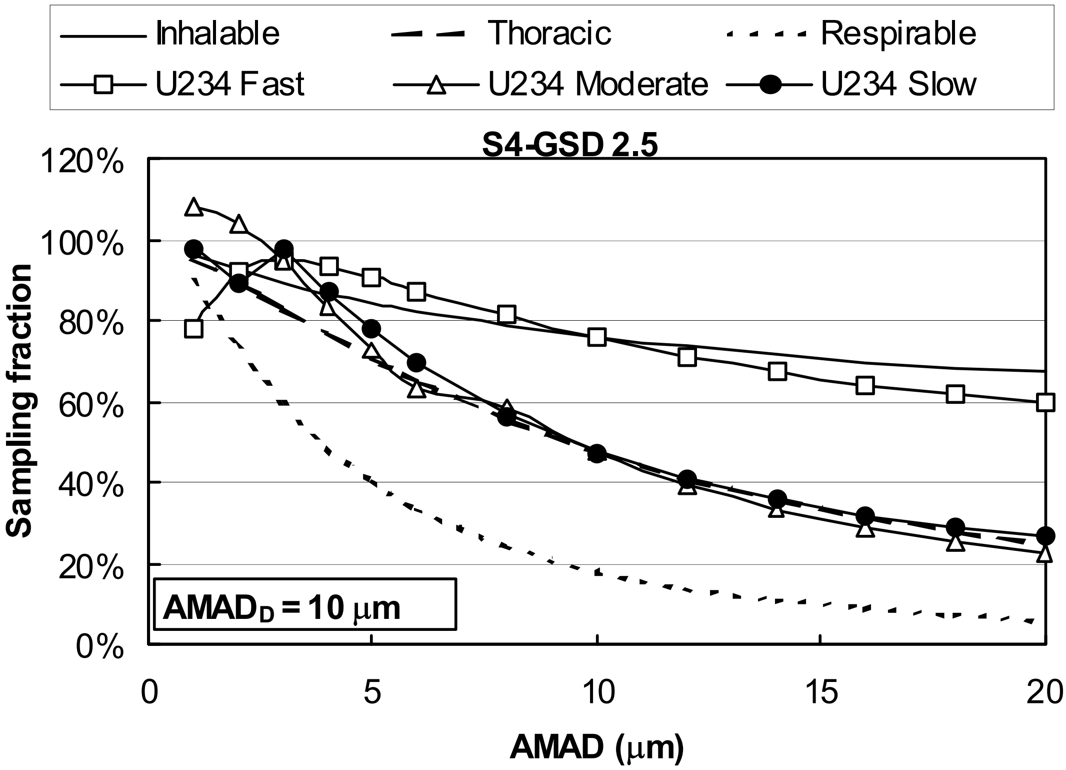

FIG. 12. Comparison of the AMAD dependency of the sampling efficiency with that of the dose coefficients for uranium compounds of different solubility — default AMAD = 10 µm

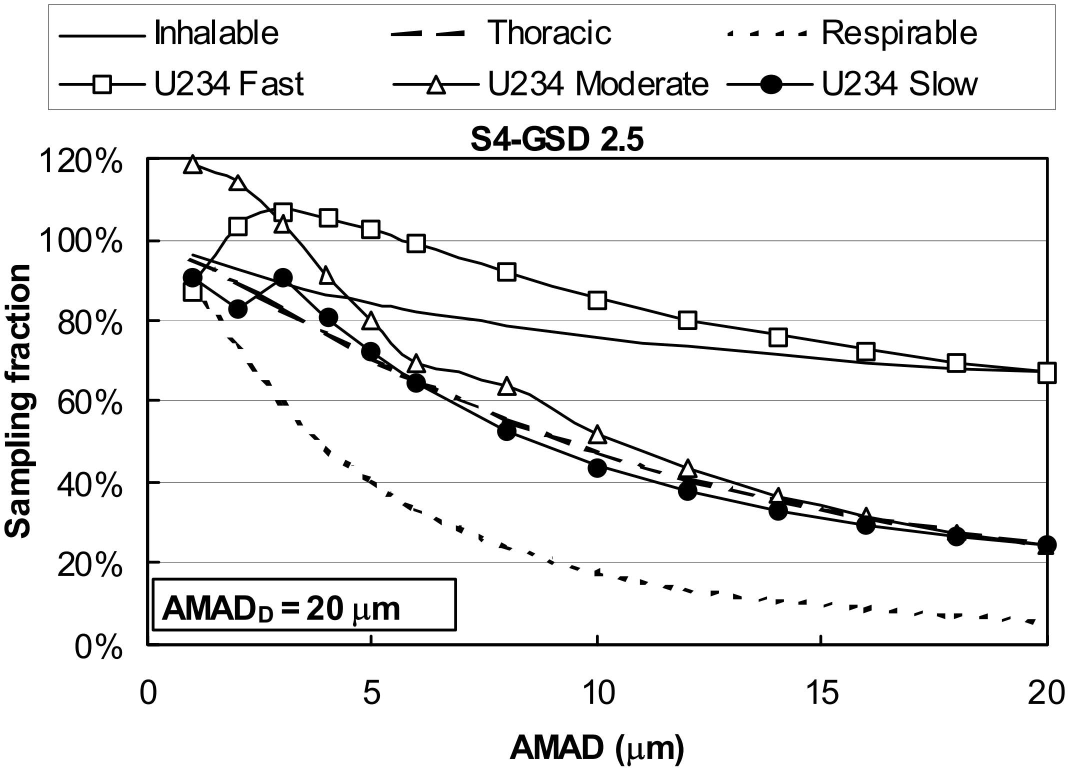

FIG. 13. Comparison of the AMAD dependency of the sampling efficiency with that of the dose coefficients for uranium compounds of different solubility — default AMAD = 20 µm

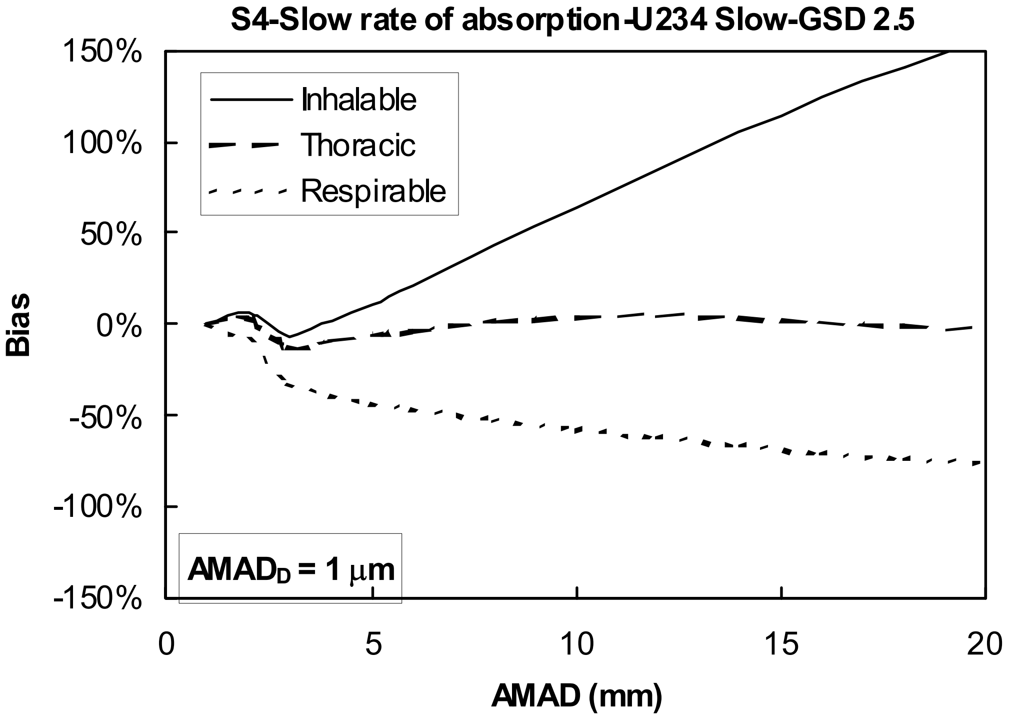

FIG. 14. Bias (relative difference) between the true and estimated effective dose arising from inhalation of a low solubility uranium compound, for the three sampling conventions — default AMAD = 1 μm

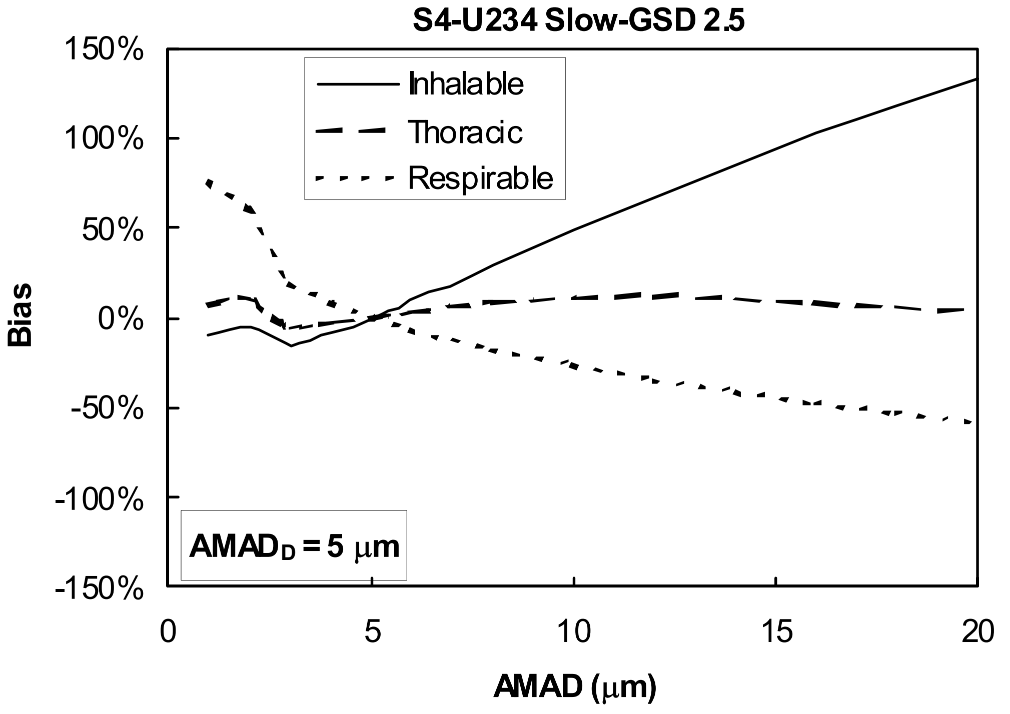

FIG. 15. Bias (relative difference) between the true and estimated effective dose arising from inhalation of a low solubility uranium compound, for the three sampling conventions — default AMAD = 5 μm

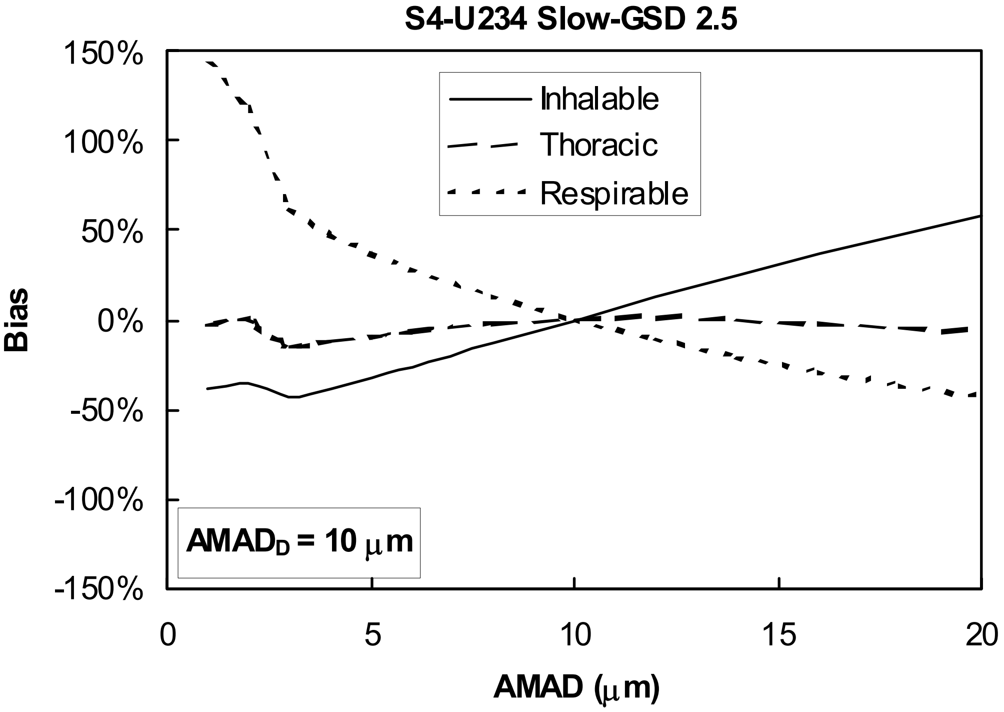

FIG. 16. Bias (relative difference) between the true and estimated effective dose arising from inhalation of a low solubility uranium compound, for the three sampling conventions — default AMAD = 10 µm

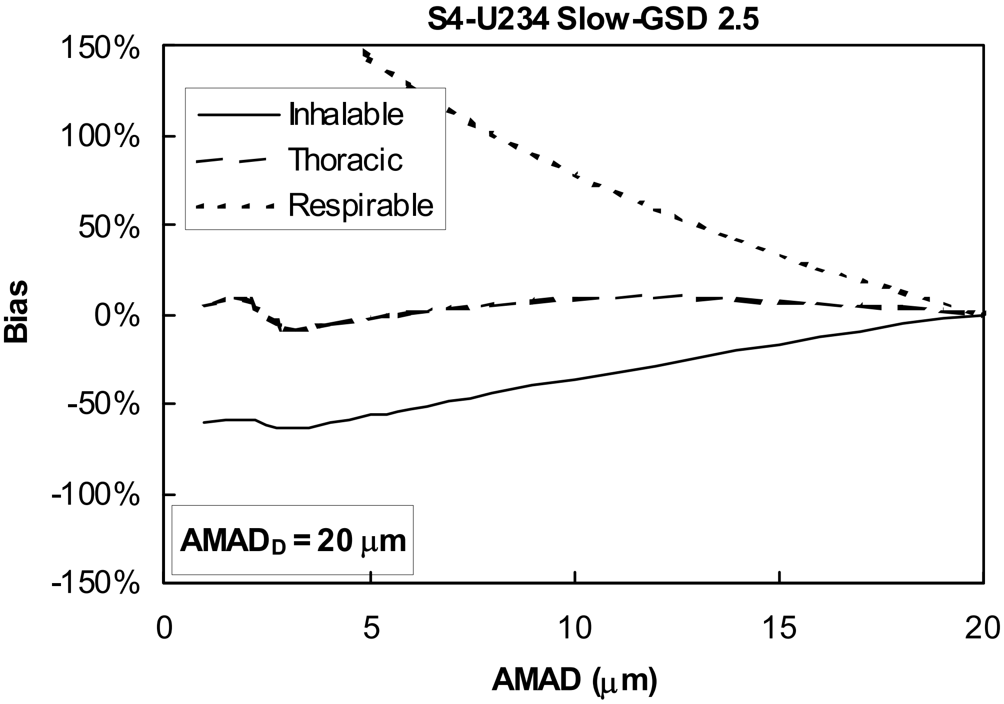

FIG. 17. Bias (relative difference) between the true and estimated effective dose arising from inhalation of a low solubility uranium compound, for the three sampling conventions — default AMAD = 20 µm

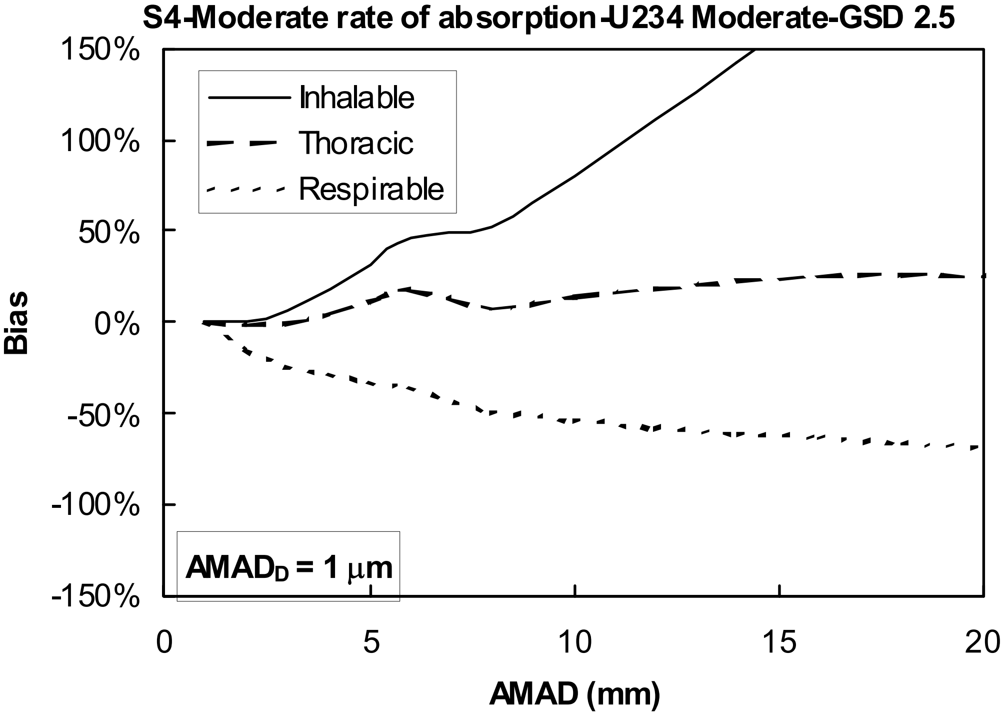

FIG. 18. Bias (relative difference) between the true and estimated effective dose arising from inhalation of a moderate solubility uranium compound, for the three sampling conventions — default AMAD = 1 μm

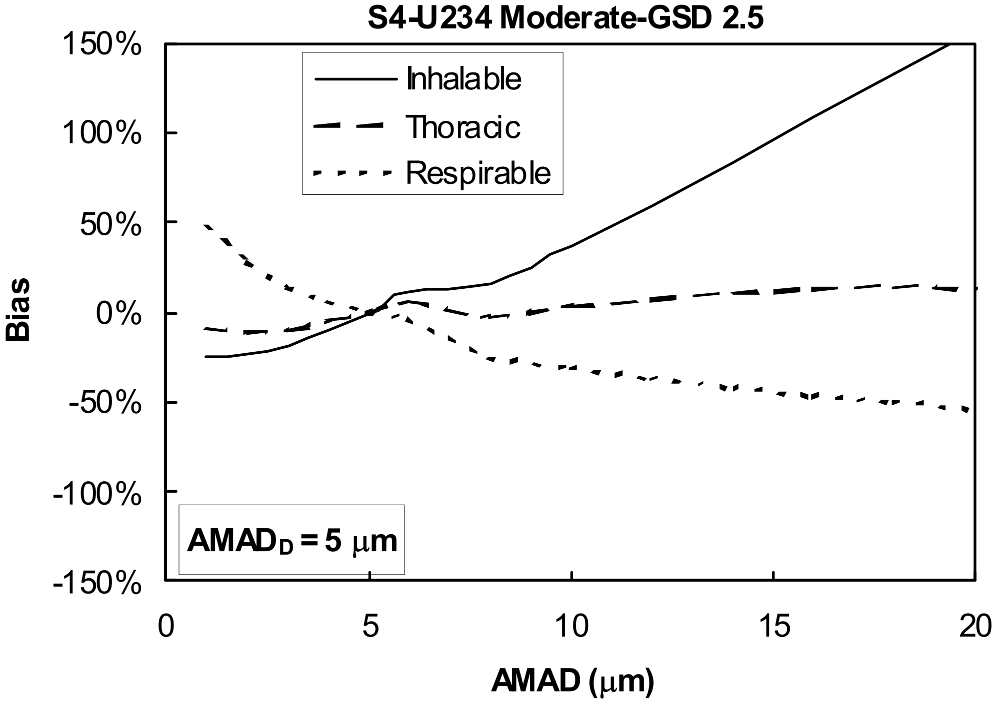

FIG. 19. Bias (relative difference) between the true and estimated effective dose arising from inhalation of a moderate solubility uranium compound, for the three sampling conventions — default AMAD = 5 μm

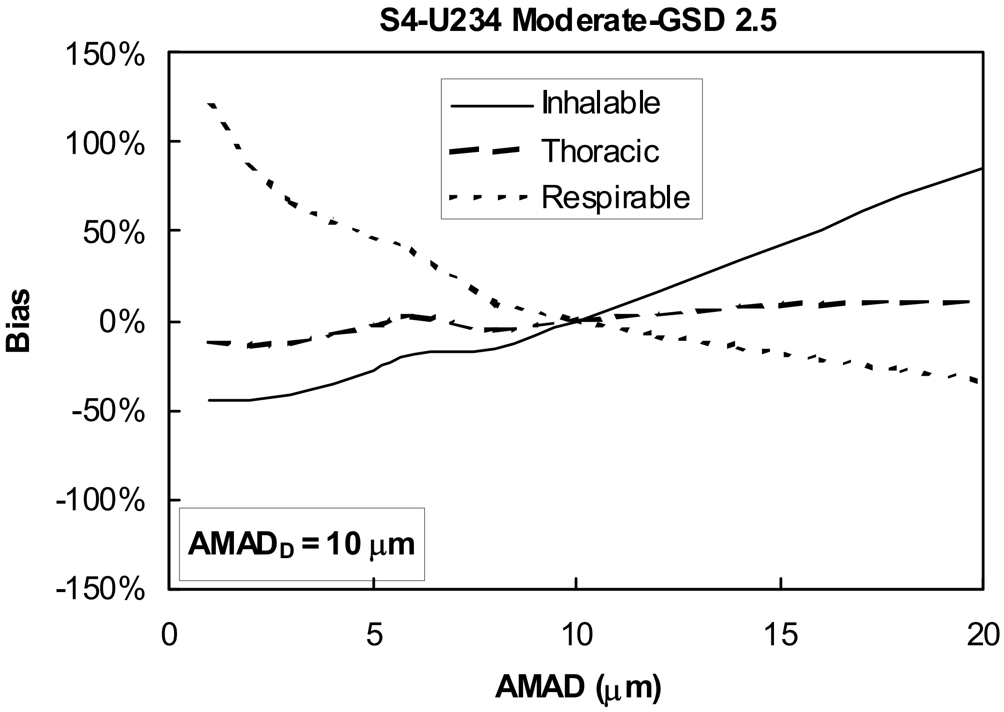

FIG. 20. Bias (relative difference) between the true and estimated effective dose arising from inhalation of a moderate solubility uranium compound, for the three sampling conventions — default AMAD = 10 μm

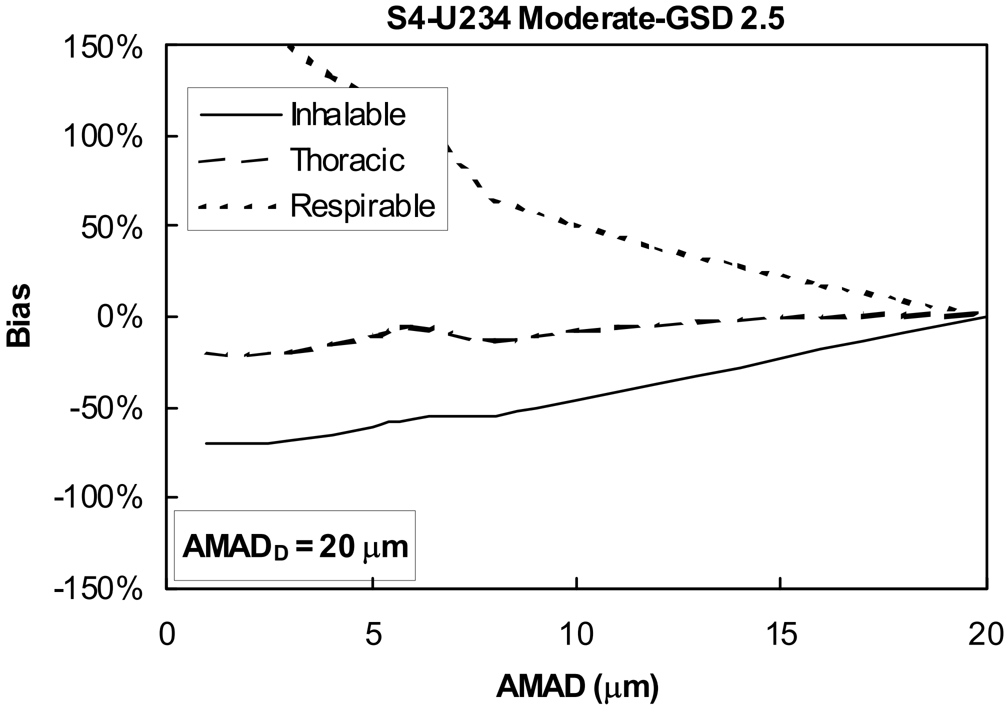

FIG. 21. Bias (relative difference) between the true and estimated effective dose arising from inhalation of a moderate solubility uranium compound, for the three sampling conventions — default AMAD = 20 μm

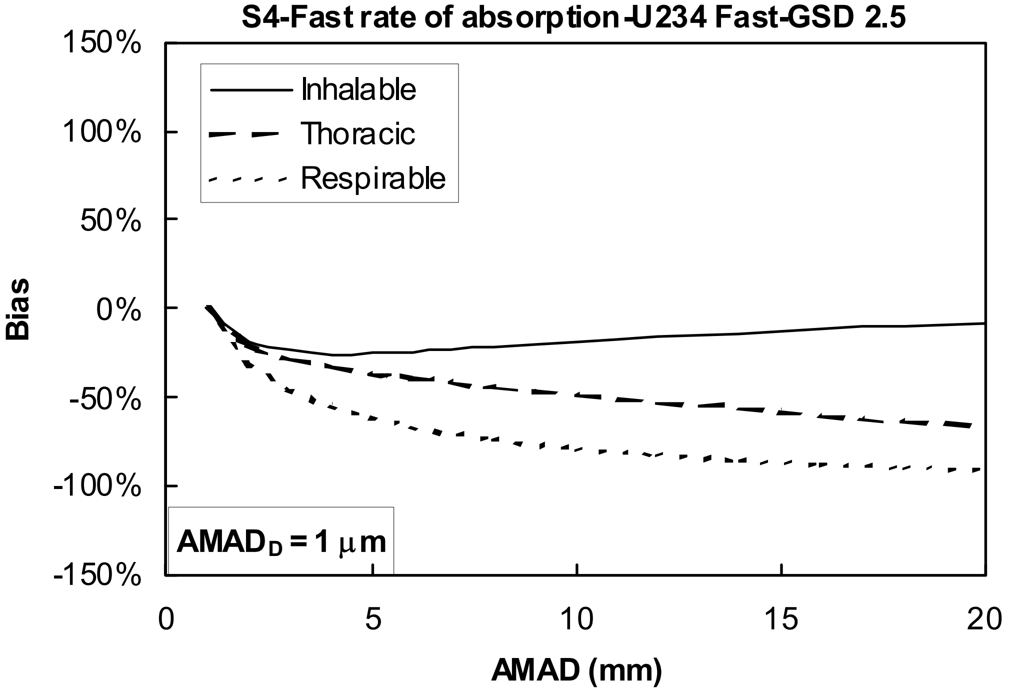

FIG. 22. *Bias (relative difference) between the true and estimated effective dose arising from inhalation of a high solubility uranium compound, for the three sampling conventions — default AMAD = 1 µm*

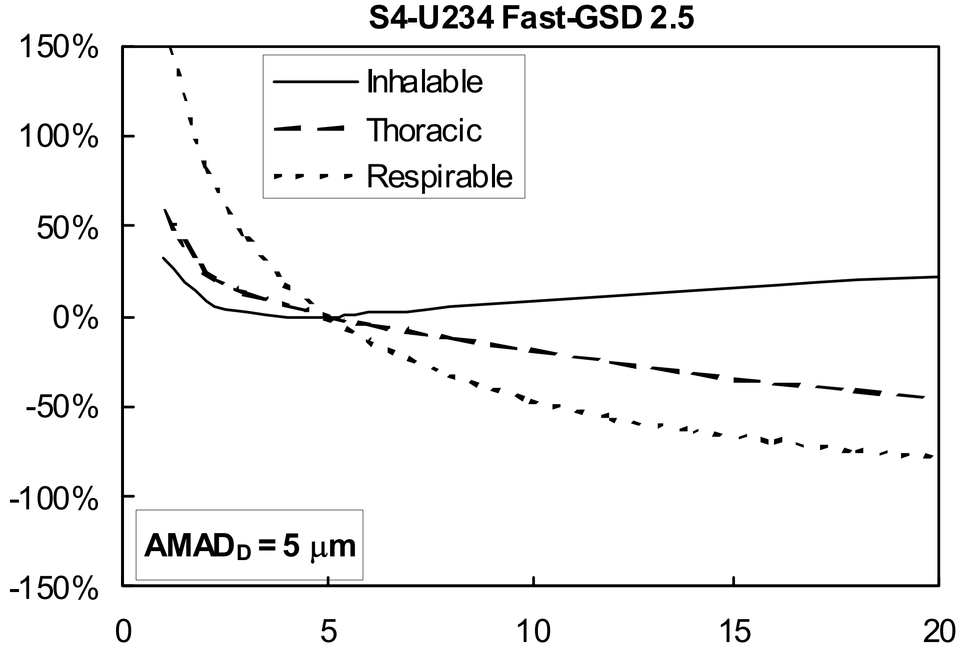

FIG. 23. *Bias (relative difference) between the true and estimated effective dose arising from inhalation of a high solubility uranium compound, for the three sampling conventions — default AMAD = 5 µm*

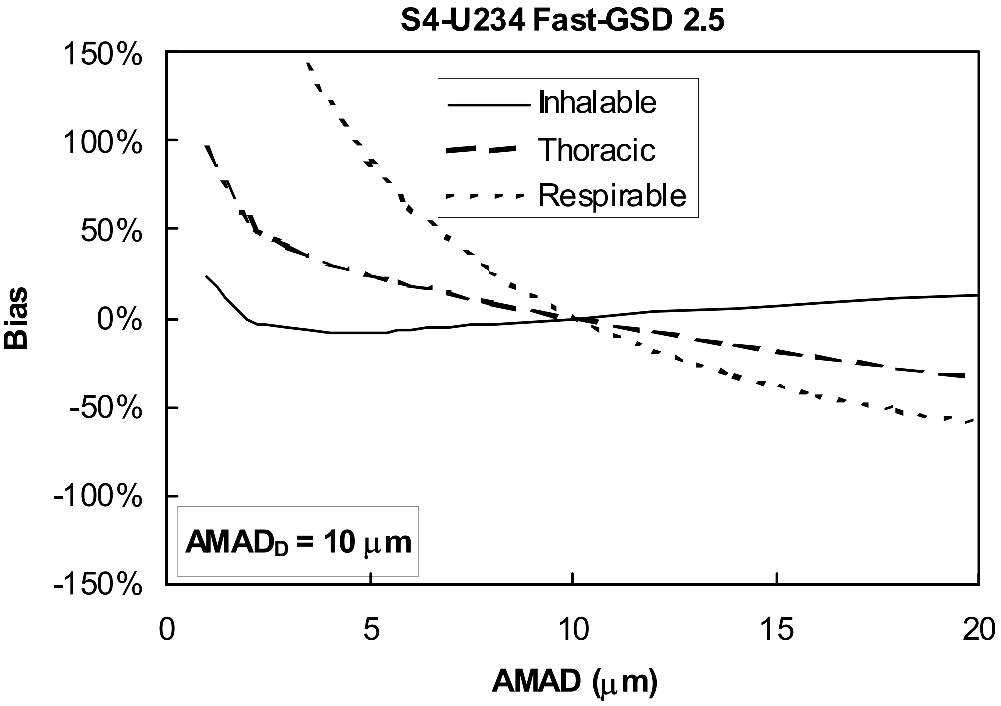

FIG. 24. Bias (relative difference) between the true and estimated effective dose arising from inhalation of a high solubility uranium compound, for the three sampling conventions — default AMAD = 10 μm

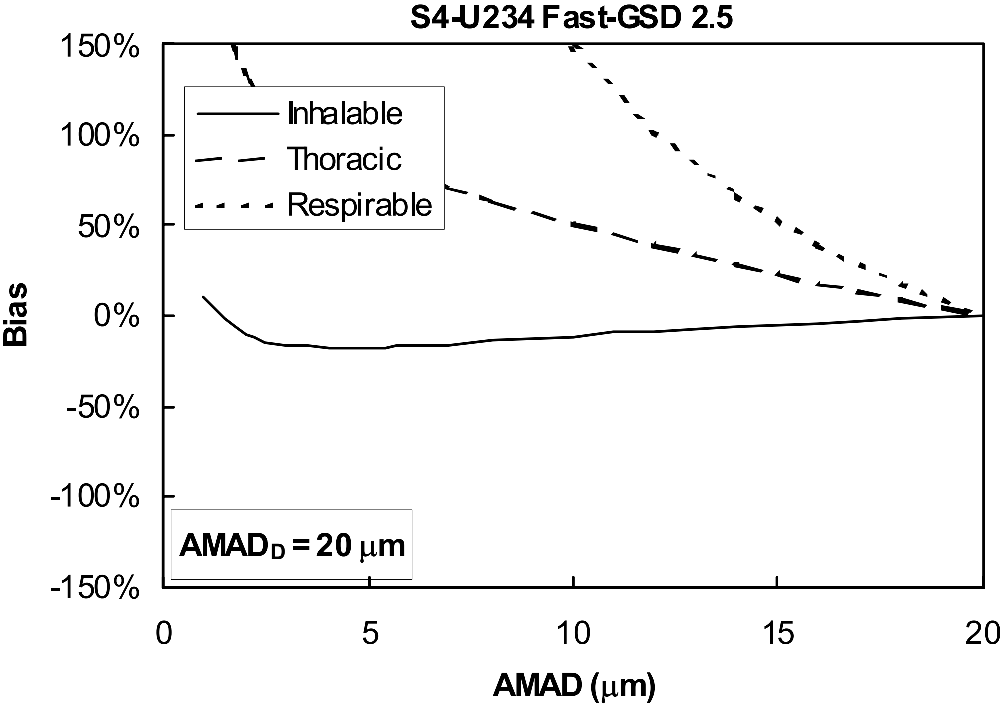

FIG. 25. Bias (relative difference) between the true and estimated effective dose arising from inhalation of a high solubility uranium compound, for the three sampling conventions — default AMAD = 20 μm

5. CONCLUSION

A generic method has been developed to facilitate the identification of the particle size aerosol sampler to select (following the inhalable, thoracic or respirable convention) for minimizing the respective biases between the true and estimated exposure and the true and estimated effective dose associated with inhalation exposure to any radioactive compound.

Calculations based on this method and applied to the various radioactive compounds of the ^{238}U and ^{232}Th natural chains radionuclides have shown that:

- For exposure and effective dose estimates, the sampling efficiency of the sampler should be known and corrected for;
- For exposure estimates, an inhalable sampler should be chosen;
- For effective dose estimates, the sampler should be chosen according to the absorption rate of the considered compound, in order to follow as closely as possible the AMAD dependency of the compound's dose coefficients:
  - A thoracic sampler should be chosen for compounds of slow and moderate absorption rate;
  - An inhalable sampler should be chosen for fast absorption rate compounds;
  - In the absence of (precise) information on the particle size characteristics of the ambient aerosol, the following default values should be chosen: AMAD = 5 μm, GSD = 2.5.

ACKNOWLEDGMENTS

The authors wish to thank Alan Birchall and colleagues from the NRPB Inhalation Studies Group for the effective dose calculation using the PLEIADES and IMBA software.

This work was partially supported by the European Commission DG Research within the framework of the 5th PCRD (SMOPIE project: "Strategies and Methods for Optimization of Internal Exposures of workers from industrial natural sources").

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MITIGATION METHODS IN THE SELECTION OF CONSTRUCTION SITES

A. Chingiz, T. Zolotovitskaya, S. Aliyeva

Geology Institute of Azerbaijan National Academy of Sciences[*], Baku, Azerbaijan

Abstract

One of the main tasks in the selection of construction sites is the study of the geologic structure. Tectonic faults within construction sites represent an additional hazard for buildings. Radiometric methods allow the activity of fault dislocations to be determined. In the radioactive fields of the earth's crust, only active tectonic dislocations and geodynamic zones manifest themselves. When planning construction works it is necessary to locate buildings away from hazardous areas. Results of surveys allowed areas with increased radon exhalation to be identified. This mitigates the risk of hazardous radiation to people. According to the level of gamma radiation, areas of different lithological composition are identified. In developed countries (USA, Canada) radon investigations were conducted to evaluate high, middle and low levels of radon exhalation. In these countries it is used to choose the less hazardous zones. Recently in Russia, radon surveys for engineered construction in different areas have been conducted more intensively. They are also used for studying the interrelation between the distribution of ground radon and the amount of radon in buildings. These problems have been discussed in China recently in connection with the mitigation of the radiation risk for the population. This problem should be discussed in the newly established Radon Centre (Poland).

1. INTRODUCTION

One of the primary tasks in the selection of construction sites is the study of the geological structure. Tectonic faults within construction sites represent an additional serious hazard for buildings. The application of radiometric methods allows us to determine the activity of fault dislocations. In radioactive fields of the earth's crust, only active tectonic dislocations and geodynamic zones manifest themselves. While planning construction works, it is necessary to locate buildings outside of hazardous areas. Results of surveys allowed us to identify areas with increased radon exhalation. According to the level of gamma radiation, land areas of different lithological composition are identified. This mitigates the risk of hazardous radiation to people.

2. RADIOMETRIC METHODS

Tectonic disturbances regardless of what they are — 'through' or 'blind' (buried) faults — play the role of hydrodynamic drainage systems. Constant microfluctuations accompanying tectonic activity form a favourable environment for rising fluid streams. Research showed that cracks in the upper beds could be formed not only in the zone of through faults, but over zones of buried active structures. The latter are more dangerous for constructions, i.e. an overlapped fault becomes a source of additional microfluctuations and fluid transportation. These faults cannot be observed in engineering research, but they can show their influence on radioactive fields regardless of the thickness of the overlapping series (Fig.1).

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[*] E-mail: radiometry@gia.ab.az

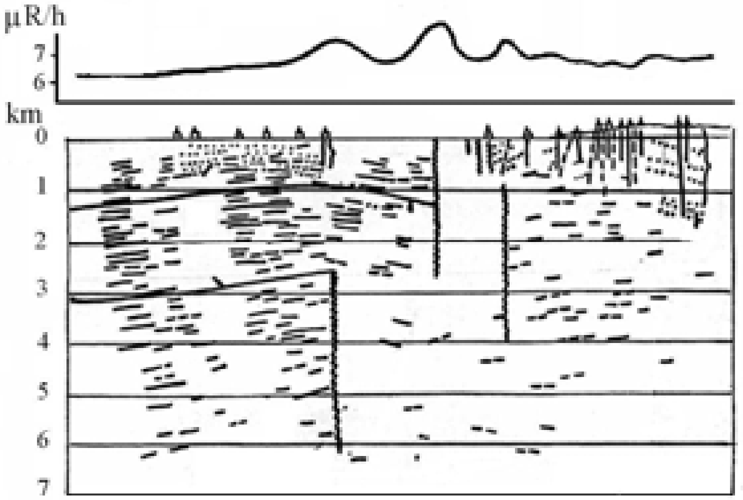

FIG. 1. Actively living tectonic disturbances manifesting in the radioactive field regardless of the thickness of the overlapping series

There is great similarity between radioactive and wave fields. So, many gamma lineaments stretch along zones of complex seismic information that are identified with zones of high density of media surrounding a fault-line area. They are large tectonic elements in both fields, like the Baku trough surrounded by a ring of anticlinal folds. These folds are represented by gradients of seismic wave rates in the wave field, and in the radioactive sense by a change of intensity of gamma radiation on the isoline 5 μR/h.[1] Especially the Fatmai-Zykh folded zone can be clearly observed in both the seismic and radioactive fields. Borders of active fault zones are clearly recognized by radiometric methods in particular by gamma survey. It is important to define the area of dynamic influence of a fault especially when the fault does not go up to the surface. By the combined study of radioactive and seismic wave fields, it has been established that the diffraction area is confined to the fault zone in the upper part of the sedimentary series. They show a high extent of microjointing and a high fluid permeability for migration of radioelements to surface. That is how anomalies of the gamma field are formed over the zones of active tectonic dislocations. In this case, the problem of danger of one or another tectonic dislocation can be solved by radiometric methods. For instance, the dislocations which are not reflected in the gamma field serve as a screen for seismic waves (here, their attenuation occurred) and this decreases the amplitude, i.e. the seismic danger is reduced (Fig. 2).

Non-traditional complexity of radiometric methods with seismic survey, electrometry, gravimetry and space data allowed us to distinguish heterogeneity in the earth’s crust on the basis of the intensity of their manifestation in radioactive fields. It has been established that geodynamically active parts of the earth’s crust are reflected by contrast anomalies both in radioactive fields and on space photos. At the same time, a number of dislocations revealed in other geophysical fields (e.g. in gravity field) manifested neither in the gamma-field nor on space photos. Considering this, the classification of zones of tectonic dislocations is presented on the basis of the intensity of their manifestations in radioactive fields and on space photos.

- Faults that have completed their development are weakly manifested in the radioactive, field although they find their reflection in other geophysical fields. These heterogeneities of the earth’s crust do not reflect on space photos.

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[1] 1 R = 2.58 × 10^{-4} C per kg of air.

- Faults inherited and continuing their development are manifested in the radioactive field by positive contrast gamma lineaments, regardless of the thickness of the sediment bulk overlapping the zone of dislocations, as under the influence of constant vibration in the layer overlapping the blind fault the zone of high fluid permeability is formed.
- Faults formed on the modern stage of development are represented by poor radioactive anomalies. The degree of their activity is determined on the relative isotope values of Ra^{228} and Ra^{226}. In accordance with this, the intensity of manifestations of geodynamical processes is estimated. They are usually reflected on space photos, but are poorly manifested in other geophysical fields.

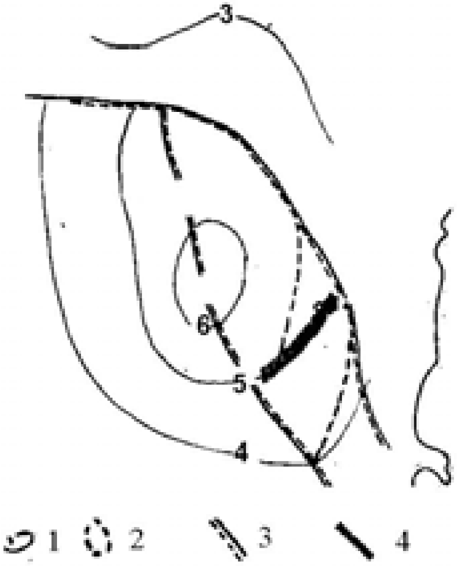

FIG. 2. Misrepresentation of the macroseismic field of the Kura earthquake dealing with screening activity of consolidated tectonic disturbances: (1) isoseismal line; (2) theoretic isoseismal line; (3,4) tectonic fault

3. EXAMPLES OF THE USE OF RADIOMETRIC METHODS

Such a non-traditional complexity of the geophysical methods with the use of remote sensing methods and macro-seismic data allowed us to contour and prove the existence of the heterogeneity zone in the earth's crust of the South-Caspian depression of the anticaucasian direction, named by us the Eastern-Mugan zone of dislocations.

Below we will give some examples of the successive use of radiometric methods during the selection of construction sites with a minimum risk of earthquake. For the first time we used radiometrical methods for micro-seismic zoning of the construction site of a radio broadcasting station in Baku. As a result of this, the zones of high tectonic activity, reflecting in the gamma field by high values of potential exposure, were determined and the place for tower construction situated on the non-geodynamic active zone was recommended as well, thus predetermining its safety (Fig. 3).

The spatial position of the North-Adjinour zone of tectonic dislocations of the Caucasian direction and zone of the Kutkashen-Chykhyrly fault which direction is transverse to the structure of Caucasus was clarified by means of the gamma field. Thus, the best options for construction area due to the active zones were chosen (Fig. 4).

The results of the work carried out become the basis for the application of the radiometric method for the final selection of a building site for a nuclear power plant. During the design process, several competitive sites were chosen, four of which were recommended for further detailed seismo-tectonic investigation (Fig. 5). For revealing the spatial position of these sites and tectonic fault zones, an auto-gamma survey of an 800 km^2 area was carried out. The area studied was represented mostly by the quaternary formations — proluvial-alluvial rocks that are homogenous in composition. Within this lithologically homogenous field, the radioactivity varied over a rather wide range — from 4 to 11 μR/h, reflecting the geological structure. On the transformed map, lineaments with high values of radioactivity showing the relationship between the radioactivity of the given rock type and the normal background were determined. When compared with geological and tectonical maps, the location of the lineaments (determined according to space photos) showed that the Adjichai-Alyat fault zone was reflected in the gamma-field. Thus, zones of tectonic dislocations were revealed and recommendations on the best site locations were given as well. As a result of the research conducted, 2 sites were rejected and, for the remainder, detailed radiometric work, allowing the seismic hazard to be estimated, was conducted (Fig. 6).

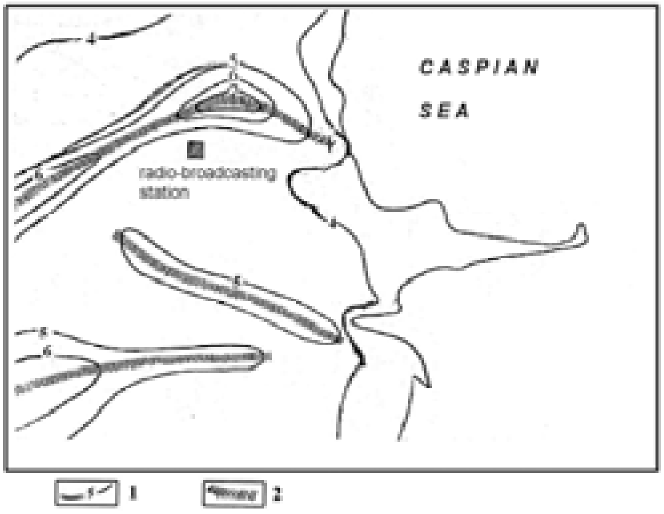

FIG. 3. The location of the construction area of an industrial complex relative to the zones of tectonic disturbances: (1) isogamms; (2) tectonic fault

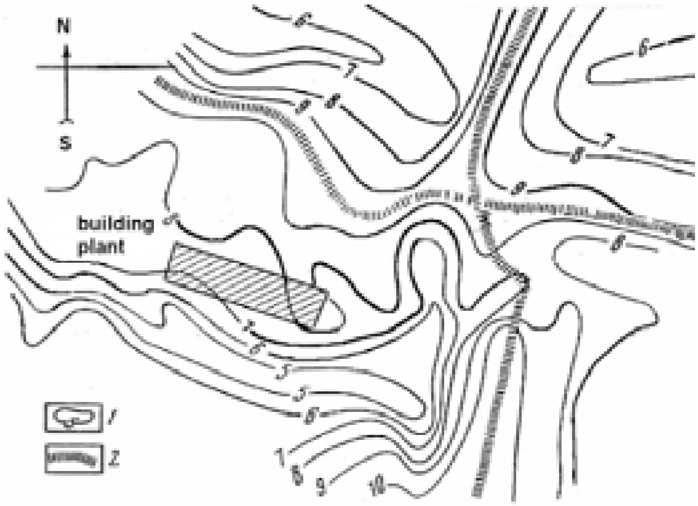

FIG. 4. The location of the construction area of an industrial complex relative to the zones of tectonic disturbances: (1) isogamms; (2) tectonic fault

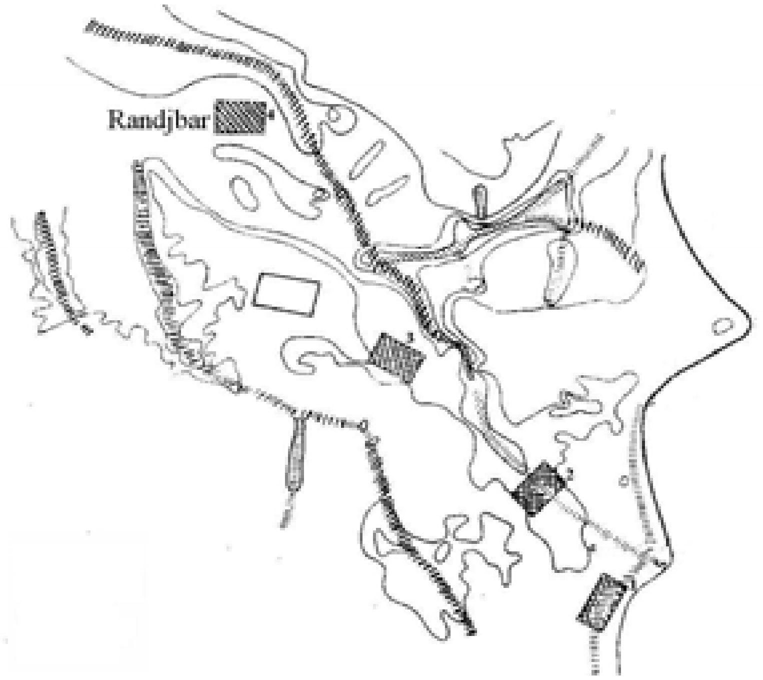

FIG. 5. The use of radiometry in a study of competitive AES areas on Azerbaijan territory

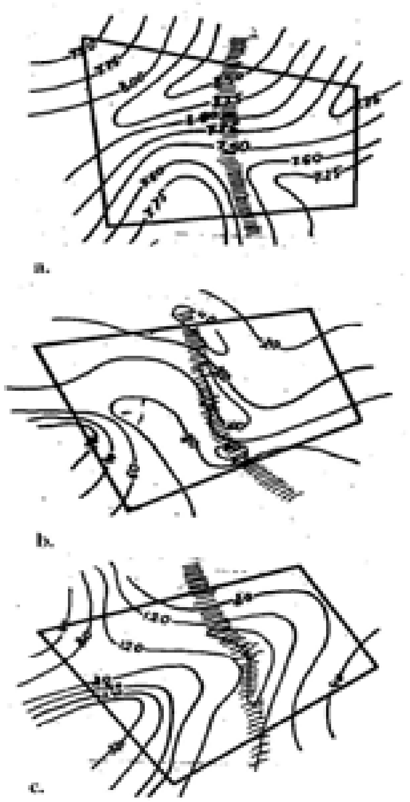

FIG. 6. Radioactive fields in the 'Salyanskaya-2' field: (a) integral gamma-field; (b) by radon; (c) by thoron

4. CONCLUSION

Radiometric methods are successfully used in Azerbaijan for the selection of the most favourable zones for construction in areas with a seismic risk, and are considered to be an important use of research in decreasing the risk of earthquakes, and radiation exposure, especially at the design stage of important state constructions.

GRAIN SIZE IN RADIOMETRIC MEASUREMENTS OF GROUND

V. Gablin[*]

Moscow Scientific-Industrial Association "Radon", Moscow, Russian Federation

Abstract

Known procedures for radiometric measurements of ground differ significantly in the grain size of the sample. The range is 0.043–0.25 mm. To answer the question about the proper grain size of the sample to be measured one must address the three types of radioactivity in ground. Natural radioactivity is distributed homogeneously through the bulk of sample. It is either in the form of radionuclides in the crystal structure of minerals (e.g. K in $KAlSi_3O_8$) or an isomorphic replacement in the crystal structure (e.g. Ra in $BaSO_4$, Th in $ZrSiO_4$, U in $CePO_4$). Model radiometric measurements of the same sample with a grain size ranging from 0.125 to 2 mm do not show significant differences between gross alpha and beta activities despite an increase in the specific surface. That is why there is no reason to grind monocrystal grains. Artificial radioactivity is caused by atmospheric fallout presenting radionuclides in dynamic form, or by 'hot particles', which are commonly uranium and plutonium oxides (silicates) and also ^{14}C. If we grind a hot particle, its fine sub-particles will cover non-active grains of matrix that will lead to an increase in surface contamination and, as a result, to an increase in activity concentration. Secondary radioactivity is a result of changes in the radionuclide concentration in the ground owing to weathering, infiltration, precipitation and other natural processes. Both natural and artificial radionuclides can be involved in these processes. Here, radionuclides occur preferentially in sorbed form on the grain surface as salts, hydroxides and complex compounds. This is another kind of inhomogeneity, but not such a sharp one. Grinding such grains increases the specific surface, decreasing the activity conentration. Thus the whole bulk of the sample to be measured should be driven to a monocrystal state, i.e. grain size does not have to be definite. If the sample of ground contains hot particles, one must try to separate it into active and non-active parts as carefully as possible with two different subsequent measurements.

1. INTRODUCTION

In the known procedures for radiometric measurements of ground, the grain size ranges from 0.043 to 0.25 mm. In order to discuss the proper grain size of the ground sample to be measured one must first consider the definition of ground in radioecology. There are many classifications of ground, which differ for the various branches of science and industry (geology, agriculture, industrial construction, etc.). Two main questions to be answered are:

- Either the ground is composed only of clay and sand or it includes silt (dust) too;
- What are the bounding grain sizes of the ground components?

The parameters distinguishing a group of sands are the mineral composition (the average contents of silica and feldspars in sand are 70 % and 15 %, respectively), the looseness (friability), the water-permeability, and the grain size. The upper bound of the grain size of sand is 2 mm. Finer fractions are usually monocrystals or their fragments, whereas larger fractions are in fact accretions of various mineral species, i.e. fragments of rocks. The lower bound of grain size is 0.05–0.0625 mm. These are the finest fractions, which can be

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[*] E-mail: vgablin@radon.ru

obtained by dry sieving. Particles of this size in the dry state still maintain their looseness. Finer fractions can be obtained only by using sedimentary methods. They are gradually being enriched by clay minerals and as a result they gain properties of clay such as sorption ability and a property of ionic exchange. The mean contents of clay minerals and silica in clays are 64 % and 34 %, respectively.

There are no evident reasons for distinguishing a group of silts. They are intermediate in composition between clays and sands, containing mainly silica, feldspars, clay minerals, carbonates and micas. They are intermediate in grain size, too. But their physical properties are much closer to those of clays. Being humid, they show fluidity as well as coherence. Silts have a property of ionic exchange, some plasticity, sticky state, linear shrinkage, and temporary resistance to pressure. These properties are of course weaker than those of clays but they are not peculiar to sands at all.

Thus for the radioecologist who deals with radiometric measurements, ground is a poly-dispersive system composed of sand and clay. It is free of organic matter, unlike soil. The grain size of sand is 0.0625–2 mm. Finer fractions are called clay.

2. RADIOMETRIC MEASUREMENTS AND GRAIN SIZE

Numerous radiometric measurements of clay and sand, obtained by sieving of natural ground sampled randomly in the Moscow region, were conducted using a Canberra HT-1000 radiometer, a sample mass of 1 g, and a measurement time of 1500 s. They show a significant distinction between clay and sand activity concentrations (Table I). Supposedly the activity concentrations of silt would have been intermediate if they had been measured.

TABLE I. GROSS ACTIVITY CONCENTRATIONS OF CLAY AND SAND IN THE MOSCOW REGION

Type of material	Alpha activity concentration (Bq/kg)		Beta activity concentration (Bq/kg)	
	Mean	Square deviation	Mean	Square deviation
Sand	103	54	110	31
Clay	894	164	1081	96

The second factor that should be taken into account concerning the grain size of the sample to be measured is related to the peculiarities of radiometric measurements. They are known to be relative, i.e. the activity of the measured sample is calculated using the known activity of a standard sample or a sample of comparison. This means that a certain requirement of the sample being measured is a correspondence of its properties, including grain size, to the properties of the standard sample. But it is possible to create a standard sample with any physical properties and radionuclide composition. Moreover, it is evident that the contribution of the grain size non-correspondence to the combined uncertainty of measurement can be neglected in comparison with the contribution of the non-correspondence of radionuclide composition.

The most important factor leading to the right choice of grain size in radiometric measurements is the existence of three types of radioactivity.

(a) *Natural radioactivity* is distributed homogeneously through the bulk of sample. It originates either from radionuclides in the crystal structure of minerals (e.g. K in $KAlSi_3O_8$) or from isomorphous replacement in the crystal structure (e.g. Ra in $BaSO_4$, Th in $ZrSiO_4$, U in $CePO_4$). Model radiometric measurements of the same sample with a grain size ranging from 0.125 to 2 mm, again using a Canberra HT-1000 radiometer, a sample mass of 1 g, and a measurement time of 1500 s, do not show a significant variation in alpha and beta activity concentrations despite the increasing specific surface (Table II). That is why there is no reason to grind monocrystal grains.

TABLE II. GROSS ACTIVITY CONCENTRATIONS OF VARIOUS FRACTIONS OF FOUR SAMPLES OF GROUND

Size fraction (mm)	Gross activity concentration (Bq/kg)							
	Sample 1 (pure silica sand)		Sample 2		Sample 3		Sample 4	
	Alpha	Beta	Alpha	Beta	Alpha	Beta	Alpha	Beta
< 0.125	<4	<69	344	893	749	824	811	739
0.125-0.16	<4	<69	272	<69	148	402	312	313
0.16-0.25	<4	<69	<4	913	437	392	312	590
0.25-0.37	<4	<69	<4	913	125	392	<4	590
0.37-0.5	<4	<69	62	541	499	432	437	442
0.5-0.7			<4	435	704	559	< 4	267
0.7-0.8			187	327	125	516	312	318
0.8-1			62	144	62	332	<4	228
1-2			<4	129	375	268	125	74

(b) *Artificial radioactivity* is caused by atmospheric fallout, presenting radionuclides in dynamic form, or by hot particles, which are commonly uranium and plutonium oxides (silicates) and also ^{14}C. If we grind a hot particle, its fine sub-particles will cover non-active grains of matrix that will lead to an increase in the surface contamination and, as a result, an increase in activity concentration.

(c) *Secondary radioactivity* is a result of changes in radionuclide concentration in ground owing to weathering, infiltration, precipitation and other natural processes. Both natural and artificial nuclides can be involved in these processes. Here, radionuclides occur preferentially in sorbed form on the grain surface as salts, hydroxides and complex compounds. This is another kind of inhomogeneity, not such a sharp one. Grinding such grains increases the specific surface, decreasing activity concentration.

3. IMPLICATIONS FOR SAMPLE PREPARATION

When preparing a sample of ground for measurement, one must take into account its poly-dispersivity and provide its granulometric representation with respect to the whole bulk of the initial sample, as follows. The initial dried sample undergoes careful grinding in order to decompose it into individual crystals and sieving, from which a fraction of sand and a fraction of clay are obtained. Both fractions are weighed and their correlation in the initial sample is calculated. A ‘proportional’ sample must be prepared for measurement by successive reduction of both fractions. The proportional sample has the same correlation of fractions as that of the initial sample. The importance of proportionality of the sample to be measured is conditioned by the following. The tight mutual relationship between the mineral composition of the rock and the size of its grains is fixed. The chemical composition of the rock depends not only on its mineral composition but also on its granulometric composition. The physical properties of the rock (e.g. density and sorption ability) and the crystal-chemical properties (e.g. the isomorphous capacity) depend obviously on the chemical and mineral composition of the rock. It means that by providing granulometric representivity one can believe with high probability that the representivity of the other parameters is provided also.

The importance of proportionality is conditioned statistically, too. The type of activity distribution (normal, logarithmic, or more complicated) for the fractions in the initial natural sample is principally unknown, but it is retained in the sample to be measured if we prepare it in the way described above. The more we grind or rather mill the initial sample, destroying individual crystals, the closer the activity approaches a normal distribution. The result of such a procedure is a collection of fine particles of absolutely equal size with an absolutely normal distribution of activity. It is obvious that such a situation is impossible if one deals with a sample of ground containing hot particles.

4. CONCLUSION

The whole bulk of the initial sample should be driven to a mono-crystal state, i.e. the grain size does not have to be fixed. This enables the granulometric representivity of the sample to be measured to be retained — the easiest kind of representivity which can be provided in the laboratory.

NORM LEGAL ASPECTS

APPLICATION OF INTERNATIONAL SAFETY STANDARDS TO WORK INVOLVING EXPOSURE TO NATURAL RADIATION

D. Wymer[*]

International Atomic Energy Agency, Vienna

Abstract

The International Basic Safety Standards (BSS), published by the International Atomic Energy Agency (IAEA) in 1996, provide the basis for the control of exposure to both artificial and natural sources of radiation. The IAEA is engaged in a programme to provide additional guidance and information on the application of the BSS to natural sources, and this programme is focusing increasingly on work activities involving naturally occurring radioactive material (NORM). This paper describes the current status of this programme and, in particular, the progress being made in the development of guidance and supporting information to help national authorities to decide which NORM activities should be regulated and how they should be regulated. Data on activity concentrations, radiation doses and appropriate control measures for various industrial processes involving NORM are being gathered as part of the development of sector-specific Safety Reports and associated training packages. Some examples are given to illustrate how these data provide support for a growing international consensus on criteria for defining the scope of regulatory control and on the need for, and the nature of, a graded approach to regulation.

1. THE IAEA SAFETY STANDARDS

The International Atomic Energy Agency (IAEA) is specifically authorized under the terms of its Statute to establish standards of radiation protection and safety in consultation and, where appropriate, in collaboration with the competent organs of the United Nations and with the specialized agencies concerned, and to provide for the application of these standards. The International Basic Safety Standards (BSS), published by the IAEA in 1996 [1], are jointly sponsored by the IAEA and five other international organizations, and are based on the most recent recommendations of the ICRP [2]. A Safety Guide on Occupational Radiation Protection [3], jointly sponsored by the IAEA and the International Labour Office and published in 1999, provides more detailed guidance on the application of the BSS to natural sources of radiation, including radon and thoron progeny. As part of its safety standards programme over the past 30–40 years, the IAEA has published various safety-related documents dealing with protection against exposure to natural sources of radiation, several of which were jointly sponsored by the IAEA and the International Labour Organization (and some also by the World Health Organization), but these have been concerned primarily with the mining and processing of uranium and thorium ores (see Refs [4–7] for publications still current). Only recently has the coverage been extended more explicitly to other activities that involve exposure to natural sources [8–10].

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[*] E-mail: D.Wymer@iaea.org

2. RECENT EVENTS IN THE DEVELOPMENT OF THE IAEA'S PROGRAMME ON EXPOSURE TO NATURAL RADIATION SOURCES

In 1998, it was concluded from an international conference on *Topical Issues in Nuclear, Radiation and Radioactive Waste Safety* [11] that further practical guidance was needed on the control of exposure to natural radiation, in particular, exposure arising from work with material containing elevated levels of natural radionuclides. Such material has come to be referred to as 'naturally occurring radioactive material' (NORM). In 2001, the IAEA held two meetings on *Assessment of Occupational Protection Conditions in Workplaces with High Levels of Exposure to Natural Radiation* to identify more precisely which industries were primarily affected and which industrial processes and materials required control as a priority. From the inputs of the 16 participating countries, it was concluded that the IAEA, in broad consultation with regulatory and advisory bodies and NORM industries, should develop Safety Reports for individual industry sectors in which the control of exposure to NORM needed to be considered. The development of a Safety Report on the oil and gas sector [9] had already been started. The other industry sectors identified included phosphates and phosphoric acid production, zircon sand and zirconia production, titanium dioxide pigment production, monazite and rare earths extraction, industrial uses of thorium, coal and coal ash, and the production of certain metals. It was also recommended that these Safety Reports should be followed up with information exchange and training courses aimed at regulatory bodies, industry personnel and service providers, and supplemented by more general assistance in identifying work activities with significant exposures to NORM and in formulating practical approaches to the assessment and control of those exposures.

In 2002, the IAEA and the International Labour Organization jointly convened in Geneva an international conference on *Occupational Radiation Protection*. One of the issues addressed was occupational exposure to NORM, and the conclusions and recommendations from this conference [12] provided further important input to the consolidation of the IAEA's programme on protection against natural radiation, the key elements of which were (a) to complete the development of supporting documents forming part of the relevant safety standards, (b) to provide for the application of these standards through the fostering of information exchange and promoting research and development, and (c) to support the provision of technical cooperation with Member States. The conference found that, while exposures to NORM were generally stable and predictable, with little or no likelihood of large accidental exposures, lack of suitable controls could in some cases give rise to doses approaching or even exceeding dose limits — these were the situations on which regulatory attention needed to be focused. At the other end of the scale, it was widely believed that, in terms of an optimized approach to protection, occupational doses below 1–2 mSv per year were unlikely to warrant significant regulatory attention and that it would be wasteful of resources, including those of the regulator, to seek further reductions. The conference therefore concluded that more explicit guidance was needed on determining which exposures arising from NORM activities should be subject to some form of regulatory control. For those exposures that did require control, the conference also highlighted the need for guidance on how to apply a graded regulatory approach that was sufficiently flexible and practicable to cater for the full diversity of exposure situations.

3. WHAT SHOULD BE REGULATED?

The question of what should be regulated can be addressed in two basic ways — by specifying either what is outside of the system of control or what is inside the system of control. The BSS make provision for both approaches, as well as for further options within each approach:

- With regard to what is outside the system of control, the BSS provide for exclusion of exposures (from the scope of application of the BSS) or exemption of practices or sources within practices (from requirements of the BSS).
- With regard to what is inside the system of control, the BSS state that certain exposures to natural sources should be automatically included, and identifies these either by specifying the practices and sources giving rise to these exposures or by specifying the exposures themselves. The BSS also make provision for the regulatory body to specify additional practices, sources and exposures that should be included.
- Exposures to natural sources not specifically excluded or included (either automatically or by regulatory decision) are considered as chronic exposure situations. Although these exposure situations are not subject to regulation as practices, some (for instance radon in homes) could be considered for intervention.

The BSS therefore provide for more than one way of defining, in national legislation and regulations, the scope of regulatory control of exposures to natural sources, and in practice different countries use different approaches to suit their own situations and preferences.

3.1. Exclusion

The decision to exclude is based on whether the exposure is essentially unamenable to control. Apart from some rather obvious examples of excluded exposures given in the BSS (i.e. exposure from ^{40}K in the body, from cosmic radiation at the surface of the earth, and from unmodified concentrations of radionuclides in most raw materials), there is no published international guidance yet on how to interpret the concept of exclusion in regulatory terms. The IAEA may be close to achieving international consensus on activity concentration levels that could be used for applying the concept of exclusion, with the derivation of such levels being based on a consideration of the worldwide distribution of activity concentrations in soil. The activity concentration levels being considered are 10 Bq/g for ^{40}K and 1 Bq/g for all other natural radionuclides. These levels could also be used as clearance levels, i.e. for release of NORM from regulatory control.

3.2. Exemption

The principal exemption criteria given in the BSS are that the risks to individuals and the collective impact be sufficiently low as not to warrant regulatory concern or control, and remain sufficiently low in all likely scenarios. Such criteria could provide a (qualitative) basis for exemption of a practice involving work with NORM[1,2]. The BSS also specify criteria based on activity and activity concentration for automatic exemption without further consideration. For natural radionuclides these levels range from 1 Bq/g upwards (mostly 1 or 10 Bq/g) and are intended to apply to the incorporation of natural radionuclides into consumer products or their use as sources or for their elemental properties. Although the numerical values were based on moderate quantities of material, they were derived conservatively and it

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[1] This is also the view expressed in guidance published by the European Commission (para. 5.3 of Ref. [13]).

[2] The BSS provide numerical dose criteria for exemption without further consideration, but the use of these is not practicable for natural sources — the individual dose criterion of 10 μSv per year is a very small increment to the average natural radiation background and an order of magnitude or two below regional variations.

is suggested in Ref. [3] that the activity concentration values could also be used as a means for defining when a practice involving work with NORM, or a source within such a practice, is exempted. Apart from this, there is no published international guidance yet on numerical criteria for exemption of practices or sources giving rise to exposure to natural radiation.

Guidance published by the European Commission [13] establishes a criterion of 300 μSv incremental dose per year for the exemption of work activities involving significant exposure to natural sources. On this basis, the following exemption levels expressed in terms of activity concentrations of radionuclides in the uranium and thorium decay series have been derived[3]: 0.5 Bq/g for ^{238}U, ^{226}Ra, ^{232}Th and ^{228}Th in secular equilibrium with their progeny; 1 Bq/g for ^{228}Ra in secular equilibrium with ^{228}Ac; and 5 Bq/g for ^{210}Pb in secular equilibrium with ^{210}Bi, for ^{210}Po, and for ^{40}K. These activity concentrations are similar to those being proposed within the IAEA as exclusion levels, although the basis for their derivation is quite different.

3.3. Exposures automatically included in the system of control

The BSS define the following exposures to natural sources as included within the system of control (unless the exposure is excluded or the practice or source is exempted):

(1) Exposure due to the (deliberate) incorporation of naturally occurring radionuclides into consumer products, or to their use as a radioactive source (e.g. ^{226}Ra, ^{210}Po) or for their elemental properties (e.g. thorium, uranium);

(2) Exposure due to any activity in the nuclear fuel cycle[4];

(3) Public exposure delivered by an effluent discharge or the disposal of radioactive waste arising from a practice involving natural sources;

(4) Occupational exposure to radon, other than exposure incidental to the work that does not exceed the action level for remedial action relating to chronic exposure situations involving radon in workplaces[5].

3.4. Exposures specified by the regulatory body as being subject to control

The Safety Guide on Occupational Radiation Protection [3] advises that the regulatory body should first undertake an investigation of the relevant occupational exposure situations to determine the extent of the exposures. For occupational exposures associated with NORM industries (i.e. the mining and processing of raw materials), a suggested approach is then to define levels of activity concentration above which the requirements for practices would apply. It is noted in the guidance that, although these levels define what is included within the system of control, they can effectively act as exclusion or exemption levels defining what is outside of the system of control. The guidance goes on to say that, for practical reasons, the

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[3] These exemption levels have been derived considering both occupational and public exposures, and apply to all materials except wet sludges from the oil and gas industry, for which higher values have been derived.

[4] The mining and milling of radioactive ores fall into this category [3]. Although the term “radioactive ore” is not defined in the BSS (in principle, all ores are radioactive to some extent), it can be taken to mean an ore mined for the purpose of extracting the radioactive elements uranium or thorium.

[5] The action level is established taking into account the benefits and costs associated with the remedial action plan, and is expected generally to be 1000 Bq of ^{222}Rn per cubic metre of air. Examples of workplaces where exposure to radon is incidental to the work include facilities for the mining and processing of ores other than uranium or thorium ores, waterworks, caves, spas, and above-ground workplaces in radon prone areas [3, 8].

regulatory body may wish to use the levels as the basis for a quantitative definition of radioactive substance and that, as mentioned earlier, the exemption levels of activity concentration given in the BSS for naturally occurring radionuclides could be used for this purpose. The guidance in Ref. [3] also refers to the relevant text in ICRP Publication 75 [14], which concludes with the following recommendations:

- Regulatory bodies should choose activity concentrations of parent radionuclides within the range 1–10 Bq/g to determine whether the exposures from these materials should be regarded as occupational — this range corresponds to worker doses of about 1–2 mSv per year.
- A single generic value or values for specific radionuclides may be chosen, above which an evaluation of the exposures and working conditions should be carried out with a view to determining whether precautions are required to limit exposure of workers.

The Safety Guide [3] also gives guidance on situations involving elevated gamma dose rates due to the presence of NORM in the ground and building materials that make up the workplace, stating that it may be appropriate to apply an approach similar to that for radon exposure — a gamma dose rate of 0.5 μSv/h for a working year would lead to an annual effective dose of about 1 mSv, and this dose rate or some multiple of it might be adopted as an action level for remedial action. As in the case of radon, the approach would be to consider whether the exposure could reasonably be reduced to below the action level (for example, by shielding). Failing this, the numerical value of the action level could be used to define when the requirements for practices apply.

3.5. Summary — the emerging international view

The direction is clearly towards the use of activity concentration levels of natural radionuclides in materials as the first step in defining what should be outside of the system of control, whether this be through exclusion or exemption. Consensus seems to be emerging around a figure of 10 Bq/g for ^{40}K and 1 Bq/g for all other natural radionuclides. In countries where activity concentration levels are already in use for this purpose, the numerical values are generally of the same order of magnitude as these figures.

The use of activity concentration levels in materials is, on its own, not enough to decide on what should be subject to control, however, since there is only a very loose correlation between activity concentration and dose. This is illustrated in Figs 1 and 2, which give data for occupational exposure to radon and to dust and gamma radiation, respectively, based on actual occupational exposure measurements made in a selection of NORM industries involving raw materials with moderate activity concentrations. Any trend towards higher doses at higher activity concentrations is very poorly defined. Table I gives some indication of the relative contributions to the total dose.

The data for exposure to radon in Fig. 1 demonstrate that the radon action level (and even the occupational dose limit) can be exceeded during work with materials that are not significantly more radioactive than normal soil. This is, of course, the reason why radon has to be treated separately using as a regulatory criterion the activity concentration of radon in air rather than the activity concentration of its parent radionuclide in the material from which it originates.

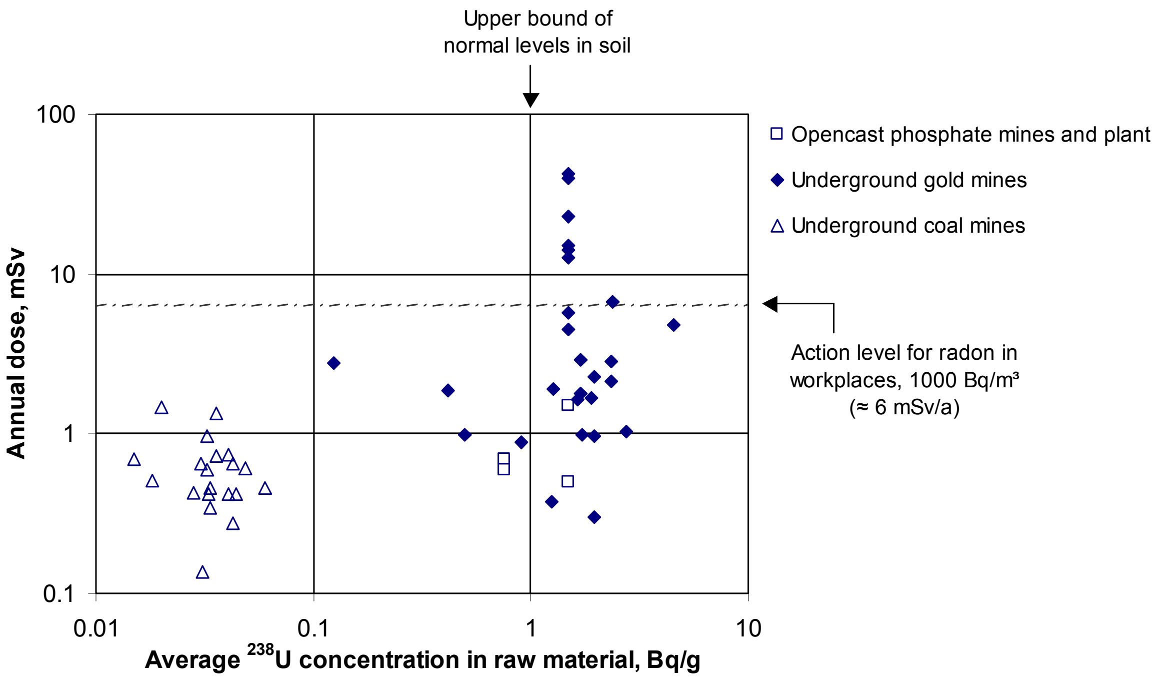

FIG. 1. Some examples of doses received by workers from radon inhalation [15–18].

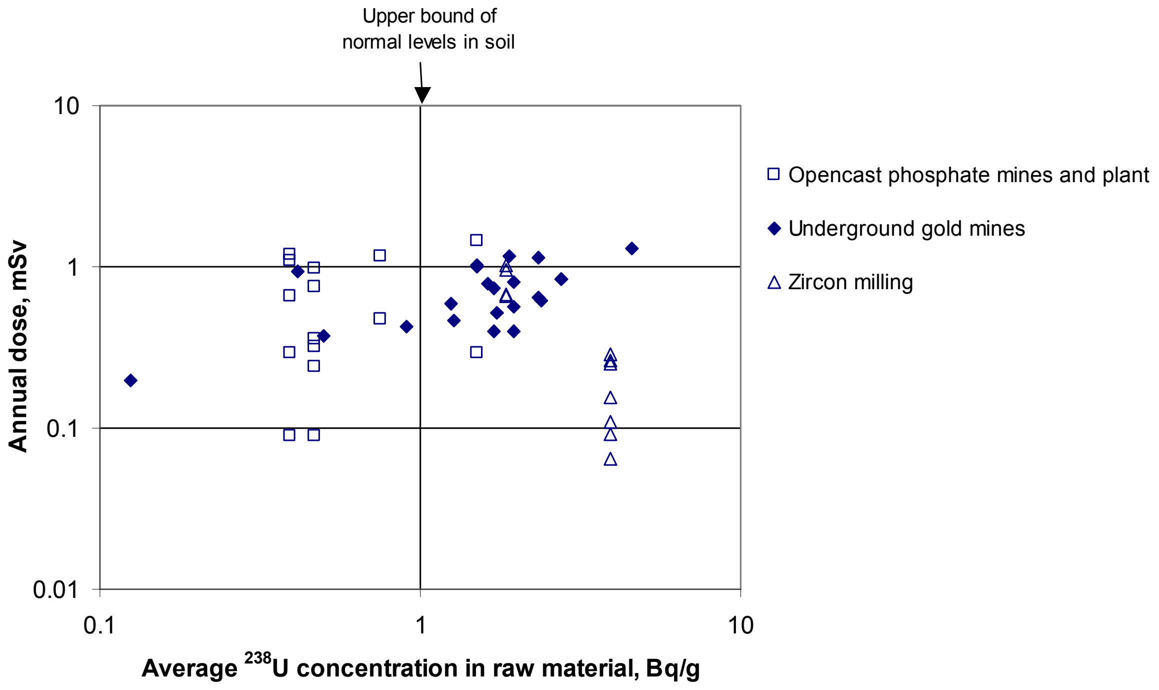

FIG. 2. Some examples of doses received by workers from external gamma radiation and dust inhalation [16, 17, 19–23].

TABLE I. SOME EXAMPLES OF RELATIVE CONTRIBUTIONS TO WORKER DOSES FROM LOW ACTIVITY SOURCES OF NATURAL RADIATION [15–23]

Type of facility	Average total dose (mSv/a) (range in parentheses)	Average contribution to dose (range in parentheses)		
		External gamma radiation	Inhalation of dust	Inhalation of radon
Underground coal mines	1 (0.1–2)	Insignificant	Insignificant	~100%
Underground gold mines	7 (1–43)	22% (2–57%)	2% (0–9%)	76% (39–98%)
Opencast phosphate mines	1 (0.1–2)	71% (44–100%)	22% (0–56%)	7% (0–32%)
Phosphate beneficiation plants	1 (0.1–2)	50% (12–100%)	37% (0–88%)	12% (0–65%)
Zircon mills	0.4 (0.06–1)	57% (15–85%)	43% (16–85%)	Insignificant

The data in Fig. 2 for exposure to external gamma radiation and dust are consistent with the statement in ICRP Publication 75 [14] and the IAEA Safety Guide on Occupational Radiation Protection [3] that work with raw materials with activity concentrations of uranium series radionuclides up to about 1–10 Bq/g is unlikely to result in workers receiving doses exceeding 1–2 mSv per year, even in relatively dusty conditions and close to large quantities of material. Doses received by members of the public are likely to be considerably lower — according to European studies, less than 300 μSv per year [13] (see also Table II below).

Reference to Fig. 2 demonstrates that for exposures to external gamma radiation and dust the use of an exclusion level of, say, 1 Bq/g for uranium series radionuclides will not be effective in screening out all of those NORM activities that do not warrant control — indeed, on the strength of the few data presented, none of the industrial operations in Fig. 2 would appear to warrant control, even though they involve NORM activity concentrations of up to five times the proposed exclusion level. There needs to be a mechanism for examining the non-excluded activities in more detail, particularly those that exceed the exclusion level by only a few times, and determining, using dose as a criterion, those activities that should remain outside the system of control. This mechanism is effectively exemption applied on a case-by-case basis. As to the choice of dose criterion to be used for this purpose, the findings of the Geneva Conference [12], the recommendations of ICRP Publication 75 [14], the guidance in the IAEA Safety Guide on Occupational Radiation Protection [3], and the guidance published by the European Commission [13] all point to a value of the order of 1 mSv per year, perhaps a little higher than this for occupational exposure and a little lower for public exposure.

4. A GRADED APPROACH TO REGULATION

The findings of the Geneva conference highlighted the need for flexibility in cases where some form of regulatory control of exposures was required. In broad terms, the BSS provide for considerable flexibility in the application of its requirements, stating that such application “shall be commensurate with the characteristics of the practice or source and with the magnitude and likelihood of the exposures … Not all the requirements are relevant for every practice or source, nor for all the actions specified …”. In terms of the administrative requirements for practices that do not qualify for exemption, the BSS specify three levels of regulatory control: (i) notification, (ii) notification and registration, and (iii) notification and licensing. Practical application of this concept of a graded approach to regulation will vary from country to country.

4.1. Notification

A legal person intending to carry out a practice must submit a notification to the regulatory body of such an intention. This is a requirement in all situations and serves as a basic form of control that can be especially useful for the regulation of many NORM activities giving rise to low doses. It ensures that the regulatory body is at least aware of the practice, even though specific radiation protection measures are not normally needed. The BSS state that “Notification alone is sufficient provided that the normal exposures associated with the practice or action are unlikely to exceed a small fraction, specified by the Regulatory Authority, of the relevant limits, and that the likelihood and expected amount of potential exposure and any other detrimental consequence are negligible”.

4.2. Authorization by registration

In terms of this requirement, the legal person must, in addition to notifying the regulatory body, apply for an authorization in the form of a registration. This is the less stringent of the two types of regulatory authorization, and is appropriate for many NORM activities where levels of exposure are moderate. The Safety Guide on Occupational Exposure in the Mining and Processing of Raw Materials [10] states that “Registration should provide for the conditions of occupational exposure to be reviewed periodically or in the event of a change in the process that could significantly affect exposures”, implying that, as a minimum, exposures must be monitored and recorded.

4.3. Authorization by licensing

This is the more stringent of the two types of authorization, and may be appropriate for some NORM activities where levels of exposure are such that the necessary level of protection would not be achieved without the adoption of specific control measures. The BSS require that the mining and milling of radioactive ores (i.e. uranium or thorium ores) be authorized by licensing.

4.4. Radiation protection measures

The radiation protection measures needed for a particular operation or process involving NORM will depend on the details of that operation or process and the characteristics of the materials involved. It is not possible to generalize, and the IAEA’s approach is therefore to examine the various exposure situations in different industry sectors through the development of the sector-specific Safety Reports referred to earlier. Data are still being gathered, but some examples of information becoming available are given in Table II. Generally, only certain processes within a particular industry sector require protective measures to be taken, and these measures may be fairly simple in nature, such as good ventilation, housekeeping and industrial hygiene, and the use of basic personal protective equipment (PPE). Work involving high activity scales may require respiratory protection to be worn. Chemical processes may require some control over discharges to the environment. These forms of protective measures may already be required under existing industrial health, safety and environmental regulations, in which case the regulatory body responsible for radiation protection may simply need to be satisfied that these measures are adequate for radiological purposes.

TABLE II. SOME EXAMPLES OF EXISTING OR POSSIBLE CONTROL MEASURES FOR INDUSTRIAL PROCESSES INVOLVING NORM

Industry/process	Dose (mSv/a or as stated)		Control measures
	Workers	Public	
Phosphate industry			
Mining/beneficiation [16, 19, 20, 24]	0.1–2	0.02	None (candidate for exemption)
Ore transport and storage [25]	0.1–0.5		None (candidate for exemption)
Thermal phosphorus plant [23, 26] (precipitator dust 1000 Bq/g ^{210}Pb)	0.2–5	0.03	Contamination monitoring/control, PPE, ventilation, decay storage of dust
Phosphorus slag in roads [23, 26]	≤0.6	0.001–0.06	None (candidate for exemption)
Wet process phosphoric acid plant [24]	0–0.8		Operation: none. Maintenance: possibly control exposure to scale
Oil and gas industry (pipe scale 0.1–15 000 Bq/g ^{226}Ra) [9]			
Gamma exposure during operation	«20		Normally none. Exceptionally distance, time, shielding
Gamma exposure while working on open equipment	0.1–300 µSv/h		Restrict access and occupancy time
Dust inhalation while decontaminating equipment	0.1–1 mSv per gram inhaled		Ventilation, PPE, contamination monitoring/control
Sulphuric acid production from pyrite (scale 100–100 000 Bq/g ^{226}Ra) [27]			
Normal operation	1 (5 max)		None
Maintenance (duration 30 days)	0.4 mSv (max 2.8 mSv)		Minimize exp. time, PPE, reduce scale formation & control disposal
Zircon/zirconia industry			
Zircon milling [21, 22]	0.06–1		Dust control in plant
Zircon in ceramic tiles [21, 28]	0.01–0.5	0.003–0.06	None (candidate for exemption)
Zircon sand landfill disposal [29]		0–0.1	Restrict disposal to landfill only
Thermal zirconia plant (zircon feed, off-gas filtration system) [21]	0.25–3.1		Dispose of off-gas dust to landfill. Maintenance/demolition: dust control
Chemical zirconia plant (baddeleyite feed) [21]	2.1–3		Minimize exposure to scale, effluent discharge control
Production of Zr chemicals [21]	<0.3–3		Effluent discharge control

5. SUMMARY AND CONCLUSIONS

For exposure to radon and to external gamma radiation from building materials making up the workplace, explicit guidance (based on action levels for remedial action) exists already on what should be inside or outside of the system of regulatory control. For other exposures arising from work involving NORM, consensus seems to be emerging around activity concentrations of 1 Bq/g for uranium and thorium series radionuclides and 10 Bq/g for ^{40}K as criteria for determining whether exposure to NORM should be excluded from regulatory consideration. For materials with activity concentrations above these levels, the regulatory body needs to decide on a case-by-case basis what should be included in the system of control. Published guidance, practical experience and informed opinion suggest that such a decision might be made on the basis of a dose criterion of around 1 mSv/a, perhaps a little more for occupational exposure and a little less for public exposure.

For situations included in the system of control, a graded approach to regulation is needed. The three tiers of regulation provided for in the BSS — notification alone, notification plus registration, and notification plus licensing — all have a role to play in the regulation of work involving NORM. Protective measures need to be matched to the particular process and material involved. Often, such measures need only be fairly simple in nature, and may even be in place already in terms of existing national health, safety and environmental regulations. Appropriate protective measures for specific industrial processes and materials are being identified by the IAEA as part of the development of a suite of Safety Reports and associated training packages focusing on various NORM industry sectors. A Safety Report and training package on the oil and gas sector has already been completed, and Safety Reports on the phosphate, zircon/zirconia and titanium dioxide industry sectors are under development (to be followed, again, by associated training packages). Other NORM industry sectors are to be similarly addressed in future.

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NORM LEGISLATION IN POLAND

J. Skowronek[1], B. Michalik[1], M. Wysocka[1], A. Mielnikow[1], J. Dulewski[2]

[1]Central Mining Institute, Katowice, Poland
[2]State Mining Authority, Katowice, Poland

Abstract

On 29 November 2000, the Polish Parliament (Seym) established a new Atomic Law, significantly changing many regulations in compliance with EU law. The new legislation has been in force since 1 January 2002. This Act regulates the peaceful uses of atomic energy, real and potential risks due to ionizing radiation from artificial sources of radiation or nuclear materials, nuclear waste and spent nuclear fuel. The regulation of nuclear safety, radiation protection of humans and the environment are also provided for in this Act. In July 2001, the Seym changed the Polish geological and mining law significantly. This Act has also been valid since 1 January 2002. In this Act the regulations for the radiation protection of workers from natural sources of ionizing radiation were significantly modified. In this paper these new regulations are described with special emphasis on the lack of detailed regulations regarding mining waste with enhanced natural radioactivity.

1. INTRODUCTION

It is common perception that the dangers of ionizing radiation are associated mostly with the use of atomic energy for military, power generation or medical purposes. Even today, not everyone realizes that humans everywhere have always been exposed to ionizing radiation, and the contribution from natural sources of such radiation is up to 75% of the dose received by the average Pole [1] (see Fig. 1).

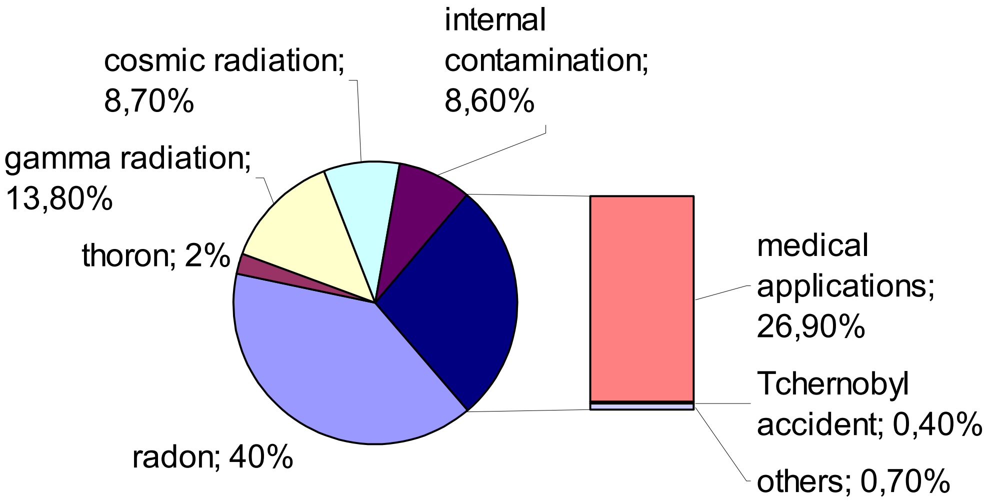

FIG. 1. Components of dose from ionizing radiation (3.3 mSv/a) received by a typical Pole

In many cases, doses from the exploitation of uranium or thorium ores and other mining and minerals processing operations are augmented as a result of processing of the material.

Until 2000 Polish nuclear legislation [2] did not mention natural radiation and the hazard it may represent. All attention was devoted to “the use of atomic energy for the social and economic needs of the country” and problems connected with endangering employees and incidental persons to ionizing radiation. In other words, it dealt with artificial radionuclides and the use of ionizing radiation from nuclear devices and systems.

Legislation in other countries was generally similar. It was only in the 1990s that international bodies involved with radiological protection started to include in their recommendations the question of protection against ionizing radiation from natural sources associated with industrial activity [3].

Several mnemonic abbreviations are used to describe materials with elevated concentrations of natural radionuclides, for example:

- NORM: normally occurring radioactive material,
- TENR: technologically enhanced natural radioactivity,

TENORM: technologically enhanced naturally occurring radioactive material. The following definition can be adopted:

TENORM: *A natural substance, raw material or other material that is not subject to legal regulations applicable to the use of atomic energy or artificial sources of radiation, that is mined, processed or present in other processes connected to any activity that may cause a relative increase in exposure to ionizing radiation and the radiation risk involved for workers or other people in the vicinity, over the natural background.*

2. RADIATION PROTECTION IN EUROPEAN UNION LEGISLATION

The importance of the potential radiological hazards from natural radiation is recognized in the Euratom Directive of 13 May 1996 [4], which introduced specific regulation in this area. Although such hazards were covered by special rules before, they were not directly included in EU regulations. The Directive does not apply to exposure to radon in dwellings or to the natural level of radiation, i.e. to radionuclides contained in the human body, to cosmic radiation prevailing at ground level or to aboveground exposures to radionuclides present in the undisturbed earth’s crust.

Article VII of the Directive obliges Member States to identify areas of work activities where exposure to ionizing radiation from natural radionuclides may be significant in terms of the need for radiation protection. Such a requirement applies particularly to:

- Work activities during which workers and/or incidental persons are exposed to alpha radiation from isotopes of radon and its daughters and gamma radiation. Underground mines and caves are given as examples.
- Work activities connected with the exploitation, processing and storage of substances not normally considered radioactive, but which contain natural radionuclides giving rise to a significant hazard to workers and incidental persons (where applicable).
- Work activities that result in the generation of waste not normally considered radioactive, but which contains natural radionuclides giving rise to a radiation hazard for incidental persons and workers (where applicable).
- Exposure of aircrew to cosmic radiation.

If a member country identifies a work activity as a real or potential radiological hazard, the Directive places such country under an obligation to monitor appropriately the hazard and if needed:

- To institute actions to decrease the radiation hazard;
- To implement radiological protection similar to that applicable to hazards arising from artificial radionuclides, resulting from the above-mentioned Directive.

Direct responsibility for implementing the radiation protection requirements is assigned, on the basis of Article 47, to the employer or producer of wastes containing TENORM substances.

Because the requirements set by the Directive are not precise as regards the definition of areas where the hazard of TENORM substances may occur, recommendations were provided by experts and issued by one of the Directorates-General of the European Commission in order to facilitate the incorporation of regulations of the Directive into the national legislation [5]. Criteria for the assessment and selection of areas, the optimization of prevention measures and requirements for monitoring are given there. Also, examples are given of NORM work activities with significant radiation protection implications, namely:

- Production of electric energy from fossil fuels,
- Processing and use of phosphates,
- Petroleum and gas production,
- Zinc and lanthanides production,
- Smelting of iron and non-ferrous metals,
- Copper production.

Generally, the Directive gives Member States flexibility in interpreting the radiation risk attributable to NORM. The basis for such actions is a compromise in the estimation of such risk, where the primary criterion is the effectiveness and measurable results. The levels of actions depend on the financial resources of the country.

EU Member States were obliged to make the necessary adjustments to their national regulations by 13 May 2000, to bring them into line with the requirements of the Directive.

3. RADIATION PROTECTION IN POLISH LAW

On 29 November 2000, the Polish Seym amended the Nuclear Law [6] by changing most of its requirements and adjusting them to comply with European legislation. The amended Act came into force on 1 January 2002. The Act describes the rules for the peaceful use of atomic energy connected to the real and potential risk of ionizing radiation from artificial sources, nuclear materials, devices producing ionizing radiation, radioactive waste and spent nuclear fuel. These actions are acceptable when requirements for nuclear safety, radiological protection of people, environment and property are met and after obtaining an appropriate authorization. According to Article 1 Point 3 of the amended Act:

The act shall be applied also to actions performed in conditions of increased hazard from ionizing radiation resulting from human activity.

Also, the Act describes the duties of a chief manager of an organizational unit performing such activity, competent authorities in nuclear safety issues and radiological protection and rules of the civil responsibility for nuclear damage. Such damage may also include negative impacts of the increased hazard from natural sources of ionizing radiation. In Article 13 Item 1 of the Act, it is underlined that:

Dose limits do not apply to the hazard of natural radiation if this hazard has not been increased as a result of the human activity, especially they do not include the hazard of the *radon in dwelling houses, of natural radionuclides being part of the human body, of the cosmic radiation at the earth's surface and of underground hazard of radionuclides in the unbroken lithosphere.*

It is regarded as controversial to exclude the danger caused by radon in dwelling houses, because in many cases its concentration may be high enough to cause the dose received by inhabitants to be close to (or even higher than) the limit; that concentration depends also on the human activity (type of building materials, type of construction or type of use of a building). This problem will be discussed in the second part of this paper.

Article 23 of the amended Act requires also that the danger from natural radionuclides in underground mines be assessed. This assessment is made on the basis of exposure measurements in the work environment. A manager of an organizational unit is responsible for such assessment and all actions to reduce the risk.

Another important requirement, contained in the Polish Nuclear Law for the first time, is that the monitoring of individual doses and internal contamination shall be performed by laboratories with accredited methods of measurement. Results of individual monitoring are stored in the central register of doses kept by the President of the National Atomic Energy Agency. The President of the National Atomic Energy Agency, on the basis of the above-mentioned act, is obliged to assess systematically the situation of the country as regards radiation. He/she is allowed to demand from every institution, organization and person to make all collected information available (Article 79).

Administrative requirements of the Nuclear Law:

The decree of the Council of Ministers of 28 May 2002 on *dose limits for ionizing radiation* [7] is fundamental to the radiation protection requirements. The decree sets the value of the dose limit, expressed as effective dose, at a level of 20 mSv/a. It allows this dose to be exceeded up to 50 mSv/a on condition that during five consecutive years the sum of the annual doses will not exceed 100 mSv. Pregnant women cannot be employed in conditions that may cause the foetus to receive a dose exceeding 1 mSv/a, and breast-feeding mothers cannot be employed in conditions that may cause internal or external contamination. For trainees and students of 16–18 years of age, the dose limit is 6 mSv/a, and for younger workers and the rest of the population — 1 mSv/a. There is no difference whether the dose is caused by radiation from artificial sources or devices emitting ionizing radiation, or increased exposure to ionizing radiation from natural sources, resulting from human activity.

The requirement to take into account the value of the radiation background when estimating the doses from ionizing radiation is a new one. The value taken to represent background should be at a level typical for the given area (or, if it is not known, the average value for Poland: 2.4 mSv/a); also, the actual time of exposure should be considered. In other words, the value of the background dose received in the given period of time should be subtracted from the measured value of the dose. Formulas to evaluate doses and risk coefficient tables are presented in annexes to the Decree.

Requirements for work with sources of ionizing radiation are given in several other Decrees concerning, among other things, documents required when submitting an application for authorization of an activity involving exposure to ionizing radiation [8], conditions for safe work with sources of ionizing radiation [9], radioactive waste [10], monitored and checked areas [11], the procedure for granting the rights of a radiation protection inspector [12], recording of individual doses [13], dosimetric devices [14], and emergency procedures in the event of radiation incidents [15].

The work activity involving exposure to ionizing radiation, described in Article 4 of the Nuclear Law, may be performed on condition that an appropriate authorization from the President of the National Atomic Energy Agency is obtained. Documents required when applying for the permission [8] have to include, among other things, grounds for embarking on such activity, information on the sources and radioactive waste generated (appropriate instructions, regulations and emergency procedure included), rights of the worker [12], the range and type of monitoring of occupational exposure, and the quality management programme of the work activity. In cases described in a separate decree, when the expected exposure is not too high, authorization by registration is sufficient [16]. It should be underlined that an employer is obliged not only to monitor the danger but also to register doses received by employees in risk category A [13]. Every person of this category will have his/her own record card in the central register of doses, kept by the President of the National Atomic Energy Agency.

Management of radioactive waste is regulated by the Decree of the Council of Ministers of 3 December 2002 *on radioactive waste and spent nuclear fuel* [10]. Levels of radioactivity content of radioactive substances are described there, which if exceeded will result in the waste being treated as radioactive waste. Wastes are assigned to an appropriate category on the basis of the value of activity and radioactive concentration of isotopes given in Annex 1 to the Decree. Radioactive wastes are divided into three categories:

- Moderate (‘warm’) — if the radioactive concentration of an isotope does not exceed 10 000 times the values given in the Annex;
- Average activity — if the radioactive concentration of an isotope exceeds 10 000 times but does not exceed 10 million times the values given in the Annex;
- High activity — if the radioactive concentration of an isotope exceeds 10 million times the values given in the Annex.

Three subcategories of wastes are set for each category, regarding the half-lives of isotopes they contain: transitory, short-lived and long-lived. Also, the Decree creates a separate category for spent sealed radioactive sources, which are then assigned according to the level of activity to one of the subcategories: moderate, average activity or high activity. Dilution of radioactive waste in order to lower the concentration of the isotopes is not permitted. The Decree sets out the requirements concerning the record and storage of wastes and formats of information tables.

According to Para. 4 of the Decree, *masses of soil or rock, removed or displaced because of an investment or exploitation of minerals, together with the processing, containing natural radionuclides, shall not be qualified as moderate radioactive waste if the sum of ratios of maximum radioactive concentrations of these isotopes, resulting from inhomogeneity of wastes, to the values described in Annex 1 to the decree, does not exceed 10 for a representative probe of waste of 1 kg.*

The above refers to the Act *on wastes* [17] as regards the exclusion of masses of soil and rock described in this way from the regulations of the Nuclear Law, on condition that the appropriate requirements are met. It allows the avoidance of a complicated legal procedure set up for radioactive wastes in the case of a huge amount of wastes containing an increased quantity of natural radionuclides produced both in mining and other industries. Now, mining sediments for which the sum of the concentrations of the radium isotopes ^{226}Ra and ^{228}Ra is lower than 100 Bq/g will not be treated as moderate radioactive waste. However, there is still the problem of how to deal with masses of rock and wastes for which the content of natural radionuclides does not exceed such limit but is much higher than the average in nature. It is undeniable that it may still cause workers or incidental persons to receive increased doses resulting form the work activity.

4. RADIATION PROTECTION IN MINING LAW

The issue of protection of miners from natural sources of ionizing radiation was addressed for the first time at the end of 1980s, in the Polish Standard *Radiological protection in underground mining plants* [18]. The sources of hazard from ionizing radiation emitted by naturally radioactive substances were defined there. The Standard set the limits of the risk for miners, both the dose limit and labour limits. The requirements for methods and devices to monitor the hazard were given. The detailed regulations concerning monitoring and prevention were to be set separately for every branch of the mining industry. For coal mining, instructions for risk monitoring [19] and guidelines for preventing the radiation hazard [20] were developed.

The coming into force of the new *Geological and Mining Law* [21] and its administrative regulations in 1994 made a part of the Standard out of date. In terms of this law, the President of the State Mining Authority issued an ordinance on criteria of estimation of natural dangers and including an excavation to an appropriate class of hazard [22], and the Minister of Industry and Trade — a decree on industrial safety [23]. These regulations were binding for all branches of the mining industry.

In July 2001, the Polish Parliament amended the *Geological and Mining Law* [24], changing the regulations fundamentally. The amended *Geological and Mining Law* became effective on 1 January 2002. Because of that fact, regulations concerning natural hazards in the mining industry were modified. Article 73 of the amended Act places an entrepreneur under the obligation not only to recognize the danger, and to undertake actions to prevent and eliminate it, but also to estimate and report the occupational risk occurring in a mining plant. Art. 73 Item 1 mentions, among other dangers in mines, the radiation hazard of natural radioactive substances, also.

The constitutional requirements concerning law sources and regulations set by the Act of 4 September 1997 on government administration divisions decided that Art. 73a Item 3 of the amended Act obliged the Prime Minister to establish, in a decree, criteria for estimating natural hazards and the procedure for classifying deposits (ledges), their parts or excavations to appropriate levels (categories, classes) of danger. The Minister for Economic Affairs had to establish detailed regulations regarding industrial safety, work running and rules of estimating and evidence of the professional risk and the use of the necessary preventive measures (Art. 78 of the Act).

The decree of the Minister of Interior and Administration *on natural dangers in mines* [25] divided underground excavations into two classes of radiation hazard:

- Class A excavations — the work area where an employee may be exposed to an annual effective dose exceeding 6 mSv;
- Class B excavations — the work area where an employee may be exposed to an annual effective dose over 1 mSv but not exceeding 6 mSv.

It should be remembered that the levels of dose presented here already include the influence of the natural background on the results of measurements and estimation of the risk — according to the requirements of the Nuclear Law. In other words, when classifying excavations to categories of the radiation hazard, the value of dose of the background received in the given period of time should be subtracted from the measured value of the dose. The decree describes the measurements of the sources of radiation hazard that shall be the basis for classification of the excavations. The following ratios of hazard from natural radioactive substances are defined there:

- The potential alpha energy concentration of short-lived radon daughters,
- The dose from external gamma radiation,
- The radon concentration in water,
- The radium activity concentration in sediments.

In the Decree of the Minister of Economy *on industrial safety, work running and technical fire protection in underground mines* [26], there are regulations concerning protection against natural sources (Section V Chapter 7) and artificial sources (Section VI Chapter 7) of ionizing radiation. The rules regarding natural sources of the radiation will be discussed here.

The decree does not use the term dose limit provided by the Nuclear Law. Par. 386 gives the definition of a dose constraint, which in practice is the same throughout the mining industry:

In underground mines, in excavations with a radiological hazard, which means those where there is a possibility of receiving an annual effective dose over 1 mSv, methods shall be introduced to preclude exceeding the usable limit of 20mSv.

Consequently, it is not possible for the hazard from natural radioactive substances in a mine in a given year to be higher than 20 mSv — that is what the Nuclear Law allows. Measurements to identify any hazard from natural radioactive substances are carried out in every underground mine, and in a mine where such a hazard occurs its level is estimated, also. Excavations of Class B radiation hazard are regarded as supervised, and excavations of Class A as monitored. Moreover, they should be marked with radiation warning signs and the entrance should be restricted to trained personnel. The decree describes the requirements regarding the monitoring in each class of hazard:

- In excavations of Class A radiological hazard, monitoring of the work environment and individual doses of employees employed there is required;
- In excavations of Class B radiological hazard, monitoring of the work environment and individual doses of employees representative for a given workplace is required.

Monitoring procedures, evidence of the results and estimation of the level of the risk are described in the Annexes to the Decree. The Decree requires that measured values be determined by a laboratory accredited on the basis of regulations on accreditation and certification [27]. It means that determinations are prepared according to the Standard PN-EN ISO/IEC 17025:2001 [28] concerning the quality system and in accordance with European requirements. It is required that persons supervising the monitoring of the radiation danger and employees taking measures in excavations are trained in an adequate scientific institution on the basis of a programme approved by the President of the National Atomic Energy Agency in agreement with the President of the State Mining Authority. Also, the basic prevention rules concerning hazards due to natural sources of radiation in mines are given in the Decree.

5. NATURAL RADIONUCLIDES IN THE ENVIRONMENT

The Nuclear Law requires the estimation of the radiation hazard and radiological situation of the country. Such estimation should also include natural radionuclides, the concentrations of which have been modified as a result of human activity. The President of the National Atomic Energy Agency, who is responsible for the estimation, is authorized to use databases of every subject collecting such information. Also, he has at his disposal the network of detecting stations of radioactive contamination and institutions measuring such contamination [29]. These institutions are involved mostly in measuring artificial radionuclides discharged to the atmosphere as the result of radiation incidents. Moreover, specialized institutions are obliged to measure natural alpha- and beta-emitting radionuclides in environmental surveys.

Also, there are regulations concerning the content of natural radionuclides in drinking water and mineral water. There are no specific demands for drinking water [30] as regards the concentration of individual radionuclides, except for ^{3}H. The maximum content of ^{3}H in drinking water is 100 Bq/L. The limit on the combined radionuclide content is specified in terms of the total dose, which is 0.1 mSv/a. According to the requirements of the Nuclear Law, this should be the incremental value above natural background. As regards mineral, spring and table waters [31], the limits for radionuclides are set in terms of the maximum concentrations of total alpha radioactivity (0.1 Bq/L) and total beta radioactivity (1 Bq/L). Moreover, it is obligatory for radon to be removed during the production process.

However, these conditions are difficult to interpret. The presence of radionuclides of natural origin (radon included) and potassium ^{40}K will influence the result. According to the requirements of the Nuclear Law, the radionuclide concentrations in the natural environment or in raw water should be subtracted from the result. The latter requires a separate measure. In the case of mineral waters, it does not seem appropriate to set the limits as total alpha or beta activities. Firstly, alpha emitters belonging to different groups of radiotoxicity may be present in water, and consequently the same activity may cause a different radiation dose to be received. Secondly, the present capabilities of national laboratories allow easy determination of radionuclides in the environmental surveys conducted, irrespective of their radiation.

6. RADIATION HAZARD IN INHABITED AREAS

Natural radionuclides in inhabited areas may cause a hazard because of the content of such substances in building materials or foundations, and because of the presence of radon in the air in rooms. These problems are discussed below in detail.

6.1. International legislation concerning hazards due to radon

In 1994 in the United States, the maximum acceptable concentration of ^{222}Rn for occupationally exposed persons was set at 370 Bq/m^3 for a 40 h working week. In 1953, the International Commission on Radiological Protection (ICRP) recommended a maximum acceptable radon concentration of 3700 Bq/m^3 in air for chronic exposure. Other limits were established in 1959: 11 100 Bq/m^3 for a 40 hour week and 37 000 Bq/m^3 for 168 hours per week. In 1985, ICRP recommended so-called annual limits on intake of radon daughters for miners at a level of 3.6 Bq·h·m^{-3}, corresponding to an average equilibrium concentration (EEC) of 1800 Bq/m^3 for an exposure time of 2000 h/a.

In several countries, Poland included, limits on radon exposure of workers were set in terms of potential alpha energy concentration of short-lived radon daughters, in units of μJ/m^3. The first reason is the fact that radon daughters, not radon itself, are the source of risk for an organism, and the second is that changes in the ventilation system, for example, will significantly influence the results such that measurements of radon concentration will not appropriately reflect the risk.

Together with the knowledge of the influence of radon and its daughters on the lung cancer hazard, the interest in dwelling houses, where we spend much more time than in a workplace, was growing. The United States was the first country where legislation concerning radon in buildings was introduced. In 1979, limits on radon concentration in buildings were set in Florida, where phosphates are exploited, and in Colorado in areas where uranium ores were mined and processed. The intervention levels, expressed in terms of EEC[1], were set at 74 and 200 Bq/m^3 in Florida and Colorado respectively.

In 1979 in Sweden, a Radon Commission was created, soon after scientists from the Radiological Protection Institute measured high concentrations of radon in buildings built on rocks enriched in uranium compounds e.g. on alum shale. In 1994, the Swedish limits were set in terms of average annual radon concentration, and are presently 400 Bq/m^3 for existing houses and 200 Bq/m^3 for new houses, following a recommendation to this effect by the European Commission in 1990 [32].

At present, regulations regarding acceptable concentrations of radon in buildings exist in most countries. In different countries the acceptable concentrations of the radon in building are defined differently. The most frequently adopted definitions are:

- Advisory (action) level — above which remedial action should be taken to reduce the radon concentration in a building;
- Intervention (enforced) limit — the radon concentration may not exceed this value, remedial action is necessary;

Apart from these, there are other definitions related to levels of radon concentration:

- Exemption (excluded) level — below which buildings are excluded from systematic monitoring;
- Investigation level — above which it is necessary to investigate and decide on a case-by-case basis.

Generally, apart from differences in names, the levels, limits and recommendations are similar in various countries. Usually, in countries where radon concentrations may vary significantly in buildings because of the complex geological structure, there are several intervention levels differently defined. Commonly, legal regulations define two levels when remedial action should be taken:

- Highest acceptable level (the higher of the two levels) — when it is necessary to undertake urgent preventive actions, usually financially demanding;
- Recommended level (the lower of the two levels) — referring to buildings where it is possible to reduce significantly the radon concentration using cheap and simple methods.

Fig. 2 shows these levels regarding existing and newly constructed buildings in EU Member States and elsewhere. It can be seen that, in most EU countries, the level is lower for new buildings than for older constructions. For new buildings, the level is 200 Bq/m^3. In Sweden, this level is defined as the highest acceptable, while in other countries it is a recommended

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[1] The equivalent radon concentration EEC is the concentration of radon in equilibrium with its daughters that is equivalent to the actual non-equilibrium potential alpha energy concentration; we get this value by multiplying the radon concentration by the radioactive equilibrium factor F.

level. Also, outside of the EU it has been decided that in new buildings the radon concentration should not exceed 200 Bq/m^3. In Latvia, the recommended level for new buildings is 300 Bq/m^3. In Switzerland two levels are used: 1000 Bq/m^3, which is the highest acceptable and 400 Bq/m^3, which is recommended.

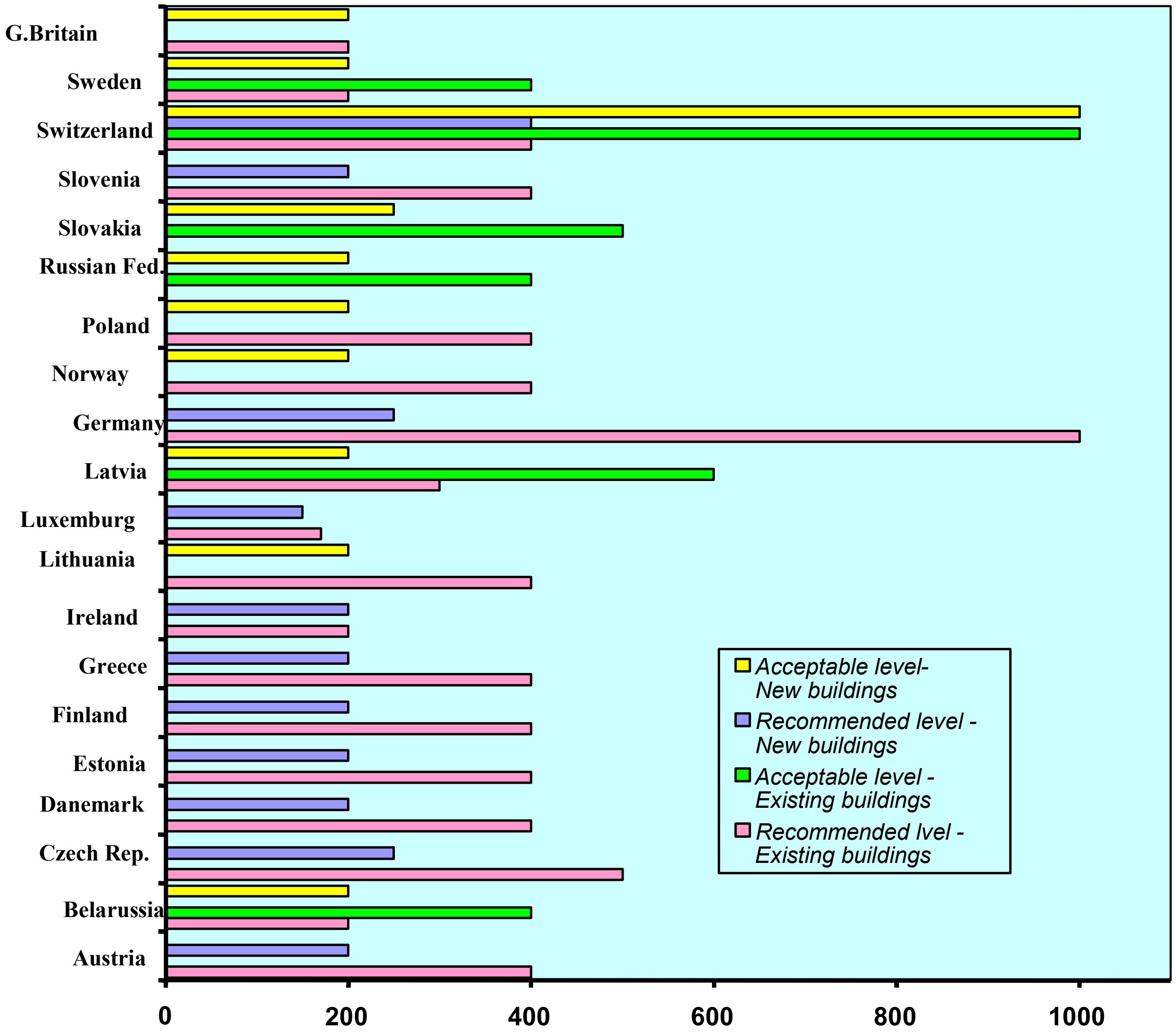

FIG. 2. Highest acceptable levels and recommended levels of radon concentration in buildings in different countries

In many non-European countries, the levels concerning both new and existing buildings are the same. In the United States, for example, the recommended level for new and existing buildings equals 150 Bq/m^3; in Canada 800 Bq/m^3; in Australia, Israel and Syria 200 Bq/m^3.

6.2. The radiation hazard in buildings in Polish law

Protection against ionizing radiation in buildings is described in the Decree of the Minister of Infrastructure of 12 April 2002 *on technical conditions that buildings and their location shall meet* [33]. In Section 8 Chapter 3 entitled: *Protection against ionizing radiation and electromagnetic fields*, the following requirements are set in §313.1 and 2:

- A building designed for people or livestock cannot be made from materials and fittings that do not meet the requirements of separate regulations on acceptable concentrations and intensities of noxious agents;
- The annual average values of equivalent radon concentration in rooms of a building designed for permanent inhabitancy by people cannot exceed the acceptable value set in separate regulations concerning radiation dose limits.

The acceptable concentrations and intensities of noxious agents are established by the Decree of the Minister of Labour and Social Policy of 29 November 2002 [34]. However, these regulations are in practice binding only for the working environment. Nevertheless, in the first paragraph it is stated that in the case of ionizing radiation the dose limits and derivative ratios are established by separate rules. In the case of the requirements set out in §313.1 of the above-mentioned Decree, the separate regulation mentioned there should be the Decree of the Council of Ministers of 3 December 2002 *on requirements regarding the content of natural radioactive isotopes in materials used in buildings designed for people and livestock and also in waste materials used in the building industry and monitoring of the content of such isotopes* [35]. Materials for the building industry are qualified on the basis of two quantities:

$$f_1 = 0.00033\,C_{\mathrm{K}} + 0.0033\,C_{\mathrm{Ra}} + 0.005\,C_{\mathrm{Th}}$$

$$f_2 = C_{\mathrm{Ra}}$$

where C_{K}, C_{Ra} and C_{Th} are the concentrations of ^{40}K, ^{226}Ra and ^{228}Ra, respectively, in Bq/kg. The quantity f_1 defines the content of natural radioactive isotopes in the examined material and is calculated on the basis of the concentrations of the activities ^{226}Ra, ^{228}Th and ^{40}K. The quantity f_2 limits the content of the radium isotope ^{226}Ra because of the danger of alpha radiation from radium and its daughters. According to the requirements of the above-mentioned Decree, the values cannot exceed the following by more than 20%:

(i) Materials used in buildings designed for people and livestock: $f_1 = 1$ and $f_2 = 200$;

(ii) Industrial waste materials used in ground-based buildings erected in urban areas or designed for buildings in a local land development plan and for levelling: $f_1 = 1$ and $f_2 = 400$;

(iii) Industrial waste materials used in ground-parts of buildings not mentioned in (ii) above and to level areas not mentioned in (ii) above: $f_1 = 3.5$ and $f_2 = 1000$;

(iv) Waste materials used in underground parts of buildings, mentioned in (iii) above, and underground buildings, rail and road tunnels included, except for waste materials used in underground mining excavations: $f_1 = 7$ and $f_2 = 2000$.

If waste materials are used to level grounds, as mentioned in (ii) and (iii) above, or to build roads, sport and leisure facilities, the absorbed dose 1 m above the ground, road or facility should be decreased to a value not exceeding 0.3 μGy/h, observing the f_1 and f_2 values. The requirement to keep to this low level of gamma dose in conjunction with the acceptable concentration of ^{226}Ra may be difficult to meet because we may expect the dose level to be exceeded even at 650 Bq/kg of ^{226}Ra in the material being used.

Also, the Decree describes requirements as regards the quality system of laboratories making the relevant measurements. Nevertheless, it is a pity that it does not refer to the Act dealing with accreditation [27], in which there is a description of the procedure for verifying whether the quality requirements are met in laboratories — such a reference is made in the case of the mining regulations. Instruction No. 234 of the Building Research Institute [36] gives the method for measuring the concentration of natural radionuclides in building materials. A part of its rules is out of date in the light of the Decree of the Council of Ministers.

As regards the radon hazard in habitable buildings, we need to say that Polish regulations have not yet been adapted to the recommendations of the European Union. As far as the criteria mentioned under (ii) above, in connection with the Decree of the Minister of Infrastructure, are concerned, we should refer to the requirements of the Decree of the Council of Ministers on dose limits [7]. However, the basic text does not mention the limits of the radon concentration. Only Para. 6 Item 2 states that the values of dose limits, mentioned in the Decree, shall be applied to the incremental hazard from natural sources of ionizing radiation as a result of human activity. It means that when the radon concentration in a building is higher that in the environment, the doses from radon should be limited also.

It is said in the Annex to the above-mentioned Decree that if the radon isotopes and their daughters, present in the air, are a source of internal exposure, the effective dose is determined by measuring or calculating the potential alpha energy. It is defined there as the total energy of alpha particles emitted during the disintegration of the daughters of ^{222}Rn down to, but excluding, ^{210}Pb and the disintegration of the daughters of ^{220}Rn down to stable ^{208}Pb, and is expressed in joules (J). The hazard is determined by converting the potential alpha energy concentration in $J{\cdot}h{\cdot}m^{-3}$ to the effective dose in Sv, with the use the following conversion factors:

- For radon in dwellings: 1.1 Sv per $J{\cdot}h{\cdot}m^{-3}$;
- For radon in workplaces: 1.4 Sv per $J{\cdot}h{\cdot}m^{-3}$;
- For thoron in workplaces: 1.5 Sv per $J{\cdot}h{\cdot}m^{-3}$.

It means that in dwellings, assuming that a person spends 80% of the time in the apartment and the equilibrium factor between the radon and its daughters equals 0.5, the dose limit is reached if the radon concentration in the apartment equals 47 Bq/m^3. The problem is that, according to the Nuclear Law, doses from radon and its daughters in dwellings in Poland are not included in the dose limits, and there are no any other reference levels for the hazard of radon and its daughters in administrative regulations.

In 1998, Instruction No. 352/98 of the Building Research Institute was issued, entitled *Methods and conditions for taking measurements of radon concentration in the air in rooms of buildings designed for permanent stay of people* [37]. It gives details of how to chose rooms for the investigations, which of the existing methods may be used for such investigations, and how to prepare documents and reports on the measurement results.

7. SUMMARY

The amended administrative regulations to the Nuclear Law and Geological and Mining Law establish the requirements as regards radiation protection of miners employed in conditions of increased hazard of ionizing radiation from natural radioactive substances. However, because of the fact that these regulations have not been issued at the same time, some of their requirements are not clear enough to the user (e.g. the necessity of including doses from the natural background when assessing the hazard). Also, some minor misprints can be found in texts of the above-mentioned Decrees.

The situation is much worse in the case of management of waste materials containing elevated radioactive concentrations of natural radionuclides, but which are not yet classified as radioactive waste. Of particular concern are the masses of soil or rock removed or displaced because of exploitation of minerals, including processing. Indeed, it is a loophole in the nuclear and environmental legal regulations.

The regulations of the Nuclear Law, specifically the Decree on radioactive wastes [10], as regards materials containing natural radionuclides, describes only in Para. 4 what *is not a radioactive waste*. For example, if the concentration of ^{226}Ra in mining sediments does not exceed 100 Bq/g, such sediments are not radioactive wastes according to the nuclear law. So, the specific procedure described in the above-mentioned Decree is not required.

But regulations concerning environment protection do not mention ionizing radiation any more. The Act on waste [17] is an example. In Annexes to that Act, radioactivity is described as neither a constituent nor a property of waste that requires it to be classified as hazardous. It means that the disposal of the waste to the environment, even if it contains natural radionuclides at enhanced concentrations such that the dose would approach or even exceed the dose limits, is still not regulated even though it may lead to an increase in the hazard from ionizing radiation in areas where it is produced, stored or utilized.

It is necessary to regulate urgently the procedure for utilizing TENORM waste, i.e. waste containing enhanced concentrations of natural radionuclides as a result of human activity.

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STATUS OF THE IMPLEMENTATION OF THE EUROPEAN DIRECTIVE 96/29/EURATOM IN IRELAND IN RELATION WITH NORM

C. Organo[*]

Radiological Protection Institute of Ireland, Dublin, Ireland

Abstract

Since 13 May 2000, following the implementation of the European Council Directive 96/29/Euratom, naturally occurring radioactive material (NORM) in Irish workplaces is subject to regulations if it is liable to give rise to a radiation dose greater than 1 mSv in a year. The Radiological Protection Institute of Ireland (RPII) is the statutory body in Ireland for matters pertaining to ionizing radiation. In 2001, the RPII undertook a review of industrial processes, which, on the basis of the literature, were thought to lead to enhanced exposure to natural sources of radiation. This paper presents the progress achieved in implementing the legislation for the gas extraction industry and for peat- and coal-fired power generation.

1. INTRODUCTION

In 1996, the European Union Basic Safety Standards Directive [1] included special provisions concerning exposure to natural sources of ionizing radiation, recognizing the specific problems that need addressing when the source of exposure has not been artificially generated but is of natural origin. In Ireland, the necessary laws and regulations to comply with this Directive were brought into force in May 2000 [2]. Accordingly, work activities where the presence of natural radiation sources (commonly referred to as NORM –Naturally Occurring Radioactive Material) is liable to give rise to a radiation dose to workers or members of the public greater than 1 mSv in a year are now controlled.

2. IDENTIFICATION OF THE RELEVANT WORK ACTIVITIES

2.1. European Commission (EC) guidance

To assist in the identification of the relevant work activities, the EC produced a series of documents mostly limited to consideration of occupational exposures. Ref. [3] recommends that the following work activities be targeted:

- Industries and work activities:
  - Coal mine dewatering plants,
  - Processing of rare earths,
  - Fertilizer/phosphoric acid production,
  - Sulphuric acid production,
  - Smelters (metal production),
  - Oil and gas industry,
  - TiO_2 pigment industry,

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[*] E-mail: corgano@rpii.ie

  - Optical industry and glassware,
- Products and materials:
  - Coal and fly ash,
  - Mg–Th alloys,
  - Foundry sands (zircon and monazite),
  - Refractories, abrasives, ceramics (zirconium minerals),
  - Thoriated welding rods and gas mantles,
  - Porcelain teeth,
  - Natural stone,
  - Fuel peat ash.

They mostly involve operations with and storage of materials as well as production of residues not usually regarded as radioactive but which contain naturally occurring radionuclides that could potentially cause a significant increase in the exposure of workers and, where appropriate, members of the public. The pathways and exposure situations that should be looked at when deciding if a work activity potentially falls under the scope of the regulations were identified in Refs [4, 5], as follows:

- Industries:
  - Phosphate industry,
  - Processing of metal ores,
  - Zircon sands and refractory materials,
  - Extraction of rare earths,
  - Manufacture and use of Th compounds,
  - TiO_2 pigment industry,
  - Oil/gas extraction,
- Types of material:
  - Mineral ores,
  - By-products and residues,
  - Products of the process itself,
- Exposure pathways:
  - External irradiation,
  - Inhalation of contaminated dust,
  - Ingestion of dirt and dust,
  - Inhalation of radon diffusing from the material,
  - Skin contamination,
- Exposure situations:
  - Proximity to large amounts of material, little shielding,
  - Dusty conditions, little respiratory protection,
  - Dirty, dusty areas, little protective clothing,
  - Enclosed room, large amounts of materials, little ventilation,
  - **Generic ES1**: stockpiles of material – exposure of warehouse operative,
  - **Generic ES2**: residues and scales – exposure of worker removing residues,
  - **Generic ES3**: process material in vessels and pipes – exposure of general worker.

2.2. NORM industries of relevance in Ireland

In 2001, the Radiological Protection Institute of Ireland (RPII) commenced a programme to identify potential NORM industries currently active in Ireland, based on the above-mentioned guidelines (Table I). Irish industries liable to produce or use diffuse NORM sources include the gas extracting and processing industry, the fossil fuel power production (peat and coal), the bauxite processing/alumina refining industry and a range of other processes producing/using bulk materials with enhanced levels of natural radioactivity (e.g. cement, fertilizers, ore extracting industries). Discrete NORM sources identified as being important in an Irish context include thoriated products and natural radioactivity in scrap, which turns up at metal dealers.

TABLE I. IRISH NORM INDUSTRIES POTENTIALLY LIABLE TO INVOLVE NORM

NORM Category	Industry
Diffuse sources	Natural gas extraction and processing
	Power generation — peat combustion/flyash
	Power generation — coal combustion/flyash
	Bauxite processing/alumina refining
	Cement production
	Handling of fertilizers
Discrete sources	Use of thoriated products (TIG welding, etc)
	Metal recycling

At the end of 2001, the RPII started a detailed investigation of the gas extraction/processing industry and of fossil fuel power production. The results obtained so far are presented in the following sections. For work activities involving NORM, the existence of a radiation risk is usually incidental to the process and the undertaking might not be aware of it. Therefore, it is always necessary to meet the staff management of a particular industry, to discuss the potential occurrence of radiological hazards and to review what a complete or partial radiological assessment will involve.

3. THE GAS EXTRACTION INDUSTRY IN IRELAND

The Kinsale Head gas field is located about 50 km off the coastline of County Cork (southern Ireland) and was discovered in 1971. It entered into production in 1978. An adjacent gas field (Ballycotton) was discovered in 1989 about 15 km north of Kinsale Head. Between the two of them, they supply approximately 16% of Ireland’s energy requirements. An additional sub sea gas well (Greensand) came on stream in 2003 to enhance the productivity of the Kinsale Head gas producing Greensand reservoir, thereby extending the exhaustion point of the Kinsale Head gas to year 2015. Since December 2003, the Kinsale Head’s operator provides firm capacity to process and transport gas extracted from another gas field (Seven Heads) located a further 35 km to the SW of the Kinsale Head field. The Kinsale Head facilities consist of two offshore production platforms, Alpha and Bravo. They both produce and process natural gas for transportation to an onshore metering station. The Bravo platform and the metering station are ‘normally unmanned installations’ (NUIs) [6].

The Corrib gas field is the second large-scale exploration project in Ireland. It is situated some 70 km west of the County Mayo coastline (NW Ireland). The operator is currently going through a planning application process for the development of an onshore terminal facility. If the project goes ahead, up to 60% of Irish domestic gas demand could be met from the Corrib field, which has a projected life of 20 years. Unlike the Kinsale Head field, there will be no manned facilities located offshore. All the Corrib's sub sea facilities will be controlled and monitored from the onshore terminal via an electro-hydraulic remote control system.

3.1. Recognized issues of radiological significance in the gas industry

Radon (^{222}Rn) is released from the gas reservoir and is transported with the extracted natural gas to the processing plant. In routine operations, as the gas flows continuously through the system and ^{222}Rn decays, its short-lived decay-products (^{218}Po, ^{214}Pb, ^{214}Bi and ^{218}Po) tend to plate out on surfaces that come into contact with the gas to form thin dark grey/black films on the internal surfaces of the equipment [7–11]. The penetrative high-energy gamma radiation they emit may result in significant occupational external gamma radiation dose rates in the vicinity of contaminated equipment. During shutdowns (repair or maintenance operations), the gas flow stops and within several hours, ^{222}Rn and its short-lived decay products have decayed. Gamma radiations are no longer emitted but the long-lived decay products of radon (^{210}Pb, ^{210}Bi and ^{210}Po) remain in the film deposits. These radionuclides emit weak gamma radiation but the energetic alpha emissions of ^{210}Po and ^{210}Pb represent a potential hazard if they become airborne and are ingested or inhaled.

Filter assemblies in gas lines remove radon decay products from the gas with other particulate matter (heavy metal decay products preferentially attach to dust particles and aerosols). Therefore, they could also become radioactive by accumulating residues with enhanced radionuclide concentrations. Sludge accumulating in separator vessels, storage tanks, gas lines and other filter assemblies contain ^{226}Ra, ^{228}Ra, ^{210}Pb, ^{210}Bi and ^{210}Po. Generally, scales do not occur at gas producing facilities as long as formation water is not produced in large quantities. This only happens towards the end of a field's life [12]. Scale inhibitors are injected in the system when formation water starts to be produced. This can raise the issue, in the future, of possible ^{226}Ra and ^{228}Ra discharges to the environment and contamination of water treatment equipment.

Extracted natural gas is not used directly as it comes from the well. It needs to undergo some processing to remove liquids and/or impurities. Depending on its composition, it might be thermally fractionated to recover Natural Gas Liquids (ethane, propane, butane, and pentane) [10]. As radon has a boiling point between that of ethane and propane, the highest radon levels are generally found in equipment associated with ethane/propane processing [7]. If the natural gas stream does not need to be fractionated (pure methane), ^{222}Rn concentrations in the production stream will remain relatively constant and will only be changed by mixing streams with different concentrations.

For workers involved in the gas producing industry, the greatest risks of exposure occur during shutdowns when the production equipment is opened or components are replaced [10, 12]. In routine operations, significant exposure to NORM is unlikely to arise as these latter are mostly contained within pipes and vessels and are therefore shielded by the walls of these vessels. However, it is possible that high energy gamma radiation can pass through the walls of such components and personnel working in close proximity of such equipment could be at risk of receiving a radiation dose.

3.2. Progress of the investigation to date

Radon gas concentrations were measured in all the Irish gas streams at the production point. The results are shown in Table II.

TABLE II. RADON GAS CONCENTRATIONS IN IRISH EXTRACTED GAS

Gas Field	Measurement location	Radon concentration (Bq/m^3)	
Kinsale Head (prior to tie-back with Seven Heads gas)	Alpha platform (inlet separator)	493; 529	Average: 696
	Terminal (export line)	775; 817	
	Terminal (calorimeter)	865	
Seven Heads (prior to tie-back with Kinsale Head gas)	Development wells	Average of 11 measurements: 147 Range: 39–252	
Combined Kinsale Head/Seven Heads streams	Terminal (calorimeter)	680	
	Terminal (calorimeter), 3 month measurement (CR-39)	411	
Corrib	Development wells	Average of 4 measurements: 99 Range: 25–190	

Samples were collected using a grab sampling technique into previously evacuated Lucas cells. In one case, radon was continuously monitored over a 3 month period (105 days) by means of passive solid state nuclear track detectors (CR-39). Combining all the measurements (excluding Corrib, as this field is not producing) gives an average ^{222}Rn concentration in the distributed Irish gas of 590 Bq/m^3. Dixon [13] demonstrated that for typical rates of gas usage and an average radon level of about 200 Bq/m^3 at point of use, the estimated annual dose for domestic users from the use of natural gas was only 4 μSv and for a critical group representing commercial users (commercial kitchens) a few tens of microsieverts. Based on these results and on the radon gas concentrations measured in Ireland, it can be concluded that the exposure of the Irish public and employees working in commercial kitchens from the combustion of gas in homes and workplaces is unlikely to give rise to an annual dose greater than 1 mSv.

It is recognized that a great part of the radioactivity in the gas extracting industry is deposited in sludge in wellhead separators and in the water/condensate separation system [14]. Both the Kinsale Head/Seven Heads and the Corrib gases are ‘dry’ and as such are mostly composed of pure methane (98.8% and 93.7% methane for Kinsale/Seven Heads and Corrib, respectively). Therefore, the main processing needed before they can commercially be distributed is dehydration. The Kinsale Head gas does not contain condensate (heavier liquid hydrocarbons extracted from the gas) although there is a possibility that some amount could be produced from the Seven Heads gas. However, at the time of writing, this was not confirmed. It is not possible to predict in advance if condensate will be produced in the Corrib field, but any condensate produced will be reused as fuel within the Terminal. On the Alpha platform, the separators are inspected every four years on average. It requires shutting down the facilities. After shutdown, the production equipment is ventilated and the inside of the vessels is cleaned. Workers are only involved at the end of the cleaning procedure to remove any residues (sludge) deposited at the bottom of the tanks. Sludges are then sent ashore for disposal and the wash-down water after the sludge is removed is discharged at sea. In 2003, the amount of sludge sent ashore was approximately 60 kg. The RPII visited the Alpha platform during a shutdown to observe the working procedures involved in the cleaning of inlet separators used in the dehydration process. A survey of the equipment (external and internal sides) was originally planned using a range of radiation monitors to determine areas of potential NORM exposure and contamination but this could not be performed for safety reasons and had to be postponed until 2005. Two sludge samples were collected from the bottom of two separators and analysed by high resolution gamma spectrometry (Table III).

Compared with results published in the literature, the Kinsale sludges contain very low levels of natural radionuclides. In Ref. [12], for example, it is reported that the maximum activity concentrations measured in sludges collected on Dutch platforms were as follows: 800 Bq/g ^{226}Ra, 500 Bq/g ^{228}Ra, 60 Bq/g ^{228}Th. Irish soils on average contain 60 Bq/kg of ^{226}Ra [15].

TABLE III. RADIONUCLIDE COMPOSITION OF SLUDGE SAMPLES COLLECTED ON THE ALPHA PLATFORM

Radionuclide	Activity concentration (Bq/kg) on a dry weight basis	
	Sludge 1	Sludge 2
^{234}Th	17.7 ± 3.6	< 6
^{226}Ra	5.5 ± 1.8	< 10
^{214}Pb	7.6 ± 0.8	1.3 ± 0.6
^{214}Bi	7.4 ± 0.8	1.5 ± 0.7
^{228}Ac (^{228}Ra)	15.4 ± 1.2	5.0 ± 1.2
^{228}Th	9.9 ± 8.7	< 17
^{224}Ra	12.6 ± 4.7	< 8
^{212}Bi	13.5 ± 2.7	5.7 ± 4.6
^{212}Pb	11.3 ± 1.3	5.4 ± 0.9
^{208}Tl	3.5 ± 0.4	1.4 ± 0.4

According to the operator, replacement of equipment (pipes, valves, pumps, etc) occurs only when the general layout of the installation needs to be modified, as was the case when the Seven Heads gas was tied back to the Kinsale Head facilities. Disused equipment is usually stored onshore in a warehouse. A visit of the storage site will be organized in 2005 to carry out a radiation survey and check that surface contaminations (^{210}Pb/^{210}Po), scales/deposits and sludges are not an issue to be considered in the future.

From 2004 onward, discharges of radioactive substances into the OSPAR region from all non-nuclear sectors will have to be reported to the OSPAR Commission [16]. Information requested will include the nature of all discharges (origin, physical and chemical properties including their radionuclide composition) and for the oil and gas industry they will also include the total discharges of radioactive substances from offshore installations (produced water, descaling and decommissioning operations and tracer experiments). For the Kinsale Head gas field, the total volume of produced water discharged at sea in 2003 was 1830 m^3.

4. FOSSIL FUEL POWER GENERATION IN IRELAND

4.1. Peat-fired power production

Annually, approximately 15% of Ireland’s electricity requirement is provided through the combustion of 3 million t of peat. While literature on the coal-fired power generation is quite abundant, studies on the peat-fired power generation industry from a radiological point of view are scarce. A study of the largest Irish peat-fired power plant, Shannonbridge (located in the Irish Midlands) was carried out in collaboration with Trinity College Dublin to review the potential occupational radiation exposures arising from the occurrence of NORM at different stages of the industrial process. Ambient gamma dose rate measurements, radon measurements, quantification of the occupational exposure from inhalation of airborne particles and gamma spectrometry analysis of peat, peat ash and effluent samples from the ash ponds were undertaken. Details of the industrial process and results are presented elsewhere [17]. The total annual effective dose likely to be received by a worker involved in the processing of peat and handling of peat ash in Shannonbridge was found to be about 0.3 mSv (312 μSv). Most of the exposure situations where workers are involved on a regular basis were investigated with the exception of maintenance duties like the cleaning of hoppers and freeing of blockages in the grit arrestors. These duties are the only ones where workers are directly in contact with the peat fly ash. However, one would not expect the associated annual effective dose to be significant as this type of work is always carried out with personal protection equipment (PPE), is undertaken in wet conditions to minimize the dust generation, occurs infrequently (3 times in a year) and is usually completed within a week. Another exposure situation is the inhalation of peat ash dust on the landfill sites (generation of windborne ash on the ash pond). This is not included in this study as the top layer of the pond, when dried out, usually forms a crust underneath which the ash is trapped. It is therefore unlikely to be wind blown.

4.2. Coal-fired power production

4.2.1. Description of the industrial process

Moneypoint is the only coal-fired power generating station in Ireland. It is located in the West of the country, along the Shannon estuary. It consumes 2 million t of world trade coal per annum and produces 40% (total capacity of 915 MW) of the total Irish demand in electricity. On its arrival at the plant, the coal is stored outdoors in a stockyard protected with a wind barrier. Two conveyor belt systems carry the coal from the stockyard to the boiler bunkers. From there, the principles of combustion and production of ash are similar to those described for the peat-firing power generation [17]. Coarse ash (bottom ash) is collected under the furnace and pulverized fly ash (PFA) is collected by electrostatic precipitators (ESPs). About 180 000–200 000 t of ash are produced annually at Moneypoint, of which 85% is PFA and the remaining 15% bottom ash. Approximately 100 000 t of PFA are sold annually to the cement industry. It enters in the composition of the cement for 5 to 10%, as a shale substitute. The remaining PFA is conditioned on site with water (to prevent dust generation) and transferred by truck to the disposal area (total capacity of 3 million m^3, approximately 10 m deep) in dry condition. The bottom ash is hydraulically transferred from the plant in a slurry form, dewatered in silos, loaded into trucks and transferred to the landfill area where it is kept separate from the PFA. Truck drivers and workers on the landfill wear dust masks. The disposal area is regularly checked for groundwater testing by the Irish Environmental Protection Agency.

4.2.2. Radiological protection issues

Clearly, the radiation doses received by individual workers at coal-fired power stations vary substantially depending on their duties, with the majority receiving trivial doses. This is illustrated by the results of the study carried out by the NRPB [18], which considered parameters such as routine operation, atmospheric releases, discharges to landfill and sales of ash. This study found that the radiological impact on the UK population of the coal-fired industry was low, with two exceptions: the use of coal ash in building materials and the possibility of high levels of naturally occurring radionuclides in scales on boiler tubes. These conclusions provided the basis of an investigation initiated by the RPII in 2003 to determine if the work activities carried out at Moneypoint were giving rise to doses liable to exceed 1 mSv to any individual in a 12 month-period.

Over the last 15–20 years, a number of studies and measurements of coal and coal ash samples have been carried out through collaborations between Moneypoint (Electricity Supply Board), the RPII, Trinity College Dublin and University College Dublin (Table IV).

TABLE IV. RADIONUCLIDE COMPOSITION OF COAL PROCESSED IN MONEYPOINT IN COMPARISON WITH COAL PROCESSED IN OTHER COUNTRIES

Data source	Country of origin of coal	Activity concentration (Bq/kg)				
		^{238}U	^{226}Ra	^{210}Pb	^{232}Th	^{40}K
Moneypoint	Poland	45	39–86	20–32	11–12	80
	Australia	—	25–40	—	2–13	20–50
	USA	5–32	6–60	10–16	5–12	30–75
	Columbia	—	25–30	—	3–9	80–100
	UK	14	24	27	8	75
Ref. [18]	UK average	20	15–20	20	7.5	—
Ref. [19]	Poland	38	—	—	30	290
	Australia	30–48	—	—	30	40
	USA	18	—	—	21	52
	UK	15	—	—	13	150
Ref. [20]	Hungary	300–500		—	—	—
Ref. [21]	Brazil		24–35		27–48	351–447

The ^{238}U series is generally in equilibrium in the coal, apart from a reduction in concentration of the later daughter nuclides due to a loss of radon during the combustion process. For each radionuclide, significant variations of activity concentrations can be observed. This is more than likely due to the different country of origin of the coal supplies. Despite this variability, activity concentrations averaged over one year of power production are generally constant.

Radionuclide concentrations in PFA are consistently higher, by a factor of ten or so, compared to those in coal (Table V). This is because at furnace temperatures, some elements originally contained in the coal are partly or completely evaporated. Between the furnace and the ESPs, the gas and fly ash stream is cooled down to remove the heat from the gas prior to its emission to the atmosphere. As the flue gases cool down, the volatilized elements condense onto the fly ash particles, giving rise to an enrichment of their concentrations in the fly ash trapped by the ESPs.

The activity concentrations of the coal processed and the ash produced in Moneypoint do not differ significantly from the ones used in [18]. Therefore, assuming similar industrial processes in Ireland and the UK, the conclusions reached in [18] should also apply to the Irish coal-fired electricity generation.

Only a small fraction of the fuel gases that contain radionuclides in gaseous form passes through the ESPs and is then discharged through the stack to the atmosphere. On average 12% of the total ash (and non-volatile elements) is removed in the furnace (bottom ash) and about 87% is removed in the ESPs (PFA). This gives a total removal in excess of 99%. Specific emissions of particulate matter are on average below 80 mg/m^3, which corresponds to an ash emission rate of about 20 g/s from each unit at 305 MW output [29] (Table VI).

TABLE V. RADIONUCLIDE COMPOSITION OF COAL ASH PRODUCED IN MONEYPOINT IN COMPARISON WITH ASH PRODUCED IN OTHER COUNTRIES

Data source	Description/coal origin	Activity concentration (Bq/kg)				
		^{238}U	^{226}Ra	^{210}Pb	^{232}Th	^{40}K
Moneypoint	Average, 1986–1990 [22]	120	134	89	53	650
	Average, 1993 [23]	116	118	—	69	545
	USA, 2002 [24]	73	137	83	72	536
	Columbia, 2002 [24]	46	71	37	34	235
	Australia, 2002 [24]	52	113	69	64	155
	Indonesia, 2002 [24]	72	118	105	90	229
Ref. [18]	UK, measurement range	43–110	44–74	98–188	19–40	—
	UK, used for dose calculations	100	100	100–200	50	900
Ref. [25]	EU, arithmetic mean	—	230	—	100	570
Ref. [20]	Hungary	1000–1500	≈ 1400	—	—	—
Ref. [26]	Poland	116–156	86–104	112–183	66–84	608–720
Ref. [27]	Greece	≤ 1443	273–1377	≤ 3986	41–65	143–661
Ref. [28]	Australia	—	96	—	170	203

TABLE VI. FLY ASH ANNUAL EMISSION INTO THE AIR FOR 5 DIFFERENT TYPES OF COAL, ASSUMING 7500 FULL LOAD HOURS [29]

Country of origin of coal	Annual emission of ash downstream of the ESPs (t)
Indonesia	386
South Africa	585
Australia	229
Columbia	71
Eastern USA	225

It is this fraction of the fly ash as well as the gaseous fraction that preferentially deposits in the pulmonary and bronchial regions of the respiratory tract and this could be an issue of concern for members of the public because of the preferential enrichment in ^{210}Po and ^{210}Pb onto the finer fly ash particles. The off-site radiological effects of the Moneypoint's operation were investigated between 1986 and 1990 using a gaseous dispersion model of radiologically active trace elements in the Moneypoint plume [30]. They were found to be negligible.

According to Ref. [18], comparing the doses arising from building materials containing 30% ash (with activity concentrations quoted in Table V) with the doses arising from materials not containing ash leads to a predicted excess external dose to that received outdoors of 600 μSv/a after subtraction of external background. This is within the range of 0.3–1 mSv/a for which the EC guidance indicates that controls on the use of such building materials should be instituted [25, 31]. Trinity College Dublin is currently investigating the significance and the extent of external doses arising from building materials containing coal ash commonly used in Ireland.

In 2001, a Dutch study [32] reported the occurrence of scale deposits on the outside of pipes within boilers of coal fired power stations, which contained ^{210}Pb at levels exceeding the Dutch regulatory limit of 100 Bq/g. Both the rate of accumulation and the composition of the scale were found to be very dependent upon the chemical environment and the temperature inside the boilers. In Ref. [18], it was conservatively estimated that a scale with a ^{210}Pb concentration of 100 Bq/g could give rise to doses in the region of 100 μSv/a for workers involved in boiler maintenance. On average, the coal processed in Moneypoint has a lower chlorine content (<2%) than the coal referred to in the Dutch study. High chlorine contents favour the establishment of reducing conditions in the boilers, which in turn lower the temperature of condensation for Pb (660°C instead of 880°C in oxidizing conditions). The Moneypoint boilers also operate at higher stoichiometry than the ones used in the Netherlands because they are fitted with the first generation of low NO_x burners, which operate in oxidizing conditions. Finally, the boilers currently in use in Moneypoint are smaller in size than in the Netherlands, which means that higher combustion temperatures are prevailing in Moneypoint. This increases the chance to exceed the condensation temperature of 880°C for Pb, thereby decreasing the chance of Pb condensation on the waterwall tubes inside the boilers. For all these reasons, the build-up of scales and therefore the potential existence of increased levels in ^{210}Pb in the Moneypoint boilers were ruled out [33]. In order to reach the future European standard for low NO_x emissions, the current generation of boilers will have to be replaced by 1 January 2008 by a second generation of large size boilers operating in forced reducing conditions. This means that from 2008 onward, the occurrence of scales will have to be controlled and monitored on a regular basis.

Radon concentrations in air at different locations throughout Moneypoint were measured in 1988. All the readings were found to be well below the Irish regulatory limit of 400 Bq/m^3. The RPII requested that a more complete radon survey be carried out to assess the radon concentrations on the totality of the premises, including offices, workshops, etc. Sixty passive solid state nuclear track detectors (CR-39) were dispatched on site for a period of 3 months and returned for analysis. They are currently being processed.

5. FUTURE INVESTIGATIONS

The largest bauxite processing plant in Western Europe is located in the West of Ireland. It produces annually approximately 1 million t of alumina from 2 million t of bauxite. A radiological assessment of the industrial process, feeding material, waste streams and work practices will be carried out. In 1992, fertilizer handling practices in Ireland were surveyed and the radiation doses to workers involved in manufacture, transport and storage, to farm workers, and to members of the public were estimated [34]. This study concluded that, since the cessation of phosphoric acid production in Ireland in 1981, the dose to the most exposed individual was unlikely to exceed 100 μSv/a and, on average, was well below this. Thorium is used as an additive in a number of industrial processes to improve heat stability of metal alloys. In the welding industry thorium is added to electrodes used in tungsten inert gas (TIG) welding to facilitate arc starting and to increase arc stability. TIG welding has particular advantages in stainless steel fabrication work and is widely used in Ireland for this purpose. It was shown in Ref. [35] that in some cases the exposure to operators involved in welding and grinding could exceed 1 mSv/a. Following an incident involving the scrapping of a radiocaesium source in the early 1990s, portal monitoring was installed at the only steel plant operating in Ireland at that time [36]. Up until the closure of the plant in May 2001, the RPII was notified of alarm activations approximately once a month and radioactive sources in scrap metal were regularly identified, the majority of which were found to be NORM materials. Dismantling/decommissioning activities of major industries such as the Irish Fertilizer Industry (IFI) and the replacement of disused equipment in still active industries (cement industry) need to be monitored and controlled for the presence of NORM contamination. Finally, disused mines and industries/companies involved in the use and transport of zircon sands and titanium dioxide will also have to be identified and reviewed.

6. CONCLUSIONS

Since May 2000 and the incorporation into Irish law by Ministerial Order of the European Basic Safety Standards Directive, industries liable to involve work activities resulting in significant exposure to natural radiation sources are subject to regulation if they are liable to give rise to a radiation dose greater than 1 mSv in a year. The gas extracting industry, the peat and coal fired power generation were the first industries to be investigated by the RPII. To date and based on the results of field and laboratory measurements, none was found to be of radiological concern, although work is still ongoing for some of the issues raised. Investigation of the bauxite processing/alumina refining industry is due to commence before the end of the current year while the TIG welding industry, disused mining activities and dismantling/decommissioning operations will be dealt with a later stage.

ACKNOWLEDGEMENTS

The author wishes to express her thanks to Mrs E.M. Lee (Physics Department, Trinity College Dublin), Mr D. Toomey (Marathon International Petroleum Ireland Ltd.), Dr J. Lyons (Environment and Chemicals, ESB Shannonbridge) and Mr F. McCarthy (Station Chemist, ESB Moneypoint) for their contribution to the work reported in this paper. The gamma spectrometry analyses of sludge were performed at the Environmental Laboratory of the RPII.

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PROPOSAL OF THE SWEDISH COMMITTEE ON MANAGEMENT OF NON-NUCLEAR RADIOACTIVE WASTE (IKA) AND THE IMPLICATIONS FOR THE MANAGEMENT AND STORAGE OF TENORM AND NORM WASTE

J.-C. Lindhé, L. Mjönes, N. Hagberg, A.-L. Söderman[*], G. Åkerblom

Swedish Radiation Protection Authority, Stockholm, Sweden

Abstract

The Swedish Government Committee on Management of Non-Nuclear Radioactive Waste (IKA) had the commitment to propose regulations regarding NORM waste to be included in the Swedish Radiation Protection Law and the Radiation Protection Ordinance. The Committee delivered its proposals to the Government by 1 December 2003. The production, handling and storage of materials classified as TENORM and NORM have previously not been subject to legal regulations, but are now to be included in the Radiation Protection Law and Ordinance. Waste that will be subject to the new regulations includes, for example, ash containing NORM and ash of bio-fuel containing ^{137}Cs from the Chernobyl accident, uranium-rich skarn from mining of iron ores (even if the mine was abandoned many years ago), gypsum waste from phosphate production, alum shale burnt to extract oil (there exist more than 50 million m^3 of such material), filters and sludge from water treatment equipment and pipes and pumps contaminated with radium due to precipitation from water. The Committee proposes that the producer that utilizes raw material containing naturally occurring radioactive substances shall have the full responsibility for future disposal of the waste. The responsibility shall include a fee to a new Government fund to cover the total costs for management and future storage of the waste. This fee is to be paid by the producer of the waste material. In case the waste consists of material from old use of natural radioactive material with no present owner, e.g. uranium use for colouring ceramics, the fund may in some cases cover the cost. This might also be the case when the disposal costs are unreasonably high for a private person, e.g. for disposal of resins used for treatment of water, which is contaminated with such a high concentration of uranium or radium that it has to be handled as radioactive waste. Radioactive waste from old abandoned mines, e.g. uranium-mineralized waste rock at old iron mines or alum shale excavations where no present owner has the responsibility for the waste are proposed to be regarded as contaminated sites and thus entitled to the same Government funds that are used for restoring land contaminated by chemical substances. The Swedish Government Committee on Management of Non-Nuclear Radioactive Waste (IKA) also has given proposals for future storage of other kinds of non-nuclear material, for example highly radioactive sources used in industry, radioactive hospital waste and smoke detectors.

1. INTRODUCTION

The following text is based mainly on a summary of the report SOU 2003:122 from the Swedish Government Committee on Management of Non-Nuclear Radioactive Waste (IKA) submitted to the Swedish Government in December 2003 [1]. In our text we have concentrated on the Committee's proposals for TENORM and NORM. At present, most TENORM and NORM materials are not subject to regulations as their content of radioactive elements are lower than the Swedish exemption levels. As an example, the exemption level for ^{238}U in equilibrium with its decay nuclides is 10 Bq/g. The IKA investigation has also

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[*] E-mail: Ann-louis.soderman@ssi.se

given proposals for future storage of other kinds of non-nuclear material, for example highly radioactive sources used in industry, radioactive hospital waste and smoke detectors. An extensive summary of the investigation is given in Safe Management of Non-nuclear Radioactive Waste: Summary of the Swedish IKA-investigation SOU 2003:122. (Copyright ÆÉ by WM Symposia, Inc. All Rights Reserved. Reprinted with permission.) For the full summary see www.sou-gov.se/ikautredningen/PDF/Summary_SOU-2003-122.pdf.

1.1. Directives

The Swedish Government on 23 May 2002 decided to set up a non-standing Committee on Non-nuclear Radioactive Waste. According to the directives of the Committee, the objective was to analyse and propose a national system for the handling and final disposal of non-nuclear radioactive waste. The system must involve a well-functioning solution with regard to organization, the environment, finance and legislation. The Committee adopted the name the IKA Committee (IKA is a Swedish abbreviation for non-nuclear radioactive waste i.e. radioactive waste unrelated to nuclear technology). Representatives from the Ministry of the Environment, the Swedish National Environmental Protection Authority, the Swedish Radiation Protection Authority (SSI), the Swedish Nuclear Power Inspectorate, the Swedish Rescue Services Agency assisted the committee. This group also included representatives from the Confederation of Swedish Enterprise and the Swedish Nuclear Fuel and Waste Management Company (SKB), owned by the nuclear power industry. The SKB now has the task of taking care of Sweden’s spent nuclear fuel and the radioactive waste from the nuclear industry.

1.2. Comprehensive aims and principal starting points

A natural starting point is the environmental objective of a Safe Radiation Environment (Säker strålmiljö) (Bill 2000/01:130 Swedish environmental aims – objectives and strategy measures) [2] that, among other things, states that:

- By 2010, the content in the environment of radioactive substances that are released by every enterprise must be so low that public health and biological diversity are protected. The additional individual dosage to the public must fall below 0.01 mSv/a per person from each separate enterprise.

To this, the government added a clarification that:

- Radiation doses are to be kept within bounds as Low As Reasonably Achievable (ALARA);
- The highest total annual effective radiation dose that a member of the public may be exposed to from an enterprise involving radiation must not exceed 1 mSv per person during a one year period.

In many cases, these aims and principals establish the absolute dose limits for people and the environment. The IAEA *Joint Convention on the Safety of Spent Fuel Management and on the Safety of Radioactive Waste Management* establishes the fundamental principal that the handling of radioactive waste must not be put onto the shoulders of future generations.

When it comes to a system for the handling and final disposal of non-nuclear radioactive waste, the principal starting points for being able to meet the above-stated aims for overall protection against radiation, as well as the aims and starting points for an environmentally adapted waste handling, can be summarized as follows:

1. With regard to *waste*, the following should apply:
   - All radioactive waste, except for that classified as cleared, should be collected and taken care of (the ‘100 % requirement’);
   - The amount of waste should be minimized and any danger due to waste is to be successively reduced;
   - The ALARA principle for radiation doses must be put into practice;
   - The handling of non-nuclear radioactive waste must fulfil the demands for protection against radiation, in accordance with the overall radiation protection aim and norms for:
     (a) The workers handling the waste,
     (b) The public and the environment,
     (c) Minimizing the discharges and risks for accidents;
   - Properties other than the ionizing radiation of waste must be taken into consideration, e.g. biological and chemical properties.
2. The *national waste system* should fulfil the following demands:
   - The waste system must be organizationally, environmentally, financially and legally well functioning;
   - A defined producer responsibility must apply, as far as possible;
   - The handling of radioactive waste must not impose undue burdens on future generations.

1.3. ‘Product waste’, ‘industrial waste’ and ‘other waste’

The Committee divides non-nuclear radioactive waste into three main categories:

(i) ‘Product waste’

This includes household products as well as products used in research, industry and hospitals etc. For this category it is easy to identify a producer who imports or manufactures the product and puts it on the Swedish market. Such activities need a licence from the Swedish Radiation Protection Authority (SSI) according to the Swedish Radiation Protection Ordinance [3].

In this category are included both products that require authorization for handling in all aspects, e.g. strong sealed radiation sources, and mass-consumption items, such as single-unit smoke detectors (with a battery), where only the manufacturer/importer is required to have authorization for handling.

(ii) ‘Industrial waste’

Radioactive substances appear naturally in nature. These substances can become concentrated in certain industrial operations that handle large amounts of naturally occurring substances. This type of waste includes TENORM, NORM and bio fuel ashes from combustion plants. Most of these processes are licensed anyway under the Environmental Code and funding for the management of the radioactive waste emanating from such practices can be settled in the licensing procedure along with specific conditions on the generation and handling of the waste.

(iii) ‘Other waste’

This concerns waste that is neither ‘product waste’ nor ‘industrial waste’. It can include certain production waste, older waste or abandoned waste without any legally responsible owner. It also includes waste with no known owner, e.g. orphan sources and radioactive waste discovered in scrap metal. ‘Other waste’ is a minor contributor of waste compared with the other two main groups, and the necessary surplus of the funding system may well cover the costs also for the management of this waste.

2. PROPOSALS FROM THE COMMITTEE

2.1. Producer responsibility

The Committee proposes the following:

- All producers of products with radioactive substances as components or products in the form of radiation sources must have imposed upon them a producer responsibility for the waste that arises when the product or the radioactive component is discarded or scrapped (‘product waste’). The term ‘producer’ means the one that produces, imports into the country or releases products on the market that give rise to radioactive waste. This responsibility must include an obligation for taking back the products after completion of use and for being in charge of the final handling of the waste.
- Producer responsibility should include a fee that would go to a special State fund for meeting the total costs of handling any radioactive waste arising, including final disposal if it is dealt with in Sweden.
- When it comes to waste to be taken back by a supplier for final disposal in the country of origin, a bank guarantee or the equivalent should be insisted on.
- The fee must meet a reasonable share of the total costs of the historic waste for which no financial producer responsibility was previously in force.
- A State fund should be established for collecting and administering the fees that producers pay for the handling of non-nuclear radioactive waste (the IKA Fund), together with making payments under the authorization of the Swedish Radiation Protection Authority (SSI).
- The Fund should be tied in with the existing Nuclear Waste Fund and share the same administrative body.
- SSI should be given a wider role when it comes to producer responsibility:
  - For checking authorization and keeping a register of producers;
  - For establishing and debiting fees;
  - For receiving compensation demands and approving disbursements;
  - For issuing instructions concerning handling and financing of non-nuclear radioactive waste;
  - For checking and monitoring the waste handling system.
- A special advisory committee with representatives of the producers and the authorities should be attached to SSI for following up and scrutinizing SSI activities within this area. The committee should also be able to make decisions on recommendations concerning the activities.

- The new system of producer responsibility for non-nuclear radioactive waste should come into effect on 13 August 2005, concurrently with the new regulations that intend to implement the EU Directive 2002/96/EG [4], concerning waste from electrical or electronic products.

2.2 'Industrial waste'

The Committee proposes the following:

- 'Industrial waste', i.e. radioactive waste that arises through enrichment of naturally occurring radioactivity or through the handling of biomass containing fallout from nuclear weapons tests or nuclear technology accidents, e.g. combustion of bio fuels, must be handled according to the Swedish Environmental Code [5] regulations, regarding ecologically harmful activities.
- Operations that can be thought of as giving rise to 'industrial waste' must, in the first place, be tested for authorization according to the Swedish Environmental Code, and this must be preceded by a description of the environmental consequences regarding radiation risks and the genesis of 'industrial waste'.
- Operations that give rise to 'industrial waste' but which have not been tested for authorization, according to the Environmental Code, must be regulated through the application of the Radiation Protection Legislation.
- It must be possible for permits for ecologically harmful operations to include conditions about preventive measures that aim to avoid or restrict radioactive waste arising, as well as conditions for how waste is to be managed and taken care of or to include delegation to the supervisory authority to issue further regulations about the management of the waste.
- In cases where the Environmental Court or a County Administrative Board issues conditions concerning the taking care of 'industrial waste' that involves demands for financial security, an enterprising party should pay a fee to the IKA Fund to guarantee that the waste can be taken care of correctly on the discontinuation of the operations. This is to be regulated in the legislation concerning the setting up of the IKA Fund.
- The radiation protection legislation should be altered so that 'industrial waste' is covered by the provisions of the legislation concerning responsibility for radioactive waste, through the Radiation Protection Ordinance being made applicable to 'industrial waste'.
- SSI should:
  - Where applicable, issue general instructions for the management and final disposal of certain 'industrial waste', with the support of the Radiation Protection Act [6], in accordance with the above-mentioned amendments;
  - Be granted the right to request a reappraisal of operations that give rise to 'industrial waste', according to the Environmental Code, and to be identified as the supervisory authority in the Ordinance for supervision [7];
  - Be given the mission of informing about problems with 'industrial waste' in the respective trade journals and to publish general advice on the management of such waste;
  - Confer with the Swedish National Environmental Protection Authority for being responsible for the supervisory and regulatory committee; SSI ought to be included in this committee.

2.3. ‘Other waste’

The Committee proposes the following:

- Those liable for payment to the IKA Fund should deposit a proportionate contribution to the Fund, in order to meet the costs for dealing with any ‘other waste’ where it is not possible to establish a legally responsible party for the waste.
- Within their present inventory programme and yearly suggestions concerning measures to decontaminate contaminated land and deal with hazardous waste in old industrial plants, the County Administrative Boards should be given the mission to include radioactive waste and radioactive contaminated land. SSI should be given the mission to assist the County Administrative Boards and the Swedish National Environmental Protection Authority with information and expert knowledge in this work. The appropriation for decontaminating and dealing with hazardous waste should, where appropriate, also be available for measures to decontaminate the radioactive waste.
- Those operating activities that give rise to radioactively contaminated matter or induced radiation must be able to be charged with paying the fee for dealing with the waste to the IKA Fund.

2.4. Clearance

The Committee proposes the following:

- SSI should be given the opportunity to make decisions about general exceptions to the Radiation Protection Act [6], when this is well founded, from the point of view of radiation protection and when it concerns the demands for an effective management of non-nuclear radioactive waste; a so called *clearance*.
- Amendments should be made to the Radiation Protection Ordinance [3] to achieve this goal.

2.5. Final disposal and the role of Swedish Nuclear Fuel and Waste Management Company (SKB) and Studsvik in the waste system

2.5.1. The Committee’s proposal for final disposal

At the earliest possible opportunity, the State should commence negotiations with the Swedish Nuclear Fuel and Waste Management Company (SKB) regarding a general agreement for the final disposal of non-nuclear radioactive waste, based on the grounds which the Committee discussed with SKB during the investigation. These imply, among other things, that SKB undertakes the final disposal of all non-nuclear radioactive waste that requires such final repositories as in any of its existing or future plants and will do this, in principle, for cost price. Furthermore they imply that SKB must be able to receive compensation also for actions taken for the adaptation of the storage and for the reappraisal of the licensing conditions for the repositories when necessary.

2.5.2. The Committee’s assessment of Studsvik AB (Ltd.)

In the 1950s, most Swedish nuclear research was located at Studsvik, on the east coast 100 km south of Stockholm. There, two research reactors were built, together with a waste handling system and an intermediate repository for low and medium level radioactive waste. Originally, the enterprise at Studsvik was State owned, but it is now privatized. As Studsvik AB is the only Swedish enterprise that handles non-nuclear waste, the company has a monopoly position on the market for services. This is now a problem as Studsvik AB has no obligation for taking care of radioactive waste and the cost for future storage of long-lived radioactive waste is not known. Thus, Studsvik can refuse to handle and dispose of radioactive waste if the cost for storage is not covered or if it contains long-lived radionuclides, e.g. radium or thorium. Also the costs for handling and storage are too high for private persons and small enterprises to bear.

However these problems will substantially decrease if the Committee's proposals for a national system for non-nuclear radioactive waste are realized. The grounds for Studsvik AB, and any other possible players on the market, for not handling certain kinds of radioactive waste, disappear partially or completely. The Committee therefore concludes that there is presently no need for any duty, regulated by law, to take care of non-nuclear radioactive waste. Nevertheless, the Government ought to closely follow the development of this issue.

3. DELIBERATIONS

3.1. Clearance

Today, SSI is unable to issue regulations on clearance (i.e. exceptions to the entire Radiation Protection Act application), although that it may decide about clearance when it comes to individual cases. However, there are good possibilities for introducing a more operative clearance system in Sweden — without waiving the basic radioactive protection demands or obstructing the environmental goal for a secure radioactive milieu from being reached — that stands in agreement with the EU regulatory framework. Further development work in SSI is needed, however, before an operative system for clearance can begin, which will meet the highest demands placed on radiation security. It is taken for granted that a change is made to the Radiation Protection Ordinance [3] that will permit general decisions about clearance from the scope of application of the Radiation Protection Act [6].

SSI has pointed out a list of problems with the current management of radioactive waste. One point concerns the case when an operator of an enterprise goes bankrupt or closes down operations. Waste from radioactive sources may then lack a legally responsible person who can cover the costs of the management and possible final disposal of the waste. The same thing concerns orphan radiation sources that occur in nature or at waste service sites. A producer responsibility, that lays the responsibility for the waste management on the producer and not on the owner, has great potential for substantially reducing the number of cases of an owner considering disposal of a hazardous radiation source illegally or in an inappropriate manner. The degree of hazard of the radioactive waste and the need for being able to take care of all waste provides motivation for a producer responsibility. A suitably formulated producer responsibility makes it also possible to successively reduce the amounts of waste and diminish the degree of hazard of the waste. Generally, there is a direct relationship between the amount of waste that a radioactive product gives rise to and the costs for dealing with the waste. Reduced activity in the product simplifies the management in all aspects when it comes to taking care of the waste. Reduced activity and short-lived isotopes diminish the demands on final disposal and, therefore, make waste management cheaper. Even when designing a product, producers have greater opportunities for taking into account these possibilities for making the products cheaper to deal with.

In the Committee's opinion, there is, therefore, motivation to develop a system of producer responsibility for radioactive products. Moreover, such a producer responsibility has to be added to the existing Radiation Protection Act regulatory framework.

A producer responsibility for 'product waste' should partly include an obligation for the producer to be responsible for the collecting, management and final disposal of radioactive waste, and partly a liability to establish financial guarantees for the management and final disposal of the waste. Producer responsibility should also include historic waste, like orphan radiation sources. In the Committee's opinion, the producer responsibility model is the system that best meets the demands made on non-nuclear radioactive waste, with regard to 'product waste'. This also has the advantage of leaving considerable room for the market to formulate the systems that can provide for collecting, managing and final disposal, if necessary, in a cost effective manner.

3.2. Demands for financial solutions

A system with financial guarantees must be created for dealing with radioactive waste, so that the resources needed can always be guaranteed. Due to the hazardous nature of the waste, there is motivation for not allowing radioactive substances to become orphaned or to be illegally utilized for malicious purposes. Even if companies go bankrupt or change the direction of their operations, the necessary resources must exist for taking care of the radioactive waste.

When it comes to non-nuclear radioactive waste, the demands have to be high. A financial system for non-nuclear radioactive waste ought to meet the following demands:

- Having the potential to result in a 100% safe keeping;
- Secure financing over a long period;
- Providing high and secure yields on established resources;
- Allowing fees or appropriations that lead to reduced amounts of waste and diminished degrees of hazard in the waste;
- Having to function well:
  - Organizationally,
  - Environmentally,
  - Financially,
  - Legally.

The demands will be especially clear if one considers that, in most instances, radioactive waste must be stored, sealed in special rock shelters, for many centuries. Suitably sealed storages do not presently exist and will not become a reality for another 30 years or so. The financial resources also have to be secured for long periods. The delay is so long that many companies might have left the market for various reasons when the costs for final disposal arise.

Today, there exist four State funds for waste. They are the Nuclear Waste Fund, the Studsvik Fund, the Battery Fund and the Car Wrecking Fund.

(i) The Nuclear Waste Fund

The Nuclear Waste Fund is a State fund system, created in 1981 to ensure financing of radioactive waste from nuclear power stations. The financing is regulated by legislation (1992:1537) concerning the financing of future expenditure for spent nuclear fuel. The fund has a book value of SEK 29.4 billion (approx. €3.2 billion) and a market value of SEK 31.3 billion (approx. €3.4 billion).

(ii) The Studsvik Fund

This is a fund for financing existing waste from, among others, the closed combined power and heating nuclear plant in Ågesta, the closed research reactor R1 in Stockholm, and waste from the research reactors at Studsvik.

(iii) The Battery Fund

The Battery Fund is a State funding system to ensure the taking care of environmentally hazardous batteries. The total balance for mercury batteries is SEK 68·4 million (approx. €7.4 million), for lead batteries SEK 262 million (approx. €28.5 million) and for nickel cadmium batteries SEK 243 million (approx. €26.4 million). The total fund balance amounts to SEK 573 million (approx. €62.3 million).

(iv) Other financial solutions

As set out above, there are several alternative solutions for guaranteeing the financing of radioactive waste. Along with the State funds for covering the costs of waste, there are also examples of private solutions. These apply to, for example, electronic waste and, in part, mercury.

The Committee proposes a State fund — on the basis of the discussion going on regarding the possibilities of meeting the demands placed on the financial mechanism for radioactive waste, a State fund is the Committee's proposal for guaranteeing resources for managing 'product waste'. As will be seen from the Committee's proposal concerning 'industrial waste' and 'other waste', the proposed State fund solution could also be utilized for 'industrial waste' as well as certain types of 'other waste'. When it comes to the administration of paid resources, the association of the IKA Fund with the Nuclear Waste Fund is the only realistic and efficient alternative.

3.3. Waste resulting from the concentration of naturally occurring radioactivity

3.3.1. Industrial waste

Radioactive substances occur naturally in nature, e.g. radium. These substances can become enriched and concentrated in certain industrial processes that deal with large amounts of naturally occurring substances. This applies, for example, to water flows in pipes and contaminated oil. Industrial water is filtered in many contexts and these filters can concentrate radioactive substances that occur naturally. This even applies to heat exchangers and municipal drinking water treatment works. Peat ash and ash from the combustion of bio fuels may contain significant amounts of radioactive substances. Ash from bio fuels may contain ^{137}Cs.

This waste, usually called NORM (naturally occurring radioactive material) or TENORM (technologically enhanced NORM), has to be introduced into the waste flow under the same criteria as for other radioactive waste. It occurs, in most cases, in activities for which the primary objective is not associated with radiation, i.e. activities that are not in operation with radiation according to the definition in the Radiation Protection Act [6]. The enriched or concentrated radioactivity is an unwanted by product, as are other types of waste or pollution from operations. Waste that occurs in this manner in enterprises that are not licensed to operate activities involving radiation, is called 'industrial waste'.

3.3.2. The Environmental Code and (radioactive) 'industrial waste'

According to the Environmental Code [5], environmentally hazardous operations are considered to be, among others, the use of land, buildings or installations in such a way that inconvenience may occur to the surroundings through ionizing or non-ionizing radiation, among other things. This makes it possible to assess such operations for authorization that give rise to inconvenience due to radiation from radioactive waste, as an example. The Code also states that it can be forbidden to release or store solid waste or other solid substances, if this can lead to land, water areas or ground water being polluted without authorization.

Furthermore, according to the Environmental Code [5], all who operate activities must take the necessary protective measures, observe the necessary limitations or practice the necessary precautionary measures for protecting against damage or inconvenience to people's health or the environment. The Environmental Court or a County Administrative Board realizes a permit appraisal for environmentally hazardous operations. According to the Environmental Code, a judgement on a permit, where appropriate, contains decisions about the conditions necessary for the management of waste and recycling and reutilization if the management, recycling or reutilization can give rise to inconvenience for the external environment. The permit appraisal organ can further commission the supervisory authority to issue detailed conditions for dealing with waste. It is, consequently, fully possible to assess (radioactive) 'industrial waste' for authorization according to the Environmental Code.

In the Environmental Code, there are regulations concerning Accounts of Environmental Consequences (MKB). These constitute an important component, when assessing 'industrial waste'. SSI has to play a proactive role in informing about problems with 'industrial waste', aimed both at the permit assessing authorities and the supervisory authorities, as to the lines of business involved.

It must be the role of SSI to be able to issue general advice and instructions for 'industrial waste', operative supervision and supervisory guidance in those cases where, according to the Environmental Code, other organs are the supervisory authorities. This could be achieved by adding SSI in the Ordinance (1998:900) regarding supervision [7], according to the Environmental Code [5]. This implies that the authority would be included in the supervisory and regulatory council of the Swedish National Environmental Protection Authority.

SSI has suggested to the Committee how the definition of operations involving radiation, in the Radiation Protection Act [6], could be expanded to make it possible to issue general advice and instructions in those cases where 'industrial waste' is not appraised, according to the Environmental Code. This would be achieved through an amendment to the Ordinance on supervision according to the Environmental Code.

The Environmental Code applies in parallel with the Radiation Protection Act. Those that operate activities with radiation are also liable, apart from the provisions in the Radiation Protection Act, to observe and put regulations of the Code into practice. If a conflict between the legislation should arise, i.e. a regulation in the Environmental Code should be inconsistent in relation to some regulation in the Radiation Protection Act, then the provisions in the Radiation Protection Act take precedence over the Environmental Code. According to the Environmental Code, the permit appraisal authority should pay attention to these relationships during the appraisal itself.

3.3.3. Connection to the financing system for 'product waste'

With the aid of the Environmental Code regulations, it is possible to make demands on operators of activities to allocate resources for after-treatment, by taking care of waste arising. The easiest way of achieving this is for the permit appraisal authority, in the permit, to enlighten the operators of the activities that they are liable to pay a fee, according to legislation for the financing of non-nuclear radioactive waste. In this way, the IKA Fund could be a general instrument for the financing of radioactive waste that demands financial guarantees for being taken care of and/or for final disposal, if necessary.

3.4. Final repository capacity

At present in Sweden, an underground repository for low and medium waste (SFR) exists at the Forsmark Nuclear Power Plant. The owner of this repository is SKB. A final underground repository for highly active and long-lived waste (SFL) is to be built within 30 to 40 years. At Studsvik, non-nuclear radioactive waste can be temporarily stored. There is a rock shelter for 6000 m^3 of packaged waste, with a large available capacity. With the information available and with today's know-how, the Committee estimates that this space will probably be sufficient for the whole period of 40–50 years until SFL is ready.

3.4.1. SKB and final disposal

Today, SKB has no direct obligation to accept non-nuclear radioactive waste, but SKB has itself expressed its ambition thus: "We take care of Sweden's used nuclear fuel and radioactive waste so that the environment and people's health are protected in the short and long term." As a basis for this, SKB has undertaken to finally dispose all non-nuclear radioactive waste that can be disposed of in a SKB final repository, under certain conditions. According to SKB, the principle would be cost price for final disposal. Resources from the IKA Fund could be requisitioned to cover the increasing general costs for the licensing or relicensing that could be demanded, so that it will be possible to finally dispose of certain substances and material that were not originally included in the planning.

As stated, the matter of final disposal should not be any great problem in the future from the aspect of capacity. Non-nuclear radioactive waste volumes are significantly less than the volumes of nuclear waste, even if the isotope combinations can vary. With the final repository that exists, SFR, and the planned final repository, SFL, it should be possible to finally dispose all non-nuclear radioactive waste within the foreseeable future. Under certain circumstances, a commercially practicable alternative could be to use additional space in the planned rock shelter repository for mercury.

3.4.2. Forms for ensuring that Studsvik accepts radioactive waste

If the Committees proposals are realized, Studsvik no longer needs to absorb risks when it comes to final disposal. Those responsible for producing waste or other parties can close their own agreements with SKB if the final disposal part and Studsvik's services can be purchased separately. With that, the Studsvik operations and services offered will be wholly independent and there will be well-defined sections in the waste management chain. The Committee expects that the market, with its prerequisites, will solve the problems for Studsvik in its present situation and the problem of Studsvik's monopoly position will mainly disappear. The new market situation could also open up to market participants other than Studsvik AB. This means that, even if it is possible to legislate for an injunction for handlers of waste to accept radioactive waste, then this solution should not be used in the situation that is expected to arise.

4. SURVEYS — TYPES OF WASTE AND WASTE FLOWS

4.1. Consumer items

Included in this category are smoke detectors and products that are sold as night-seeing aids in the form of telescopic sights, bearing compasses and bearing binoculars. A great deal of radioactive waste also occurs from consumer items from former times, when it was permitted to use clocks with luminous faces and uranium compounds could be used to give a lustre to colours on ceramics and, sometimes, even on crockery and glass.

4.2. NORM, TENORM etc.

This type of waste comes mainly from industrial processes that use large volumes of NORM. These have, as a rule, been enriched through the processes. A technical term for this is TENORM. Residual waste, such as slag from mining operations, sand filters or the equivalent from water works etc. are, in certain cases, so enriched with natural radioactive substances with long half-life, that the waste must be taken care of in a special manner.

Combustion of bio fuels and peat gives rise to ash with increased contents of radioactive caesium, predominantly from fallout after the Chernobyl accident. About 100 000 t of bio fuel ash from wood fuel and 30 000 t of peat ash are produced annually.

Depleted uranium is a residue product that remains when natural uranium is enriched to form nuclear fuel or nuclear weapons. It is only when the depleted uranium has to be taken care of as waste that it presents a radiation protection problem. By a rough estimate, there are a few dozen tonnes of it in Sweden. The biggest environmental hazard comes from the chemical toxicity of uranium.

4.3. Open and sealed radiation sources

Sealed radiation sources in industry are sometimes returned to the supplier when they are scrapped, but it is often the owners themselves who are responsible for the waste being taken care of within the country. Non-nuclear radioactive waste from hospitals, research and education often consist of *open* radiation sources, e.g. when the radioactive substance is found in the form of a liquid solution. At a rough estimate, Sweden generates a few dozen kilograms of waste from radioactive chemicals each year, which does not cause any great waste problem. Solid waste from these operations can be protective clothing, glass jars etc. with small amounts of radioactive substances. The suppliers take most of the sealed radiation sources back as a rule, in some kind of exchange system. For practical reasons, the scrapped sources are always sent abroad to the country they came from, in such cases. However, radiation sources from the medical care sector still occur which, after many years' usage, must be sent to Studsvik to be taken care of. Activities in research, hospitals and education are expected to continue at the present rate.

To sum up, it concerns 100–200 strong to medium strength radiation sources from industry, hospitals, research and education that need to be finally disposed of in Sweden, every year.

Abandoned radiation sources lack known lawful owners responsible for their scrapping. In today's circumstances, the one who finds such an orphan source becomes likewise its owner and, with that, according to the Radiation Protection Act [6], is responsible for taking care of it. It is important to build an efficient system for reducing risks from abandoned sources, since these can be the cause of grave consequences with financial damages and acute radiation injuries. The IAEA has also warned against terrorists using orphan radioactive waste to make terror bombs, the so-called dirty bombs. In Sweden, abandoned radiation sources are reported to SSI once or twice a year.

5. EXPECTED OUTCOME

The IKA Committee's proposals are now handed over to the Government. After remittance the Government's final proposal will probably be presented to the Parliament in early 2005. It is expected that the new regulations and agreements will be in force later in 2005.

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NEW REGULATORY DEVELOPMENTS AND GUIDANCE IN THE EU WITH REGARD TO NORM

T.P. Ryan[1*], A. Janssens[1], E. Henrich[1], J.-L. Daroussin[2]
[1]European Commission, DG TREN, H4, Radiation Protection, Luxembourg
[2]IRSN/DEI/SARG/LERAR, Fontenay-aux-Roses Cedex, France

Abstract

A framework for a regulatory system for the control of exposure of workers and members of the public to natural radiation sources was introduced in Council Directive 96/29/Euratom 13 May 1996. The Directive deals with basic safety standards for the protection of the health of workers and the general public against the dangers posed by ionizing radiation. In particular Title VII of the Directive deals with significant increases in exposure due to natural radiation sources. This applies to 'work activities' or industries within which the presence of natural radiation sources leads to a significant increase in the exposure of workers or members of the public and which cannot be disregarded from the radiation protection point of view. In accordance with Articles 40 and 41 of the Directive, each Member State is directed to ensure the identification of such work activities and to setting up the appropriate means for monitoring exposure and applying radiation protection measures as set out in the Directive. To assist Member States with the implementation of the Directive in general and Title VII in particular, the Commission has published a number of guidance documents. However, no guidance has yet been developed in relation to discharges from NORM industries. In order to begin to address this, a study was carried out, the results of which have now been delivered. The aims of this study were: to review the regulatory framework within Member States regarding the implementation of Title VII of the Directive with respect to effluent discharges; to provide guidance for a realistic dose assessment methodology for NORM discharges and to establish criteria allowing the rapid identification of effluent discharges potentially requiring regulatory control. The results of this study will be considered by the Article 31 Group of Experts with a view to advising the Commission on appropriate guidelines. In addition, the Commission has awarded a contract with a view to developing a Network for stakeholders involved in NORM issues to share experience and to build a common understanding of the inherent problems and workable solutions. The Network will aim to identify and promote good practice, to enhance risk awareness and to create a common risk culture between stakeholders. It will act as an archive for relevant documentation that will be available to the members of the Network.

1. INTRODUCTION

The objective of this paper is to provide an update on activities by the European Commission (EC) in the domain of NORM and in the context of the basic safety standards laid down in Council Directive 96/29/Euratom (the 'Directive') [1]. Two recent initiatives in particular are summarized:

- The outcome of a study of progress in implementation into national legislation of regulations concerning NORM in Member States [2];
- A proposal for the creation of a network of NORM stakeholders in Europe (NORMNET).

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[*] E-mail: thomas.ryan@cec.eu.int

In addition, the conclusions of a recent study, MARINA II [3], as they relate to NORM industries are also presented providing an example of the impact of some NORM industries on the European marine environment. MARINA II was commissioned by the EC as part of its ongoing commitment to the OSPAR[1] process.

2. BACKGROUND

2.1. Chapter III of the Euratom Treaty

The Treaty establishing the Atomic Energy Community (Rome, 1957) introduced, at a very early stage of the development of nuclear energy, the need to ensure adequate protection of the health of workers and of members of the public in relation to the dangers arising from ionizing radiation. Article 2b of the Treaty lays down that the EC shall "establish uniform safety standards to protect the health of workers and of the general public and ensure that they are applied". Chapter III (Health and Safety, Articles 30–39) is concerned with radiation protection, in particular with safety standards (Article 30–33) and specifically with environmental radioactivity (Articles 34–38).

2.2. European Standards

The first standards were laid down in 1959 and they have been continuously updated in the light of international guidance (via the International Commission on Radiological Protection (ICRP)) on radiation effects and related concepts and taking into account practical experience with national legislation and operational radiation protection. The most recent revision to the standards was adopted in May 1996 in the Directive. Implementation of these standards through national legislation was scheduled for completion in May 2000.

2.3. The Basic Safety Standards Directive and NORM

The provisions on work activities involving exposures to natural radiation sources are set out in Title VII of the Directive. Articles 40 and 41 establish a stepwise system in which Member States are required:

- To identify, by means of surveys or by any other appropriate means, work activities that may be of concern;
- To set up appropriate means for monitoring exposure in the identified work activities;
- (As necessary) to implement corrective measures to reduce exposure pursuant to Title IX of the Directive (Intervention);
- To apply all or part of the system of radiological protection for practices, as prescribed elsewhere in the Directive.

The structure of the Directive is such that a priori all work activities are within its scope. It is for Member States to identify those work activities that are of concern and that require an appropriate form of regulatory control. Surveys will relate to the characteristics of industries processing materials with (enhanced levels of) naturally occurring radionuclides (NORM).

The approach of Title VII of the Directive is thus rather general offering flexibility for Member States to take into account national circumstances. Such flexibility is necessary in

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[1] Oslo and Paris Commission

view of the fact that in many Member States there may be little experience with the regulation of natural radiation sources.

The economic implications of controls imposed on industries processing raw materials may be such as to require a harmonized policy within the European Community. The Group of Experts set up under Article 31 of the Euratom Treaty have recognized this need and have provided technical guidance on the implementation of a system of protection for workers, not only in NORM industries but also for radon in workplaces and for exposure of aircrew to cosmic radiation [4].

3. REVIEW OF PROGRESS ON IMPLEMENTATION BY MEMBER STATES

3.1. Context

Following the publication of the Directive, the EC funded research to assist Member States in the area of NORM and subsequently published related guidance (see in particular Refs [5, 6]). Such documents are not regulations but guidance, and carry no obligations for Member States. Ref. [5] provides reference levels for identifying those industries for which workers exposure should require regulatory control. Ref. [6] relates to exemption and clearance and is of particular relevance to the workplace. Significantly, no guidance has yet been developed in relation to discharges.

Within the Directive, activities involving naturally occurring radionuclides (other than those used for their radioactive, fissile or fertile properties) likely to result in a significant increase in exposure of workers or the public were defined separately in Title VII as ‘work activities’. A limited review of the regulatory framework in EU Member States in relation to the regulation of work activities has been undertaken as part of the current study. The objective of the study was not a legal review of Member States’ compliance but of the regulation of the impact on the public of work activities and, specifically, of discharge control for such activities. Information gathered for the review consisted of data from recent papers and publications and in particular from the responses, by national regulators or by other national advisory bodies, to a questionnaire.

The main provisions relating to work activities are contained in Title VII of the Directive. In terms of Article 40, these activities should be identified by Member States. Once a work activity has been identified as of concern, Article 41 states that Member States shall require exposure to be monitored and corrective/protective measures implemented, as necessary, pursuant to part or all of the requirements set out in rest of the Directive: in Titles IX (intervention), III (reporting and authorization), IV (justification and optimisation), V (estimation of effective dose), VI (fundamental principles of radiation protection for workers) and VIII (radiation protection for the public).

Ref. [6] provides Member States with some guidance in this area. Two significant conclusions of this publication were:

- For NORM, one simple set of levels covering the concepts of both exemption and clearance is appropriate;
- Rather than an individual dose criterion, a dose increment in addition to background exposure of the order of 0.3 mSv/a for workers as well as members of the public is appropriate.

Although one set of values is recommended, it is also emphasized that while, for exemption, the levels must be fixed (to allow industries to decide whether reporting is necessary), some flexibility for clearance will be necessary to allow for the best option for waste management and for the specifics of particular industries. So, although the levels may be the same, the concepts remain different, requiring separate approaches.

3.2. Main findings of the review

3.2.1. General

On reviewing the available information, it is noted that all EU Member States have acknowledged the issue of 'work activities' within their regulatory structure. Often Member States have concentrated in the first instance on the impact on workers. However, Member States appear to be at an early stage in the area of identification of significant exposure to the public from wastes and discharges.

Initial identification of general groups of industries that may be affected, based on published reports, has been completed in 11 of the 15 countries, with the remaining 4 countries currently in the process of their initial identification process (Fig. 1). A number of countries are beyond the initial identification stage and have completed detailed studies into the industries within their countries establishing those processes that require regulation. Such countries include Germany, the Netherlands, Finland, Sweden and the UK. Denmark and Greece have completed detailed studies into some industries, but the identification process is still ongoing. In the other Member States where the initial identification process is complete, detailed investigations are either planned or are ongoing.

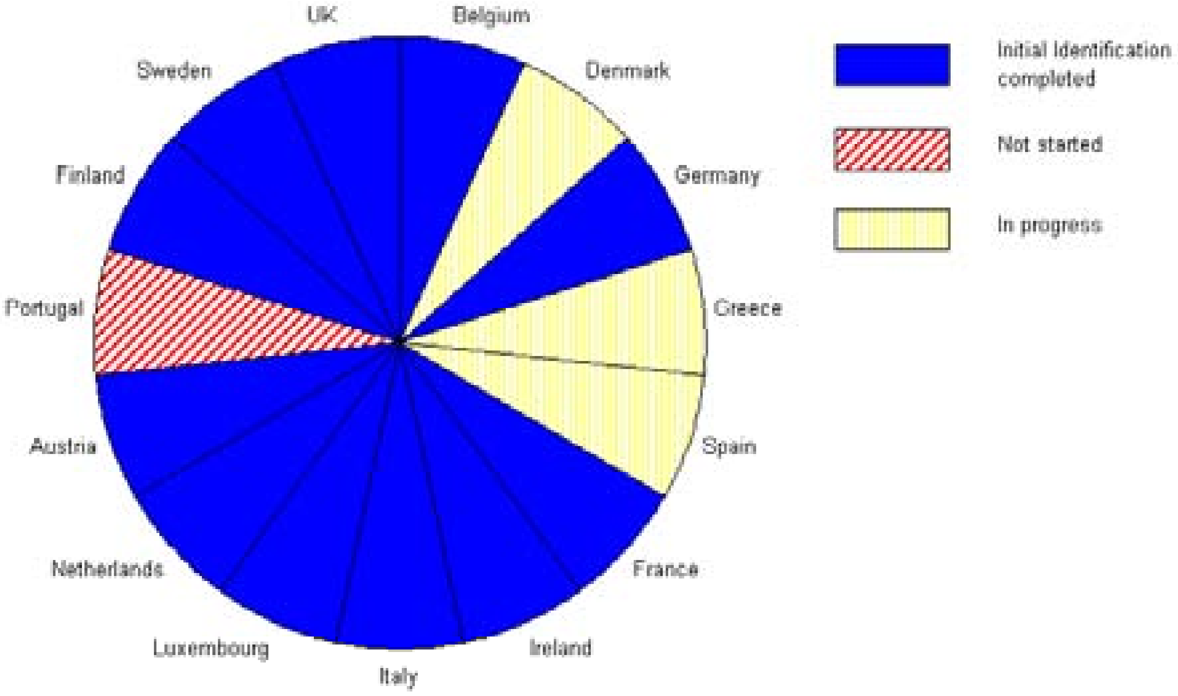

FIG. 1. Progress in the identification of work activities in Member States

Of those Member States responding to the questionnaire issued as part of the study, about 75% had regulations relating to NORM and have used the concept of exemption within their legislation (Figs 2 and 3). By restricting regulatory control to those industries where, for example, effective doses could exceed 1 mSv/a, regulatory resources can be concentrated on those industries of significance.

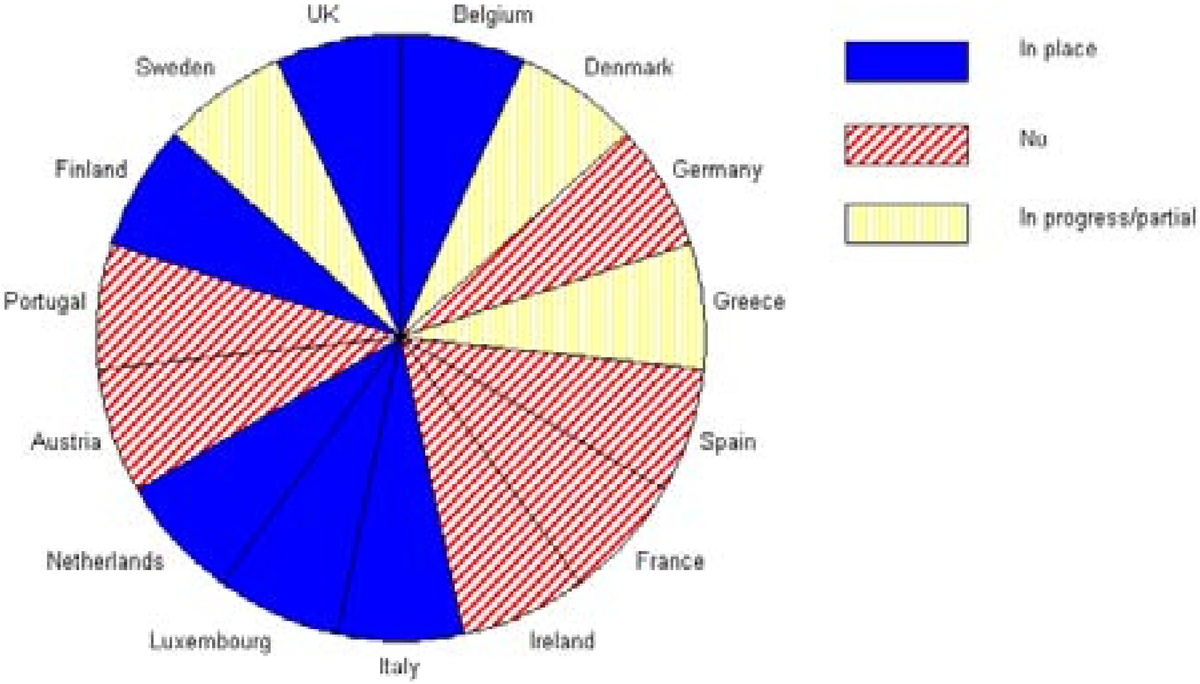

FIG. 2. Existence of discharge controls for NORM within Member States

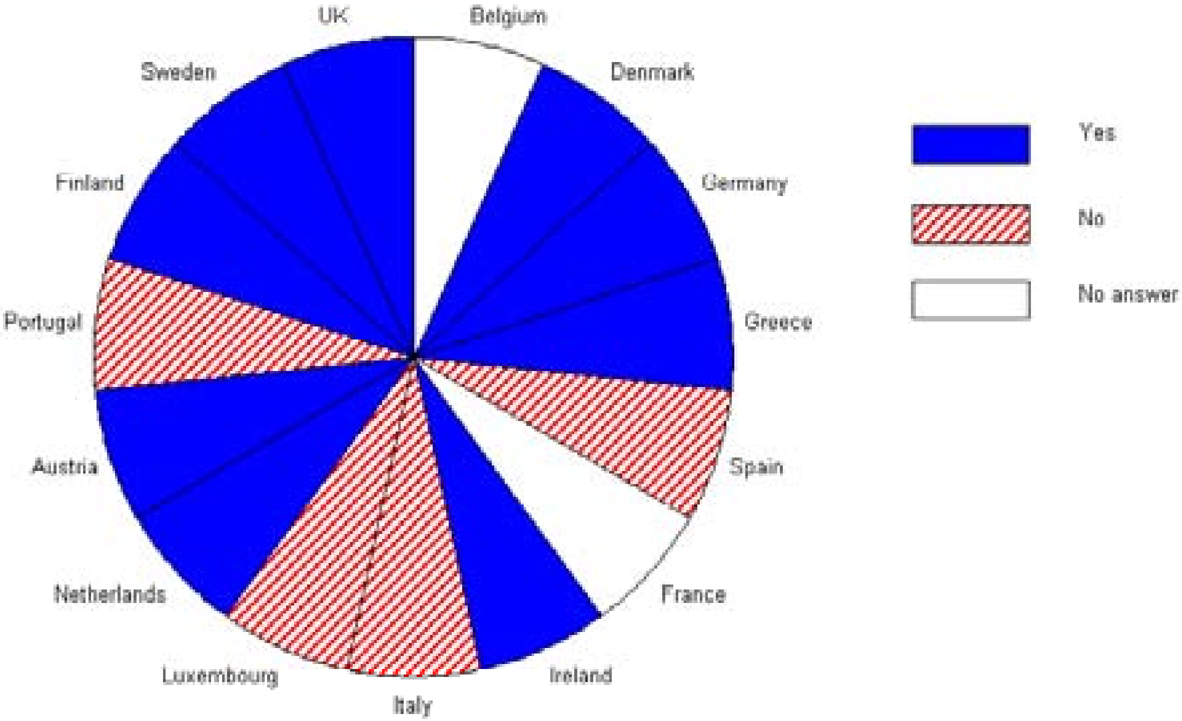

FIG. 3. Application of the concept of exemption to NORM within Member States

At present there are no specific discharge controls, specific assessment procedures or constraints for wastes from work activities in the majority of countries. A number of countries including Spain, Ireland, Austria and Sweden indicated an intention to review their discharge controls with respect to NORM wastes in the near future.

There appears to be little radiological control in the area of liquid and aerial discharges specific to the NORM industries. It should be noted that environmental protection measures in place to control particulate emissions, heavy metal releases, etc. may have the additional benefit of also limiting radiological releases and this was highlighted by Ireland who suggested that they may fall within the scope of their 'Environmental Protection Act 1992'. Solid waste controls are more common. In Germany, for example, there are detailed regulations for the disposal of solid material.

3.2.2. Dose limits, constraints and NORM

According to Article 41 (b) of the Directive, Member States shall apply radiation protection measures including Title IV — dose limits — as necessary. It can be concluded, therefore, that these dose limits could be applied to NORM. The current state of application of these concepts in the case of Member States can be summarized as follows:

- In relation to the dose criterion for the disposal of solid wastes and NORM residues, Greece and Denmark have both adopted a value of 0.3 mSv/a, the value recommended in Ref. [6]. Several countries, however, including Belgium, Germany, Luxembourg and the Netherlands, stated that they did not incorporate this criterion due to a mismatch in timing between the release of advice and implementation of legal provisions. The Netherlands uses 0.3 mSv/a as an effective dose criterion for exposure of the public from solid residues containing natural radionuclides, but for workers the criterion is 0.1 mSv/a under normal conditions and 1 mSv/a under unfavourable but realistic conditions.
- Ireland, Austria and the UK, in particular, incorporate the concept of dose constraints within secondary legislation. However, values are not stated in the legislation and are likely to be determined by the relevant regulator as directed by government policy.
- Austria and Denmark do not consider a lower boundary below which further optimization is no longer required. In Greece, dose constraints provided in their legislation are set within the process of optimization and so there is no optimization requirement below the dose constraints.
- Finland has a provision within tertiary legislation for dose constraints for exposure from natural radiation in the range 0.1–0.5 mSv/a, which can be applied to effluents as well as solid disposal. However, despite these regulations being in place since 1992, no occasion has arisen up to now requiring the application of dose limitation to discharges. In Greece there are no discharge limits because, similarly, no significant liquid or gaseous NORM waste has yet been found to be present at the identified work activities.
- In Sweden and the UK, existing dose constraints are not NORM-specific and were largely formulated for the purpose of controlling discharges from practices. Nevertheless, they can be used in relation to NORM. Sweden, however, is undertaking a review of its controls over exposure to sources of natural radiation in view of Title VII of the Directive. Spain and Ireland are also reviewing discharge controls. At present there are no specific discharge provisions.

In conclusion there are few NORM-specific discharge controls in place at present, and where these do exist, such as in Finland, there have been few occasions when the limits have been applied.

4. OBJECTIVES OF THE NORM NETWORK (NORMNET)

The European Commission is aware that the provisions of Title VII of the Directive have not yet been fully implemented in practice in all Member States, and intends to encourage harmonization of the approaches used by Member States. The Commission also wishes to contribute to the circulation of information and to increase the risk awareness of the various stakeholders in relation to NORM. In this context, the Commission wishes to create a 'NORM Network'. The network will be established as a web-based forum. The NORM Network aims to provide a tool to:

- Develop links and share expertise between European NORM stakeholders;
- Sustain the efforts made in different countries through the exchange of information;
- Identify good practice and to promote it;
- Enhance risk awareness and create a common risk culture between stakeholders;
- Gather and organize documentation made available to the members of the network;
- Prepare periodic summaries of the information;
- Provide a basis for recommendations for further action (reports, conferences, etc.).

Members of the NORM Network will be requested to agree to some terms and conditions. They must be active within the existing EU Member states, the EU accession States and candidate States, Iceland, Liechtenstein, Norway or Switzerland. In particular, members will be those stakeholders who deal with NORM and are involved in the various themes proposed within the Network. They will include regulators (local, national and international organizations), NGOs, consultants and professionals in research and industry.

5. MARINA II

The primary objective of the MARINA II study was to provide EC input to the work of OSPAR in support of the implementation of the OSPAR strategy with regard to radioactive substances. It provided information on radioactive discharges, including those from NORM industries as well as concentrations of radioactivity within the marine environment and an assessment of their impact on humans and marine biota. It followed an earlier MARINA I study [7], which considered data up to the mid-1980s. The main conclusions of the study with respect to NORM industries discharging into the OSPAR region (North East Atlantic) were as follows:

- The overall discharge of alpha emitters into the OSPAR region has remained constant since 1986 due to discharges from the phosphate industry and the production of oil in the North Sea. By 1999, the estimated discharges of produced water (from oil and gas installations) alone contributed 90% of the discharge of alpha activity into the OSPAR region. Since at least 1981, the discharges of phosphogypsum from the phosphate industry have dominated the collective dose to the population of the European Union. This is because of the higher radiotoxicity of the radionuclides discharged by these industries compared to that of the radionuclides discharged from nuclear reprocessing plants.
- The peak collective dose from NORM industries occurred in 1984 — in that year it was just over 600 man·Sv. This collective dose was almost entirely due to discharges from the phosphate industry with the important sources being discharges into Cumbrian waters from the UK and into the North Sea from the Netherlands. Discharges from the phosphate

industry, particularly in the UK, were reduced in the 1990s but the phosphate industry is still a major contributor to the collective dose rate.

- Discharges from the oil and gas industry, which made a small contribution over much of the period 1981–1999, have become relatively more important. In 2000, discharges from the oil and gas industry contributed about 39% to the total collective dose from NORM industries.
- It was found that discharges and collective doses resulting from the production and application of radiopharmaceuticals were negligible in comparison with those from either nuclear reprocessing or oil production. The same applied to discharges from shipyards servicing nuclear submarines in the UK, historic dumping of wastes at sea and submarine accidents.

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THE INVENTORY AND RADIOLOGICAL IMPACT OF NATURALLY OCCURRING RADIONUCLIDES IN SOME ITALIAN NON-NUCLEAR INDUSTRIES

F. Trotti[1*], C. Zampieri[1], E. Caldognetto[1], A. Tacconi[1], L. Filipozzi[1], M. Lanciai[1], G. Clauser[2], M. Facchinelli[2], D. Desideri[3], L. Gaidolfi[4], G. Jia[5], G. Torri[5]**

[1]ARPA Veneto: Regional Agency for the Environmental Protection of Veneto, Verona, Italy
[2]APPA Trento: Provincial Agency for the Environmental Protection of Trento, Trento, Italy
[3]Institute of General Chemistry, Urbino University, Urbino, Italy
[4]ARPA Emilia Romagna: Regional Agency for the Environmental Protection of Emilia Romagna, Piacenza, Italy
[5]APAT: National Agency for Environmental Protection and Technical Services, Rome, Italy

Abstract

The importance of NORM in Italy, from the radiation exposure point of view both for workers and for the public, is confirmed by a national decree (n. 241/2000) implementing the EU Basic Safety Standards Directive, which provides the execution of controls for a set of work activities. A project aimed at estimating the environmental impact for some activities dealing with NORM is being carried out by the National Topic Centre on Physical Agents (CTN-AGF) and co-ordinated by the Regional Environmental Protection Agencies (ARPA). It supports the National Agency for Environmental Protection and Technical Services (APAT) in collecting environmental information about physical pollutants (ionizing and non-ionizing radiation, noise). By now, the following working categories have been chosen: phosphate and fertilizer industry, integrated steelworks, processing of zircon sands, oil and gas extraction, uranium mines, and coal-fired power plants. Radiological surveys have been carried out and technical data related to the various work activities have been collected by means of specific questionnaires sent to most of the involved factories. A centralized database has been set up.

1. INTRODUCTION

A project aimed at estimating the environmental impact of some activities dealing with NORM and co-ordinated by the Regional Environmental Protection Agencies (ARPA) is being carried out by the National Topic Centre on Physical Agents (CTN-AGF). The project, which is part of the research activities concerning physical pollutants (ionizing and non-ionizing radiation, noise) launched by the National Agency for Environmental Protection and Technical Services (APAT), deals with the following working categories: phosphate and fertilizer industry, integrated steelworks, processing of zircon sands, oil and gas extraction, uranium mines, and coal-fired power plants.

The importance of NORM in Italy, from the radiation exposure point of view both for workers and for public, is confirmed by a national decree (No. 241/2000) implementing the EU Basic Safety Standards Directive that provides the execution of controls for a set of working activities. Information about the presence and features of different working cycles has been obtained through field reports and representatives of sector associations or of the

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[*] E-mail: ftrotti@arpa.veneto.it
[**] E-mail: czampieri@arpa.veneto.it

companies themselves. Radiological surveys have been carried out to increase the knowledge — for some working activities — on dusts, residues and products as far as the environmental impact is concerned. Technical data, related to the various working activities and sent by most of the involved factories, have been collected by means of specific questionnaires, and a centralized database has been set up. Preliminary results were presented at the Seventh International Symposium Natural Radiation Environment (NRE-VII), Rhodes, Greece, 20-24 May 2002 and the project is reported in this paper.

2. DATA ON NORM INDUSTRIES

A synthesis of data collected on industries involved with NORM is shown in Table I. A database of NORM industries, containing sufficient information to characterize the environmental implications of work-related activities and to give input data for radiological impact estimates, has been set up. This database comprises three sections:

- Private data of companies and all its plants;
- The type, quantity and characteristics of raw materials (phosphate ores, zircon sands, bauxite, etc.), products (fertilizers, refractory materials, aluminium, etc.) and residues (dust, sludge and waste water), and technical data on the emissions (e.g. temperature, height and stack emission rates);
- Activity concentrations of ^{238}U and ^{232}Th series radionuclides and ^{40}K in materials (raw materials, products and residues) used or produced in working cycles of selected industries.

The database is being compiled with data collected through questionnaires distributed to companies in selected sectors, and through measurement results from specific samples. Some data base input forms are shown in Figs 1 and 2.

3. RADIOLOGICAL STUDIES FOR DIFFERENT NORM INDUSTRY SECTORS

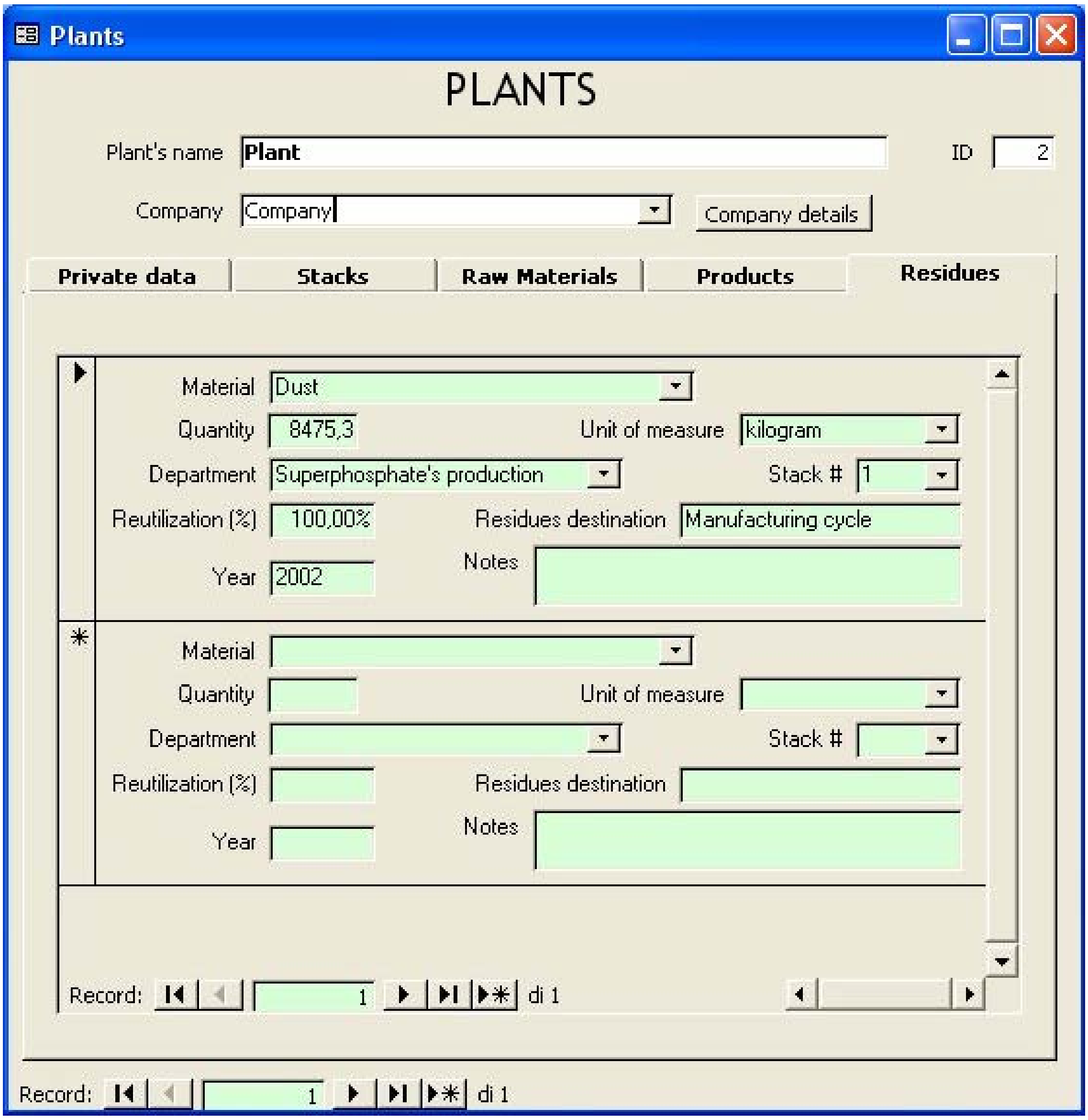
3.1. Fertilizer industry

In Italy, on the basis of information provided by Assofertilizzanti (the main fertilizer companies association), there are about 50 associated companies that produce complex, simple phosphate and simple potassium fertilizers, of which 17 are the main producers. Amongst them, 3 companies produce superphosphates by a balanced reaction between phosphates and sulphuric acid [1]. Additionally some new data are available from ARPAV for raw materials and products, as shown in Table II (the previous data were presented by the authors at the Seventh International Symposium Natural Radiation Environment (NRE-VII), Rhodes, Greece, 20-24 May 2002).

The breaking of the ^{238}U chain between ^{238}U and ^{226}Ra has been confirmed in measurements samples of Moroccan mono ammonium phosphate (MAP) and triple superphosphate. The moderate ^{238}U content in Russian MAP may be due to phosphates not being used in its production. For a bone superphosphate sample, the use of organic raw materials instead of conventional phosphate ores can explain the moderate concentrations of all natural radionuclides.

TABLE I. A SYNTHESIS OF DATA ON NORM INDUSTRIES

Sector	Work activity	No. of NORM-related companies or sites	Annual national production or quantity	Remarks	Source
Phosphates	Fertilizer industry	50 main companies	3.5 Mt	Simple and complex mineral fertilizers	ISTAT 2003 and Assofertilizzanti 2002
	Phosphogypsum disposal	5 sites	0.2–6 million m^3 each	Reclamation complete at 2 sites	Enichem 2001
Zircon sands	Tile industry	50 main companies	600 million m^2	—	Assopiastrelle 2004
	Refractories industry	9 companies	556 kt	—	
	Ceramic colouring, ceramic products	65 companies (potential)	—	Direct use of zircon sands in ceramic product manufacture not documented	Ceramicolor and Federceramica 2002
Energy	Oil and gas extraction	ENI: ~7000 wells, Edison: ~100 units	Gas (m^3): 13.8×10^9 (ENI) 1.4×10^9 (Edison)	1.38×10^6 m^3 connate water, ≤2000 t sludges, 15–20 production tubing per year may have significant activity (ENI)	ENI, AGIP Division and Edison Gas 2001
	Coal-fired power plants	12 plants	31 000 GWh gross energy produced from 11 Mt coal	Annual effective dose estimates: individual 0.42 μSv, collective 0.055 man·Sv	ENEL Group 2001
Metals	Integrated steelworks	4 plants	26.7 Mt	—	Federacciai 2000
	Aluminium industry	1 alumina producer, 1 aluminium (from alumina) producer	1.02 Mt (alumina)	—	Assomet 2004 and personal communication from a company

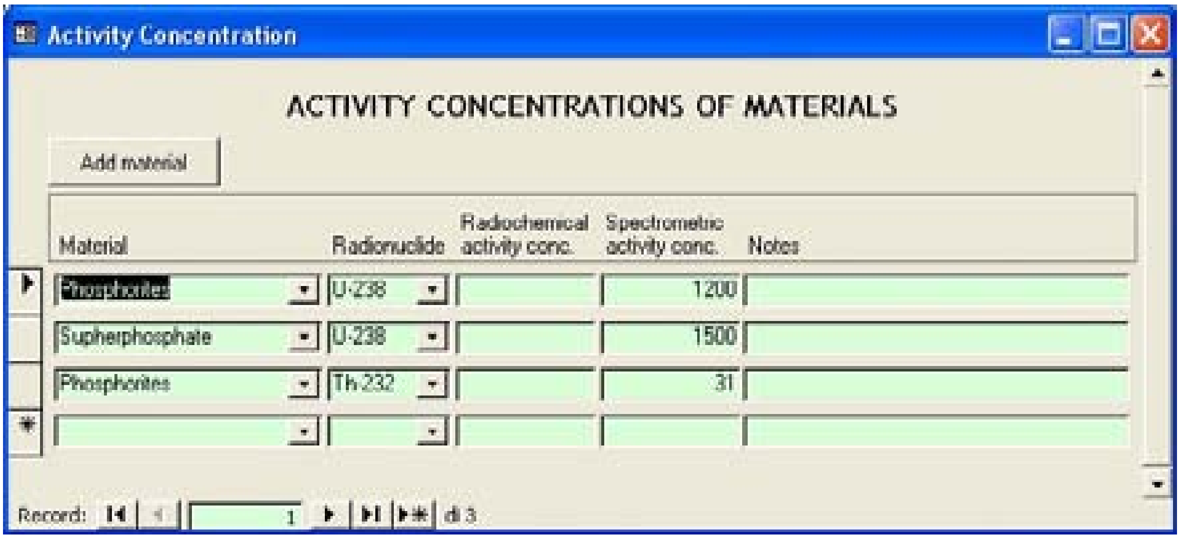


Plant's name: Plant
ID: 2
Company: Company

Material: Dust
Quantity: 8475,3
Unit of measure: kilogram
Department: Superphosphate's production
Stack #: 1
Reutilization (%): 100,00%
Residues destination: Manufacturing cycle
Year: 2002
Notes:

Material:
Quantity:
Unit of measure:
Department:
Stack #:
Reutilization (%):
Residues destination:
Year:
Notes:

FIG. 1. Input form for type, quantity and characteristics of residues



Material	Radionuclide	Radiochemical activity conc.	Spectrometric activity conc.	Notes
Phosphorites	U-238		1200	
Supherphosphate	U-238		1500	
Phosphorites	Th-232		31	

FIG. 2. Input form for activity concentrations of materials

TABLE II. ACTIVITY CONCENTRATIONS IN FERTILIZER RAW MATERIALS AND PRODUCTS

Sample	Activity concentration and uncertainty at the 68% confidence level (Bq/kg)				
	^{238}U	^{226}Ra	^{232}Th	^{40}K	^{235}U
Moroccan MAP	2741 ± 15%	39 ± 6%	9 ± 7%	28 ± 6%	131 ± 5%
Russian MAP	41 ± 16%	1 ± 8%	14 ± 6%	37 ± 5%	2 ± 12%
Triple super phosphate	1506 ± 15%	352 ± 6%	7 ± 9%	92 ± 6%	69 ± 6%
Bony super phosphate	57 ± 18%	34 ± 6%	4 ± 7%	45 ± 6%	3 ± 21%

The collective effective dose for the Italian population due to the use of fertilizers in agriculture has been estimated by means of the simplified model given in paras 64–65, Annex C, p116 of Ref. [2]. This model, which takes into account intakes (ingestion of contaminated food and inhalation of resuspended material) and external irradiation, is the same as that used previously to assess dose from the deposition of radionuclides emitted from a refractory plant [3]. Only the radionuclides of ^{238}U chain and ^{40}K were considered, because the concentrations of ^{232}Th and ^{235}U in fertilizers are not significant. The concentrations of radionuclides distributed in Italian soil were derived from data obtained in 2003 from ISTAT for the quantity of fertilizers country-wide and from average activity concentrations measured in various samples [3–5]. These data are presented in Table III. For the purpose of the calculations, it was assumed that the population stood on fertilized ground for 1% of the time.

TABLE III. ITALIAN FERTILIZER USAGE AND RADIOACTIVITY CONTENT, 2003

Fertilizer	Annual usage (Mt)	Mean activity concentration (Bq/kg)				No. of samples
		^{238}U	^{226}Ra	^{210}Pb	^{40}K	
Simple phosphate	0.25	667	295	295	—	3
Simple potassium	0.15	—	—	—	14000	2
Complex phosphate	1.39	262	107	157	—	15
Complex potassium	1.02	—	—	—	3379	15

Table IV and Fig. 3 show the results of the modelling calculations. The collective committed effective dose in a year was about 40 man·Sv. This is not a very high value and can be compared with the estimated annual collective dose worldwide of 10 000 man·Sv due to the use of fertilizers in agriculture [6]. A crude estimate of the per caput dose, obtained by the ratio of the collective dose to the Italian population, is about 1 μSv/y, far below the action level of 300 μSv indicated by Italian law [7]. The main contribution to the dose is received via the ingestion pathway and the most relevant radionuclides are ^{210}Pb and ^{210}Po. Caution is necessary in interpreting these results due to the nature of the model — it ignores site-specific data, single radionuclide transfer coefficients, etc. To overcome this limitation, an assessment using deterministic modelling, oriented particularly towards analysing the exposures of eventual critical groups, would have to be planned.

TABLE IV. COLLECTIVE DOSE ARISING FROM THE USE OF FERTILIZER IN ITALY

Radionuclide	Collective committed effective dose in a year (man·Sv)			
	Ingestion	Inhalation	External gamma	Total
^{238}U	0.145	0.000 122	0.446	0.256
^{234}U	0.162	0.000 151	—	0.274
^{230}Th	0.336	0.000 278	—	0.448
^{226}Ra	1.95	0.000 063 3	—	2.06
^{222}Rn	—	1.14	—	1.14
^{210}Pb	8.91	0.0127	—	8.93
^{210}Po	27.1	0.003 82	—	27.1
^{40}K	—	—	0.578	0.578
Total	38.6	1.16	1.02	40.7

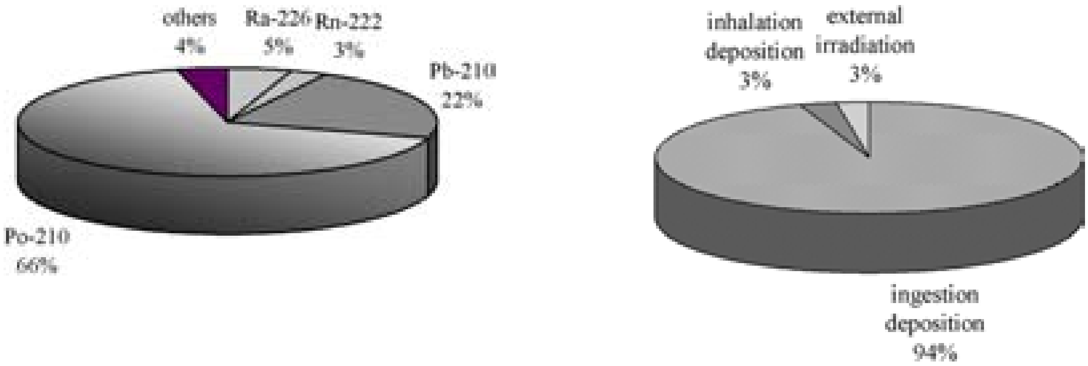


FIG. 3. Contributions of radionuclides and exposure pathways to the collective dose

3.2. Tile and refractory materials industry

The production of tiles and refractory materials has been investigated by ARPAV because of the zircon sand or silicate content that may result in elevated concentrations of natural radionuclides [4].

3.2.1. Tile industry

The Italian ceramic tile industry enjoys an overall world leadership position, accounting for 43% of the tile production of the entire European Union and 13% of total world production. The industry comprises nearly 280 manufacturing facilities throughout Italy and has an output of more than 600 million m^2. Assopiastrelle represents the main sector association with a 90% market representivity [8]. From the Assopiastrelle database, a set of 50 associated companies (70% market representivity) was selected and a simplified questionnaire was sent to them. The questionnaire dealt with the quantities of zircon sand or silicate used in the bulk of porcelain stoneware and in enamels preparation. Only 32% of the interviewed companies have answered up to now — based on these responses, the quantities of materials used in 2003 were as follows:

- Zircon sands: 720 t;
- Zircon silicates: 19 000 t;
- Zircon sand/silicate based enamel, preparation: 6000–11 000 t;
- Zircon sand/silicate based enamel, purchases: 15 500 t.

3.2.2. Refractories industry

The Italian refractories industry is made up of 39 companies, 20 of which have joined the main sector association, Assopiastrelle (75% market representivity) [8]. Ten companies belonging to Assopiastrelle use zircon sands or semi-finished zircon-silicate-based components in the process, but only two of them use significant amounts (thousands of tons) of zircon sands. A study concerning NORM in the refractories industry [3] reported on the following:

- Activity concentration measurements by gamma spectrometry and radiochemical analysis;
- An estimate of the collective effective dose using a simplified model;
- A national overview.

3.3. Steelworks

Dust samples from thermal processes in a non-integrated steelworks were collected. The samples were radiochemically analysed for their ^{210}Pb and ^{210}Po content to confirm the expected moderate contamination related to dusts coming from integrated steelworks. The radiochemical analyses were carried out in 2004 by the University of Urbino and APAT. The averages of the results from the two laboratories are shown in Table V. The slight enrichment of ^{210}Pb and ^{210}Po in the samples investigated possibly arises from the consumption of refractory materials in the thermal process.

TABLE V. RADIOACTIVITY CONTENT OF DUST FROM A STEELWORKS

Dust sample	Mean of two independent activity concentration measurements, with deviation from the mean in parentheses (Bq/kg)	
	^{210}Po	^{210}Pb
Converter electrofilter dust	422.0 (5.2)	360 (18.9)
Blast furnace dust	58.7 (4.7)	50.2 (13.5)

3.4. Aluminium industry

Natural radionuclides are contained in bauxite ores at only moderate concentrations, but may become more highly concentrated in the emissions from the high temperature treatment of the ore, particularly ^{210}Pb and ^{210}Po [9]. At present, there are 50 alumina refineries in the world with a combined production of 55 Mt/a. In Europe, there are 6 alumina refineries with a combined production of 6.4 Mt/a. In Italy the extraction of aluminium from bauxite is carried out by only one company and its production amounts to 1.02 Mt/a.

The process is based on the digestion of bauxite with caustic soda at high temperature and pressure. The alumina contained in the bauxite (about 50%) dissolves in the caustic phase and is separated. The alumina is subsequently precipitated as a hydrate and subjected to calcination where, at temperatures of about 1000°C, the hydrate is transformed into aluminium oxide product (alumina) by elimination of the water of crystallization. The other unextracted components represent the process residues (red mud), which are pumped to storage.

Measurements of radionuclide concentrations in bauxite samples were carried out by ARPAV using gamma spectrometry. The concentrations, together with the uncertainties at the 95% confidence level, were as follows:

- ^{238}U: 333 Bq/kg ± 14%;
- ^{232}Th: 383 Bq/kg ± 12%;
- ^{40}K: 35.5 Bq/kg ± 8.5%.

These results confirm the data reported in the literature [9] and indicate that the radionuclide concentrations are elevated above the average values in normal soil.

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IMPROVING CRITERIA FOR REMEDIATION OF MONAZITE BY-PRODUCTS CONTAMINATED SITES IN BRAZIL

C. Briquet[*], **K.M. Silva**[**], **M. Cipriani**[***]

Comissão Nacional de Energia Nuclear (CNEN)
Rua General Severiano, 90 Rio de Janeiro, Brazil

Abstract

In 1999, the first Brazilian decommissioning process occurred in São Paulo State at a monazite physical and chemical treatment plant, closed down since 1992. The decommissioning process comprised equipment, piping, buildings and land decontamination with the final site release for unrestricted use. At the present time, another monazite site is being decommissioned in the same State. Regulations for intervention situations in the mining and milling of ores with associated uranium and thorium are currently being developed. Due to this, the decommissioning activities were based on case-by-case analyses and ALARA criteria. Investigations are being made to propose suggestions for public participation in the process and to establish a method of working together, in order to obtain more effective communication between the regulatory agency and society. This paper presents an overview on the situation of three sites in São Paulo State: a past and a present remediation case and a site to be decontaminated in the future. All sites were contaminated with radioactive residues produced by outdated monazite chemical processing. We also propose some improvement in procedures, based on past experience and international guidelines. This paper also suggests the implementation of public participation in the evaluation of the remediation process.

1. INTRODUCTION

One of the thorium occurrences is in beach monazite sand. These sands are found over a large extent of the Brazilian coast, from the northern border of Rio de Janeiro State to south of Bahia State. Monazite is an orthophosphate of thorium and rare earths — $(Ce, La, Y, Th)PO_4$ — and contains an average of 6% ThO_2, 0.3% U_3O_8 and 50% to 60% rare earth oxides. The Brazilian practice for monazite treatment was made in two phases. First the monazite was separated from silica and other minerals (ilmenite, rutile, zircon) by a combination of gravity, electrostatic and magnetic separation techniques. A concentrate containing more than 90% of monazite was obtained. In this physical phase of the process no relevant waste was produced. In the second phase the monazite was attacked by sodium hydroxide solution in autoclaves, transforming the mineral into water-soluble trisodium phosphate and mixed hydroxides of rare earths and thorium. Then the rare earth elements were solubilized by hydrochloric acid (pH 3.5– 4.0) and separated from thorium hydroxide by filtration.

Fig. 1 shows the chemical processing of monazite, which took place in Brazil until 1992, resulting in two main radioactive by-products:

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[*] E-mail: cbriquet@cnen.gov.br
[**] E-mail: kmsilva@cnen.gov.br
[***] E-mail: cipriani@cnen.gov.br

- Thorium hydroxide concentrate, a precipitate named cake II (20% ThO_2, 1% U_3O_8), with a specific activity around 1820 Bq/g;
- Barium–radium sulphate crude residue, a precipitate named mesothorium (Ba(Ra) SO_4), with a specific activity around 4360 Bq/g.

Cake II retains most of the thorium and uranium from the monazite. For each 100 t of monazite processed chemically, 2 t of cake II and 7 t of mesothorium are produced [1]. There are no estimates for the total amount of cake II and mesothorium produced in Brazil from 1949 to 1992. The monazite chemical process phase produces large quantities of residues with low level long-lived natural radionuclides from the ^{238}U and ^{232}Th series.

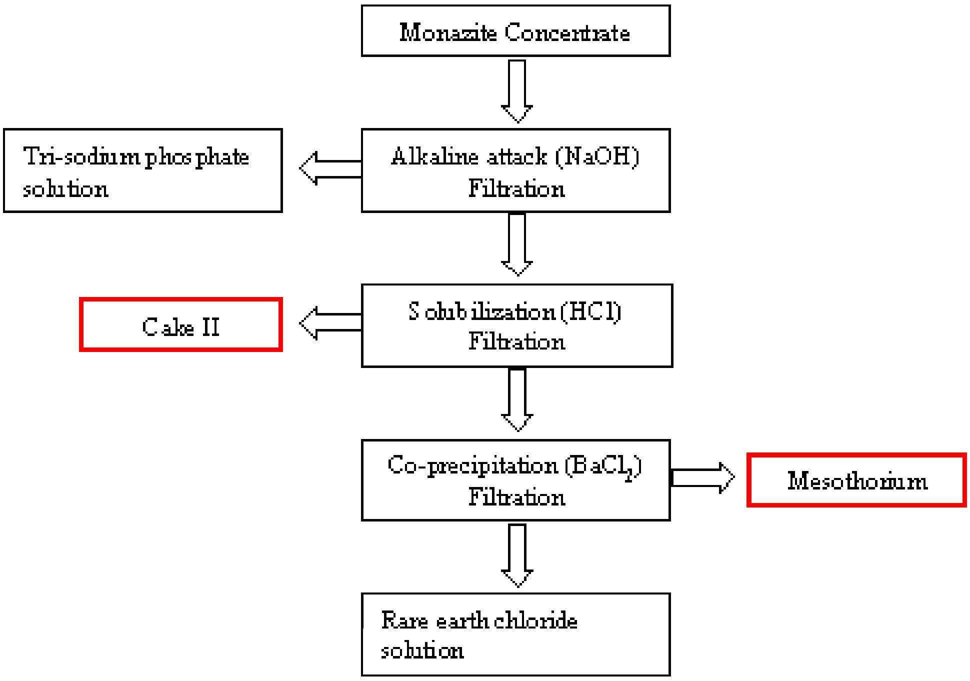

FIG. 1. Monazite chemical process

2. REGULATORY ASPECTS

The chemical processing of monazite sands to produce rare earths began to be explored in São Paulo State in 1949, before the establishment of the National Nuclear Energy Commission (CNEN) in 1956 (Decree 40110/56), and almost 30 years before the setting up of the Brazilian Institute of the Environment and its Resources (IBAMA) in 1989 (Law 7735/89) with responsibility for environmental licensing. This kind of industry produced large quantities of radioactive by-products according to the process described above. Regulations for intervention situations in mining and milling of ores with uranium and thorium associated are being developed by CNEN [2].

In accordance with the Brazilian Nuclear Policy Act (Law 4118/62 as amended by Laws 6189/74 and 7781/89), CNEN has the responsibility for establishing regulations and implementing nuclear policy. The Licensing and Control General Co-ordination Board of CNEN is responsible for performing regulatory control of nuclear facilities: issuing licenses and authorizing construction, operation and decommissioning. The Brazilian Environmental

Policy Act (Law 6938/81 as amended by Laws 7804/89 and 8028/90) was enacted almost 20 years after the Brazilian Nuclear Policy Act.

IBAMA's responsibilities include the environmental licensing of undertakings and activities with significant environmental impact at a national or regional level, which includes all stages of exploration, mining, processing, storage and disposal of radioactive material, and activities that use nuclear energy in any of its forms and applications, according to CNEN's evaluation. IBAMA carries out the licensing process after considering the technical evaluation made by the State and Municipal environmental agencies where the activity or undertaking is established, as well as the evaluation of the other pertinent Federal, State or Municipal agencies involved in the licensing process (CONAMA 237/97).

3. DECOMMISSIONING ACTIVITIES, CASE 1

A monazite processing plant named USAM (Usina de Santo Amaro), located at São Paulo, started operation in 1949 and closed down in 1992. The site with an area of 11 000 m^2 consisted of three units: physical separation of raw mineral, chemical treatment of monazite, and rare earth separation. The justification for intervention was:

- Over the years, the place had turned into an urban area;
- From 1979 onwards, with the evolution of radiological protection concepts, critical aspects of the site have been shown to be the inadequate dust generation control system and the limited storage capacity for the by-products — cake II and mesothorium [3].

The decommissioning process began in 1994 in the physical separation unit, the simplest one. The procedures adopted included radiological characterization of the site, decontamination of equipment and buildings, and material classification considering the final destination: reuse, landfill, sale as scrap or radioactive waste, in accordance with CNEN regulations [4]. The higher risk areas were the area of monazite milling, due to dust deposition, and the area of chemical treatment. CNEN surveyed the dismantling and the decontamination activities — the worker doses were below the limits and there were no accidents while the work was being done.

The waste generated in the process was transferred to another site, located near the facility described below as Case 2. The Environmental Agency of São Paulo State (CETESB) gave the authorization for this temporary storage in 1995.

The site release for unrestricted use was based on a conservative residential scenario, considering all exposure pathways for a dose limit 1mSv/a to derive an activity concentration level of 600 Bq/kg ^{228}Ra. Before release, a final survey was conducted by CNEN to confirm the release criteria adequacy.

As it was the first decommissioning to take place in Brazil it was done under critical and diligent CNEN evaluation, not only to guarantee compliance with the established limits, but with all safety criteria. The process ended in 1999.

4. DECOMMISSIONING ACTIVITIES, CASE 2

This site is presently undergoing the decommissioning process. It is located in São Paulo city, with an area of around 60 000 m^2, of which 4500 m^2 were occupied by 3 storage sheds: A, B and C, and 55 500 m^2 comprises an open area with weedy vegetation. Storage shed A (2060 m^2) is being used as temporary storage for the waste generated in the decommissioning Case 1. Storage sheds B and C, out of operation since 1992, were demolished in 2002 under CNEN surveillance.

In the past the owner first used the site for storage of residues of mineral processing, and then for a period of time storage shed A was used as a rare earth extraction unit.

Two contamination sources were identified at the soil site: monazite sand and cake II. Investigations are in progress to verify if there is underground water contamination.

5. DECOMMISSIONING ACTIVITIES, CASE 3

During 1975–1981, 3500 t of cake II were stored in seven concrete constructions, built especially for this purpose, in a rural property located in a farming region of São Paulo State. A river crosses the property and flows to a station that supplies water to a city 12 km away. The local population is very concerned about the situation.

Monitoring programmes carried out at the site revealed two areas with ^{226}Ra contamination and two others with ^{228}Ra. In August 1983, technicians of the local environmental agency recorded an activity concentration of 0.8 Bq/L ^{226}Ra in a well located inside the site. In March 1993, the same well showed a value of 4.0 Bq/L. Since 1989 the well has been sealed.

Presently, a soil characterization is being made at the site using a triangular grid of 11 m, in accordance with MARSSIM methodology [5] to determine the extent of the contamination.

The property owner has not yet shown interest in decommissioning the site. Should the owner intend to keep it as a storage facility, very detailed studies must be developed.

6. PUBLIC PARTICIPATION

Despite the importance of the nuclear industry, laymen always associate radiation with weapons, war and accidents. Although its most harmful consequences are rare, this is incomprehensible to most citizens [6].

The first release of an urban site in São Paulo for unrestricted use continues to evoke questions to CNEN. It is clear that non-radiological factors affected the public. Perhaps, if during the decommissioning process, public representation had been involved, the acceptance of the results would have been enhanced with a decisive influence in the final release. Dialogue can increase support for decisions, although it is a lengthy process.

7. FINAL REMARKS

Remediation is a complex process. We propose the adoption of an integrated strategy (Fig. 2) in which the justification of the remediation action will be based not only on impact criteria, but also on a social and economic approach to obtain an optimization of the decision-making process. An effective contaminated land management process is suggested, adopting environmental legislation and considering the evaluation of the other pertinent State or Municipal agencies and authorities involved in the licensing process. Four preliminary steps are proposed within this strategy:

- An evaluation of public perception;
- An evaluation of stakeholder interests;
- An effort to establish a link between technical and social evaluation;
- Definition of a methodology to consider the engagement of social and local authorities.

As yet, there is no disposal site for this low level long-lived waste in Brazil. CNEN is selecting an adequate site for permanent storage of this material. Specific regulations or guides concerning decontamination and decommissioning are necessary to advise on the appropriate evaluation actions.

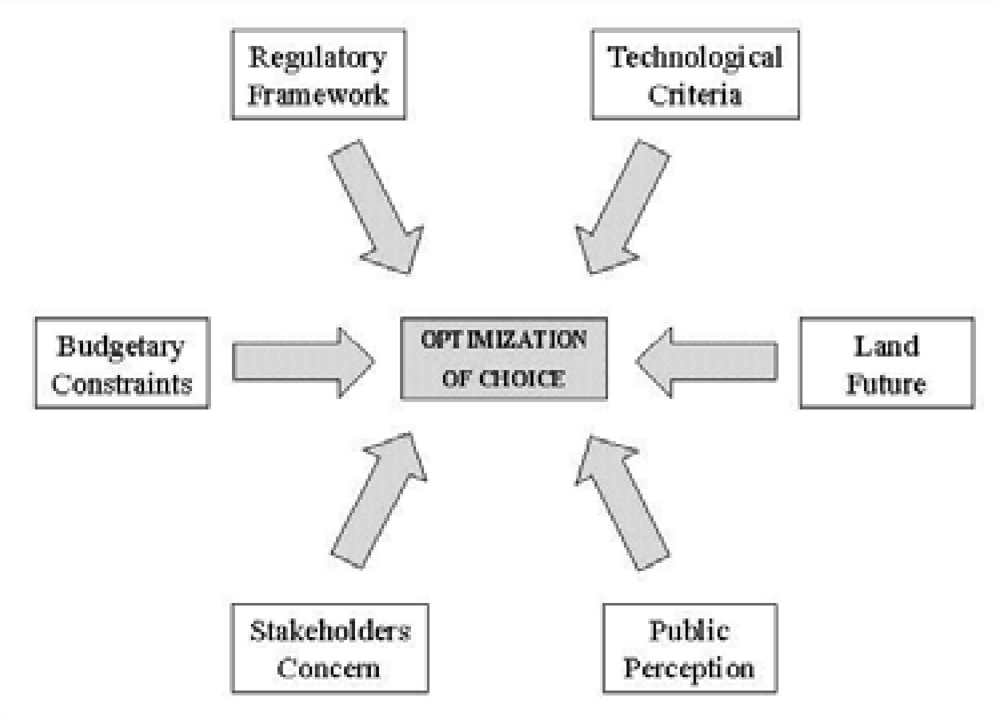

FIG. 2. Remediation evaluation framework

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RADON AND AIR POLLUTION

ASSESSMENT OF THE RADON CONTRIBUTION FROM MINING SITES TO THE GEOGENIC ENVIRONMENT

R. Rolle*

Goettingen, Germany

Abstract

An issue associated with NORM in mining areas is the mean radon exposure assignable to surface mining residues. Outdoor radon decay chain concentrations (at breathing height), compared with elevated indoor levels, are relatively low and they fluctuate widely with time and location. Differentiating a mining contribution to the geogenic radon exposure is a challenging metrological task, particularly in the later stages of remediation. The activity concentrations of radon decay chain members can be determined accurately with good time resolution down to low outdoor concentrations using (quasi-) continuous on-filter concentration measurements. Such measurements showed continuous diurnal concentration cycles ranging from a general minimum concentration to a widely varying maximum for different cycles. Correlation with chain activity ratios and diurnal wind velocity clarifies the build-up of concentrations near the ground during minimal vertical air exchange, above an otherwise generally low concentration over the height of the atmosphere. Ways of assessing radon exhalation and of the exhalation ratio ^{222}Rn/^{220}Rn are indicated, and these may provide a better measure for assessing possible mining influence on local radon exposure.

1. INTRODUCTION

Radon concentrations fluctuate widely in time and space, and outdoors at breathing height, apparently of interest to some groups, it is difficult to differentiate relatively small increases in ‘average’ radon concentrations, which could possibly have resulted from current or past mining activities. At this height above ground, diurnal concentration cycles of varying magnitude generally occur due to diurnal cycles of air movement. To assess the possible contributions from mining activities, diurnal cycles of different character were investigated to elucidate the processes leading to long-term mean concentrations. Many previous studies with long-term (seasonal) integrated measurements had not yielded mean geogenic radon concentrations at hoped-for small error margins. An explanation for this has been derived here from the diurnal cycle periods of vastly different intensity that have been investigated so far.

The radon exhalation rate from the ground has a much closer link to possible effects from mining activities than the radon concentration in air and a new method of local exhalation assessment is proposed.

2. RADON MEASURING INSTRUMENTS

For the measurement of outdoor radon concentrations down to a few Bq/m^3, a range of instruments is available — from low sensitivity instruments for long term (monthly to annual) integrated measurements to much higher sensitivity instruments for continuous measurement of concentrations differentiated hourly or shorter. With long-term integrating measurements,

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[*] E-mail: rrolle@gwdg.de

the individual processes dominating the average radon concentration over short time periods cannot be unfolded.

In any measuring instrument, all members of the sampled decay chain are involved and ought to be considered when accurate evaluation is favoured. Direct gas measuring instruments are generally equally sensitive to ^{222}Rn and ^{220}Rn. With an often very substantial contribution from ^{220}Rn outdoors (even to a height of many metres above the ground), not considering ^{220}Rn can lead to significant errors in the conversion of measurement signals to ^{222}Rn concentration. As shown in Table I, outdoor ^{222}Rn concentrations can generally be measured far more accurately with on-filter concentrating, alpha-spectrometric instruments than with direct radon gas instrumentation, and the former are insensitive to ^{220}Rn and ^{216}Po concentrations. On-filter concentrating instruments, in addition to providing the ^{222}Rn concentration, can simultaneously furnish also the potential alpha energy concentration (PAEC) of ^{222}Rn and ^{220}Rn, as well as the ^{222}Rn PAEC equilibrium factor F. With quasi-continuous sampling, and so much the better using beta-alpha spectrometry, the individual member concentrations of the radon decay chains can be evaluated delay-free. Concurrent inline sampling on screens, and free of entrance losses, will also provide the unattached radon decay product concentrations.

TABLE I. STEADY STATE SENSITIVITY OF VARIOUS TYPES OF ALPHA SPECTROMETRIC MEASURING SYSTEMS FOR RADON GAS[1]

Instrument	Alpha counts per hour					
	^{222}Rn	^{218}Po	^{214}Bi/Po [2]	^{220}Rn	^{216}Po	^{212}Bi/Po [2]
Radon track-etch dosimeter	~0.02	~0.02	~0.02	~0.02	~0.02	~0.02
Track-etch environmental monitor[3]	0	0.02	<0.3[4]	0	0	<4.5[4]
½ L radon ionization chamber	12	9	9	12	9	9
½ L electrostatic radon monitor	0	9	9	0	9	9
2 L/min on-filter concentrating	0	80	<1300[4]	0	0	<18 000[4]

Note that probably with most measurement systems, evaluation algorithms are used that yield concentration values that are not adequately corrected for measurement delay — the systems are generally calibrated only for steady state situations, and thus strictly are not suited for the accurate assessment of concentrations that vary significantly in measuring intervals of the order of the respective half-lives; alerting to 'data quality' errors, as from some instruments, does not alleviate the situation. The delay effect is due to the time development of the various chain member activities in the instrument subsequent to the sample intake. The effect of delays for a half-life of up to 3 min (^{218}Po) is generally negligible for diurnal (hourly) measurements. Delays for a half-life of up to 30 min (^{214}Pb … Bi) can be significant for diurnally rapidly changing concentrations, and instrumental response for ^{212}Pb (half-life 10.6 h) definitely requires appropriate evaluation if diurnal cycles are to be evaluated, irrespective of radon gas or decay product concentration determination.

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[1] Approximated as detected radionuclide alpha counts per hour at a radon concentration of 10 Bq/m^3 (36 radon atom decays per hour per litre). The Bi/Po alpha signals require incorporation into the radon evaluation.

[2] Delay from the half-lives of ^{214}Pb, ^{214}Bi and particularly ^{212}Pb and ^{212}Bi needs to be taken care of.

[3] 2 L/min concentration on filter with collimated track-etch detection (ALGADE).

[4] Equilibrium-dependent rates from respective decay product concentrations should normally be compensated for.

The calibration of some measurement systems is not always reliable at concentration levels of a few Bq/m^3, making some measurement comparisons rather inaccurate.

3. RADON CONCENTRATIONS, GLOBAL AND LOCAL

The *total* ^{222}Rn activity in the global atmosphere is in equilibrium with the total ^{222}Rn exhalation from the continental surfaces — as required for the compartment balance of source and decay. Since ^{222}Rn exhalation from soil generally is far greater than from the oceans and ice cover, the large-scale lateral distribution of ^{222}Rn over the globe is influenced to a variable degree by offshore and onshore movement rates of air masses relative to the ^{222}Rn half-life of 3.8 days.

In the atmosphere the fraction of vertical air mass exchanged (mixed) per unit time, λ_v, is usually much higher than the fraction of ^{222}Rn decay per unit time in the air, i.e. $\lambda_v + \lambda_{Rn\text{-}222} \cong \lambda_v$, so that a nearly homogeneous vertical ^{222}Rn concentration (Bq/kg air) can be expected over all altitudes above ground, at a concentration level probably somewhere below 4 Bq/kg air ($\approx$ 5 Bq/m^3 NTP). Only for situations where and when the vertical air exchange is much reduced near the source of ^{222}Rn, i.e. the ground, so that the constant $\lambda_{Rn\text{-}222}$ value becomes competitive with λ_v,, can the ^{222}Rn concentration close to the source accumulate to values significantly above the mean concentration, to a local value which depends mainly on the duration and relative residual value of λ_v, and decreases with (vertical) distance from the ground.

Vertical mixing of air λ_v is linked (in a complex way) to differences in wind speed of air layers parallel to the ground, the ground contact layer having zero speed. The diurnal cycle of insolation produces a diurnal cycle of vertical air mixing. During calm weather there may be vertical mixing cycles, parts of which are practically windless so that the usual turbulent, eddy diffusional mixing stops, leaving only molecular diffusion near the ground, a period during which the ^{222}Rn can accumulate there to raised concentrations. The occurrence and duration of such adequately windless, minimal vertical mixing intervals is also strongly dependent on the surrounding topography, the plant or tree cover, and structures. An adequately calm interval usually starts late in the afternoon and may last until the onset of turbulent diffusion in the morning, when the raised local concentration near the source is again rapidly diluted to the mean vertical concentration. For diurnal cycles where a lower threshold in wind speed is not crossed, vertical mixing can prevent substantially raised concentrations (to above the vertical mean concentration) near the ground. Stable inversion layers can persist in some locations for days and present the opportunity for still more extended accumulation of the various concentrations.

Over the height of the atmosphere the activities of the short-lived decay chain members of ^{222}Rn are in equilibrium with the ^{222}Rn concentration, except for washout during rain or snow and for about an hour after. However, when the $\lambda_{Rn\text{-}222}$ value becomes competitive with λ_v near the ground and ^{222}Rn can accumulate near the source to elevated concentrations, then the short-lived decay chain members follow suit with appropriate decay chain timing. This timing results in activity disequilibrium of the chain members and can be measured as activity ratios, a compounded ratio being the ^{222}Rn potential alpha energy concentration equilibrium factor $F_{Rn\text{-}222}$.

4. MEASUREMENT RESULTS

In support of the above interpretation, hourly measurements were made at 4 measuring sites a few kilometres apart. Over a period of more than 20 days, hourly values of the ^{222}Rn and ^{222}Rn PAEC were taken with 7 different alpha spectrometric instruments. As all the data show continuous diurnal cycles with corresponding patterns, only a subset of measurement data is presented in Fig. 1 with ^{222}Rn concentration and wind speed. These show particularly two types of diurnal cycles: starting late afternoon in the 7 day period with hardly any wind for part of the 24 h (12–19 October 2003) and 6 cycles (starting 9–11, 22, 24 and 25 October 2003) selected with at least some wind all during the cycle. Data from an on-filter continuously concentrating spectrometer are presented, as this instrument efficiently provides additional ^{222}Rn decay chain ratio data (F factor) to corroborate the vertical air mixing model.

The seven diurnal cycles starting on 12–19 October are superimposed in Fig. 2a, and the ‘always some wind’ cycles in Fig. 2b. Since ^{222}Rn accumulation cycles do not start with a minimum concentration at 00:00, the concentration values on a diurnal scale >24 h are repeated at >0 h of the following day. The corresponding ^{222}Rn equilibrium equivalent concentration F factor is shown restricted to $F \leq 1$, as it was determined without measurement delay correction.

5. INTERPRETATION OF MEASUREMENT RESULTS

A comparison of Figs 2a and 2b shows that only during a diurnal cycle with several hours of practically no wind does the ^{222}Rn concentration build up to an elevated level. If the wind velocity does not go below some minimum value, the concentration approximates the general low concentration at higher wind velocity, i.e. with far better vertical mixing, to the low value of the vertical mean concentration.

The diurnal course of the measured F factor corroborates the above explanation: only the excess (above the mean) of freshly accumulated ^{222}Rn near the source can produce a decay chain concentration mixture with an F factor reduced below $F = 1$, as expected higher up.

6. DISCUSSION AND IMPLICATIONS OF THE FINDINGS

The mean value of the radon (decay chain) concentration near the ground is usually considered over one or several months, seasons or years. This value, on the one part, has a more or less steady contribution from the generally low radon concentration in the upper atmosphere, and at a given site possibly a few very enhanced contributions from local exhalation during individual periods of several hours of minimal vertical air mixing. The mean radon value over a longer term thus depends on the particular choice of the period with its weather-dependent, site-specific ratio of minimal vertical air mixing intervals to normal mixing time, and, during these minimal mixing periods, on the radon exhalation rate from the ground. Only the last term, exhalation, could possibly be, or have been, affected by current or past mining activities, and its assessment is blurred (very imprecise) in longer term radon mean value determinations. Also the radon exhalation is influenced by precipitation and ground temperature, but the superimposed variability from vertical air mixing usually strongly dominates the variability of long term mean concentrations.

The foregoing measurements have illustrated that with on-filter collecting instruments, low outdoor concentrations of decay chain members can be quantified in hourly steps, and they have elucidated the behaviour of outdoor concentrations near the ground. These instruments will soon be operated in an optimal quasi-continuous sampling mode so that the individual concentrations of all short-lived decay chain members can be assessed with instrumental measurement delay corrected. The activity concentration ratios of decay chain members (as well as the derived F factor) are functions of the air exchange in a given compartment mixing model with source and decay. From hourly concentration measurements plus concentration ratio measurements during a pronounced diurnal cycle(s) of the ^{222}Rn as well as ^{212}Pb decay chain concentrations, the ^{222}Rn and ^{220}Rn exhalation and the exhalation ratio can thus be determined. Attempts by previous authors to determine, from monthly or longer integrated measurements, a ratio signature of the two decay chains ascribable to possible mining influence was fraught with high imprecision. The high concentration variability in and of diurnal cycles in longer periods, and of the local topography influence on lower levels of vertical air exchange had not been adequately considered. The relative effect of precipitation on local exhalation of ^{222}Rn and ^{220}Rn may need clarification, but the wide-area diurnally resolved exhalation rate and/or exhalation ratio should be a more reliable indicator of the possible influence of mining activities in a given area than the mean ^{222}Rn concentration.

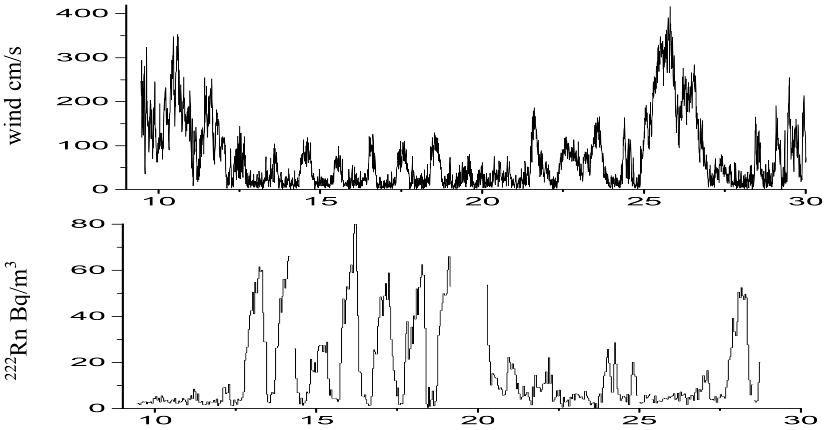
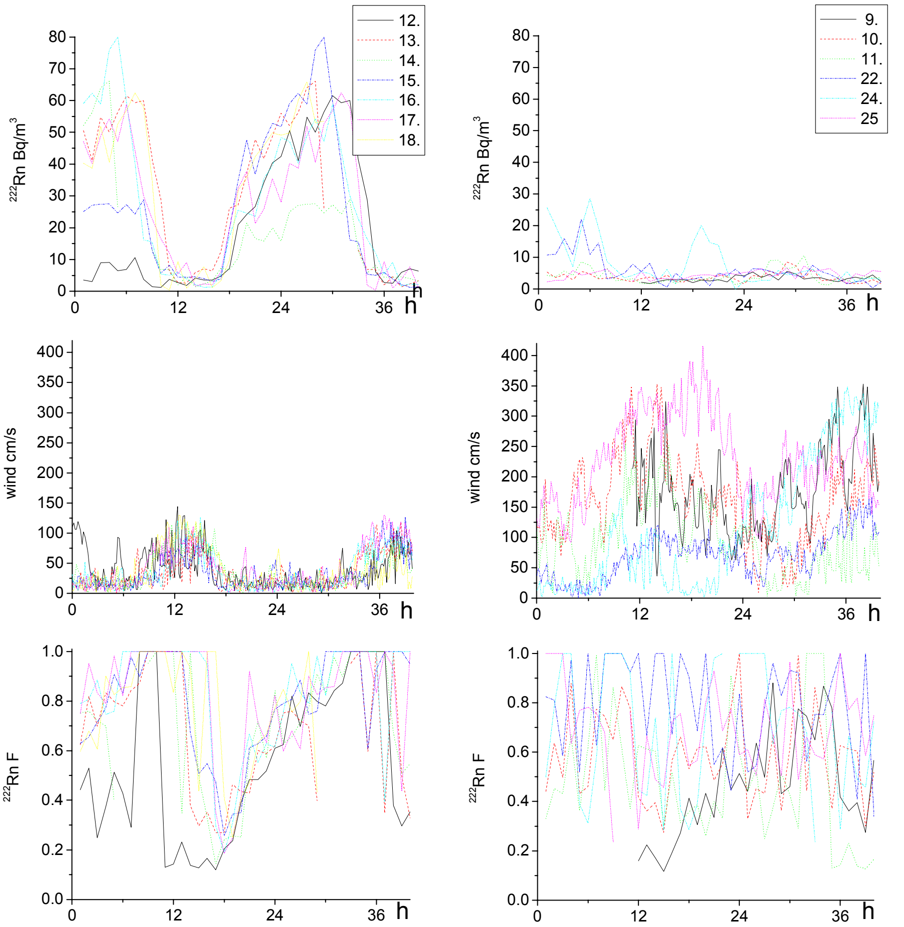


Fig. 1: Measurements 9 - 30 Oct. 2003



a: diurnal cycles starting 00h00 on 12th to 18th Oct

b: diurnal cycles starting 00h00 on Oct 9,10,11,22,24&25

Fig.2 Diurnal cycles selected to show different nature -
a) minimal wind period for ^{222}Rn accumulation @ F low
b) always at least some wind - thus elevated F and low ^{222}Rn

TEST OF THE MATERIAL FOR RADON SEAL LAYER AT THE MINE WASTE DISPOSAL SITE JAZBEC

J. Rojc[1*], **P. Jovanovic**[2**]

[1]Todraz 1, Slovenia
[2]Institute of Occupational Safety, Ljubljana, Slovenia

Abstract

About 1.4 million t of mine waste was deposited at the mine waste disposal site Jazbec during the mining of ore at the Zirovski vrh uranium mine. The average concentration of uranium in the mine waste is about 60 g/t, the average specific activity of ^{226}Ra is 730 Bq/m^3. To reduce the radon exhalation rate and the penetration of rainfall water into the waste pile, it should be covered with an appropriate material. The surface of the waste pile is about 5 ha. The thickness of the cover should be about 2 m. A test field on the waste pile Jazbec (100 m long and 12–20 m wide) was constructed in 2003. The surface of the test field was separated into two parts: one part with a multi-layer cover (5 layers), the second part with only two layers. For the seal layer, fine clayey silt and sand were used. Measurements of radon exhalation were carried out on the mine waste material, on the seal layer, on the protection layer and finally on the humus layer. For the radon exhalation measurements, the method with charcoal absorbers was applied. The time of exposure was 48 h. The results of the radon exhalation rates confirmed that clayey silt and sand mixture is an adequate material to use as a radon barrier. The average results of the radon exhalation rates were 50% and more lower than the prescribed authorized limit of 0.1 Bq·m^{2}s^{-1}. The results of the water penetration measurements were not as low as is required by the regulations. The improvement of clayey silt and sand characteristics with bentonite was also evaluated.

1. INTRODUCTION

The Zirovski vrh uranium mine is located in the north-western part of Slovenia, 35 km west of the capital city of Ljubljana. The facilities consist of the underground mine, several mine waste deposits and the mill tailings site. The mill has already been demolished and the area decontaminated. The uranium ore deposit was discovered in 1960. Twenty two years later, uranium ore extraction started. The first yellow cake was produced at the end of 1984. At the end of June 1990, production was stopped permanently. In the three decades, about 60 000 m of adits, galleries, stopes and shafts, about 2.7 Mt of rock and 0.63 Mt of uranium ore were mined. The average uranium concentration in the ore was about 715 g/t.

The Jazbec mine waste disposal site is situated at the main entrance of the uranium mine P-11. About 1.4 million t of mine waste and red mud has been deposited since 1982. The average concentration of uranium in the deposited materials was about 60 g/t, and the ^{226}Ra activity concentration was about 730 Bq/kg. The amount of red mud is 48 000 t, with a ^{230}Th activity concentration of approximately 60 Bq/kg. It is planned that an additional 0.4 Mt of mine waste from other mine deposits, rubble from the demolition of facilities, and contaminated soils will be disposed at the site by 2005. The site is located in a deep ravine of

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[*] E-mail: joze.rojc@rudnik-zv.si
[**] E-mail: peter.jovanovic@zvd.si

the Jazbec brook. The surface area of the facility is about 5 ha, and the altitude difference between the lowest and highest point is presently 65 m [6, 7]. After depositing the mine waste and material from the decontamination and demolition of the mine surface facilities, the surface of the facility will be reshaped. Then the whole site will be covered with a layer of natural material about 2 m thick. The main reasons for such cover are:

- To assure the stability of the disposal facility;
- To protect the surface of the disposal facility from water erosion (the annual average precipitation over the last 40 years was 1750 mm, with a maximum of 100 mm/day);
- To restrict/prevent the entrance of rain water into the body of the waste and to reduce the dissolved uranium, the uranium decay products and the chemical components in the seepage water from the site;
- To reduce the radon exhalation from the waste into the atmosphere.

In 1994, a small test field was constructed on the upper plateau of the facility. For the seal layer, a special clay from Novo Mesto (150 km from the uranium mine) was applied. The test field of 200 m^2 was divided into three parts, with layer thicknesses of 0.2, 0.3 and 0.4 m. The radon exhalation was measured with the charcoal method by the Jozef Stefan Institute, Ljubljana. The test measurements confirmed that the 0.4 m thick layer of clay reduced the radon exhalation from the mine waste into the atmosphere from 0.8 to 0.02 $Bq{\cdot}m^2s^{-1}$. On the basis of these radon exhalation measurements, an exhalation limit of 0.1 $Bq{\cdot}m^2s^{-1}$ and a multi-layer cover were suggested. In 1996, the Health Inspectorate adopted this limit for radon exhalation and prescribed it as the authorized limit for the Jazbec mine waste disposal site. The design of the cover and the procedure for its construction were defined in the project for the long term settlement of the mine waste disposal site [6, 7].

In late autumn 2002, the construction of the seal layer was tested at the Borst mine tailings site. The dimensions of the test field were 100 × 15 m. The activities started during heavy rain, and the temperatures were 10°C or less. After one month the testing was temporarily stopped. In April 2003, testing began on a test field at Jazbec. The test field was situated on the slope of the waste facility. In the meantime, a new proposal for the cover structure was prepared. The test field was divided in two parts:

- the lower part had dimensions of 50 × 12 m, and comprised a multi-layer cover of five layers, one of which was a drainage layer (original project proposal for the cover structure),
- the upper part had dimensions of 50 × 20 m, and comprised a two-layer cover without the drainage layer, (new proposal for the cover structure).

The local community was opposed to the transport of the large amounts of construction materials through the 1000-year-old town Skofja Loka and the local villages in the Poljanska valley. To avoid conflicts with the community, the clay material for the sealing layer was substituted with local material obtained from a location close to the Jazbec disposal site. The local material (carnian silty and clayey gravel) was tested in the Building and Civil Engineering Institute, Ljubljana. By testing, it was established that the permeability of this material for water was higher than for the clay material. The content of the fine fraction was not large enough, but it was possible to improve this deficiency with the addition of a fine material such as bentonite. Local materials were tested at the Borst mill tailings site in 1996. The construction of the test field was in the rainy period, the best local materials were selected for the seal layer (clayey gravel – carnian clayish sandstones/clay sand), the applied materials were technically improved and the results of the radon exhalation rates were also excellent. All conditions for a successful test were assured. The test of the local materials was carried out on a small, flat surface of about 300 m^2. But the Jazbec disposal site has a surface of about 50 000 m^2, nearly half of which is on a steep slope. Was it possible to assure such a small radon exhalation rate also for the cover of the Jazbec disposal site? The answer was no. Dry weather (no precipitation, high temperatures) was technically more convenient for the construction of the cover layers, but it was difficult to assure the required characteristics of the material used. The appropriate period for the construction of cover layers was from May to October, but in this time the temperatures in Zirovski vrh can be very high, with very long dry periods without rain.

2. CONSTRUCTION OF THE TEST FIELD, PREPARING FOR THE RADON EXHALATION RATE MEASUREMENTS

The construction of the test field at the Jazbec disposal site began in December 2002. The original slope of Jazbec was planed and the incline of the slope was reduced to 20°. In the second part of April, the construction of the multi-layer cover started. The slope was flattened with a roller and then the seal layer was built in two separate layers with thicknesses of 0.3 and 0.2 m. After this, the drainage layer followed, then the shielding layer in two separate layers and finally a layer of humus. The total thickness of all five layers was 2.05 m. The seal and shielding layers were compacted with a stamp foot roller. After this the two-layer cover on the upper part of the test field followed. On the left part of the test field, particular layers 0.3 m thick were flattened with a bulldozer and then compacted with a stamp foot roller. On the right part of the test field, layers were flattened with a bulldozer. Details of the two types of cover are shown in Table I.

TABLE I. COVER STRUCTURE AND LAYER THICKNESSES

Layer	Thickness (m)
Multi-layer cover (original project proposal):	
Vegetation: grass and bushes	
Vegetation layer: humus or soil	0.25
Protecting layer: silty gravel (crushed carnian solid sandstone)	0.8
Filter layer: sand, gravel or grit	0.3
drainage layer: crushed stone	0.2
Sealing layer: clay	0.5
Waste rock: mine waste	
Total thickness of cover	2.05
Two-layer cover (new proposal):	
Vegetation: grass and bushes	
Vegetation layer: locally available soil	0.25
Protecting layer: silty gravel (crushed carnian solid sandstone 0/63 mm)	1.3
Sealing layer: clayey gravel (separated weathered carnian clayish sandstones/clay sand)	0.5
Total thickness of cover	2.05

Daily temperatures during the test were 20–35°C. To avoid the loss of moisture in the gravel, the gravel was transported directly from the place of the excavation to the Jazbec test field. The moisture in the seal layer was 11–19% (15% on average). The seal and shielding layers were moistened with water after the compaction. The measurements of radon exhalation were organized on the next morning. The placing of charcoal canisters started at 06:30. For each plastic cylinder, a small plateau with dimensions 0.15 × 0.15 m was prepared. The contact between the plateau and the cylinder was sealed with clayey material. About 0.3 m above the plateau, a 0.5 m long cross channel was hollowed out to take away the surface water in case of rain. In the early afternoon, the near surroundings of each measuring point were moistened with water to avoid the formation of cracks in the ground caused by dry weather. Subsequent to this test, we substituted the moistening of the surface layer with the application of a 3–5 cm thick layer of fine, non-compacted clayey gravel. A thin layer of gravel or other material is more appropriate than the moistened one.

3. MEASUREMENT METHODS

A simple method for measuring ^{222}Rn exhalation from the surface was used. It consisted of placing the activated charcoal canisters on the ground to adsorb the emitted radon gas from the soil [1–4]. By using this method, problems caused by back diffusion and leakage were largely eliminated because the activated charcoal virtually adsorbed all the radon entering the exhalation container. Variations of atmospheric pressure during the time of exposure have a strong influence on the radon exhalation rate [5] and cause it to change. This method gives as a result the average value of the radon exhalation rate for the exposure time used.

The canisters were made of metal with a diameter of 9 cm and a height of 3 cm, and filled with 100 g of charcoal. The charcoal was activated by heating the can, open end up, on an electric frying pan for at least 4 h at about 150^{o}C. The cans were sealed with caps and adhesive tape. After opening, the canisters were fixed to the ground surface simply by pushing the rim of an outer protective plastic shell into the soil to a depth of about 1cm. The canisters were recovered after two days and resealed with their metal caps. They were then left for least 3 h to allow the radon daughters to grow into equilibrium with radon.

Counting was done inside a lead-brick shield to reduce the background from external radiation. The gamma activity of the canisters was measured using a high purity Ge detector on a multi-channel analyser system. Three gamma peaks of radon daughters were used for analysis: 295 keV and 352 keV of ^{214}Pb and 609 keV of ^{214}Bi. The efficiency of the detector for charcoal canisters was determined using the reference charcoal canister from Isotope Products Laboratories, Source No. 236-4-5-8 filled with a standard radium solution in radioactive equilibrium between radon and radium.

4. RESULTS OF THE RADON EXHALATION MEASUREMENTS

The geophysical measurements, as measurements of material compression, showed that it was not possible to assure the same geomechanical characteristics in the layer on the steep slope as those on the flat surface. But with a cover thickness of 2 m this deficiency did not have a measurable impact on the passage of radon through the seal and shielding layers. The average measured radon exhalation rates on the different layers were lower than the prescribed authorized limit of 0.1 $\mathrm{Bq{\cdot}m^2s^{-1}}$. The results of radon exhalation measurements for the different types of layers and with different thicknesses of layers are presented in Table II. In June 2004, a new series of measurements will be performed to check the radon exhalation rates after one year of existence of the Jazbec test field.

To reduce the flow of radon from the mine waste through the cover layer, the preservation of moisture in the gravel before being built in, and compression, are of great importance. This statement was confirmed at the Borst test field constructed in 1996. The seal layer (0.5 m clayey gravel) was not protected with an additional shielding layer. During the 7 winters (frost) and 7 summers the clayey gravel broke up. The radon exhalation rates, measured in dry weather in September 2003, were a few hundred times larger than during the rainy autumn in 1996 [6, 7].

TABLE II. AVERAGE RADON EXHALATION RATES AT THE JAZBEC TEST FIELD

Type of layer and thickness	Average Rn exhalation rate ($Bq\cdot m^{-2}s^{-1}$)	Effect of covering layer (%)
Mine waste covered with 0.1–0.25 m layer of soil	1.19	21
Mine waste planed with bulldozer, compacted with stamp foot roller	1.50	0
Sealing layer (0.5 m clayey gravel) flattened with bulldozer, compacted with stamp foot roller, lower test field	0.02	99
Drainage layer (0.2 m grit) + filter layer (0.3 m grit) + protecting layer (0.8 m crushed silty gravel) flattened with bulldozer, compacted with stamp foot roller, lower test field	0.05	97
Sealing layer (0.5 m clayey gravel) flattened with bulldozer, minimally compacted with stamp foot roller, left part of upper test field	0.08	95
Sealing layer (0.5 m clayey gravel) flattened with bulldozer, not compacted with stamp foot roller, right part of upper test field	0.05	97
Protection layer (1.8 m crushed gravel) flattened with bulldozer, not compacted with stamp foot roller, upper test field	0.04	97
Final covering with humus, deposited and flattened with excavator	0.07	95
Obligatory authorized limit	0.1	93

5. CONCLUSION

The results of the radon exhalation rates confirm that clayey gravel is an adequate material to use as a radon barrier at the Jazbec mine waste disposal site. A thickness of 0.6 m of clayey gravel is enough to limit the radon flux to within the required value. The efficiency of such type of layer is higher if the clayey gravel is intensely compacted and if the layer is built up in several thin layers. It is very important to preserve the natural moisture in the clayey gravel during the building-in procedure and to apply the protection layer as soon as possible on the sealing layer to prevent the drying of the gravel.

On the basis of the radon exhalation rates from the Jazbec disposal site, the emission of ^{222}Rn to the environment was estimated to be up to 2 TBq/a. After the cover is complete, the emission of radon will be about 0.2 TBq/a. The additional contribution of radon from the mine waste to the radon concentration in the Jazbec area is estimated to be <10–20 Bq/m^3.

The charcoal canister method is adequate for measuring ^{222}Rn exhalation. The deficiency of this method is sometimes the time of sampling (48 h). No other activities are allowed at the same time in the surroundings. During sunny weather and higher temperatures, it is very important to control the formation of cracks in the ground in the near surroundings of the measurement points. Moistening of the surface with water or the application of 3–5 cm of clayey gravel have been effective in protecting the layer from crack formation.

The two-layer cover will replace the multi-layer cover at the Jazbec mine waste disposal site and at the Boršt mill tailings site. The reasons for this decision are the following:

- The two-layer cover is much easier to construct;
- Its stability on a steep slope is much higher;
- Damage is much easier to repair;
- Maintenance is simpler and cheaper;
- The radon exhalation rate is the same as that for the multi-layer cover.

A new project for the long-term settlement of the Jazbec mine waste disposal site has been prepared. The structure of the cover is shown in Table III.

TABLE III. SINGLE-MATERIAL COVER PROPOSED FOR THE JAZBEC MINE WASTE DISPOSAL SITE

Layer	Thickness (m)
Vegetation: grass and bushes	
Vegetation layer: locally available soil	0.25
Storage (interim) layer: crushed silty gravel (carnian solid sandstone 0/63 mm)	0.5
Protecting layer: crushed silty gravel (carnian solid sandstone 0/63 mm)	0.8
Sealing layer: clayey gravel (separated weathered carnian clayish sandstones/clay sand)	0.5
Total thickness of cover	2.05

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RADON MEASUREMENTS AS A MONITORING POSSIBILITY FOR MINING SUBSIDENCE OCCURRENCES

A. Kies[1*], A. Storoni[2], Z. Tosheva[1], H. Hofmann[1]

[1]Laboratoire Physique des Radiations, Université du Luxembourg, Luxembourg
[2]Cellule de Recherche en Géographie Physique, Luxembourg

Abstract

The objective of the current research is to check whether or not subsurface radon concentrations can be related to mining and mining subsidence voids in order to allow the creation of a subsidence risk map. The chosen test site is located in the former Luxembourg mining basin. Under an overburden of 65 m thick limestone and marls, iron ore bearing formations have been mined between 1920 and 1950. Mining subsidence has progressively occurred for more than 50 years and is currently going on. We report on intensive investigations on radon-in-soil measurements, distributed over parallel traverses. Radon concentrations plotted against sample spacing are very irregular showing inhomogeneous subsoil. The maps of radon concentrations document these irregularities; furthermore it is possible to identify a trend corresponding to the main directions of the old mine roadways. The location of enhanced radon concentrations may point to a local increased subsidence risk, consecutive to a fractioning of the underground.

1. INTRODUCTION

The Luxembourg mining basin covers 3670 ha, located in the southwest of the country (Fig. 1(a)) and is the northern continuation of the French ‘minette’ iron ore basin. The minette ore was extracted from the middle of the 19th century until 1981 at which time the last mine was closed. The extraction technique used in the underground mines was the room-and-pillar working where the ore is taken from a panel while pillars are kept in place temporarily in order to maintain the solidity of the roof. On the retreat, the pillars are gradually removed allowing the roof to collapse. In older mines, the geometry of the workings was often irregular and many pillars remained in place keeping the rate of extraction sometimes as low as 50 % [1]. Most of the undermined surface has been affected by ground subsidence during and after the mining period due to the fact that the thickness of the overburden, comprehending the overlaying sterile strata as well as the non exploited seams, reaches from a few metres at the outcrop of the ore layers to a maximum of 80 m along the French border.

Mine subsidence occurred and continues even more than 50 years after closure; the rate of surface collapse has nevertheless perceptibly diminished in the course of the last 30 years. The two types of ground subsidence that dominate in Luxembourg are crown holes and fissures. Crown holes mostly form on top of the wider mine voids, as they are the direct result of roof collapse between pillars. Sometimes they trace the pattern of the underlying mine. Individual subsidences may coalesce into depressions of different shapes. The depth of the resulting deformations vary from a few tenths of a metre to as much as 8–10 m, depending on the local bulk factor and the number and thickness of the extracted layers.

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[*] E-mail: antoine.kies@univ.lu

Throughout the mining period, subsidence-related disturbances caused comparatively little damage as the mining area is scarcely occupied. Merely secondary roads, a few buildings, a municipal park, and a camping ground were damaged and had to be abandoned. New subsidence risks emerged at the end of the 20th century when notably undermined areas started to be considered apt to support urban facilities necessary for the development of the crowded industrial towns of the mining basin where about a third of the country's population lives. Time alone will not solve this risk problem because in areas prone to pillar failure and sinkhole development the subsidence risk may last for decades and even centuries after underground mining has stopped.

Experience has shown that the only safe management policy for mining areas prone to pillar failure under a thin overburden is to abandon them altogether or at least to ban any residential or industrial development from this land. On the other hand it cannot be excluded that sooner or later the development of the urban infrastructure will encroach on the mining land. Such a development will probably be delayed temporarily or it may be limited to restricted areas, so that managing the subsidence risks is not an urgent matter. On a few occasions though, positive expertise based on erroneous data had been forwarded, which shows that data on past mine workings and on former ground subsidence are not readily available. In fact, the greater part of the mining company records have disappeared by now or are in the hands of private collectors. The archives of the mining inspection authority are still available, but they offer only limited information. Recorded data on ground subsidence are extremely scarce, except for the first two decades of the mining period. Old air photographs may show ground subsidence on some occasions, but only if it was localized outside the forest and had not yet been reclaimed at the moment of the coverage. The only effective ways to document the type of subsidence and to determine the spatial aspects of the disturbances is a close and often tedious field investigation. Due to the poor information on the underground mine conditions and to the undeniable fact that under the prevailing conditions no zone of the mining area can be considered to be safe construction ground, new means of monitoring mines from the surface have to be investigated. Among different possible geophysical investigations we decided for a monitoring based on radon in soil air measurements.

2. MATERIALS AND METHODS

The chosen test site called 'Baraque Bleue' is located in a forested area on the plateau of the Luxembourg mining basin. Under an overburden of 65 m thick limestone and marls, two iron layers have been mined between 1920 and 1950, in tunnels approximately 3 m high The site is depicted in Figs 1 and 2, which show examples of sinkhole occurrence over the old mine roadways and the location of the transects where soil-radon was measured. The locations of the underlying main galleries are approximate. Along the western boundary a long surface fissure has developed and some 30 subsidence pits occurred over a period of several decades; the last developed in 1995 (Fig. 2).

The site was chosen mainly because it is situated in a forest area, it has a more or less uniform surface, the old mining maps still exist and further subsidence may be expected especially under the neighbouring busy road in the vicinity of which the most recent crown holes appeared.

The ease with which radon can leave the site of production in the soil and rocks, and the differences in the subsequent possibility of migration and concentration in underground voids, give the possibility to locate underground inhomogeneities by a survey based on radon soil measurements. Normally mining voids situated at a depth of 60 m have no influence on radon concentrations measured at 1 m depth. But due to mining subsidence and the important brittleness of the rocks, fractures can develop and radon will be able to move up to the surface; as a consequence we expect locally increased radon concentrations. We report on an intensive investigation on radon in soil measurements, distributed over 10 parallel transects. Along a transect, the spacing between the measurement points was 4 m and 10 m between each transect. The last two transects had an offset of 30 m (Fig. 2).

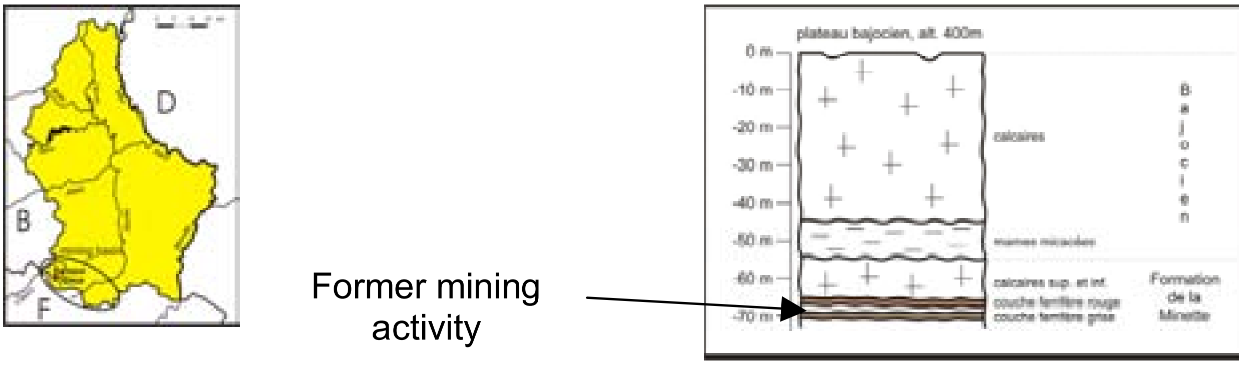

FIG. 1. (a) Location of the Luxembourg mining basin, (b) Thickness and nature of the overburden at the investigated site 'Baraque Bleue'

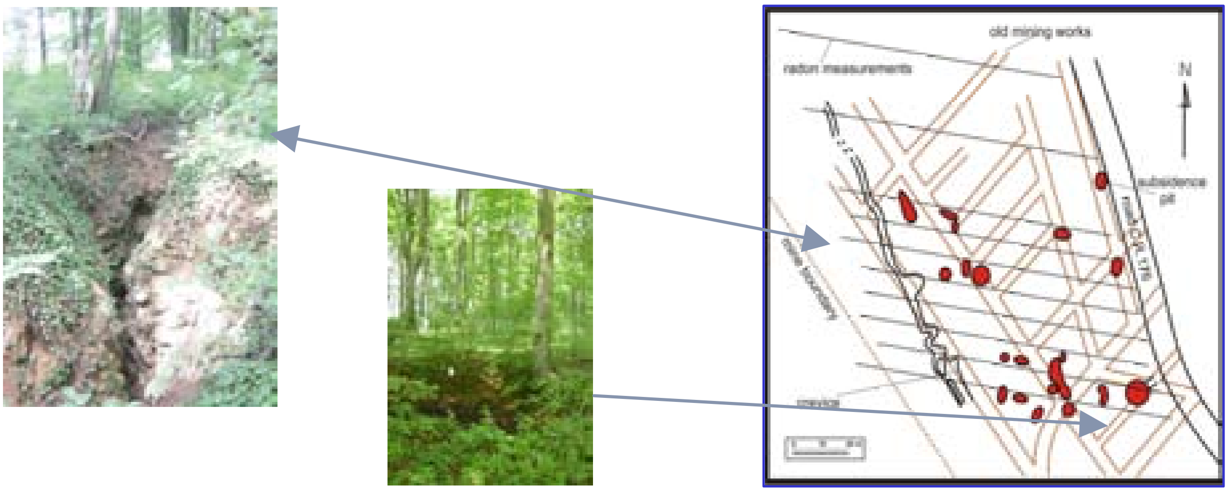

FIG. 2. The chosen test site "Baraque Bleue"

The distribution of radon activity concentrations in the subsurface gives very useful information and applications in many different domains. Variable concentrations often mean variable emanation and variable migration possibilities in a fractured medium. For indoor radon surveys, radon potential maps based on radon activity concentrations in soil gas are taken as an estimation of the geogenic radon potential [2]. In geology, geophysics and archaeology they give hints on underground inhomogeneities as faults, fractures, underground voids [3–5].

A steel tube was hammered 1 m below the soil surface and a small void of several cubic centimetres was freed at the end of the rod. Compaction of the soil was small due to the small diameter of the rods. After venting a certain volume in order to purge the system, soil air samples were sucked into a syringe; 100 ml were introduced from the syringe into an evacuated Lucas cell. The measurements were performed after at least 3 h in order to reach the equilibrium between radon and its short-lived decay products in the measuring cells.

For the present survey, all measurements were performed in a couple of days, thus minimizing an eventual seasonal variation; furthermore during the survey the weather conditions were dry and stable. The measurements were done without repetition, only for some holes soil gas was collected twice for a quality check.

3. RESULTS AND DISCUSSION

For the present study we were fortunate to have information from the old mining maps [1]. As the subsurface features we wanted to detect by the survey were elongated, the transects were taken across them, perpendicular to the underground directions of the main galleries. Fig. 3 shows 7 of the resulting profiles displayed one above the other. It can be seen that the choice of the transect directions was a good one.

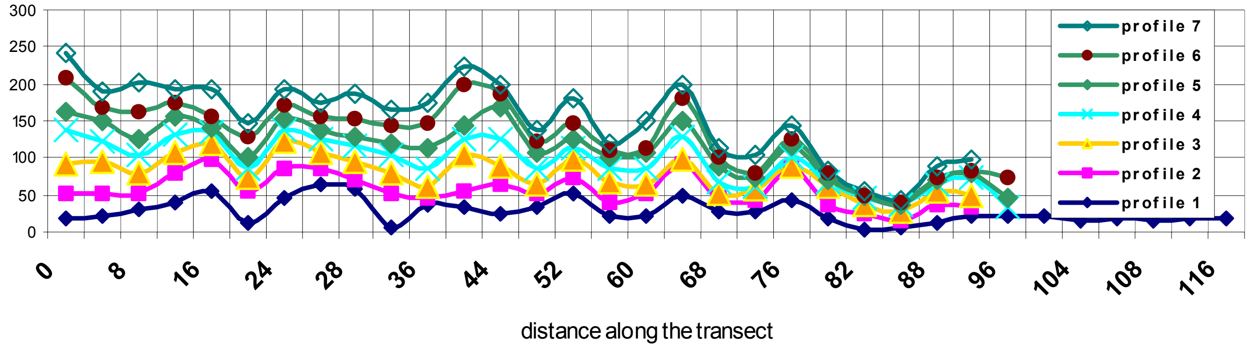

FIG. 3. Stacked profiles of the 7 parallel transects, inter-distance 10 m

As expected, the measured concentrations are lognormally distributed, with the exception of some unusually low values (lower than 5 Bq/m^3) that were omitted from the mapping. The median value was 25 kBq/m^3. Very low measured radon concentrations indicate an incorrect sampling or a disturbed soil; they introduce undesired lows during the mapping procedure (Fig. 4).

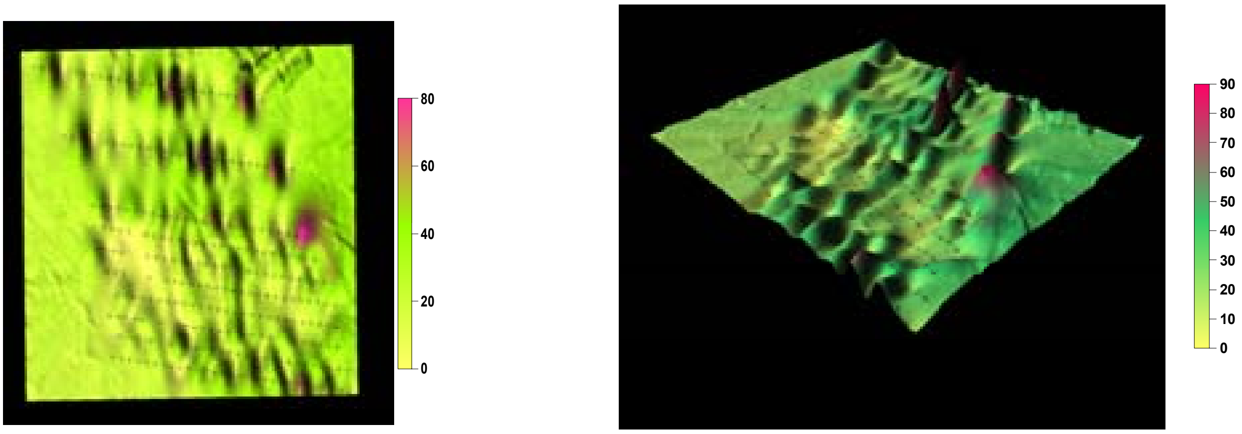

FIG. 4. Surfer maps show the distribution of the radon concentrations and the transects with the exact locations of the measuring points (radon concentrations in kBq/m^3)

The radon concentrations plotted against sample spacing were very irregular, documenting an inhomogeneous subsoil. The maps of the radon concentrations (Figs 3 and 4) show these irregularities. Through the maps obtained, after 'kriging' by the Surfer program, it was possible to identify a trend from east to west, corresponding to the main direction of the underlying main tunnels. Locations of increased radon activity concentrations may present an increased risk for subsidence in the near future. An alarming fact is that the points where radon concentrations are highest are situated close to a busy road.

Presently a study is being initiated to duplicate the investigations with gravity measurements. It will be interesting to compare the results.

4. CONCLUSION

The present study, based solely on radon in subsoil measurements, shows a promising possibility to investigate subsidence due to past mining activity. Locations with enhanced radon concentrations may imply an increased subsidence risk as a consequence of the underground fractionation. It is evident that a radon survey should be part of a vast investigation effort incorporating other geophysical techniques.

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ESTIMATION OF RADON DOSE IN SEVERAL WORKPLACES USING DOSIMETRIC MODEL FOR INHALATION OF AIRBORNE RADIONUCLIDES

K. Mamont-Cieśla[*], **O. Stawarz**

Central Laboratory for Radiological Protection, Warsaw, Poland

Abstract

There are two approaches to the estimation of the effective dose associated with the inhalation of ^{222}Rn short-lived progeny. One of them based on Publication 65 of the International Commission on Radiological Protection (ICRP) using a single dose conversion factor, called a conversion convention, is derived from the results of epidemiological studies on uranium miners. However, the extrapolation of the lung cancer risk for uranium miners to the general population is highly questionable, due to the large difference in radon exposure (2–3 orders of magnitude) and differences in the exposure environments (e.g. concentration, size distribution and chemical composition of aerosols), breathing rates, smoking patterns and so on. The second approach is based on ICRP Publication 66, which strongly recommends the use of dosimetric models for inhalation of airborne radionuclides. These models reveal that the dose per unit intake of radon progeny depends on the site of particle deposition in the respiratory track, which, in turn, strongly depends on the particle size distribution. It is particularly important in the estimation of the dose to take into account the contribution of the ultrafine particles below 10 nm in diameter. To recapitulate, for the reliable estimation of the radon dose it is necessary to know not only the potential alpha energy concentration (PAEC), but also the full size distribution of radon progeny particles in the range 1–1000 nm, which penetrate the lung with the air. The dosimetric model approach uses a weighted dose conversion factor, which combines radon progeny size distribution with the particle-size-dependent dose conversion factors in a particular exposure location. By means of our radon progeny particle size spectrometer, manufactured by ARPANSA, Australia, we measured PAEC and radon progeny size distribution in five workplaces — an attorney's office, the Faculty of Physics at Warsaw University (two locations), the Central Laboratory for Radiological Protection, and the 'Barbara' experimental coal mine. The measurements were conducted in two aerosol conditions: natural and high level aerosols from smoking cigarettes. We applied both approaches for the estimation of the annual effective doses from inhaled radon progeny for an adult male with a breathing rate appropriate for occupational exposure (1.2 m^3/h) and for environmental exposure (0.78 m^3/h) and compared them. The ratios of the doses estimated by the dosimetric model to those estimated with the use of the constant conversion convention ranged from 0.5, when the free fraction was about 5%, to 1.7 when the free fraction was about 30%.

1. INTRODUCTION

The deposition of inhaled short-lived radon progeny in the respiratory tract is a main contributor to the radiation dose arising from exposure to radon. The dose is calculated as a product of the potential alpha energy concentration (PAEC) and a dose conversion factor (DCF). There are two approaches to the estimation of the DCF. One of them, based on Publication 65 of the International Commission on Radiological Protection (ICRP) [1] using a single dose conversion factor called a conversion convention, is derived from the results of epidemiological studies on uranium miners. However, the extrapolation of the lung cancer risk for uranium miners to the general population is highly questionable, due to the large

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[*] E-mail: kalinam@clor.waw.pl

difference in radon exposure (2–3 orders of magnitude) and differences in the exposure environments (e.g. concentration, size distribution and chemical composition of aerosols), breathing rates, smoking patterns and so on. The second approach is based on ICRP Publication 66 [2], which strongly recommends the use of dosimetric models for inhalation of airborne radionuclides. These models reveal that the dose per unit intake of radon progeny depends on the site of particle deposition in the respiratory track, which, in turn, strongly depends on the particle size distribution. It is particularly important in the estimation of the dose to take into account the contribution of the ultrafine particles below 10 nm in diameter. To recapitulate, for the reliable estimation of the radon dose it is necessary to know not only the PAEC, but also the full size distribution of radon progeny particles in the range 1–1000 nm, which penetrate the lung with the air. The dosimetric model approach uses a weighted dose conversion factor, which combines radon progeny size distribution with the particle-size-dependent dose conversion factors in a particular exposure location.

2. RADON PROGENY PARTICLE SIZE SPECTROMETER

The Central Laboratory for Radiological Protection (CLOR) owns a radon progeny particle size spectrometer (RPPSS) manufactured by ARPANSA, Australia (Fig. 1), a unique research tool that allows the radon dose to be estimated using the dosimetric model for inhalation of airborne radon progeny. The RPPSS comprises 8 stages operated in parallel: one open face stage, a four-stage diffusion battery system and a three-stage inertial impactor system. In the diffusion battery system, filters are preceded by wire screens with increasing numbers (1, 2, 13 and 32) and mesh (100, 100, 100 and 200) in the consecutive stages. In the three impactor stages, aluminized Mylar foil is used as a collector. The activity collected on the filters and foil are counted simultaneously by silicon detectors mounted adjacent to them. The counts are processed by deconvolution analysis for 43 size ranges between 0.60 and 2493.9 nm. It is done by means of two different algorithms: the Twomey non-linear iteration [3] and the expectation maximization method [4]. In the continuous mode, the deconvolution yields overall particle size distributions for ^{222}Rn daughters. The RPPSS produces, among other things, the following data: the total PAEC, the distribution of PAEC for 8 stages, the unattached fraction defined as the smallest particles collected by stage 2, the distribution of alpha-active aerosol sizes with information on each peak (activity median thermodynamic diameter (AMTD), geometrical standard deviation (GSD) and percentage contribution to PAEC), and the size-weighted dose conversion factors (for an adult male with breathing rates of 1.2 and 0.78 m^3/h) derived from the ICRP66 respiratory tract model implemented in the computer program RADEP (RAdon Dose Evaluation Program) [5]. The dependence of the DCF on the particle diameters applied in the software of the RPPSS is shown in Fig. 2. It reveals that for a particle diameter (AMTD) of 2.9 nm (the free fraction), the DCFs are about 22 times higher than for particles of about 500nm (the attached fraction). The RADEP-derived values of DCFs are adjusted by a factor of 0.3 to provide consistency with the results derived from the epidemiological risk estimate using the ICRP65 conversion convention.

The collection efficiency curves for all eight stages applied in the RPPSS software, for diameters of 0.6–2494 nm, are shown in the Fig. 3.

FIG. 1. Radon progeny particle size spectrometer

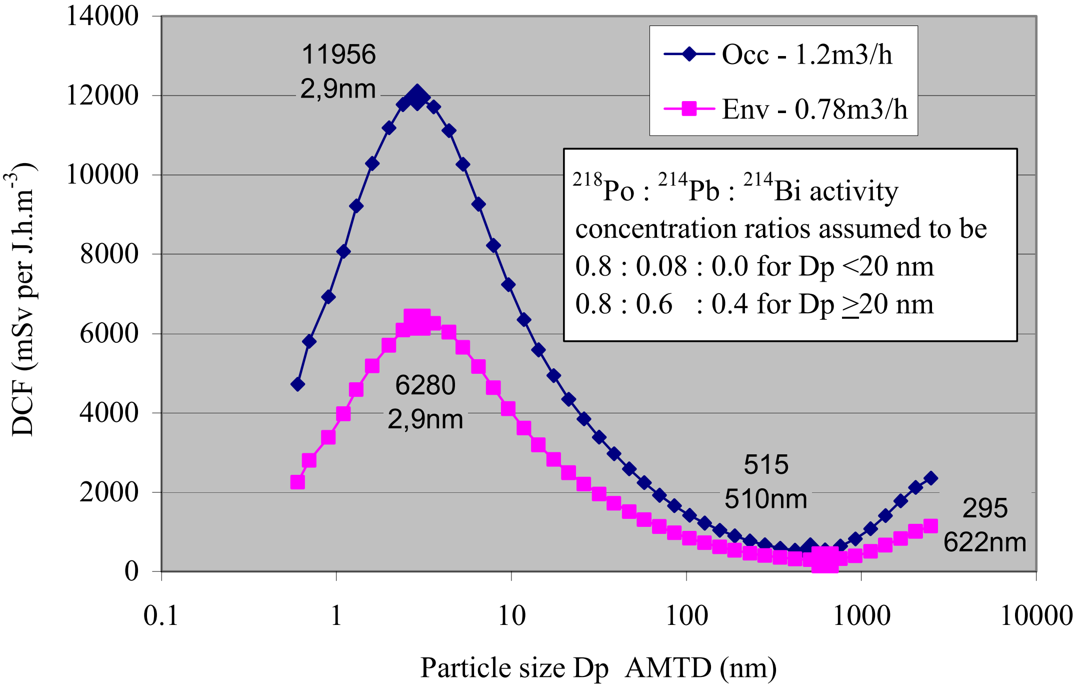

FIG. 2. RADEP DCF as a function of particle size for monodispersed particles

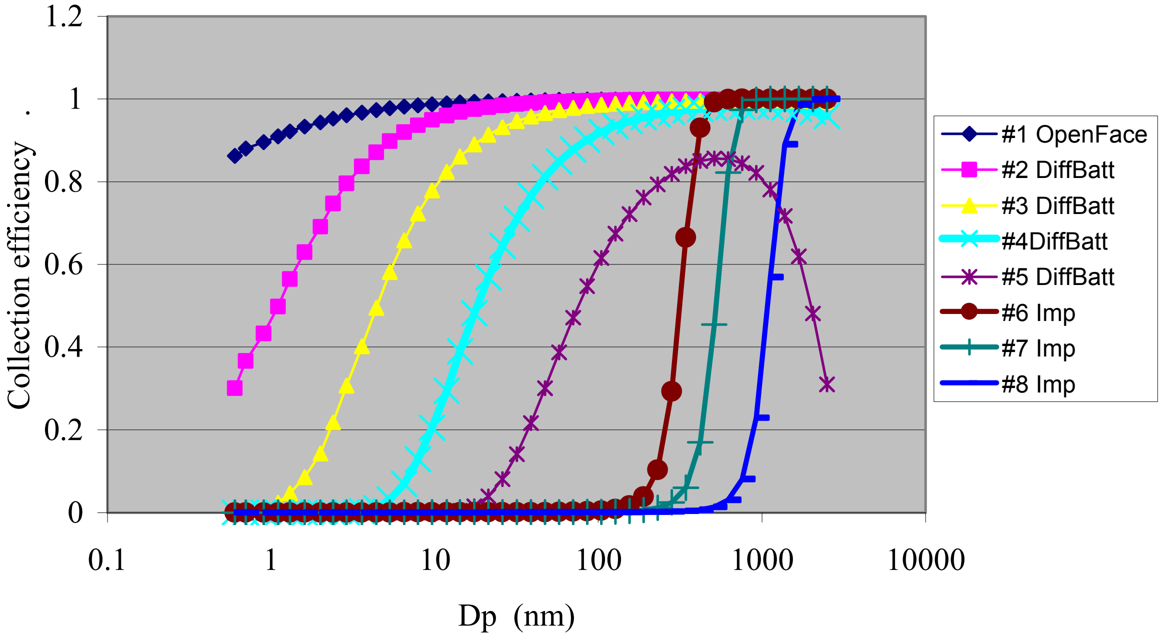

FIG. 3. Collection efficiency of all 8 stages

3. MEASUREMENTS AND RESULTS

Measurements of PAEC and radon progeny size distribution were performed with the RPPSS at four workplaces: an attorney's office with an elevated radon level, the Faculty of Physics at Warsaw University, the Central Laboratory for Radiological Protection, and the 'Barbara' experimental coal mine. The measurements were conducted in two aerosol conditions: natural and enhanced level aerosols from smoking cigarettes. Simultaneously, radon concentration was measured with an AlphaGUARD monitor to estimate the equilibrium factor *F*.

Table I summarizes the results of measurements of the average radon concentration, the PAEC, the equilibrium factor *F* and the unattached fraction *fp* at the four workplaces in both natural conditions and in an atmosphere of smoking cigarettes. In the Barbara coal mine, the measurements were performed on two separate days in natural conditions, characterized by a high aerosol level. The unattached fraction ranged from 0.3% in high aerosol conditions at the CLOR bunker to 30% in the attorney's office (computer server room) in a low aerosol level due to air conditioning. In the Barbara mine the unattached fraction was about 5%, with a high value of equilibrium factor *F* of 74–89%.

In Table II, data on the peaks in the particle size distributions expressed in terms of AMTD, GSD and percentage contribution to the total PAEC are given. Examples of the measured full distributions of particle size are shown in Figs 4 and 5. In the Barbara mine, an additional ultrafine particle peak of 7.9 nm occurs.

To estimate the annual effective doses, both of the above-mentioned calculation approaches were applied: the epidemiological approach using the ICRP65 dose conversion convention (1.425 and 1.1 Sv per J·h·m^{-3} for occupational and environmental exposure, respectively) and the dosimetric approach, which is based on the size-weighted dose conversion factors for each particle size distribution. The doses were calculated for an adult male with breathing rates of 1.2 and 0.78 m^3/h for occupational and environmental exposure, respectively, and are compared in Table III. The ratios of the doses estimated by the dosimetric model to those estimated with the use of the single conversion convention range from 0.5 when the unattached fraction is about 5% to 1.7 when the unattached fraction is about 30%. Similar results were obtained in studies performed with the use of an 'effective dosimeter' in a cave environment in Australia [6] — in these studies, the effective doses calculated according to the ICRP65 dose conversion convention were lower than those calculated using the dosimetric model by a factor of up to 2.

TABLE I. MEASUREMENT RESULTS

Workplace	Aerosol condition	^{222}Rn concentration (Bq/m^3)	PAEC (nJ/m^3)	Equilibrium factor (%)	Unattached fraction (%)
Attorney's office	Natural	1407	614	8	30
	Cigarette smoking	1400	1410	18	19
UW Hoża pavilion	Natural	224	39	3	10
	Cigarette smoking	426	216	9	0.8
CLOR bunker	Natural	118	430	65	5.8
	Cigarette smoking	102	460	81	0.3
Barbara mine	Natural	971	4040	74	5.3
	Natural	915	4550	89	5.3

TABLE II. DATA ON PEAKS IN THE PARTICLE SIZE DISTRIBUTIONS

Workplace	Aerosol condition	Peak 1			Peak 2			Peak 3		
		AMTD (nm)	GSD (nm)	Contrib. to PAEC (%)	AMTD (nm)	GSD (nm)	Contrib. to PAEC (%)	AMTD (nm)	GSD (nm)	Contrib. to PAEC (%)
Attorney's office	Natural	0.6	1.16	30	153	2.07	70	599	1.36	1.3
	Cigarette smoking	0.6	1.15	19	141	1.76	80	655	1.3	2.5
UW Hoża pavilion	Natural	1.0	1.66	10	151	1.49	80	721	1.19	9.7
	Cigarette smoking	1.4	1.82	0.5	152	1.51	88	713	1.23	11
CLOR bunker	Natural	0.92	1.55	5.8	160	1.54	80	755	1.35	14.2
	Cigarette smoking	1.0	1.71	0.3	170	1.38	90	711	1.20	9.5
Barbara mine	Natural	0.7	1.33	5.3	131	2.0	83	622	1.22	12
	Natural	0.7	1.33	5.3	135	1.87	81	681	1.25	14

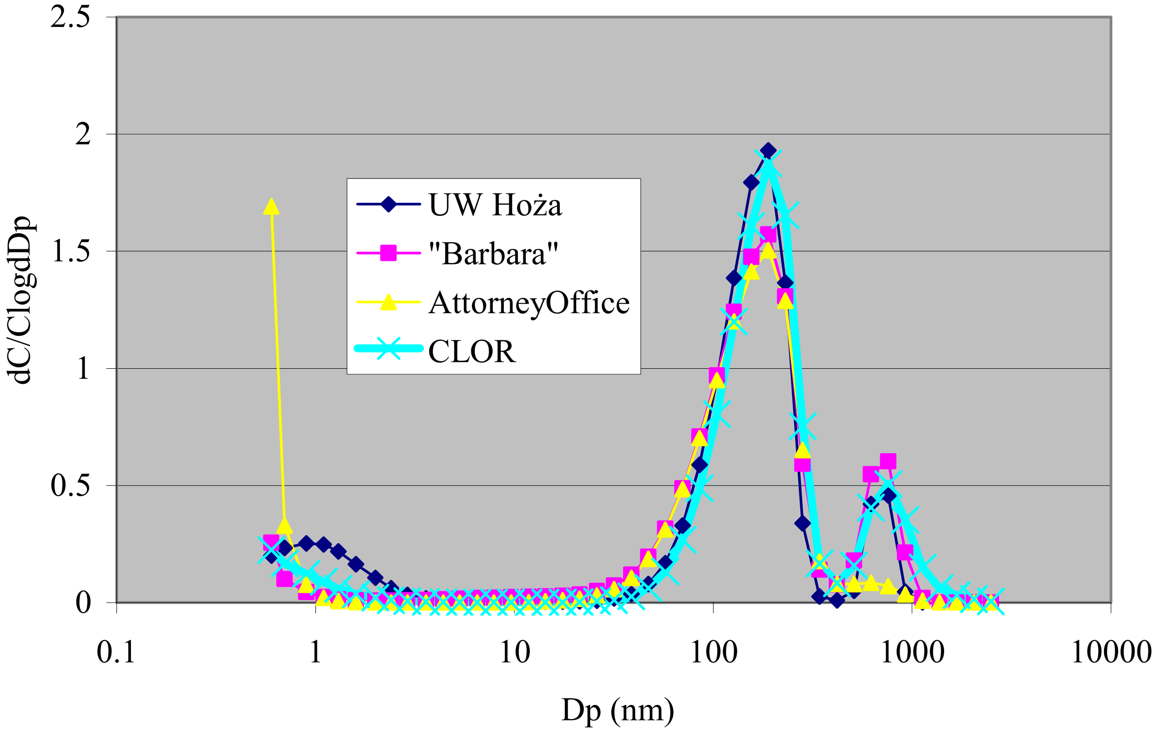

FIG. 4. Examples of particle size distributions

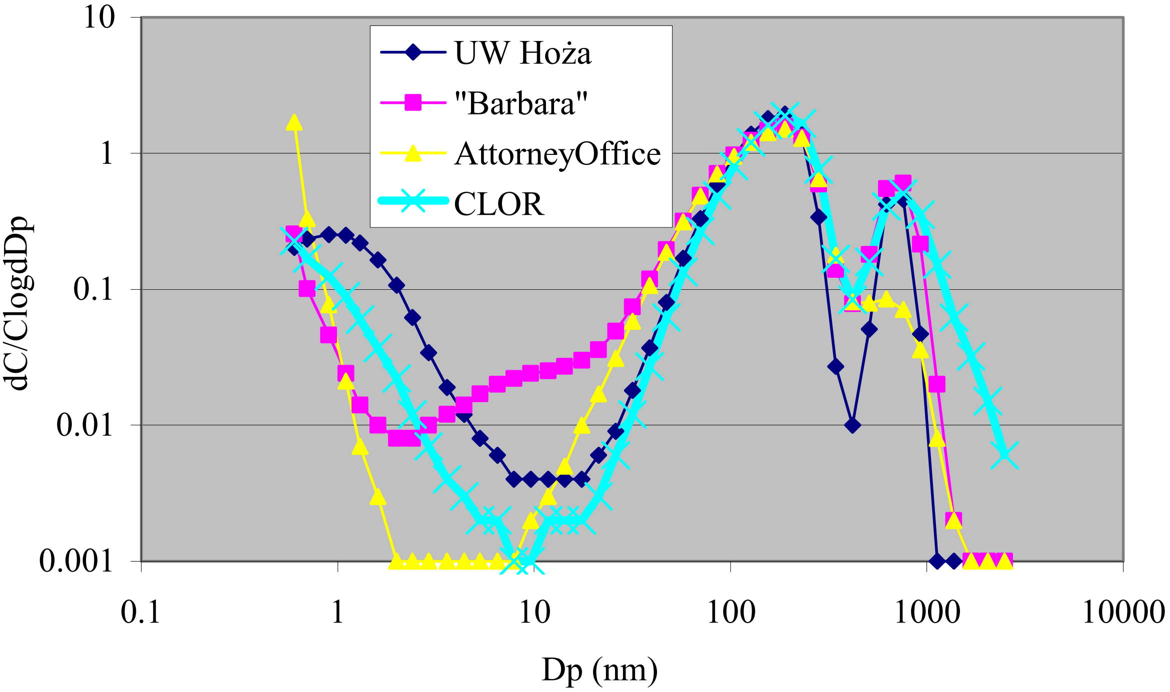

Fig. 5. Examples of particle size distributions

TABLE III. COMPARISON OF ANNUAL EFFECTIVE DOSES ESTIMATED USING DOSIMETRIC AND EPIDEMIOLOGICAL APPROACHES

Workplace	Aerosol condition	Annual effective dose (mSv)				Ratio of doses (epidemiological approach to dosimetric approach)	
		Epidemiological approach		Dosimetric approach			
		Occupational	Environmental	Occupational	Environmental	Occupational	Environmental
Attorney's office	Natural	1.46	0.76	0.87	0.68	1.7	1.1
	Cigarette smoking	2.70	1.45	2.00	1.55	1.4	0.9
UW Hoża pavilion	Natural	0.08	0.04	0.06	0.04	1.3	1.0
	Cigarette smoking	0.25	0.15	0.31	0.24	0.8	0.6
CLOR bunker	Natural	0.60	0.34	0.61	0.47	1.0	0.7
	Cigarette smoking	0.48	0.28	0.66	0.51	0.7	0.5
Barbara mine	Natural	6.20	3.50	5.80	4.50	1.1	0.8
	Natural	6.70	3.80	6.50	5.00	1.0	0.8

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INTERCOMPARISON OF INSTRUMENTS FOR MEASURING RADON AND RADON PROGENY HELD IN THE CLOR CALIBRATION CHAMBER

K. Mamont-Cieśla*, O. Stawarz

Central Laboratory for Radiological Protection, Warsaw, Poland

Abstract

Intercomparisons among radon laboratories are of particular importance because calibrated standards for radon activity concentration and for radon progeny activity concentration in air are not available. An intercomparison exercise for radon and radon progeny instruments was conducted at the Central Laboratory for Radiological Protection (CLOR) on 9–13 June, 2003 to verify comparability of mainly continuously measuring instruments for radon and potential alpha energy concentration (PAEC). Seven Polish institutions participated in the intercomparison of ten radon and six PAEC monitors. Among radon devices there were: six Genitron AlphaGUARD monitors, two Pylon AB-5 monitors, a radiometer RMR1 and a radon probe SRDN2. Among PAEC devices there were five monitors measuring in the continuous mode: three T/N Rn WL Meters co-working with AlphaGUARD monitors, a Pylon WLx monitor and a radon progeny particle size spectrometer (RPPSS), and one grab sampling device: an aspirator SKC equipped with an ALFA unit. All the instruments were simultaneously exposed in the large calibration chamber at CLOR, with a volume of 12.35 m^3 and a radon atmosphere of 700–2500 Bq/m^3 under different controlled climatic and aerosol conditions. The relative humidity varied from normal (45–50%) to very high (95–99%) and, for both values of relative humidity, the concentrations of condensation nuclei varied over the range 200–31 000 CN/cm^3. Aerosols were injected from the TSI water generator. The total exposure time was 44 h. A value of radon concentration calculated on the basis of the activity of radium ^{226}Ra in the certified Pylon flow-through radon generator constituted the reference value for radon at the beginning of the exposure. Later, the average results for four time periods from all instruments could be compared only among themselves due to the loss of radon while walking in and out the chamber. In the analysis of the PAEC results, the RPPSS spectrometer was considered as the reference because it measured radon progeny particle size distribution and applied it to correct the PAEC value for plate-out of small particles upstream in the inlet of the device. AlphaGUARD monitors were also compared in the atmosphere of thoron in the small calibration chamber of volume 0.32 m^3. Thoron was pumped into the chamber from the certified Pylon flow-through thoron generator in a closed circuit with a flow rate of 1 mm^3/min. The monitors worked equally well in the diffusion mode as in the flow mode with two different flow rates: 0.5 and 1 mm^3/min. The results of average radon concentrations for all AlphaGUARD monitors indicated very good agreement for the whole exposure time in the large chamber. For six AlphaGUARD monitors, standard deviations of mean values for four selected periods ranged from 1 to 2.8%, while for all monitors they ranged from 5.5 to 20%. The comparison of the means for AlphaGUARDs in the thoron chamber, where readings were below 100 Bq/m^3, gave significantly worse results. The comparison of the PAEC results from the T/N Rn WL Meters and the Pylon WLx monitor with the reference value from the RPPSS indicated differences of 30–42% in the calibration factors determined in high aerosol conditions (unattached fraction 5%), and 38–55% losses of PAEC possibly due to plate-out in the inlets of filter holders at low aerosol concentrations (unattached fraction 62%).

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* E-mail: kalinam@clor.waw.pl

1. INTRODUCTION

Intercomparisons among radon laboratories are of particular importance, because calibrated standards for radon activity concentration and for radon progeny activity concentration in air are not available. An intercomparison exercise for radon and radon progeny instruments was conducted at the Central Laboratory for Radiological Protection (CLOR) on 9–13 June 2003, to verify the comparability of mainly continuously-measuring instruments for radon and potential alpha energy concentration (PAEC). Seven Polish institutions participated in the intercomparison of ten radon and six PAEC monitors. Radon devices included: six Genitron AlphaGUARD monitors, two Pylon AB-5 monitors and two Polish instruments: RMR1 and a radon probe SRDN2. Among PAEC devices there were five monitors measuring in the continuous mode: three T/N Rn WL Meters co-working with AlphaGUARD monitors, a Pylon WLx monitor, a radon progeny particle size spectrometer (RPPSS) designed and manufactured at ARPANSA, Australia and one grab sampling device: an aspirator SKC equipped with an ALFA unit.

2. CALIBRATION FACILITIES

CLOR maintains a walk-in radon/aerosol chamber with anteroom, shown in Fig. 1, for use in the quality assurance programme for radon and radon progeny measurements. The chamber body is an airtight climatized room made of sandwich elements covered inside with stainless steel. Its inner volume is 12.37 m^3 and the surface-to-volume ratio is 2.6 m^{-1}. The climatic conditions (temperature and relative humidity) may be controlled manually or automatically. The temperature may be set up from –30°C to +60°C and the relative humidity from 10 to 95% within ±5% (for the temperature range from +10 to +60°C). The chamber contains a radon atmosphere that can be varied from several Bq/m^3 to 52 000 Bq/m^3. Radon is delivered from two dry Pylon ^{226}Ra sources traceable to NIST standards, and its concentration is continuously measured by one of two AlphaGUARD monitors. The aerosol conditions in the chamber can be altered as required for studies and calibrations using a TSI water aerosol generator to raise the aerosol level or an air conditioner to lower the aerosol level.

The concentration of neutral condensation nuclei is measured by a RICH 100 condensation nuclei monitor. The PAEC in the chamber and the particle size distribution of carriers of radon progeny are continuously monitored by an RPPSS, a unique research tool from ACJ & Associates, Inc. designed and manufactured by ARPANSA, Australia. This device is considered as a reference PAEC monitor. The RPPSS consists of eight stages operated in parallel — one open face stage, a four stage diffusion battery system and a three stage inertial impactor system — and measures, among other things, total PAEC corrected for the loss of unattached fraction activity due to the plate-out effect in the inlet of the first stage, and the distribution of the alpha-active aerosol sizes. The first peak of the distribution corresponds to the unattached fraction *fp* with particle diameters of about 1 nm.

The calibration factor, converting count/min to PAEC expressed in nJ/m^3, is calculated for the average radon progeny alpha particle energy for decays on the filter of 7.2 MeV and a conversion factor of 1.6×10^{-13} J/MeV. The value of the unattached fraction in the chamber may be varied over a wide range of 0–80%, and the value of the equilibrium factor *F* may be varied up to 99%.

CLOR also owns a small chamber with a volume of 320 L, which was used as a thoron chamber provided with thoron from a dry flow-through ^{228}Th source working in the continuous mode.

FIG .1. The radon chamber at CLOR

3. DESCRIPTION OF RADON AND THORON EXPOSURES

Instruments submitted for the intercomparison were placed 0.5–1.5 m above the floor of the chamber and started. The radon source was connected to two ports on opposite sides of the chamber and radon was pumped into the chamber in a closed in-series circuit. The total exposure lasted 44 h and consisted of four intervals that differed in relative humidity and concentration of condensation nuclei. In the first interval, continuing overnight, the relative humidity was ambient, about 45%, with the concentration of condensation nuclei becoming lower and lower. In the second interval, the relative humidity remained the same and the TSI generator was operated, injecting aerosols. In the third interval, lasting overnight, the relative humidity was increased to 95% and the level of aerosols was low. In the fourth interval the relative humidity remained high, at 95%, and the TSI generator again injected aerosols to increase their concentration in the chamber.

The radon concentration decreased from 2500 Bq/m^3 to 700 Bq/m^3 during the whole exposure. The PAEC varied in the range 1400–6000 nJ/m^3, the concentration of condensation nuclei varied from <200 to 31 000 CN/cm^3, the equilibrium factor F from 15 to 99%, and the unattached fraction fp from 0 to 62%. The time variations of radon concentration according to six AlphaGUARD monitors and of the PAEC according to PAEC meter readings are shown in Figs 2 and 3. In Fig. 4, the time variations of the equilibrium factor F and the unattached fraction fp are illustrated. The four intervals of interest are marked in the Figures. An example of the particle size distributions for various aerosol conditions during the exposure is given in Fig. 5.

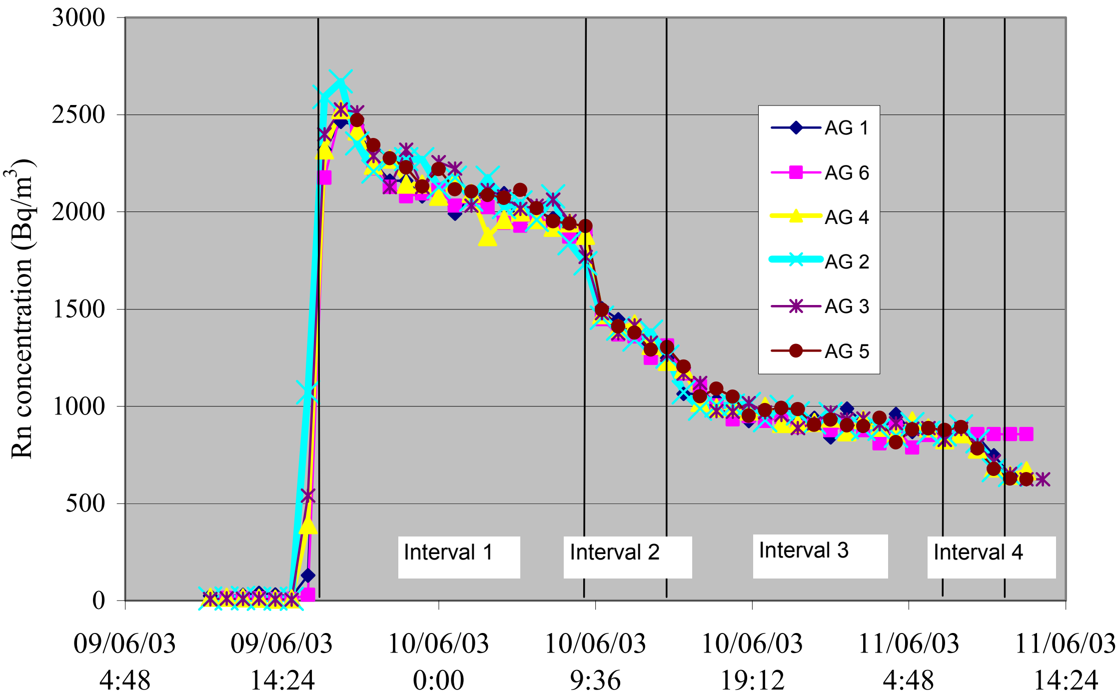

FIG. 2. Time variation of radon concentration — comparison of 6 AlphaGUARDs

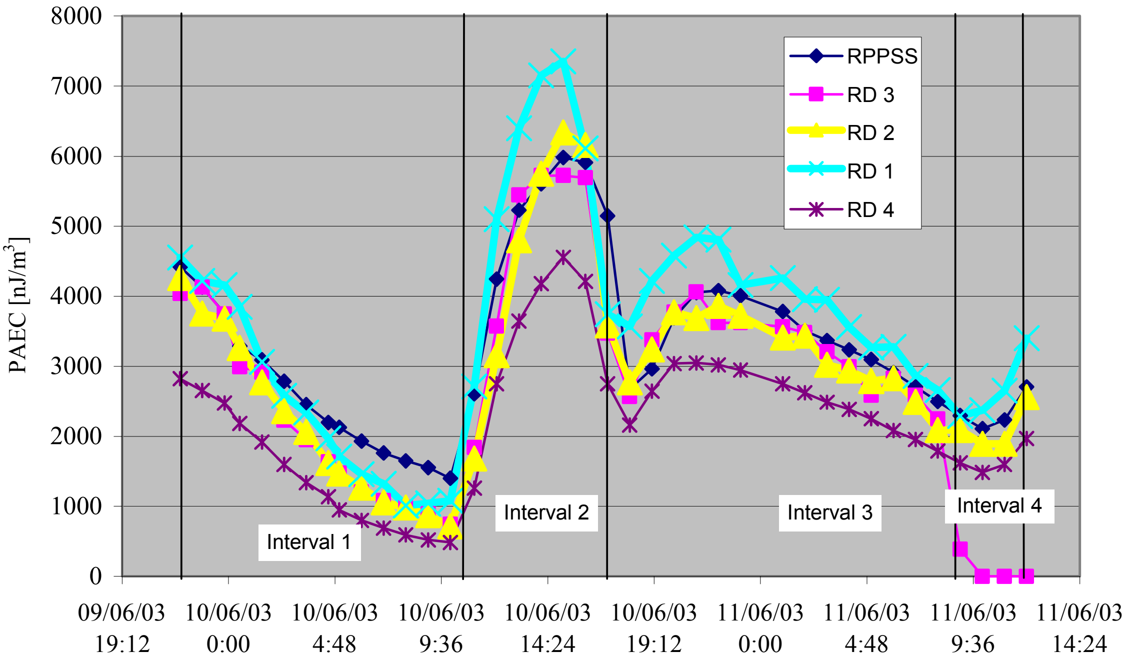

FIG. 3. Time variation of PAEC — comparison of 5 PAEC monitors

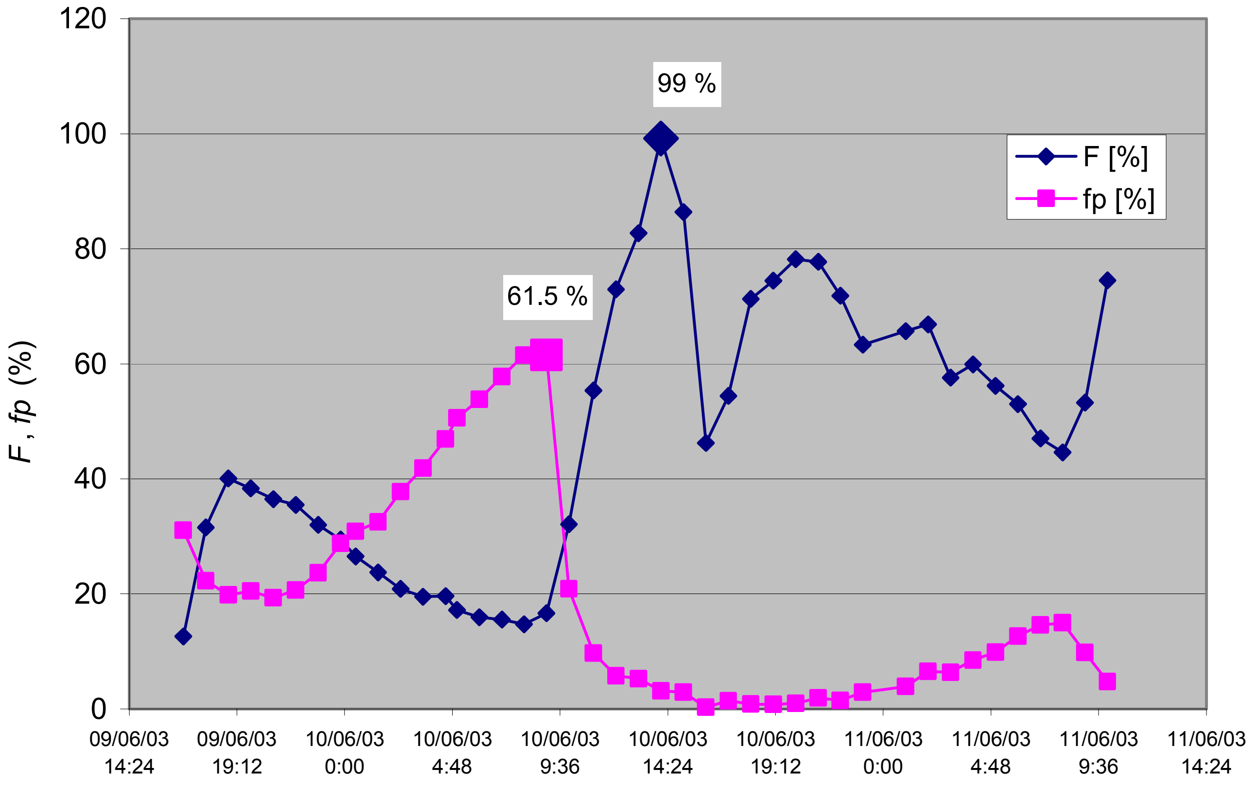

FIG. 4.Time variation of F and fp

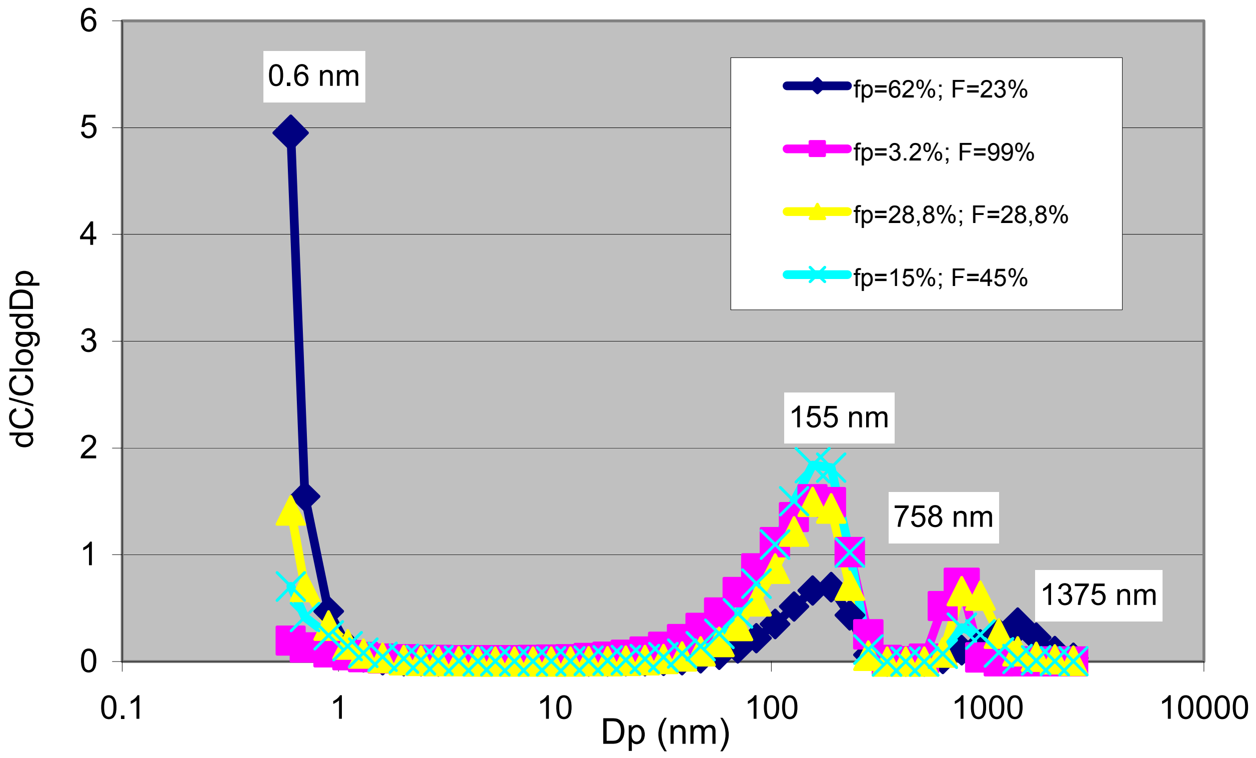

FIG. 5. Particle size distributions for various aerosol conditions

The AlphaGUARD monitors were also compared in an atmosphere of thoron in the 320 L chamber. Thoron was delivered from the Pylon dry flow-through ^{228}Th source working in the flow mode, which resulted in a lowering of the air pressure in the chamber. The activity of the source was 77 Bq. The monitors worked in the diffusion and flow modes in turn, for 17 h each. The background radon concentration in the chamber was 20 Bq/m^3 and the sum of the radon and thoron concentrations was 65 Bq/m^3.

4. RESULTS AND DISCUSSION

After the exposure had been completed, the instruments were taken for analysis. Upon analysis, the results of the mean values of radon concentration and PAEC and their uncertainties in the four intervals of exposure were sent to CLOR for comparison and evaluation. For the AlphaGUARD monitors, values of temperature, relative humidity, pressure and gamma dose rates were also compared.

The results of radon concentration from all devices in the four intervals are summarized in Figs 6–9. Two mean values are marked in each of them: one for the six AlphaGUARD monitors and the other for all devices together. The mean values for the AlphaGUARD monitors are within 0.4–4 % of each other, showing very good agreement among the monitors in all intervals with the worse result (4 %) in Interval 4. The standard deviations of the means for all instruments were 1.8–6 % in the four intervals. The highest value of 6 % was due to the value for the device ‘Rn 7’ differing markedly from others in Interval 2, i.e. in the high aerosol atmosphere. It can be explained by the filter not completely protecting the detector chamber against radon progeny. Unfortunately, the participant did not report the result in Interval 4, when the aerosol concentration was also high.

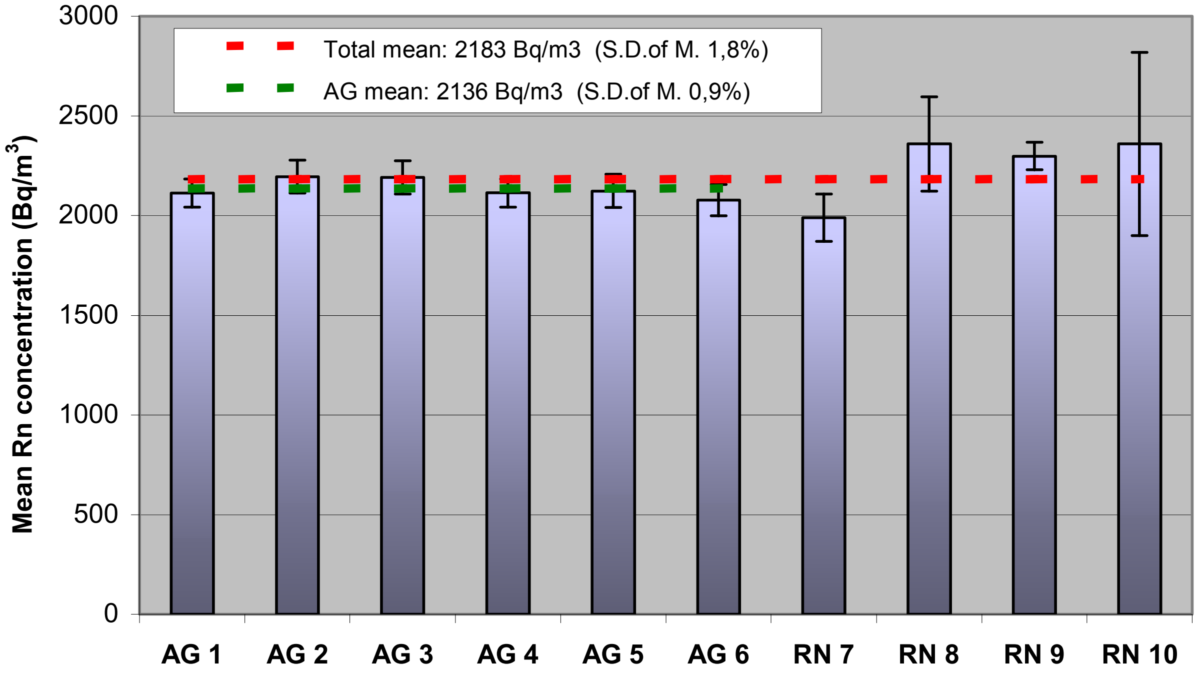

FIG. 6. Results from radon monitors, Interval 1 (45% relative humidity, low aerosol level)

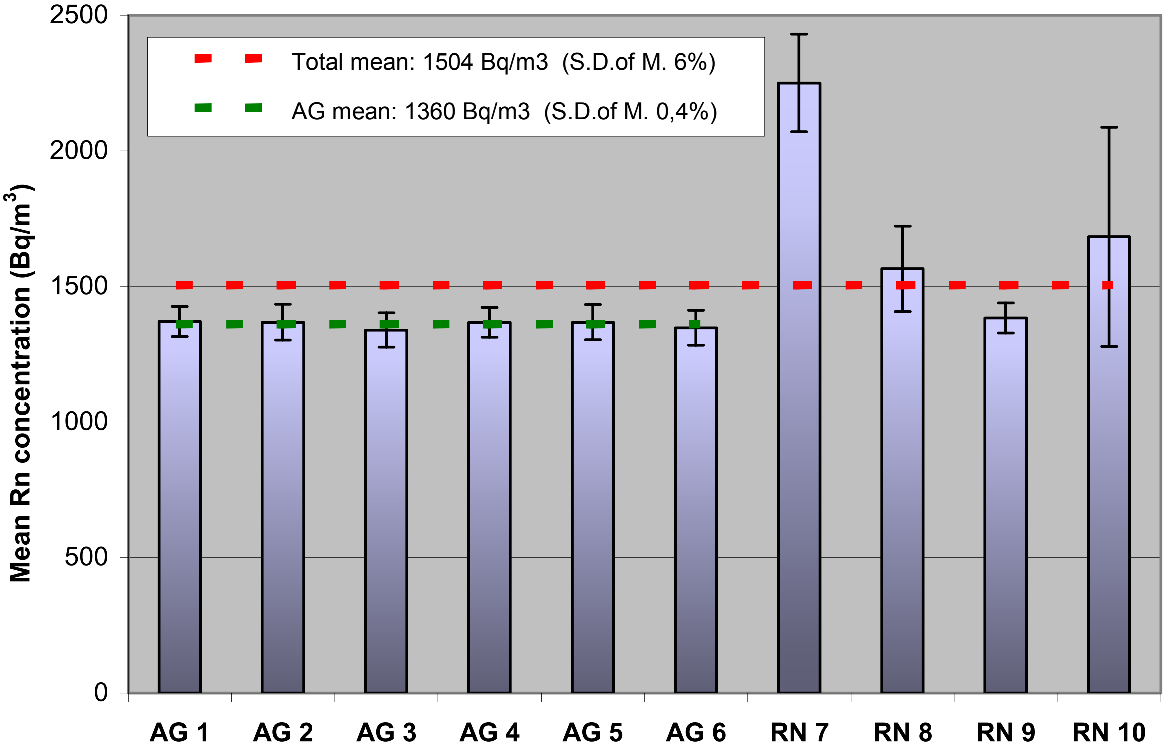

FIG.7. Results from radon monitors, Interval 2 (45% relative humidity, high aerosol level)

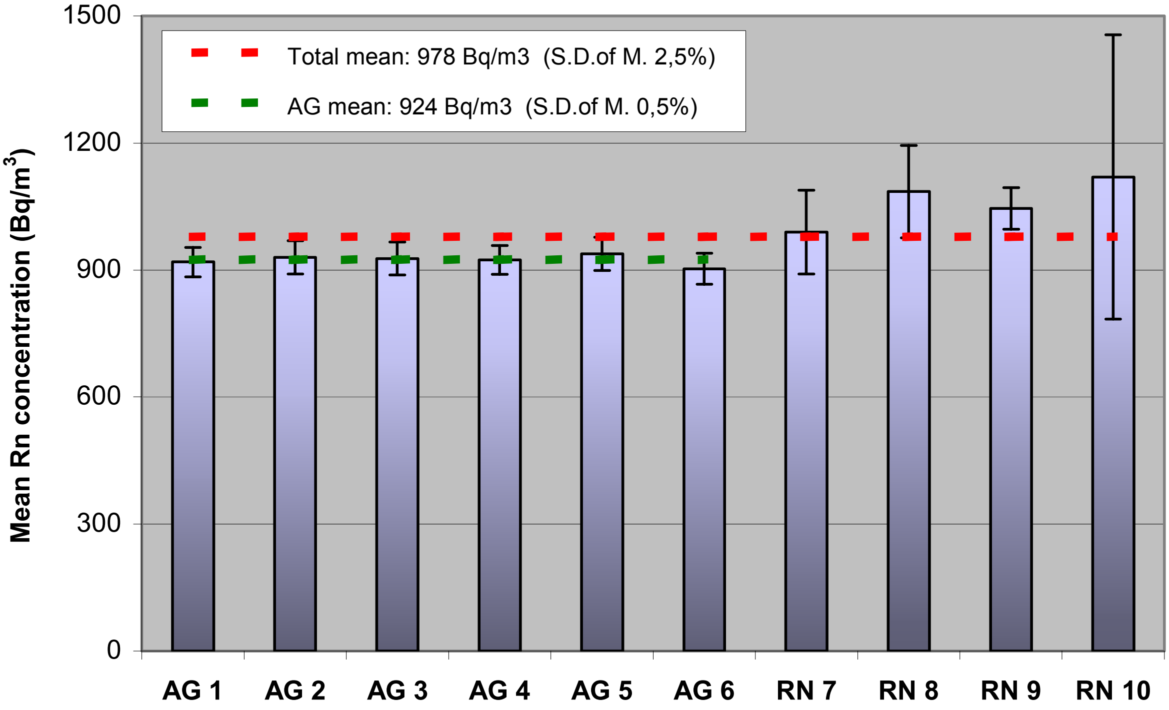

FIG. 8. Results from radon monitors, Interval 3 (95% humidity level, low aerosol level)

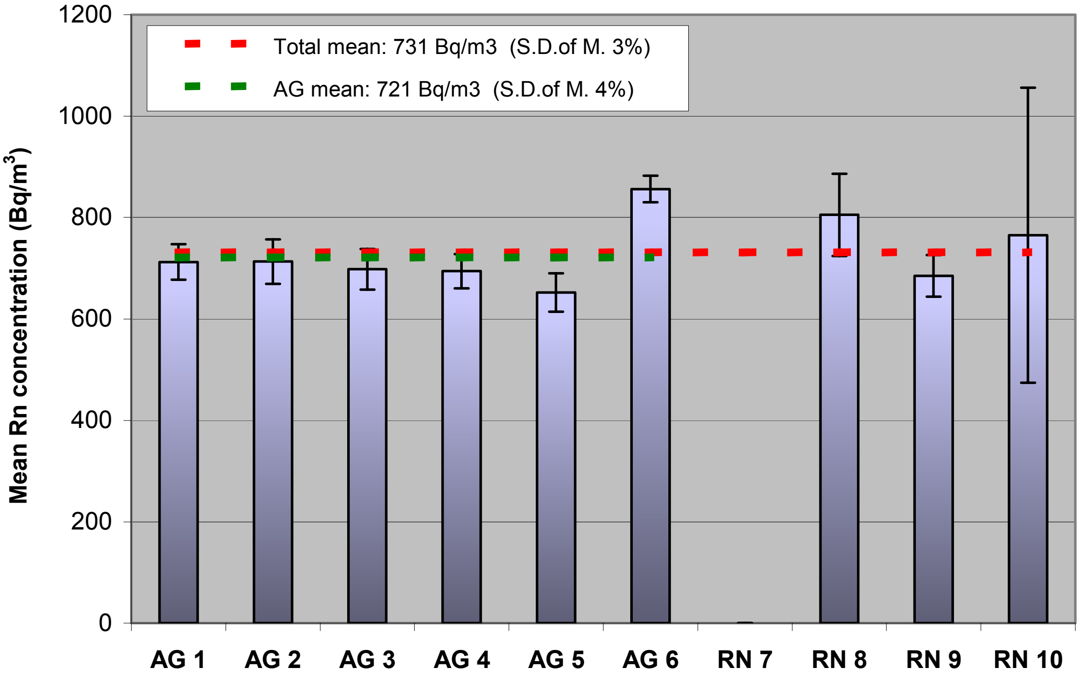

FIG. 9. Results from radon monitors, Interval 4 (95% relative humidity, high aerosol level)

To evaluate each device on the basis of its results in the four intervals, a factor of merit was calculated. This factor was defined according to the following formula:

$$\delta_j = \frac{1}{n_j}\sum_{i=1}^{n_j} b_{ij}\text{-}1$$

where δ_j is the factor of merit of the method j; b_{ij} is a bias of the particular result i against a reference value or an average value of several methods (ratios of results obtained with the method j to the reference or average value), and n_i is the number of results obtained with the method j. The summing over i for the method j is from $i=1$ to $i=n_j$. It should be kept in mind that the better the method the lower the factor. The factors of merit of the methods, calculated in terms of the mean value for all AlphaGUARD monitors, are presented in Table I. They range from 0.009 to 0.062 among AlphaGUARD monitors and up to 0.265 for all devices.

Results of thoron concentration measurements using AlphaGUARD monitors working in the diffusion mode are summarized in Table II, and reveal significant discrepancies, possibly due to low values of measured concentrations.

Mean values of the climatic parameters (temperature, relative humidity and pressure) and gamma dose rates readings for the AlphaGUARD monitors in six exposure intervals are compared in Table III. The relative humidity shows the largest scatter of results — 9 percentage points, or 14% of the mean. The readings of temperature and pressure do not scatter more than 0.7ºC (2% of the mean) and 2 mbar (0.2% of the mean), respectively.

The results of the intercomparison of PAEC instruments in the four intervals are shown in Figs 10–13. The standard deviations of the means for each interval range from 5.3 to 10.8%. The factors of merit of the methods calculated in terms of the RPPSS readings are given in Table IV. They range from 0.072 to 0.306.

In order to estimate the PAEC losses associated with the unattached fraction, due to the plate-out effect in the inlets of the devices, the time variations of PAEC were normalized against the maximum value of the PAEC reading for the RPPSS, which corresponds to the maximum value of the equilibrium factor *F* (99%) and to a very small value of the unattached fraction *fp* (3.2%). The normalized time variations for four radon progeny meters are shown in Fig. 14. In the region of the highest value of the unattached fraction, 62%, the loss of PAEC estimated in the comparison with the RPPSS reading ranges from 44% for the RD 4 meter to 60% for the RD3 meter.

TABLE I. FACTORS OF MERIT FOR THE RADON CONCENTRATION MONITORS

Radon concentration monitor	Factor of merit
AG 1	0.009
AG 2	0.013
AG 3	0.019
AG 4	0.013
AG 5	0.031
AG 6	0.062
Rn 7	0.265
Rn 8	0.137
Rn 9	0.069
Rn 10	0.154

TABLE II. THORON EXPOSURES MEASURED USING THE ALPHAGUARD MONITORS

AlphaGUARD monitor	Thoron concentration (Bq/m^3)	
	Diffusion mode	Flow mode at 1 L/min
AG 1	57 ± 4	39 ± 4
AG 2	42 ± 3	55 ± 4
AG 3	41 ± 3	—
AG 4	129 ± 7	—
AG 5	92 ± 6	76 ± 5
AG 6	38 ± 2	88 ± 6
Mean ± S.D.	67 ± 15 (22%)	65 ± 11 (17%)

TABLE III. CLIMATIC PARAMETERS AND GAMMA DOSE RATES MEASURED USING THE ALPHAGUARD MONITORS

Interval	Parameter	Measurement						Maximum difference
		AG 1	AG 2	AG 3	AG 4	AG 5	AG 6	
I	Temperature	31.5	31.6	31.4	31.2	31.7	31.4	0.5
	Relative humidity (%)	46	48	52	46	51	50	6
	Pressure (mbar)	1008	1009	1008	1008	1008	1008	1
	Gamma dose rate (nSv/h)	—	153	142	—	153	—	11
II	Temperature	33.1	33.6	33.1	32.9	33.1	33.3	0.7
	Relative humidity (%)	45	47	51	45	49	49	6
	Pressure (mbar)	1010	1011	1010	1010	1010	1010	1
	Gamma dose rate (nSv/h)	—	153	147	—	153	—	6
III	Temperature	33.7	33.8	33.6	33.6	34	33.8	0.4
	Relative humidity (%)	99	99	99	97	99	99	2
	Pressure (mbar)	1008	1008	1007	1008	1008	1008	1
	Gamma dose rate (nSv/h)	—	150	145	—	152	—	7
IV	Temperature	33.3	33.3	33.3	33.3	33.4	33.7	0.3
	Relative humidity (%)	96	99	99	90	98	93	6
	Pressure (mbar)	1006	1006	1005	1006	1005	1005	1
	Gamma dose rate (nSv/h)	—	154	152	—	151	—	3
Thoron (diffusion mode)	Temperature	25.7	25.7	25.2	25.2	25.6	25.6	0.5
	Relative humidity (%)	60	64	68	59	64	63	9
	Pressure (mbar)	994	995	995	993	994	994	2
	Gamma dose rate (nSv/h)	—	111	117	—	118	—	7
Thoron (flow mode)	Temperature	26.5	26.7	—	—	26.2	27.3	1.1
	Relative humidity (%)	59	59	—	—	61	57	4
	Pressure (mbar)	975	976	—	—	975	972	2
	Gamma dose rate (nSv/h)	—	107	—	—	119	—	12

TABLE IV. FACTORS OF MERIT FOR THE PAEC MONITORS

PAEC monitors	Factor of merit
RD 1	0.072
RD 2	0.148
RD 3	0.145
RD 4	0.306
RD 5	0.162

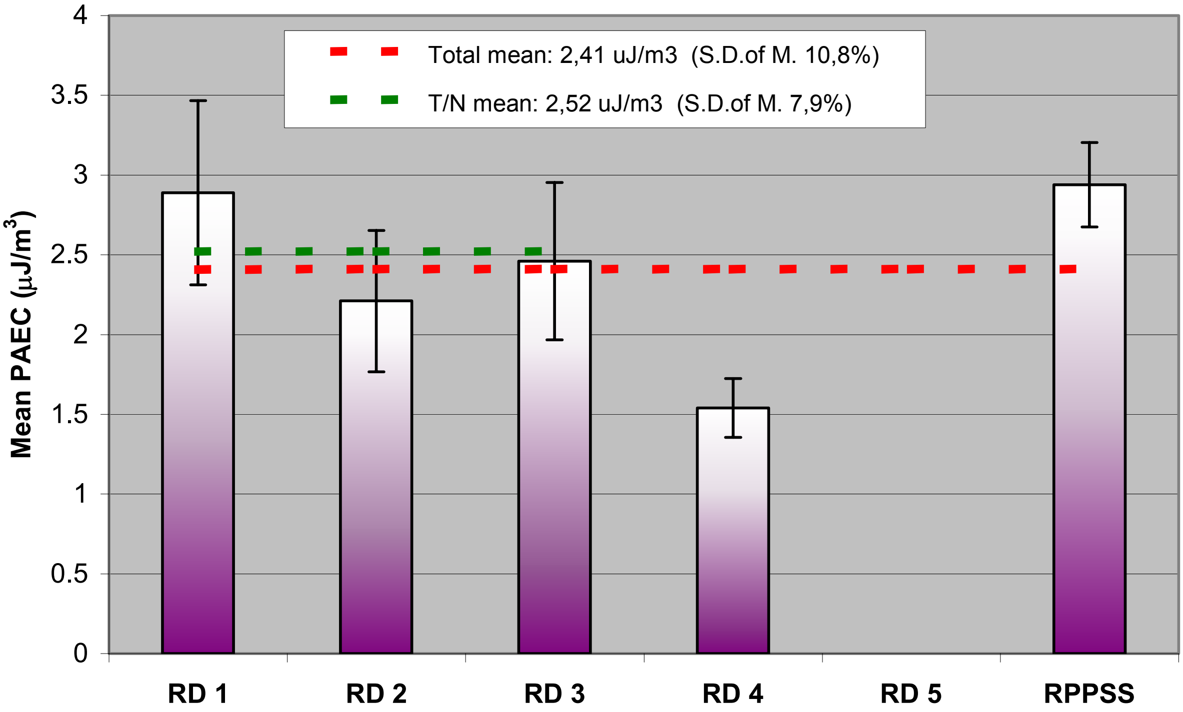

FIG. 10. Results from PAEC monitors, Interval 1 (45% relative humidity, low aerosol level)

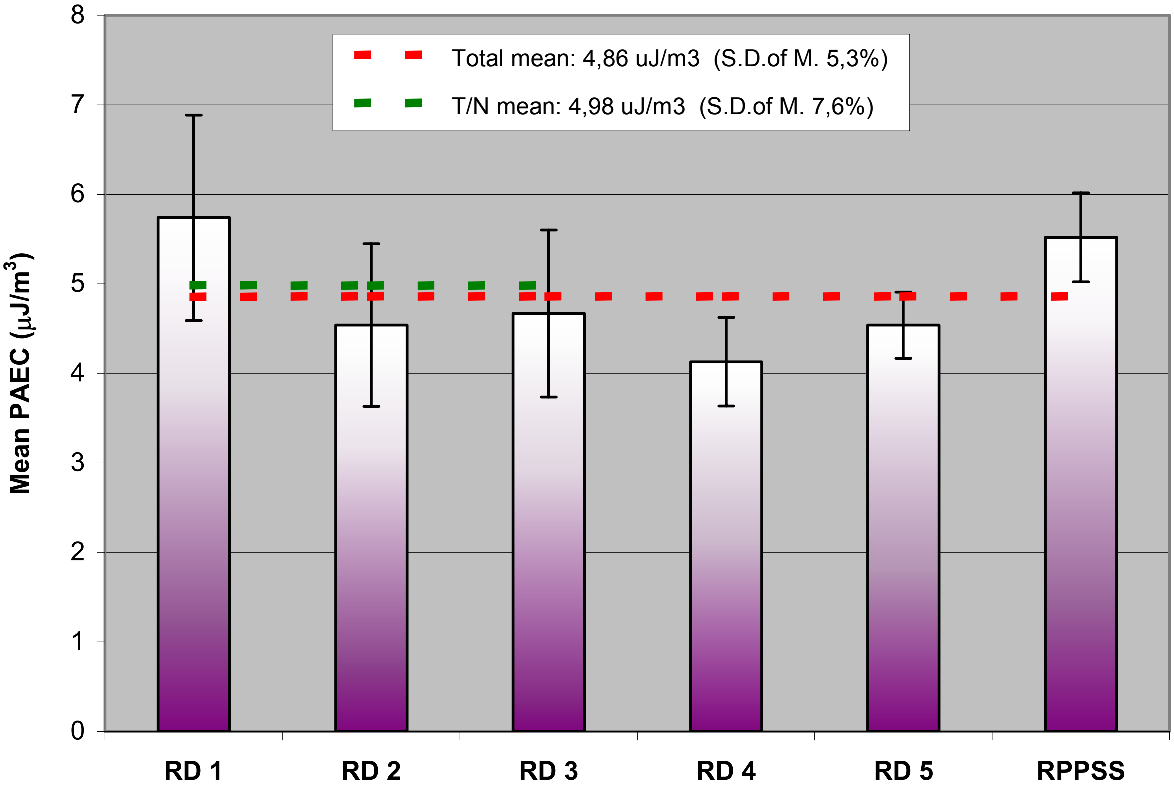

FIG. 11. Results from PAEC monitors, Interval 2 (45% relative humidity, high aerosol level)

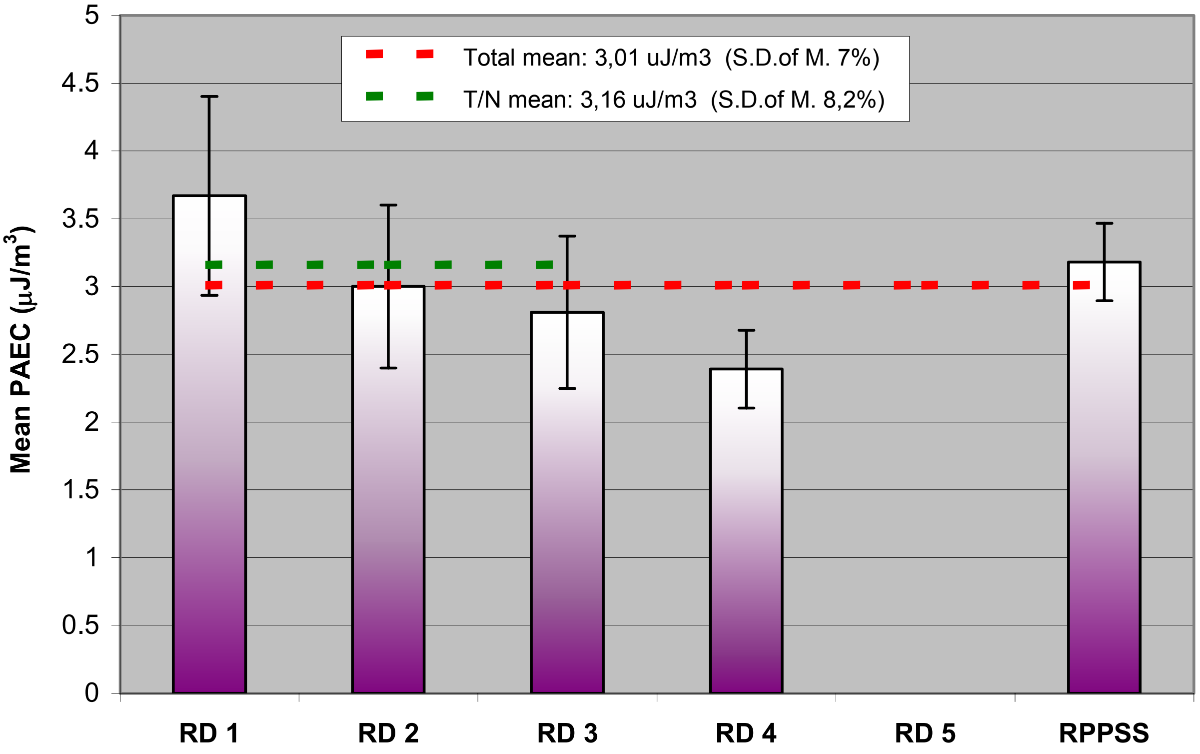

FIG. 12. Results from PAEC monitors, Interval 3 (relative humidity 95%, low aerosol level).

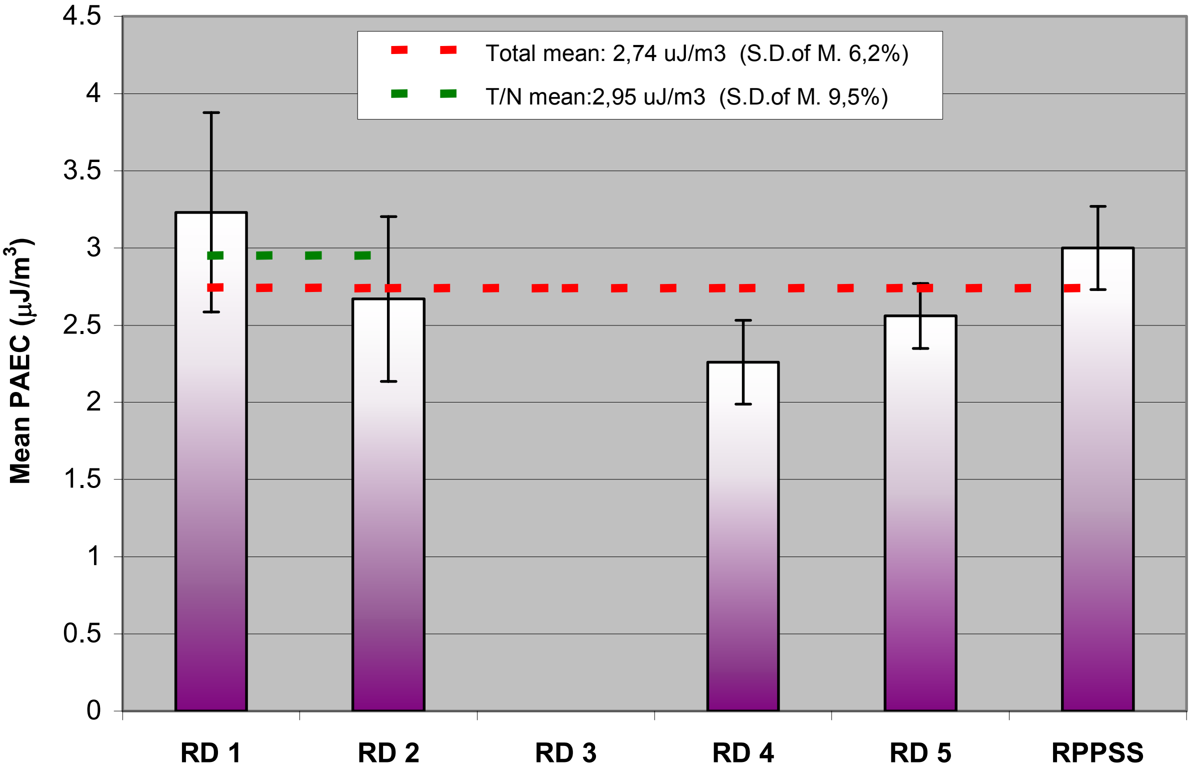

FIG. 13. Results from PAEC monitors, Interval 4 (relative humidity 95%, high aerosol level)

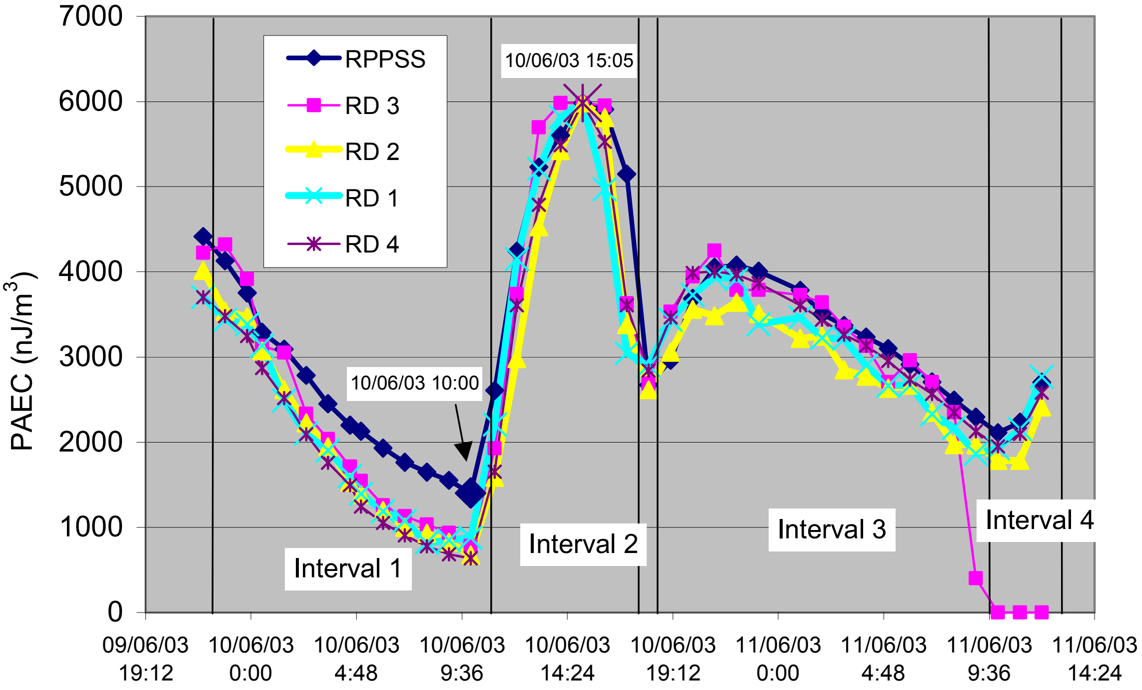

FIG. 14. Time variation of PAEC results normalized against the RPPSS at 15:05 on 10/06/03

5. SUMMARY

The results of the intercomparison of radon monitors in a radon atmosphere with concentrations from 700 Bq/m^3 upwards showed quite good agreement except in the case of one monitor, which differed considerably from the others in high aerosol levels in Interval 2. This implies that, in high aerosol conditions, not only PAEC monitors but also radon monitors need to be intercompared. It should be emphasized that the agreement between the radon concentration results in various aerosol and climatic conditions for the AlphaGUARD monitors was very good in the applied range of radon concentration, and the factors of merit for them are correspondingly low (0.01–0.06). The unsatisfactory results of the intercomparison of AlphaGUARD monitors in a thoron atmosphere of low concentration and low air pressure suggest the need to compare the instruments in low radon concentrations, below 100 Bq/m^3, and to check them in low air pressure conditions.

The results for the PAEC instruments show bigger discrepancies than those for the radon monitors. This is due to many contributing factors, such as the stability of the flow rate in various climatic and aerosol conditions, the efficiency of the detector system, the integrity of the filter and filter holder and, depending on aerosol conditions, the radon progeny plate-out effect upstream.

STAFF FROM PARTICIPATING INSTITUTIONS

Kalina Mamont-Cieśla, Olga Stawarz (Central Laboratory for Radiological Protection); Tadeusz Przylibski, Anna Adamczyk (Wrocław University of Technology); Krystian Skubacz, Stanisław Chałupnik (Central Mining Institute); Krzysztof Kozak (Henryk Niewodniczański Institute of Nuclear Physics of the Polish Academy of Sciences); Nguyen-Dinh Chau (AGH University of Science and Technology); Jakub Bartak (Institute of Nuclear Chemistry and Technology); Jerzy Wroblewski (National Atomic Energy Agency, Office for Financial Claims of Former Workers of Uranium Ore Facility in Jelenia Góra).

POLISH NATIONAL INTERCALIBRATIONS OF MEASUREMENT METHODS OF ^{222}Rn CONCENTRATION IN WATERS

T.A. Przylibski[1*], K. Mamont-Cieśla[2], O. Stawarz[2], B. Kłos[3], J. Dorda[3]

[1]Wrocław University of Technology, Faculty of Geoengineering, Mining and Geology
Institute of Mining, Division of Geology and Mineral Waters, Wrocław, Poland
[2]Central Laboratory for Radiological Protection, Dosimetry Department,
Radon Dosimetry Group Warsaw, Poland
[3]University of Silesia, Institute of Physics, Department of Nuclear Physics and its
Application, Katowice, Poland

Abstract

This paper presents the results of intercalibration exercises to measure ^{222}Rn concentrations in water samples. In total, 11 laboratories from many Polish research and commercial institutions took part in the above-mentioned exercises. Seven of them participated in 3 intercalibration exercises organized in 2001–2003. In 2001 and 2002, the intercalibration measurements were carried out in the Sudety Mountains (at the Szczawno Zdrój and Świeradów Zdrój health resorts, respectively). During these two experiments, water samples were taken from mineral springs, considered medicinal in Poland. They are characterized by an increased CO_2 concentration (0.53–2.54 g/L), as well as different values of total dissolved solids (0.15–3.82 g/L) and radon concentrations (10–1170 Bq/L), and other distinct differences in chemical composition and physical properties. In 2003, experimental measurements were carried out in water samples prepared in the Central Laboratory for Radiological Protection in Warsaw. The samples were produced by the aeration of a 10 L container filled with tap water with air enriched by ^{222}Rn coming from a Pylon™ source comprising 502.5 kBq of ^{226}Ra. During all the intercalibration exercises, the concentration of ^{222}Rn in 7 water samples (2, 3 and 2 in 2001, 2002 and 2003, respectively) was determined. Special care was taken to ensure the same conditions of collecting water samples for each participant. The laboratories participating in the experiments applied different techniques to determine the concentration of ^{222}Rn in the water samples: a liquid scintillation method, gamma detectors, Lucas cells and ionization chambers. The results confirmed that keeping the containers with water samples closed tightly from the moment of collecting until the measurement was of great importance. It happened twice, in different laboratories, that a leakage in the measurement set-up (in the AlphaGUARD™ + AquaKIT™ system) resulted in underestimates of ^{222}Rn concentration. The best consistency of results in all 3 intercalibration exercises was obtained by the laboratories using the liquid scintillation method. It has been observed that the number of laboratories that obtained consistent results (within error limits) increased from about 50% in 2001 to nearly 100% in 2003. This confirms that the organized experiments met the main task, i.e. improving the correctness of the results obtained in particular laboratories. Thus, it seems necessary to organize such experiments in coming years.

1. INTRODUCTION

In 2001–2003, three national intercalibrations of methods used for measuring ^{222}Rn concentrations in water samples were organized in Poland. Twice, in 2001 and 2002, they were organized by Wrocław University of Technology, while the 2003 comparative

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[*] E-mail: tadeusz.przylibski@pwr.wroc.pl

experiment was organized by the Central Laboratory for Radiological Protection in Warsaw (CLOR). In 2001 and 2002, measurements of ^{222}Rn concentrations dissolved in natural groundwaters flowing out of the Sudetes (in Szczawno Zdrój in 2001, and in Świeradów Zdrój in 2002) were compared (Fig. 1). In 2003, water samples for comparative measurements were prepared in a laboratory. Overall, 11 laboratories from different Polish scientific institutes and commercial organizations dealing with measurements of radon concentrations in water took part in the comparative experiments. Seven of them participated in all three comparative experiments.

FIG. 1. Sites of the comparative experiments in the Sudetes on the background of an outline map of Poland (1: Szczawno Zdrój, 2: Świeradów Zdrój)

2. WATER SAMPLES

In 2001, intercalibration measurements were based on samples of groundwater flowing out of two springs (‘Marta’ and ‘Mieszko’) in Szczawno Zdrój (Fig. 1). The water from the Mieszko spring is a HCO_3-Na type of water, with temperatures oscillating between 7.3 and 13.1ºC. The total dissolved solids (TDS) varies from 2.34 to 3.82 g/L. The water is also characterized by a high concentration of dissolved CO_2, oscillating between 0.81 and 2.24 g/L. The concentration of ^{222}Rn in the water from this spring varies from 10.4 to 55.1 Bq/L, with an arithmetic mean of 30.3 Bq/L obtained from 26 measurements conducted during 1974–1998. The spring discharge is not big and varies from 0.16 to 0.51 m^3/h. The water from the Marta spring belongs to the HCO_3-Na-Ca type. Its TDS oscillates between 1.13 and 2.70 g/L, the temperature reaches 8.3–14.3ºC, and the content of CO_2 oscillates between 1.23 and 2.15 g/L. The concentration of ^{222}Rn dissolved in the water from the Marta spring varies from 103.6 to 325.6 Bq/L, with an arithmetic mean of 214.1 Bq/L obtained from

860 measurements conducted during 1974–1998. The spring discharge is very low and fluctuates from 0.016 to 0.07 m^3/h [1].

In 2002, groundwater samples for comparative measurements were taken from 3 wells in the 'Górne' intake in Świeradów Zdrój (Fig. 1). In these wells, an HCO_3-Ca-Mg type of water is extracted, with the total self-outflow discharge varying between 0.11 and 1.86 m^3/h. The water temperature oscillates in time between 8 and 16°C and is similar in all the wells situated in the cellar of the spa house. TDS values change in time from 0.15 to 0.63 g/L and are comparable in all three wells, just as the concentrations of the dissolved carbon dioxide, whose values change in time from 0.53 to 2.54 g/L. The concentrations of ^{222}Rn in the water in wells 1, 2 and 3 are, respectively, 155–614 Bq/L with an average of 336 Bq/L (27 data), 81–1145 Bq/L with an average of 210 Bq/L (27 data), and 37–1170 Bq/L with an average of 510 Bq/L (1953 data). The measurements were conducted during 1986–2002 [2].

In 2003, at CLOR, two 10 L bottles with a faucet near the bottom were prepared and filled with tap water. The radon produced in the flow through a radon source of activity 502.5 kBq manufactured by Pylon™ was used to saturate the water in both bottles. In order to get a radon concentration of about 500 Bq/L on the day of the intercalibration exercise, the full production of radon from the source (closed 30 days earlier) was pumped through a plastic hose to the volume of water in one bottle. The pumping, at a flow rate of 0.05 L/min, lasted 80 min. Next, the water was left for 7 days before sampling for the intercalibration. The water with a low radon concentration (about 30 Bq/L) was prepared directly before sampling. First, the radon source was unloaded of radon and only the running production of radon was pumped into the water during one hour, with a flow rate of 0.05 L/min. It was observed that while using the flow rate of 0.05 L/min., 5–6% of the pumped-in radon was dissolved in the water.

Jointly, in all the experiments, ^{222}Rn concentration values measured in 7 water samples were compared: 2 in 2001, 3 in 2002 and 2 in 2003.

3. MEASUREMENT METHODS

The organizers of individual experiments paid particular attention to ensuring that conditions were identical for the taking of water samples by all the participants, regardless of the volume (according to the requirements of each of the applied measurement methods). This concerned chiefly minimizing the time of taking samples by all the participants. The time usually did not exceed 20 min for one intake or one sample for all the participants altogether. This was especially important in the case of taking groundwater samples. After the moment of sample taking, each laboratory followed its own measurement procedure, paying special attention to a fast transfer to the laboratory and ensuring the impermeability of the container used for transporting the water sample. Particular laboratories used different methods to determine the concentration of ^{222}Rn in the water samples.

3.1. Method 1

Five of the 11 laboratories participating in the intercalibration measurements of ^{222}Rn concentration applied the liquid scintillation technique (Laboratories 1, 2, 3, 5 and 11). The procedure for radon determination by liquid scintillation counting is fast and simple. A sample of 10 ml of water is drawn by a disposable syringe and transferred immediately into a vial containing 10 ml of liquid scintillator solution. The vial is capped, shaken and taken to the laboratory for measurement. Radon will permeate from the water phase to the organic scintillant solution phase. The alpha activity of ^{222}Rn and its decay products is measured with a liquid scintillation counter (Wallac™, Quantulus™, TRI-CARB™).

3.2. Method 2

Two laboratories measured radon concentration in water using the professional radon monitor AlphaGuard™ (Laboratories 4 and 7). This is an ionization chamber, designed for measuring radon in air, soil and water. For measuring ^{222}Rn concentration in water, an additional piece of equipment, the AquaKIT™, is used. In a closed gas cycle, radon is extracted from a water sample (placed in a degassing vessel) by means of a pump. The security vessel is connected to the degassing vessel. All drops are deposited in it if they get into the gas cycle during the degassing process. By doing this, the stress of the water vapour is minimized for the radon monitor. The radon concentration in this system was determined with the AlphaGuard™, whose ionization chamber is also part of the gas cycle.

3.3. Method 3

A detector with a Lucas cell was used by Laboratory 9 for detecting and measuring radon in water samples. The detector consists of a Lucas cell coupled to a photomultiplier tube. The inside walls of Lucas cells are covered with a scintillator of activated zinc sulphide (ZnS(Ag)), which responds to alpha radiation from radon decay, but is insensitive to beta and gamma radiation. Air flowing through the investigated water washes away the radon contained in it. After reaching the equilibrium state between radon and its daughters, the container with air is placed in the Lucas cell. When decaying, radon and its daughters emit alpha particles that hit the zinc sulphide within the cell. The alpha particle interacting with the scintillator produces a pulse of light that is converted into an electric pulse by the photomultiplier tube. The electric pulses are amplified and counted. The light output is proportional to the alpha particle energy.

3.4. Method 4

An electrometer SG-11 was used by Laboratory 8 to determine the content of ^{222}Rn in water samples. The electrometer measures the ion current produced by the radioactivity of radon in the ionization chamber. The radon enters the chamber from the water sample by blowing some air through the measured sample. The electrometer is mounted on the microscope stage so that the electrometer fibre can be viewed through the lens. A scale inserted in the microscope eyepiece permits a quantitative measurement of the fibre's deflection during the observation period. The velocity of the fibre's deflection is a measure of the concentration of ^{222}Rn in the ionization chamber.

3.5. Method 5

Special equipment was used by Laboratory 6 for measuring radon in water. The main part of this detection device is a scintillation chamber in the form of a 6 L tube. The tube contains 2 photomultiplier tubes that work concurrently. The collecting electrode is covered with a scintillator of activated ZnS(Ag). The alpha radiation from ^{222}Rn and its daughters is converted into light that, in turn, is converted into electric pulses that are amplified and counted. The measurements are made after 180 min (in the equilibrium state).

3.6. Method 6

The measurement of ^{222}Rn concentration by Laboratory 10 was performed by a NaI scintillation detector SSU-70™. The scintillation detector collecting gamma radiation is connected with an electronic system. The window of a single-channel analyser is set on a gamma line of ^{214}Bi, a short-lived decay product of ^{222}Rn. The measurements are made after 4 h, when the equilibrium state between ^{214}Bi and ^{222}Rn is achieved. The scintillation detector is sunk inside an open vessel containing a 1 L water sample. The content of ^{222}Rn in this sample corresponds to the counting rate in the counter.

4. RESULTS AND DISCUSSION

In the first two comparative experiments, the ^{222}Rn concentration in the investigated waters was unknown, except for the range of values measured during the last few decades. Therefore, it was impossible to determine the concentration to which the obtained results should be referred. Consequently, the comparative measurements of radon concentrations in groundwater were aimed chiefly at checking the consistency of the results obtained by particular laboratories. An important element of the comparative measurement was examining the influence of the increased content of carbon dioxide dissolved in these waters, as well as an increased TDS in some intakes, on the quality of the results.

During the first comparative experiment, ^{222}Rn concentrations were measured in water samples from the Marta and Mieszko intakes in Szczawno Zdrój. The results obtained by particular laboratories are presented in Figs 2 and 3. The results from Laboratories 1–6 were regarded as reliable for the water samples from the Marta intake. All of them were comparable within error limits. These laboratories included all those using the liquid-scintillation technique. The results obtained by the remaining laboratories are much underrated, which is probably related to the degassing of the samples before or during the measurement, or even during the sample taking. In the case of Laboratory 7, a leakage in the measurement circuit was detected after the experiment, which could verify the above interpretation. It is difficult to interpret the results obtained for the samples from the Mieszko intake without a reference value. The only obvious thing is the underrated value obtained by Laboratory 7 due to the leakage discovered in the measurement circuit. The higher results obtained by Laboratories 1, 2, 5 and 6 seem more probable. It is also possible that the conditions of sample taking had changed during the process, resulting in the lowering of radon concentration in the water taken for the experiment. Hence, it can be concluded that four out of the nine laboratories participating in the intercalibration measurements obtained satisfactory results, and another 2 obtained good results for one sample.

In view of the inconsistency of the results produced in the first comparative experiment, and the significant number of laboratories that obtained unsatisfactory results, another experiment was organized. This time, samples were taken from three wells of the Górne intake in Świeradów Zdrój. The results obtained by particular laboratories are presented in Figs 4–6. Again, a leakage was found in a measurement set, this time for Laboratory 4, which resulted in a considerable underestimation of the results for all samples. In the water samples from well no. 1, only four laboratories (2, 3, 5, and 7) obtained results within the error limit. The results obtained by the remaining laboratories should be considered as underestimated. In the water samples from wells 2 and 3, the results obtained by Laboratories 1, 2, 3, 5, and 7 were within the error limit, and simultaneously the highest, and they should be considered as accurate. These laboratories included all of those applying the liquid-scintillation technique. Thus, among nine laboratories participating in the 2002 comparative experiment, five obtained satisfactory results, including four that had also obtained satisfactory or good results in 2001. These are the laboratories using liquid-scintillation technique.

The latest experiment, carried out in 2003 at CLOR, involved water prepared in such a way as to enable an estimation of a reference value, for comparison with the results obtained by particular laboratories. The measurement results for two samples with radon concentrations of about 500 and 30 Bq/L are presented in Figs 7 and 8, respectively. For the sample with the higher radon concentration, 7 out of 8 laboratories participating in the experiment obtained satisfactory results, i.e. within the measurement error limit. At the same time, they were slightly (about 10%) lower than the estimated reference value. As for the water sample with the lower ^{222}Rn concentration, all laboratories obtained results within the measurement error limit and about 10% lower than the estimated reference value, i.e. satisfactory. Also in this comparative experiment, very good results were obtained by the laboratories using the liquid-scintillation technique. Equally good results were obtained in the laboratories using the AquaKIT™ set and the AlphaGUARD™ monitor equipped with an ionization chamber.

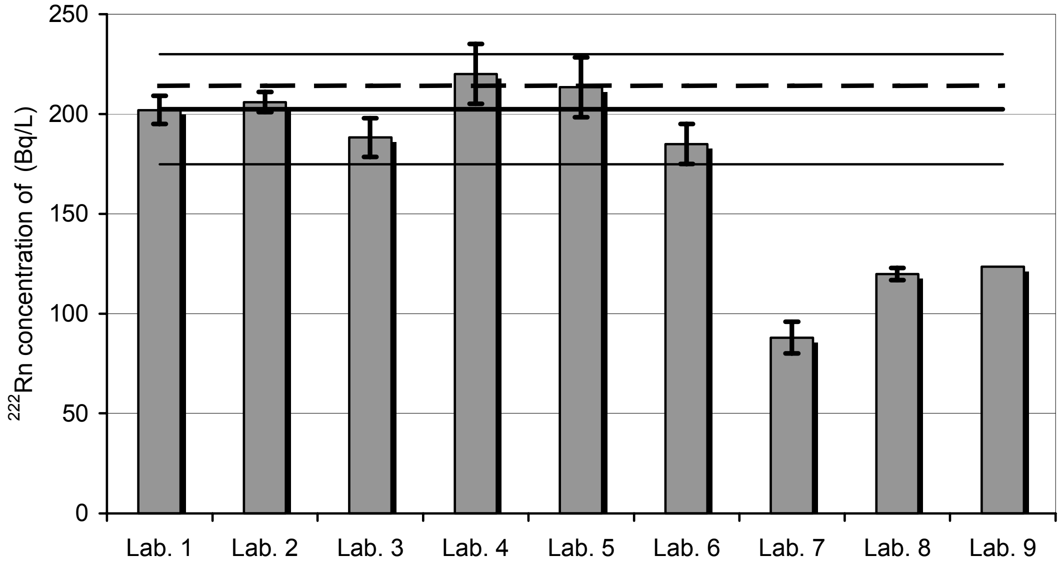

FIG. 2. Rn-222 concentration measurements, Marta intake water (Szczawno Zdrój)[1]

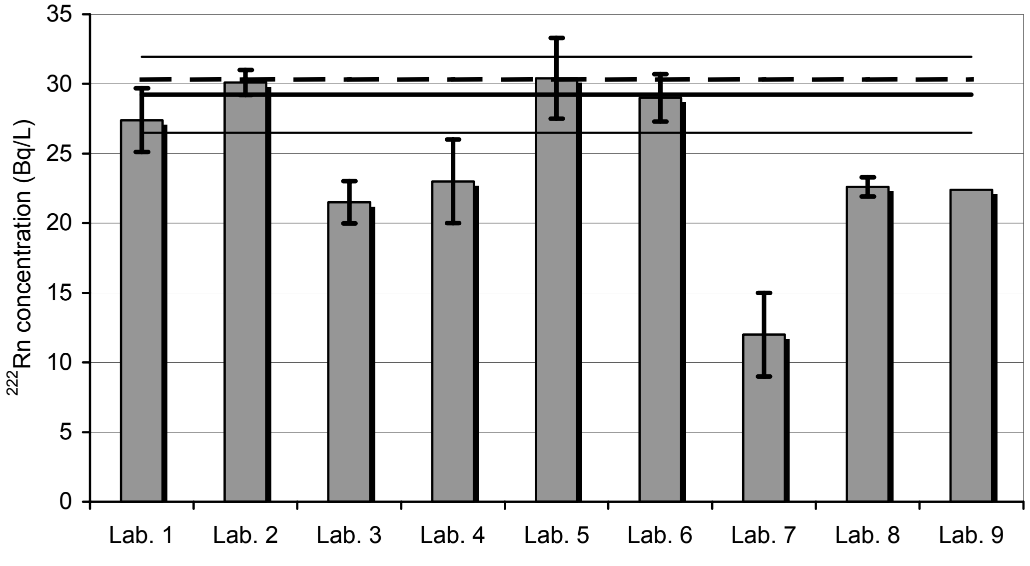

FIG. 3. Rn-222 concentration measurements, Mieszko intake water (Szczawno Zdrój)[1]

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[1] The dotted line is the arithmetic mean of the 1974–1998 measurements; the thick solid line is the arithmetic mean of the highest results in the present exercise, i.e. those from Laboratories 1–6 (Fig. 2) or 1, 2, 5 and 6 (Fig. 3), these being the only ones within measurement error limits; the thin solid lines are the standard deviation from the aforementioned mean.

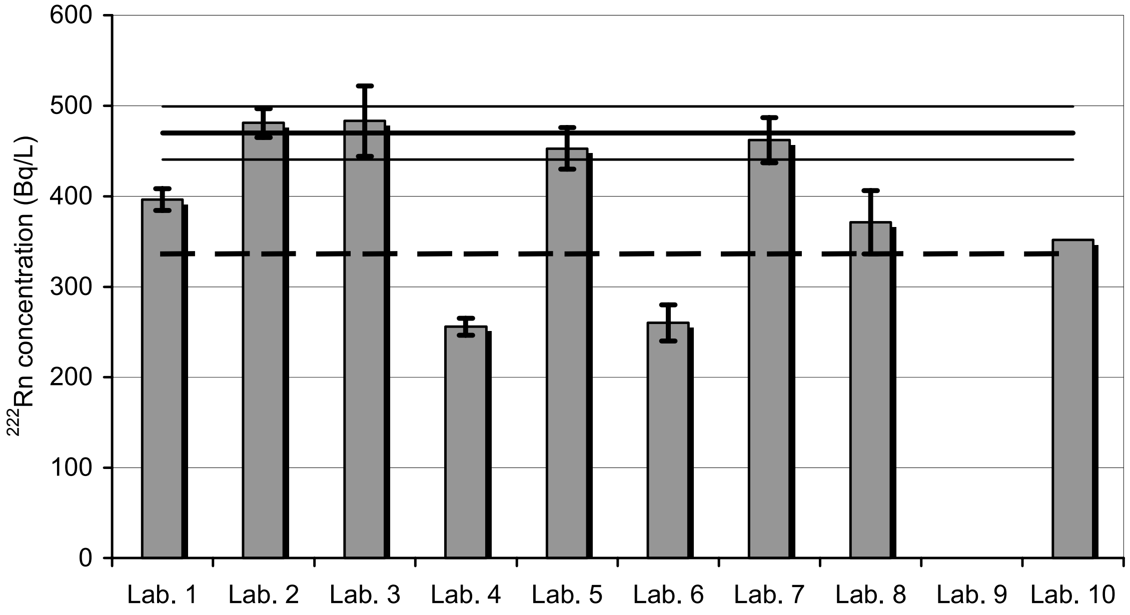

FIG. 4. Rn-222 concentration measurements, Górne intake, well no. 1 (Świeradów Zdrój)[2]

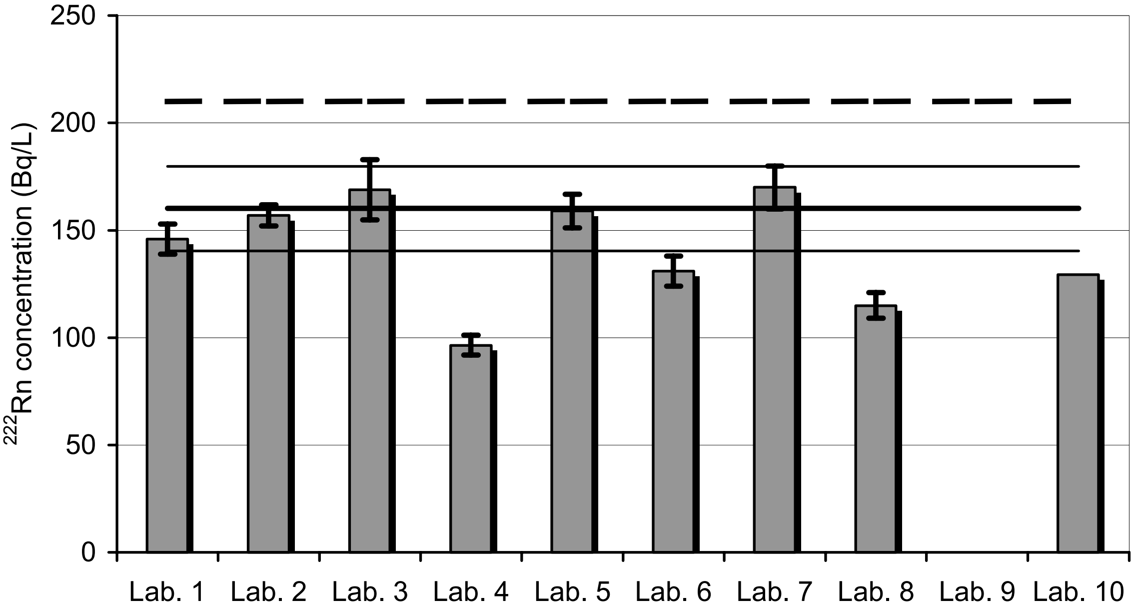

FIG. 5. Rn-222 concentration measurements, Górne intake, well no. 2 (Świeradów Zdrój)[2]

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[2] The dotted line is the arithmetic mean of the 1986–2002 measurements; the thick solid line is the arithmetic mean of the highest results in the present exercise, i.e. those from Laboratories 2, 3, 5 and 7 (Fig. 4) or 1, 2, 3, 5 and 7 (Figs 5 and 6), these being the only ones within measurement error limits; the thin solid lines are the standard deviation from the aforementioned mean.

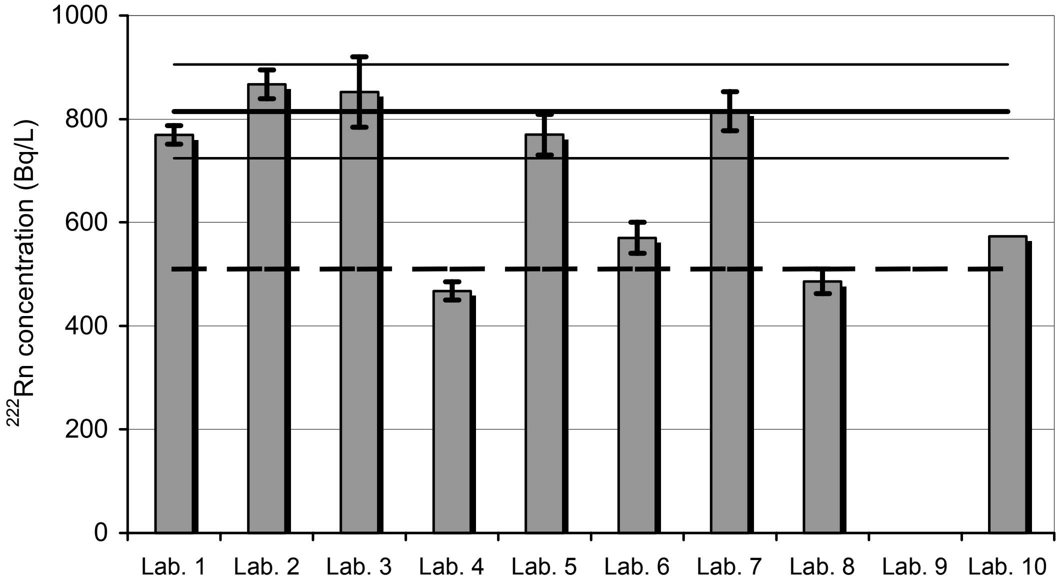

FIG. 6. Rn-222 concentration measurements, Górne intake, well no. 3 (Świeradów Zdrój)[2]

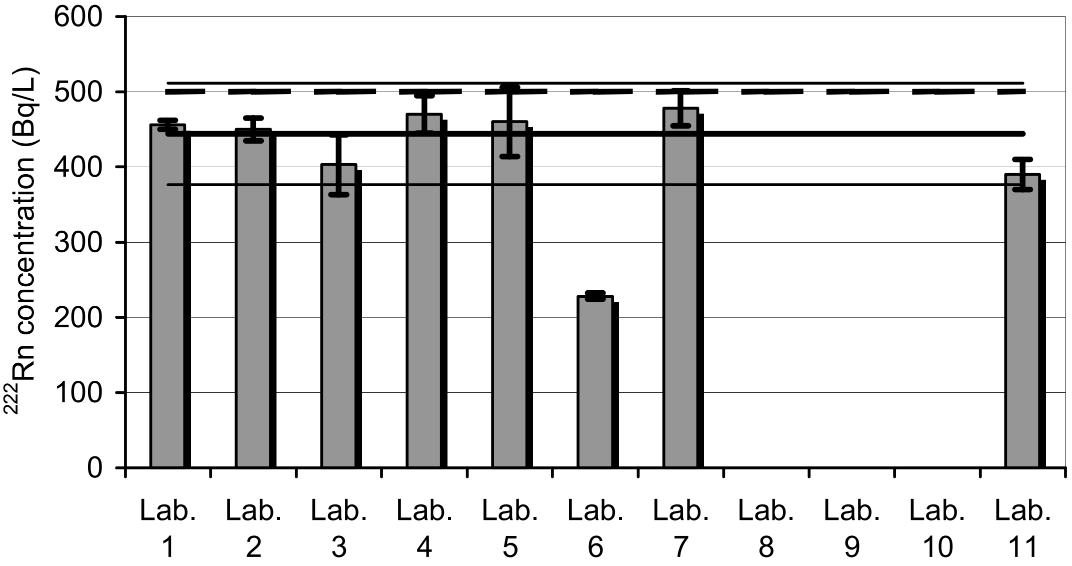

FIG. 7. Rn-222 concentration measurements, water sample 1 (higher concentration) prepared at CLOR[3]

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[3] The dotted line is the estimated value in the prepared sample; the thick solid line is the arithmetic mean of the highest results in the present exercise, i.e. those from Laboratories 1, 2, 3, 4, 5, 7 and 11 (Fig. 7) or all laboratories (Fig. 8), these being the only ones within measurement error limits; the thin solid lines are the standard deviation from the aforementioned mean.

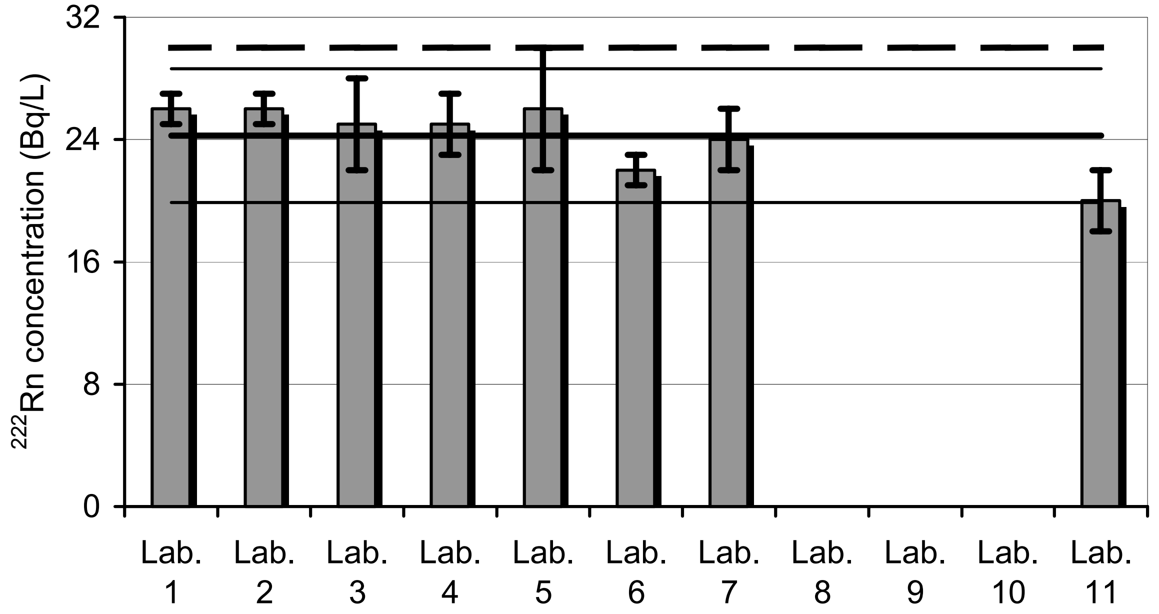

FIG. 8. Radon-222 concentration measurements, water sample 2 (lower concentration) prepared at CLOR[3]

5. CONCLUSIONS

The organization of successive intercomparisons of ^{222}Rn concentration measurements in groundwater brought about the expected effect, namely, increasingly convergent results by all laboratories. In the 2001 intercalibration measurements, barely 50% of the participating laboratories produced satisfactory results while, in 2003, practically all laboratories measured radon concentrations comparable within the error limit and close to the estimated reference value. The results of the subsequent intercalibration experiments proved that a very good method of measuring ^{222}Rn concentrations in this type of water, including groundwater, is the liquid-scintillation technique. Equally good results were obtained using an ionization chamber to measure radon previously extracted to a gas phase.

In view of the indisputable benefits to all laboratories measuring ^{222}Rn concentrations in water for human consumption, water regarded as medicinal, groundwater and surface water used for geochemical and other research, the next experiments of this kind are planned for the coming years within the activities of the Radon Centre — a non-governmental international scientific network. The slightly poorer results of the experiments based on groundwater samples suggest that future intercalibration measurements should include samples of both natural water and laboratory-prepared water with a defined reference concentration of radon.

ACKNOWLEDGEMENTS

The authors would like to thank the following people for enabling them to take samples of medicinal groundwater in the health resorts Szczawno Zdrój and Świeradów Zdrój and for the extensive help during their stay in the resorts: Ms Teresa Dragunowicz from the Resort Mining Institute in the resort Świeradów-Czerniawa Sp.z o. o., and Mr Paweł Filbier from the Resort Mining Institute in the resort Szczawno-Jedlina S.A.

The intercalibrations in 2002 and 2003 were carried out within the activities of the Radon Centre and in 2003 they were also financed by this organization.

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STAFF FROM PARTICIPATING INSTITUTIONS

Anna Adamczyk (Wrocław University of Technology); Monika Kuzyk (Central Laboratory for Radiological Protection); Beata Kozłowska (University of Silesia); Małgorzata Wysocka, Stanisław Chałupnik, Antoni Mielnikow (Central Mining Institute); Krzysztof Kozak, Mirosław Janik, Elżbieta Kochowska, Jadwiga Mazur (Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences); Maria Karpinska (Medical School of Białystok); Zbigniew Kaminski (Nofer Institute of Occupational Medicine); Nguyen-Dinh Chau (AGH University of Science and Technology); Bogdan Ciekot (Lądek-Długopole S.A. Health Resort); Katarzyna Kania (Analytical Laboratory in Świeradów Zdrój); Zdzisław Rafalski (Private Laboratory in Szczawno Zdrój).

FACTORS CONTROLLING MEASUREMENTS OF MASS RADON EXHALATION RATE

N. Dinh Chau, E. Chruściel, Ł. Prokólski

Faculty of Physics and Nuclear Techniques, AGH University of Science and Technology, Krakow, Poland

Abstract

The mass radon exhalation rate of soil samples was measured using a tight emanation chamber of 10 L volume and a Lucas cell. The results showed that the mass of sample, grain size fraction and water content influence the radon mass exhalation rate. For soil with a radium activity of about 2500 Bq/kg, the values of the mass radon exhalation rate for a sample mass of 0.2–0.5 kg are higher than those at other sample masses. The dependence of the measured exhalation rate on sample mass supposedly can be explained by a heterogeneous distribution of radon atoms in the air space of the emanation chamber and an enlarging of sample dimensions due to the mass increasing. The observed radon exhalation rate decreased with the enlarging of grain sizes; it increased intensively at a water content of a few percent by weight, then decreased with moisture growth. Due to these influences, the measured values of the mass radon exhalation rate should be reported together with the data of the physical parameters of the sample material.

1. INTRODUCTION

The contribution of radon and its progeny to the entire radioactive dose from natural radionuclides is above 50% [1], so the mitigation of radon concentration in indoor air from day to day has become more important — one should investigate the radon exhalation rates of building materials. One of the kinds of radon exhalation rate is the mass exhalation rate. The determination of the mass radon exhalation rate is based usually on the measurement of the growth rate of radon content in the air in a tightly closed emanation chamber containing the sample of the investigated material. The procedure seems to be simple, but the measured results for the same material differ over a wide range [2]. To find an explanation for this ambiguity, the authors have examined the influence on the measurement results of the following factors: sample mass, grain size fraction and moisture of the investigated material.

2. MEASUREMENT METHOD

To measure the mass radon exhalation rate, a 10 L emanation chamber (20×20×25 cm) and a Lucas cell coupled to a Pylon Electronic device AB-5 were used. A sample of known physical parameters such as mass, volume and moisture was placed in the tightly closed emanation chamber. Fig. 1 shows the measurement stand, and the connection of the Lucas cell to the emanation chamber by plastic pipes and valves. The connecting system enabled the air in the measurement system to be moved only from the emanation chamber to the Lucas cell and the other way round. In order to shield the radon progeny from the emanation chamber to the Lucas cell, a filter paper was located in the inlet to the Lucas cell. The radon content in the air chamber was measured every day, until it had reached a saturation value. This measurement can be described as follows — pumping the air from the emanation container to Lucas cell by the AB-5 pump for a time interval of 10 min, then starting the pulse counting cycle 3 h after pumping stopped. One cycle consisted of at least 6 pulse counting intervals of

10 min each. The radon content in the Lucas cell $N_L(t)$ (Bq) after time t (the interval between closing the emanation chamber and stopping the pump) was calculated by the following formula (in accordance with the manufacturer's instructions):

$$N_{\mathrm{L}}(t) = \frac{1}{n}\sum_{i=1}^{n}\frac{NCP_i \times C}{3 \times 600 \times \varepsilon \times A_i} \tag{1}$$

where NCP_i is the count rate less background of the i^{th} time of pulse counting in the 10 min counting interval, ε is the counting efficiency, n is the number of pulse counting times (6 in this case), C is the correction factor for decay during the 10 min counting interval, and A_i is the correction factor for decay during the time interval between stopping the Lucas cell pumping and starting the i^{th} time of pulse counting. The values of C and A_i can be found in the instruction manual [3]. The value 3 in equation (1) reflects the fact that after 3 h of stopping the pumping, the radon in the Lucas cell is in equilibrium with its two alpha-emitting daughters.

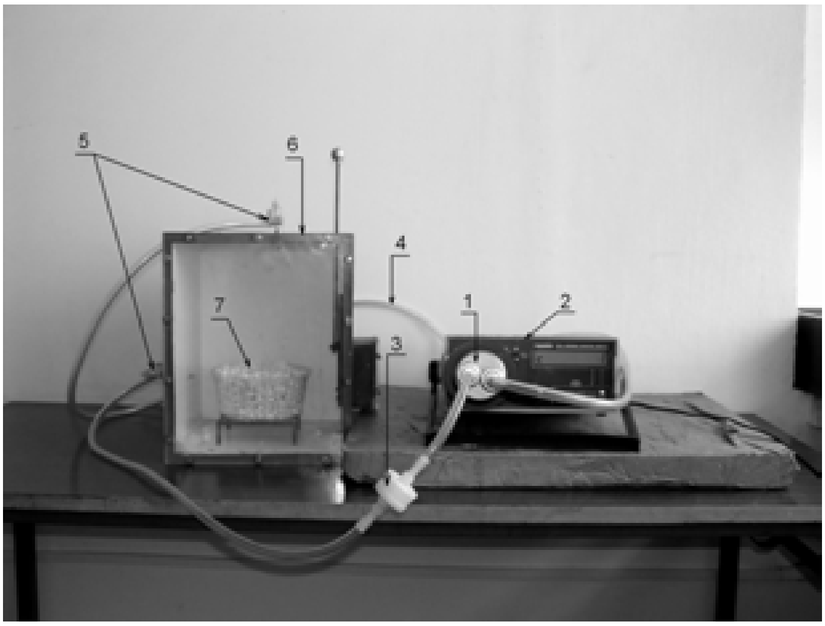

FIG.1. The view of the measurement stand.

The radon content in the emanation chamber at the time of stopping the pump, $N_C(t)$, was calculated using the formula:

$$N_{\mathrm{C}}(t) = \frac{N_{\mathrm{L}}(t) \times V_{\mathrm{C}}}{V_{\mathrm{L}}} \tag{2}$$

where V_{C} and V_{L} are the volumes of the emanation chamber and Lucas cell respectively. A typical curve describing the growth of radon content in the emanation chamber, $N_C(t)$, is presented in Fig. 2. It can be expressed by an equation of the form:

$$N_{\mathrm{C}}(t) = a\left(1 - e^{-bt}\right) \tag{3}$$

where b is in this case the radon decay constant (λ) and a is related to the mass radon exhalation rate by the expression $E_m = \frac{a \times b}{m}$ (with m being the sample mass in kg).

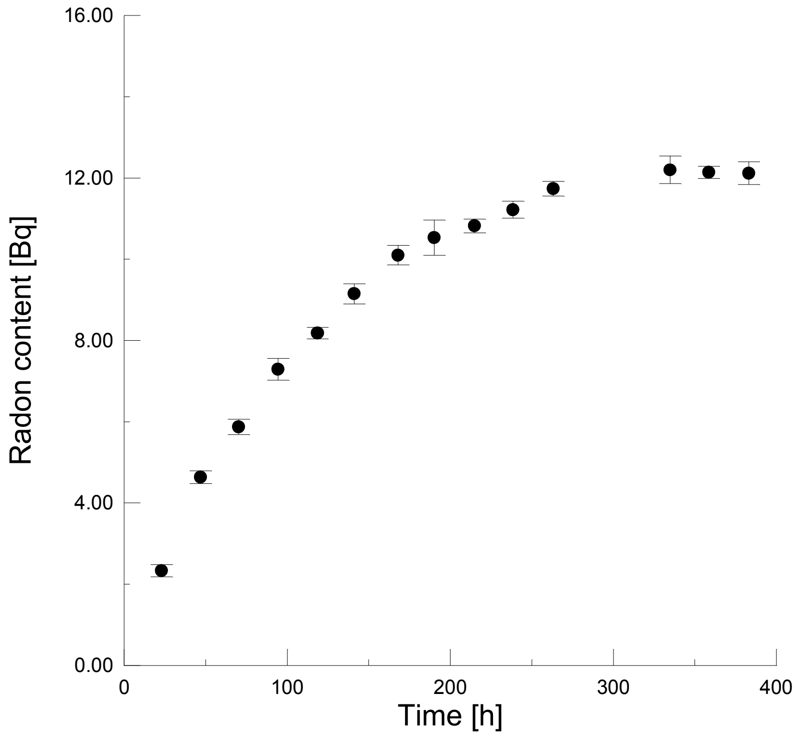

FIG. 2. Typical radon growth observed in a tightly closed emanation chamber containing a sample under investigation

3. INFLUENCE OF SOME FACTORS ON THE MASS RADON EXHALATION RATE

To investigate the influence of some sample parameters on the mass radon exhalation rate, a particular soil was chosen for preparing samples with different parameters. The soil was of various grain sizes and the concentrations of ^{226}Ra, ^{232}Th and ^{40}K, measured using gamma spectrometry, were 2560 ± 30, 73 ± 2 and 443 ± 12 Bq/kq, respectively.

3.1. Sample mass

In order to investigate the mass influence on the mass radon exhalation rate, samples of various masses were prepared from the above-mentioned soil. For each sample, the mass radon exhalation rate was measured by the method described above. Table I presents the masses, volumes V_S of samples and adequate measured mass exhalation rates E_m. The dependence of E_m on sample mass m is presented in Fig. 3. The shape of the curve of the dependence could be explained by:

- Heterogeneous distribution of radon atoms in the space of the emanation container due to gravitation effects;
- Enlarging of the sample dimensions due to the increase of its mass.

Due to gravitation effects, the majority of the escaped radon atoms settle in the area surrounding the soil sample. Therefore, if the sample mass is small, and thus its volume is small in comparison with the chamber volume, more radon atoms will settle in the area surrounding the sample and less atoms will settle in other places. This can cause a decrease in the measured radon exhalation rate. If the mass of the sample is too big, the sample dimensions become too large, so a portion of the emanated radon atoms could be confined to the sample. Consequently, the apparent radon exhalation rate could be smaller than the true rate.

TABLE I. SAMPLE MASS AND VOLUME, AND ADEQUATE MEASURED EXHALATION RATES

Sample mass (kg)	Sample volume (L)	Mean radon mass exhalation rate and two standard deviations (Bq·s^{-1}·kg^{-1})
0.05	0.057	185 ± 15
0.10	0.140	189 ± 12
0.20	0.273	209 ± 8
0.35	0.412	215 ± 7
0.50	0.570	212 ± 6
0.70	0.800	175 ± 8
1.00	1.130	168 ± 4

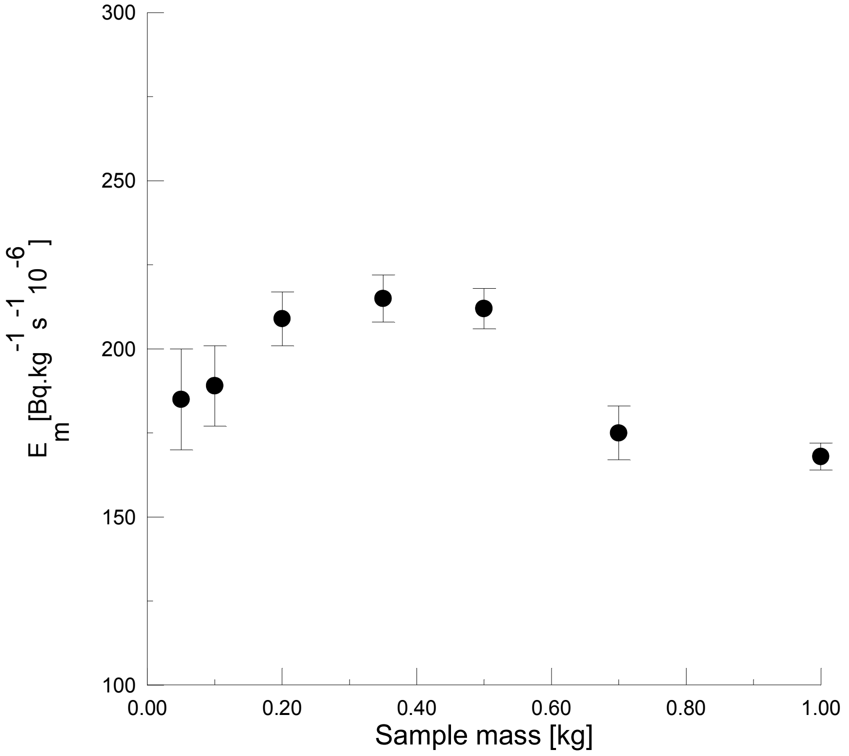

FIG. 3. Measured radon mass exhalation rate as a function of sample mass

3.2. Size fraction

To investigate the influence of grain size fraction on the mass exhalation rate, four samples with different grain sizes (diameters <1, 1–2, 2–4 and >4 mm) were created by sorting the above-mentioned soil. In the sample with a grain size >4 mm, it was confirmed that there were grains of up to 8 mm in diameter. The mass of the sample with a 1–2 mm grain size was the smallest (200 g), and therefore the masses of the other three samples were adjusted to the same value. Fig. 4 shows the dependence of the measured radon mass exhalation rate on the grain size fraction. One could expect that the radon exhalation rate should decrease with increasing grain size [4], due to the decrease in total surface area and hence the number of radon atoms emanated. However the phenomena is not entirely visible in Fig. 4. This could be explained by the possibility of different distributions of radium atoms in the different size fractions and by the size of the deviations in the measured results.

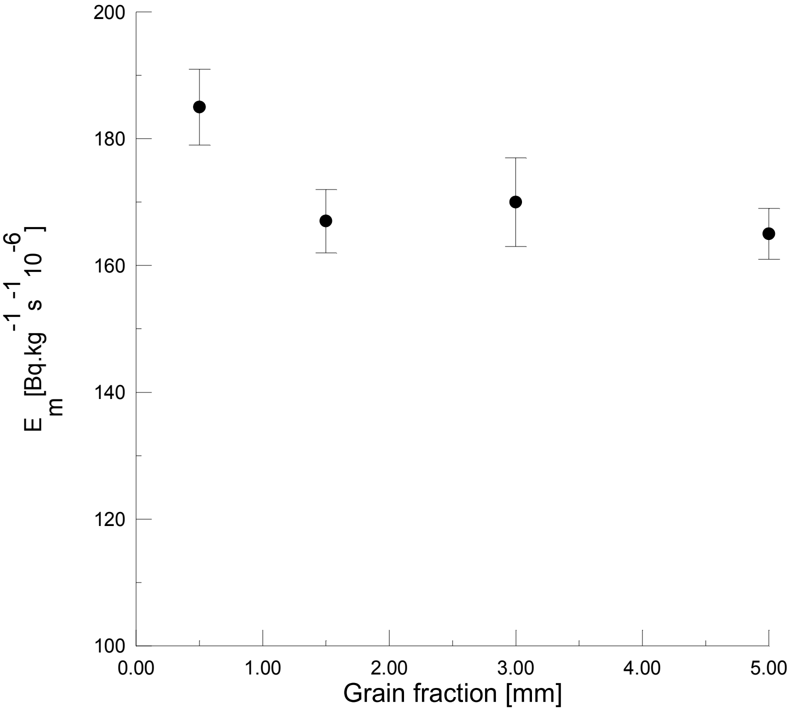

FIG. 4. Measured radon mass exhalation rate as a function of sample grain size

From Figs 3 and 4, one can notice that the average value of the measured exhalation rates for the samples of the mixed grain sizes is higher than that for the samples of the sorted grain sizes. The fact is due to the higher porosities of the samples of mixed grain sizes than those of the other samples.

3.3. Sample moisture

To prepare samples of different moisture content, 3 kg of the investigated soil was first dried at a temperature of 105°C until its mass ceased to change. Then, four samples each of mass 0.5 kg were made from the dried soil. To prepare four samples with different moisture contents (0, 2, 6 and 10% by weight), different masses of water (10.2, 32.0 and 55.5 g) were added to the second, third and fourth samples. Each sample was then measured by the method described above. The results are presented in Fig. 5, showing that at first the radon mass exhalation rate increased with water content, reached a maximum at a certain value of moisture, and then decreased with further increase in water content. This can be explained by the 'target' phenomenon [1, 4–6]. If the soil is dry, a certain portion of radon atoms originating from radium decay on the mineral surfaces, due to a sufficiently high ejection energy (83 keV), could pass through the pores (if the pores are small enough) and stick to other minerals. Thus, less radon atoms would exist in the pores and the exhalation rate would be small. If the soil is moist but not wet, the radon atoms could be caught by the water in the pores and could move out the sample. This results in more radon atoms entering the free air, so in consequence the radon exhalation rate would be increased. If the soil is wet, the water can cover the mineral surfaces and lead to less radon atoms in the air pores. So the radon exhalation rate could again be small.

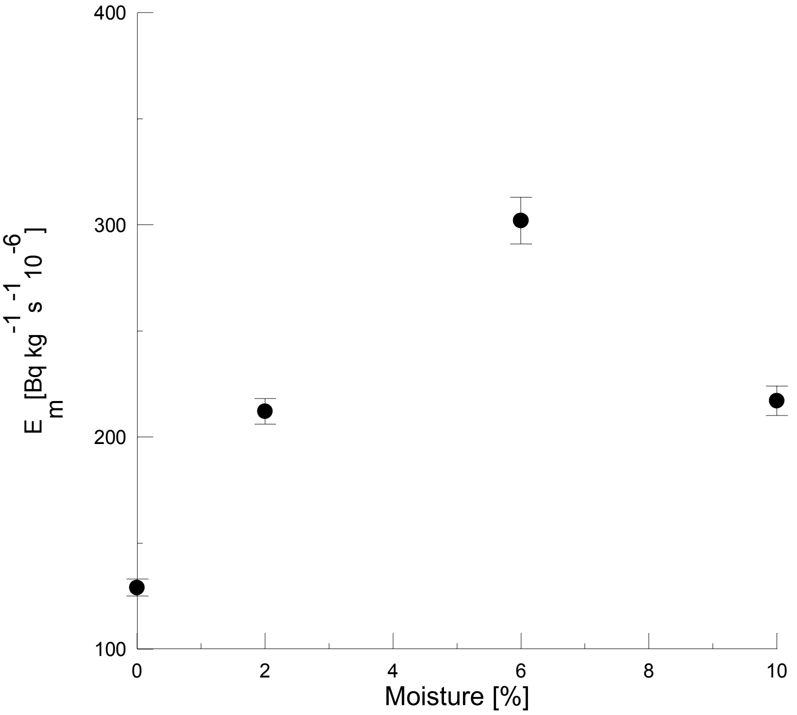

FIG. 5. Measured radon mass exhalation rate as a function of sample water content

4. CONCLUSION

The mass radon exhalation rate E_m depends on the measurement conditions and the physical parameters of the sample. The dependence of E_m on the sample mass and the volume ratio V_S/V_C is explained by the heterogeneous distribution of exhaled radon atoms in the chamber and by the decrease in the relative portion of exhaled radon atoms due to the increase in sample mass. The exhalation rate decreases with increasing grain size. The shape of the curve relating the radon exhalation rate to the water content in the sample is explained by the 'target' phenomenon. Therefore we propose that a given radon mass exhalation rate should be qualified by stating the physical parameters of sample under investigation.

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ATTEMPTS ON DETERMINATION OF RADON EXHALATION RATE FROM A WASTE-DUMP OF BOGDANKA COAL MINE WITH USE OF THE PICORAD DETECTORS

A. Komosa[1*], S. Chibowski[1], M. Klimek[1], S. Chałupnik[2]

[1]Department of Radiochemistry and Colloid Chemistry, Maria Curie-Sklodowska University Lublin, Poland

[2]Central Mining Institute, Katowice, Poland

Abstract

The Bogdanka coal mine is located in the Pojezierze Łęczyńsko-Włodawskie district in the vicinity of the Poleski National Park. From the beginning of mining activity, i.e. for the last 20 years, waste rock has been deposited close by. It consists mainly of clumps (about 88%) of a few centimeters grain-size, while sandstones, siderite and mudstones form the rest. A storage yard, filled to about 30%, covers an area of 83 ha and is partly cultivated. It is well known that deposited waste rocks of coal mines may be a source of radon. The emission rate of this element from a spoil dump depends on many factors, so direct measurements of the exhalation rate are the most reliable. Passive detectors containing activated carbon (Picorad, Niton-Canberra-Packard), designed for the detection of stable concentrations of indoor radon were used. An application of these detectors in open areas may produce errors associated with the higher humidity and variable concentrations of exhaled radon. The radioactivity of radon and its daughters was determined using a liquid scintillation spectrometer (Quantulus, Wallac-Perkin-Elmer). Measurements were made at several points on the spoil dump, including where waste was most recently deposited and cultivated sites. A calibration of the detectors with various radon concentrations and humidity levels was performed in a radon chamber at the Central Mining Institute.

1. INTRODUCTION

The Bogdanka coal mine is located in the Pojezierze Łęczyńsko-Włodawskie district in the vicinity of the Poleski National Park. From the beginning of mining activity, i.e. for the last 20 years, waste rock has been deposited close by. A storage yard, filled to about 30%, covers an area of 83 ha and forms a 25 m high waste dump hill. The north and southwest hill slopes were stabilized, covered by a thin soil layer and planted with small trees. The deposited gangue consists mainly of clumps (about 88%) of a few centimeters grain-size, while sandstones, siderite and mudstones form the rest [1].

It is well known that deposited waste rocks of coal mines may be a source of radon [2]. Such areas are potentially hazardous and, according to radiological protection standards, should be monitored [3]. The emission rate of radon from a dump depends on many factors, so direct measurements of the exhalation rate are the most reliable. The aim of this work was to use Picorad detectors to measure the radon exhalation rate from the waste dump of the Bogdanka Coal Mine. The Picorad vials containing activated charcoal and silica gel are so called passive detectors. Radon from the air is absorbed by the charcoal (usually for 48 h) and a radioactivity measurement is performed after desorption of radon by a liquid scintillation

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[*] E-mail: akomosa@hermes.umcs.lublin.pl

cocktail. These detectors are intended for the detection of radon in areas of rather stable concentration.

2. METHODS

The measurement points for the exhalation of radon were chosen near the top of the waste dump on a partly reclaimed area and on open waste gangue. The geographical coordinates of the sample collection points were: 51°19"01 N and 22°59"38 E. The Picorad vials were placed at twelve locations (scattered over a distance of about 100 m) and covered with steel bowls of 2.5 L volume and 25 cm in diameter. Measurement took place in January 2004 when a small layer of snow covered the heap. The bowls were pressed firmly into soil or rock layer, and snow or soil was used to prevent the gas from leaking. The collection of radon was performed over a 3 h period at an air temperature of -5°C, a relative humidity about 75% and an atmospheric pressure 99.5 kPa. Next the vials were brought to the laboratory where, one hour after ending the radon collection, they were subjected to routine analysis.

For measurements, an Instafluor (Packard) scintillator was added and a Quantulus 1220-002 (Wallac-Perkin-Elmer) spectrometer applied. Radiation emitted by radon and its daughters was measured in the 466–902 channel range as high energy beta, without the background reducing option. The counting rate (counts/min) was calculated by the computer program Picorad 5.9 (Niton) to obtain the concentration of radon in Bq/m^3.

The program calculating the radon concentration assumes at least a 12 h period of radon sorption in the vial with minimal changes of its concentration level in air. For shorter exposure times of the vials with the activity possibly still growing, the application of the calculation program may be limited. Therefore, the calibration of the Picorad detectors was conducted in a radon chamber at the Radiometry Laboratory of the Central Mining Institute (CMI) as described below.

The chamber of 7.25 m^3 volume was ventilated to obtain a concentration of radon at the same level as in the open air. Directly before beginning the exposure of the Picorad vials, the air was pumped through a radium source type Ra-1025 PYLON for about 15 min to remove radon from the source. Then, the Picorad vials, CMI coal detectors and radon source equipped with a small pump for continuous pumping of air were put in the chamber.

The 4 h exposure was begun after the chamber had been locked. Detectors were removed after 2, 3 and 4 h, respectively, and closed. At the same time, air samples were collected in two Lucas cells to measure the radon concentration in the chamber. The Picorad detectors were sent to the M.C. Sklodowska University laboratory within 24 h for analysis.

3. RESULTS AND DISCUSSION

3.1. Calibration of the Picorad detectors

The results of the Picorad detector calibration, conducted in a radon chamber, are presented in Fig. 1. The Figure shows the true radon concentration in the chamber (determined by calibrated coal detectors and Lucas cells) during the exposure time, the measured counting rate of Picorad detectors, as well as the radon concentration calculated by the computer program Picorad 5.9. As can be seen, the true concentration of radon in the chamber grew linearly with time at a rate of about 450 Bq·m^{-3}·h^{-1}. The linear correlation of the points described by Pearson's coefficient was 0.986. The counting rate measured by the spectrometer with the liquid scintillator in the Picorad detectors grew linearly in a similar fashion. The data points lie on a straight line, also with a high correlation coefficient.

However the radon concentration calculated from the counting rate by the Picorad 5.9 program strayed markedly from a linear plot — the values obtained after 2 h of exposure were too high The reason for this is probably the short exposure time, which led to incorrect calculation by the Picorad 5.9 program. The relation between the counting rate and the true concentration of radon in the chamber is shown in Fig. 2, while a similar relationship, but this time for the radon concentration calculated with the Picorad 5.9 program, is shown in Fig. 3.

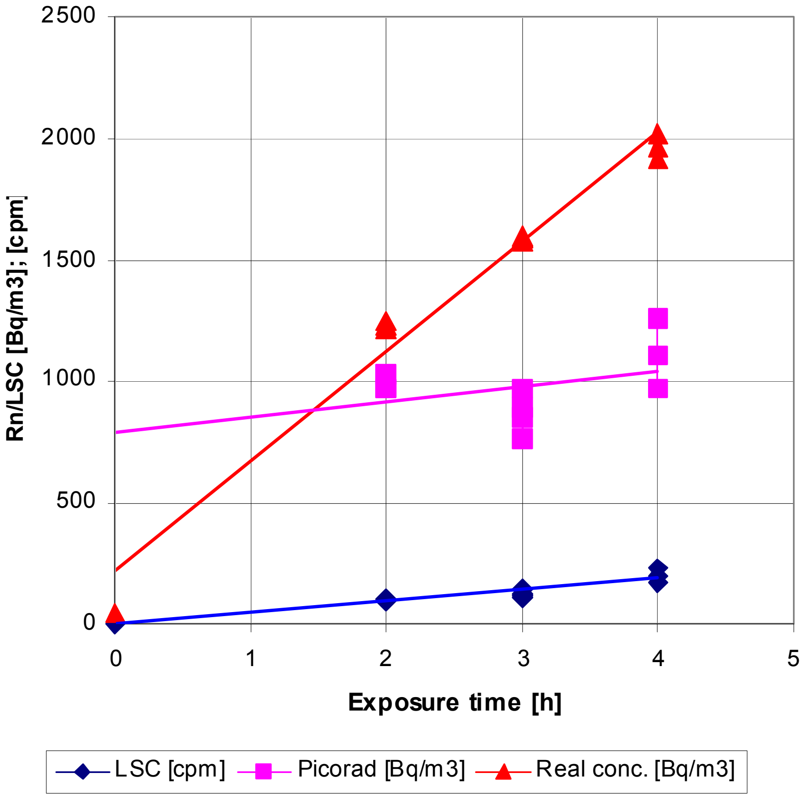

FIG. 1. Calibration of the Picorad detectors, showing the time variation of the real radon concentration ('Real conc.'), the count rate in the liquid scintillator ('LSC') and the concentration calculated by the Picorad 5.9 program ('Picorad')

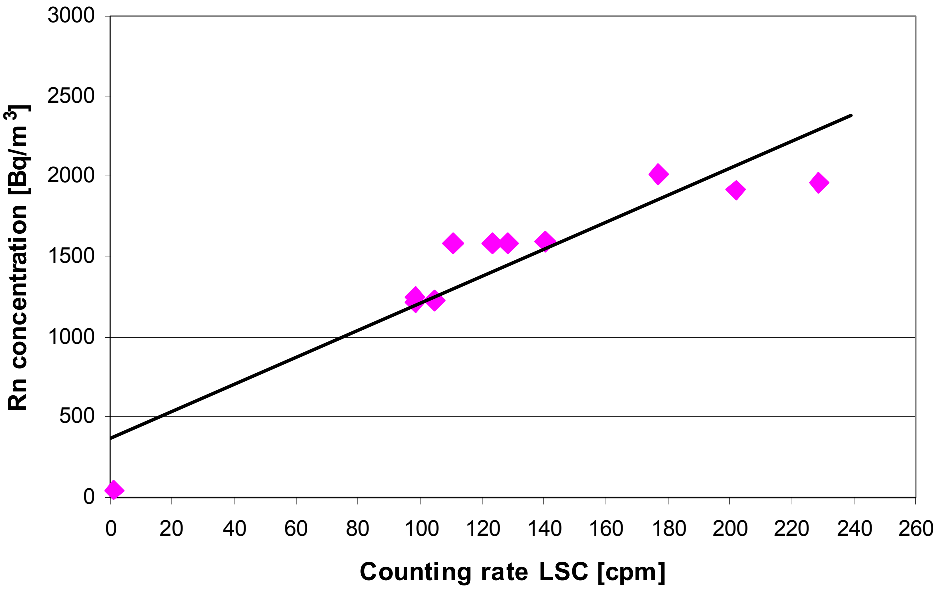

FIG. 2. True radon concentration vs. counting rate in the liquid scintillator

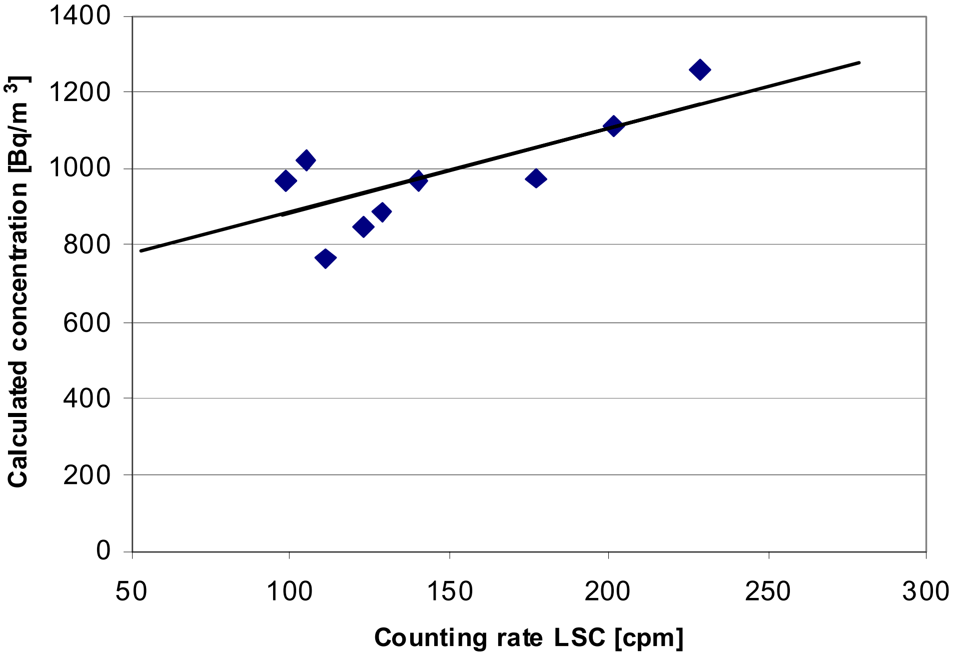

FIG. 3. Radon concentration calculated with Picorad 5.9 program vs. counting rate in a liquid scintillator

The relationship between the real concentration of radon in the chamber and the counting rate in the liquid scintillator, shown in Fig. 2, approximates a linear dependence quite closely — the Pearson's correlation coefficient is 0.87. However, the radon concentration calculated with the Picorad 5.9 program shows a worse correlation with the counting rate in the liquid scintillator, i.e. 0.73. The data points obtained after the shortest time of exposure (2 h) cannot be accepted. Their removal improves the correlation to a value of 0.93.

The analysis of the above-mentioned dependencies allows one to conclude that the real concentration of radon in the chamber is better correlated with the counting rate using the liquid scintillator over the concentration range studied than that calculated with the Picorad 5.9 program. For this reason the relationship presented in Fig. 2 is more reliable.

3.2. Results of radon exhalation measurements on the waste dump

The results of the 3 h measurements of radon exhalation are shown in Table I, indicating the counting rate of the Picorad detectors in the liquid scintillator, the activity of radon and its daughters calculated with an assumed 100% measurement efficiency, and a radon exhalation coefficient defined by the following equation [4]:

$$\varphi_{\mathrm{Rn}} = \frac{A_{\mathrm{Rn}}}{S \times t} \tag{1}$$

where φ_{Rn} is the radon exhalation coefficient (Bq·m^{-2}·s^{-1}), A_{Rn} is the activity of radon (Bq), S is the exhalation surface area (m^2), and t is the time of radon accumulation (s). The calculated radon exhalation coefficients turned out to be small in comparison with the literature data, which range from several to tens of Bq·m^{-2}·s^{-1} [4]. However, one should remember that investigations were carried out in winter, with an air temperature of -5°C remaining for a long time. The soil was frozen, making the radon diffusion more difficult. The measurements will be repeated shortly in different weather conditions. The radon exhalation coefficients are presented in Fig. 4 for the various measuring points. Points 1–7 were associated with the reclaimed surface, while the remaining ones were associated with the surface of fresh gangue. From Table I and Fig. 4, one can determine that the average values of radon exhalation coefficient for the reclaimed surface were about 2.5 times greater than those for the fresh rock. The values are, respectively: 0.138 ± 0.075 and 0.051 ± 0.033 mBq·m^{-2}·s^{-1}. Such results may have been influenced by the frozen soil.

TABLE I. RADON EXHALATION MEASUREMENTS

Location	Net count rate LSC Picorad (count/min)[1]	Activity (mBq)	Exhalation coefficient (mBq·m^{-2}·s^{-1})
Reclaimed surface	4.34	72.3	0.136
	2.32	38.7	0.073
	3.74	62.3	0.118
	8.48	141.3	0.267
	7.27	121.1	0.229
	3.03	50.5	0.095
	1.51	25.2	0.047
Fresh gangue surface	2.12	35.3	0.067
	0.20	3.33	0.006
	1.82	30.3	0.057
	3.23	53.8	0.102
	0.81	13.5	0.025

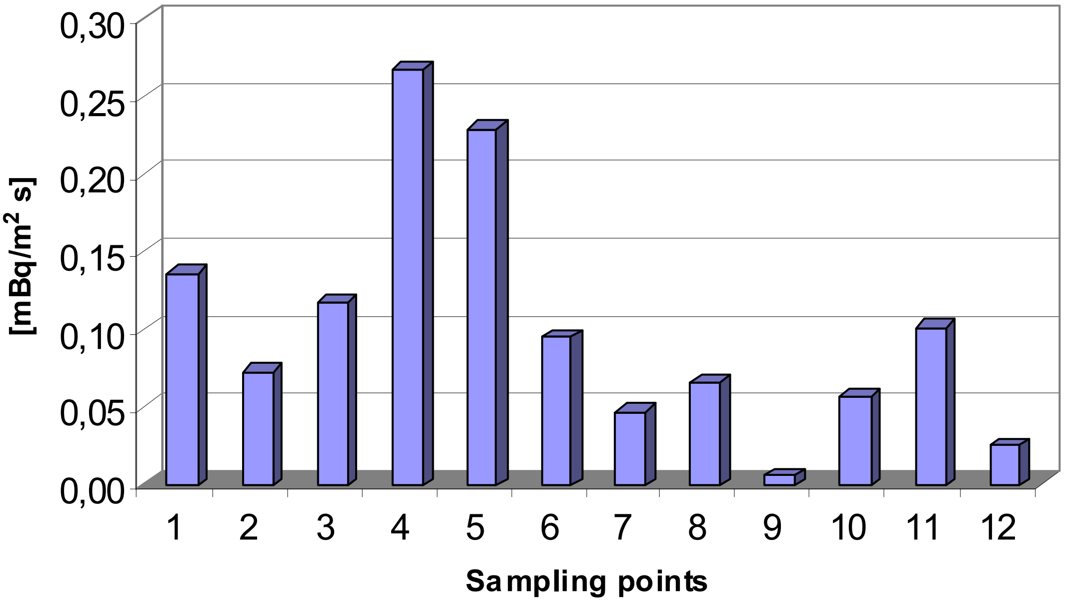

FIG. 4. Radon exhalation coefficients from frozen soil, Bogdanka coal mine waste dump

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[1] The background count rate was 0.9 count/min.

The average concentration of radon was calculated by the Picorad 5.9 program from the counting rate. Results are shown in Fig. 5 as the calculated concentration of radon versus the counting rate. This dependence is characterized by a good approximation to a linear relationship, with a Pearson's correlation coefficient of 0.99. It shows that the 3 h measurements are satisfactory for the determination of radon concentration from the counting rate data using the Picorad 5.9 program.

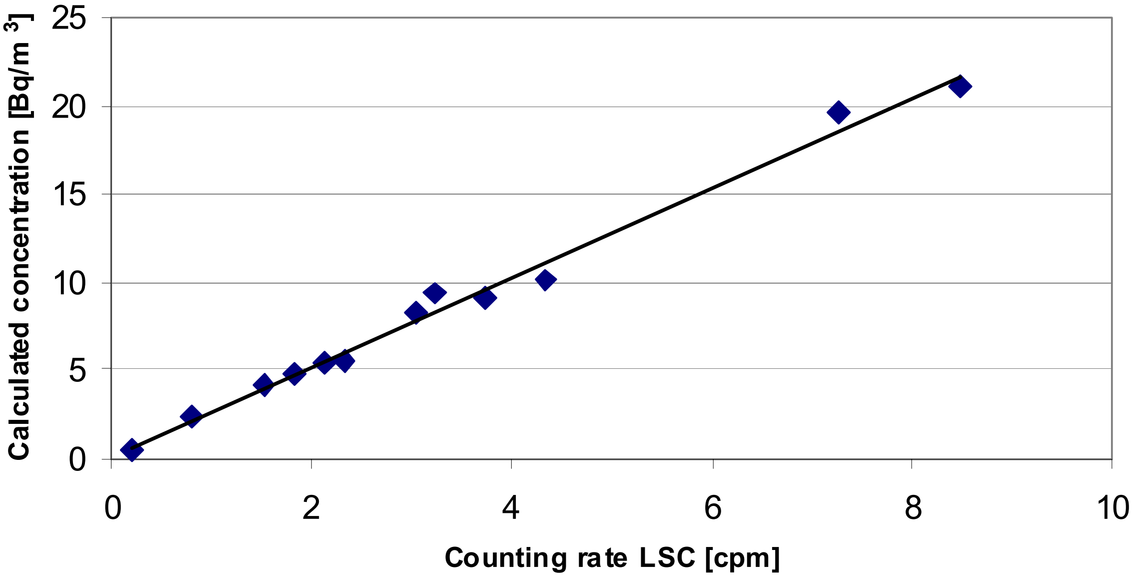

FIG. 5. Radon concentration calculated with the Picorad 5.9 program vs. counting rate in a liquid scintillator

To confirm the results, measurements were made, in addition, of the ^{226}Ra content in the samples of gangue taken earlier from different places of the waste dump. The use of the high-resolution gamma spectrometer with germanium detector allowed the average content of this radionuclide, about 60 Bq/kg, to be evaluated. The radon exhalation coefficient φ_{Rn} is related to the radium content in the material by the following equation [5, 6]:

$$\varphi_{\mathrm{Rn}} = \varepsilon \times A_{\mathrm{Ra}} \times \rho \times \lambda_{\mathrm{Rn}} \times R \times f \qquad (2)$$

where ε is the emanation coefficient, A_{Ra} is the radium concentration in soil (Bq/kg), ρ is the soil density (kg/m^3), λ_{Rn} is the radon decay constant (2.0974×10^{-6} s^{-1}), R is the range of diffusion (m), and f is the porosity factor including moisture. The distance of diffusion R is dependent on the diffusion coefficient, as follows [5, 6]:

$$R = \frac{\sqrt{D}}{\sqrt{\lambda_{\mathrm{Rn}}}} \qquad (3)$$

where D is the diffusion coefficient of radon in soil (m^2·s^{-1}). The diffusion range R may be calculated from equation (2) using exhalation coefficient values obtained from measurements (Table I) and assuming rational values for the remaining parameters It allows the radon diffusion coefficient in particular conditions to be estimated using equation (3) in the next stage. For this purpose an emanation coefficient ε of 0.2 and a porosity factor f of 0.4 were adopted [5]. The other factors, i.e. radium concentration and the density of material, were determined experimentally. The average radon diffusion range R and the associated diffusion coefficient D calculated in the above-mentioned manner are shown in Table II.

TABLE II. AVERAGE RADON DIFFUSION RANGE AND DIFFUSION COEFFICIENT

Location	Diffusion range (cm)	Diffusion coefficient ($m^2 \cdot s^{-1}$)
Reclaimed surface	1.0	2.6×10^{-10}
Fresh gangue surface	0.4	$4.0 \times \cdot 10^{-11}$

The values obtained are much smaller than expected for soils in normal conditions, and approximate more closely to values for rocks (marble, granite, sandstone) or construction materials (concrete) [6, 7]. This confirms the earlier conclusion that the diffusion of radon is limited under the conditions studied.

4. CONCLUSIONS

The possibility of using Picorad detectors for measuring the radon exhalation rate for the waste dump of the Bogdanka Coal Mine proved to be successful. Calibration of the Picorad detectors in the radon chamber confirmed that 3 h is the minimum time of exposure needed to ensure reliable values of the radon concentration calculated by means of the Picorad 5.9 program. Knowing the calculated rate of radon exhalation and the radium concentration, one can estimate the average radon diffusion range. In our study, the calculated mean radon diffusion range in gangue of the waste dump was 1 cm (reclaimed surface) and 0.4 cm (surface of fresh gangue). The respective diffusion coefficients were, respectively, 2.6×10^{-10} and 4.0×10^{-11} $m^2 \cdot s^{-1}$, similar to those for low permeability materials such as rocks.

ACKNOWLEDGEMENT

This study was supported by the Polish Committee of Scientific Research (KBN) with Grant No. 4T09D 05824.

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THE EFFECT OF EARTHQUAKE-INDUCED RADON RELEASE ON THE POPULATION IN THE SEISMIC ACTIVE REGIONS OF ARMENIA

E. Saghatelyan[*]**, A. Petrosyan, Y. Aghbalyan, M. Baburyan, A. Davtyan**

Armenian State Engineering University, Armenia
Centre for Ecological-Noosphere Studies of NAS RA, Yerevan, Armenia

Abstract

For the first time, on the basis of the Spitak earthquake experience (Armenia, December 1988), it was found that an earthquake causes intensive and prolonged radon releases that are strikingly displayed in covered premises (dwelling houses, schools, kindergartens) even if they are at a considerable distance from the epicentre of the earthquake. The duration of the release includes the period starting from the first foreshock and ending with the last aftershock, i.e. several months. The radiation intensity and duration of the influence are in direct correlation with the force of earthquake. The area affected by radiation is larger than the territory of Armenia. The scale of this impact on the affected population was 12 times higher than the number of people injured in the Spitak earthquake.

1. INTRODUCTION

The reality of the radon problem is universally recognized today. According to IAEA data, natural sources of radiation are responsible for the main contribution (up to 70%) to the total radiation dose. The main contributions are materials with an increased content of natural radionuclides and radon accumulating in buildings. About 44% of the total radiation dose arises from radon and its daughters. Mortality attributable to this is about 80 000 people per year. Among the main consequences of radon exposure are cancer of the upper respiratory tract and lungs, and leukaemia in children. In many countries (e.g. United States of America, Sweden, United Kingdom) this problem has become the subject of national programmes.

The attention of studies in other countries is focused on the harmful effects of radon for those who inhabit houses with high radon concentrations for long periods. The main sources of radon are building materials, mainly soils. According to IAEA data, localities with a high content of radioactive elements in rocks are considered as ‘hot spots’ with increased levels of radon.

According to the results of investigations in the former USSR, humans are affected by ‘radon storms’ caused by geomagnetic storms. In geology, the use of radon emanation from groundwater and soil for detecting seismicity became famous worldwide after the Tashkent earthquake in 1966 and after the discovery made by Gorbushina and others. Japanese investigators found a small increase in radon concentration in the atmosphere during earthquakes.

There is no information in the literature about the influence of the seismic focus and the radius of its effects on radon concentrations in dwellings. There are no data concerning the

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[*] E-mail: sagatelyan@fromru.com

radiological implications of dust during destruction caused by earthquakes. This paper is one of the first in which these deficiencies are taken into consideration to a significant extent.

Significant hazards are associated with sites at which radon and radium concentrations are high in minerals and groundwater, and with oil-bearing basins and areas on which oil–water precipitation tanks are located. Areas in which rocks containing high concentrations of uranium, thorium, and radium are exploited also present a potential hazard. The presence of high radon concentrations in seismically active regions is a different issue. Here, radon concentrations are influenced by earthquake areas and active tectonic fault zones — in addition to the natural radioactivity of the rock, a major role is played by the physical-mechanical properties of the rock, textural-structural peculiarities that stipulate the percentage of rock porosity, and radiometric parameters such as the ‘estimation coefficient’. Moreover, soils behave not in an isolated way but as a constituent of the engineering-geological peculiarities of the site, with all the ensuing consequences. The extended occurrence of the radon emanation field is rather a significant factor; opinions concerning its formation differ. As a matter of fact, a significant increase in radon concentration is a function of the earthquake.

The problem of populated areas in the general sphere of problems connected with earthquakes is usually considered only from one aspect, namely, that of seismically stable buildings and structures. But, as the results of our mainly ecological investigations have shown, catastrophic destruction caused by earthquakes, with all ensuing consequences, are only the tip of the iceberg. It is possible to predict an earthquake correctly, to have seismically stable houses, and to avoid direct fatalities, but it is impossible to avoid the danger of death when there is no knowledge of such danger — this danger is radiation.

In this report we shall speak about alpha radiation (radon radiation), on which we have firm data, although it should be noted that, as the analysis of the literature has shown, other types of radiation resulting from earthquakes are not excluded. As the results of our investigations have shown, the same houses at the same time of the year are characterized by different concentrations of radon during stable and extreme (earthquake) conditions of the earth’s crust. Thus, using the example of the Spitak earthquake, it has been determined that earthquakes are accompanied by intensive and long-term alpha radiation releases (radon releases) — local radiation effects that are constantly manifested in closed buildings (dwellings, schools, kindergartens) even at a considerable distance from the epicenter of the earthquake, thus repeatedly increasing the risk of alpha exposure of the population. These releases are quickly dispersed in the open air, and that is why they are not usually registered.

Preliminary work financed by the Ministry of Education and Science of the Republic of Armenia started in 1989, and was conducted by a small scientific group in the Department of Geology and Exploration Techniques, SEUA.

2. SUBJECT AND METHODOLOGY OF MEASUREMENTS

The research is underpinned by the results of indoor radon monitoring conducted in Yerevan (Armenia) and its surroundings from 1987 to 1993 (during stable and unstable situations of the earth’s crust). The area is characterized by low activity volcanogenic sedimentary rocks. Armenia is a highland region, characterized by young volcanism. The volcanic regions have not yet cooled and the region is seismically active. These active geotectonic processes and increasing industrialization make public safety an issue with regard to natural and industrial catastrophes. Measurements were made using a radon meter (model FAS-P-2 supplied with a filter type AFA-PSP-20, manufactured in Russia). The instrument assures a 95% efficiency of radon aerosol gathering and a measurement error of about 40%.

Air samples were taken in basements and measured in underground, single- and multi-storied buildings throughout the study period. While carrying out the investigations, recommendations were made on the methodology for measuring the volume activity of radon and its daughter products in the air of dwellings and other buildings in Armenia.

The total number of samples taken and analyzed was 5228. Mean monthly values of measurements were generated, irrespective of the type of building, through a moving average formula, and graphs were constructed from the data obtained.

3. RESULTS AND DISCUSSION

Statistical processing of the radon monitoring data (Fig. 1) superimposed on the dynamics of the earthquake showed clearly that, irrespective of seasonal oscillations, the radon concentration in dwellings during 1987 was within normal levels. A growth in radon concentration occurred from the beginning of 1988, and in July and August exceeded by 8–10 times the concentration during the previous year. In January 1989, the mean radon concentration had increased by nearly 14 times. As may seen from Fig. 1, three spikes are evident, characterizing intensive releases of radon corresponding, with some delay in time, to the first foreshock, the main shock, and the late aftershocks. The time interval between the first foreshock and the last aftershock, characterized by multiple increases in radon concentration in closed buildings, could be clearly seen.

It is interesting to note that the radon concentration peaks in the houses of Yerevan were generally a mirror image, delayed in time, of the graph of subsoil radon monitoring registered at Gyumri regime station (Fig. 2); they differ only in the change of concentration levels. In using the soil radon method, the investigator can determine by intersection only short-term anomalies, which are characterized by an increase or decrease of concentrations of only 20% of the original background. As for the indoor radon monitoring, the question is not only about the repeated increase of the concentration long before the earthquake, but also about the possibility of correlating the whole pattern of variations in indoor radon with instabilities in the earth’s crust.

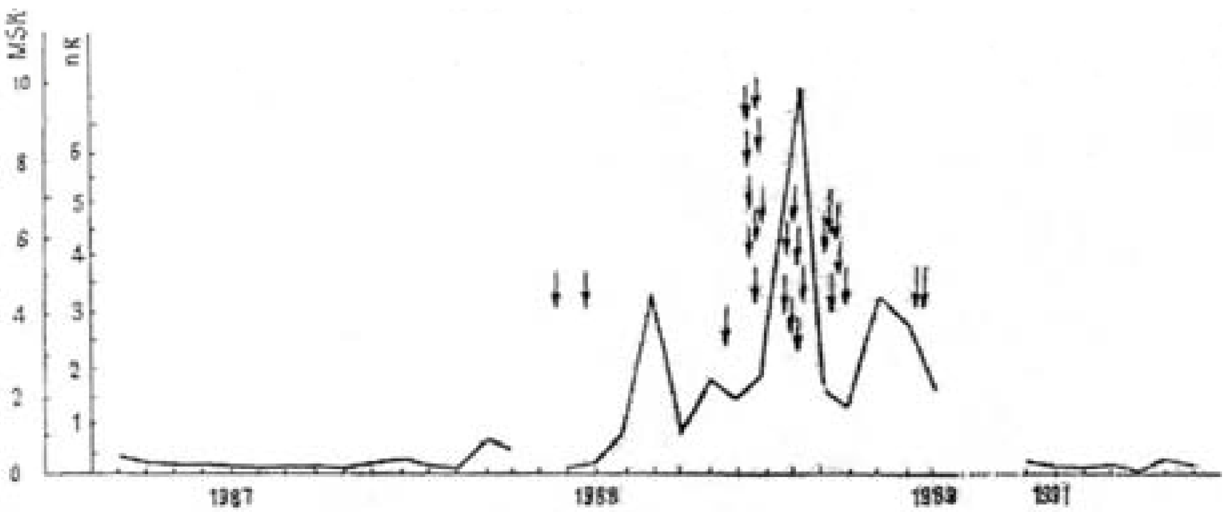

FIG. 1. Dynamics of changes in the concentration of indoor radon and the intensity of the Spitak earthquake, Yerevan

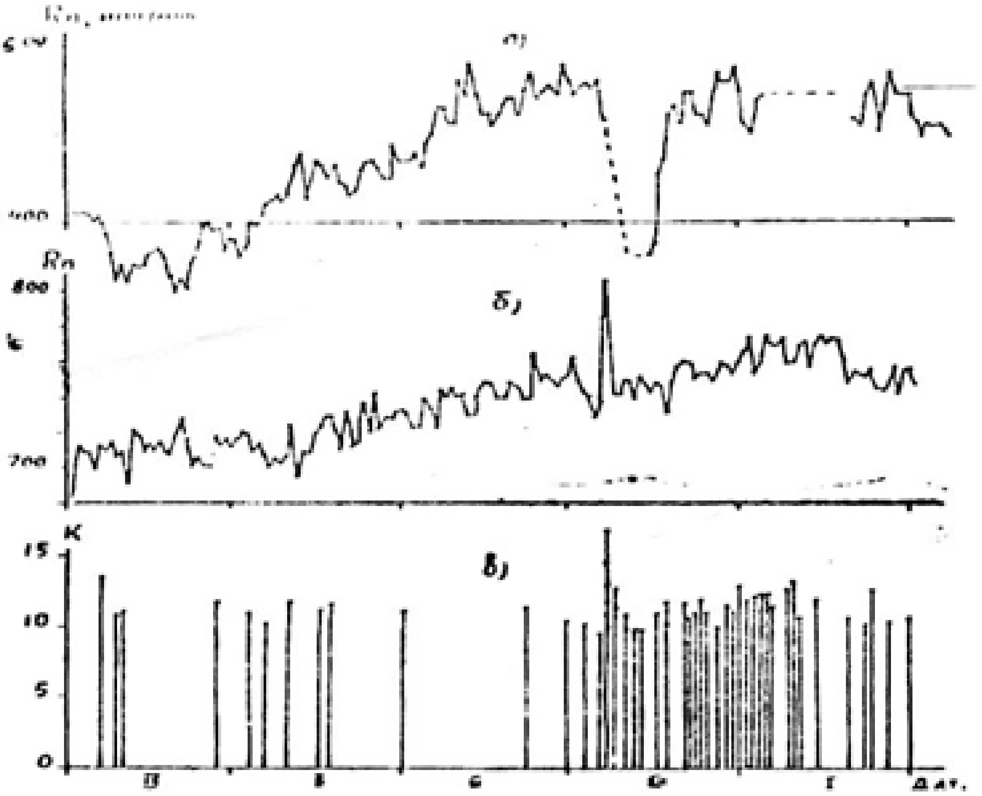

FIG. 2. Spitak earthquake operational precursors: (a) Leninakan seismic station; (b) Jermuk seismic station; (c) seismic activity in the region

Annual average indoor radon concentrations in Yerevan in 1987, 1988, 1989 and 1991, and the indices of the variations, are shown in Table I. They show clear differences between stable periods (1987, 1991) and unstable periods (1988, 1989) of the earth's crust.

TABLE I. INDOOR RADON CONCENTRATIONS IN YEREVAN

Year	Mean concentration	Dispersion, α^2	Root mean square dispersion, d	Variation coefficient V (%)
1987	0.25	0.0106	0.0103	41.32
1988	1.126	0.864	0.924	82.5
1989	2.977	4.444	2.109	70.81
1991	0.17	0.004	0.069	37.05

At the same time, as may be seen from Figs 1 and 2, the radon concentration curve coincides with the positive spike at Jermuk seismic station. These results demonstrate the release of radon into the atmosphere at the epicentre and its intensive accumulation in the subsoil layer a considerable distance from the epicentre. It is important to note that actually there is no vivid central spike and, according to the results of daily measurements, this whole interval before and after the earthquake is characterized by dozens of spikes (Fig. 3).

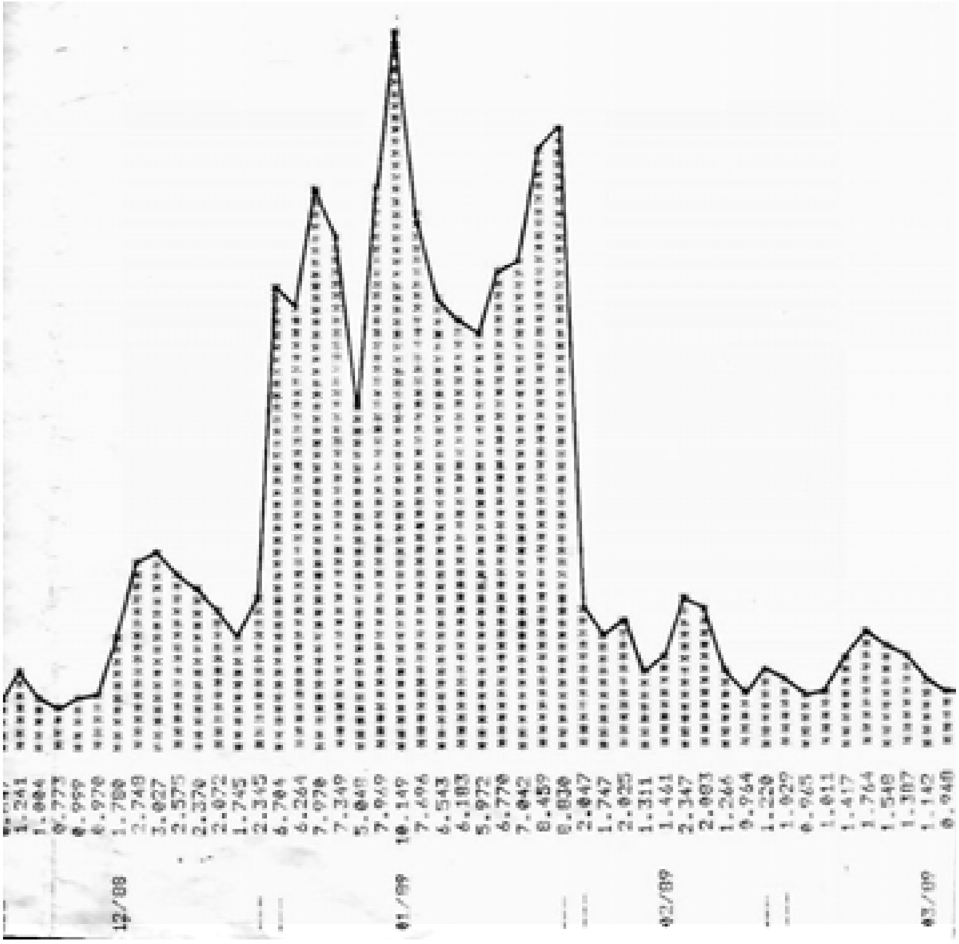

FIG. 3. Extract from the graph of daily radon measurements

Fig. 4 shows the effective dose calculated at monthly intervals and projected to an annual figure. Here also, curves characteristic of the stable state and for the state during the earthquake are distinctly seen. In January 1989, the projected annual dose from radon and its daughters was about 16 mSv. If the 1987, 1991, 1992, and 1993 data, showing doses from 0.183 to 0.435 mSv (less than twice the global average), are taken as typical, then the dose in January 1989 was 50 times more than that in the 'stable' periods and 16 times more than the global average.

Near the epicentre of the earthquake (Nalband, Spitak and alongside the whole disaster zone), the indoor radon concentrations, and hence the effective dose from radon, were many times higher.

The following facts which have not received explanation till now can be considered as a consequence of the prolonged radiation effect on humans: a prolonged state of apathy and indifference typical for the population of Armenia during a period of more than a year after the earthquake, a prevalence of respiratory diseases and digestive system diseases (Fig. 5), a prevalence of malignant cancer in disaster zones and of lung cancer over other forms of oncology diseases (Figs 6 and 7), a prevalence of mental disorders in children (Fig. 8), etc. (Source: Ministry of Health of Republic of Armenia, Statistical data on public health). The area affected by radiation is larger than the territory of Armenia. The scale of this impact on the affected population is 12 times higher than the number of people injured in Spitak, Leninakan and other settlements (the number of injured was 25 000 people, compared with a projected number of more than 300 000 diseases caused by high levels of radiation.

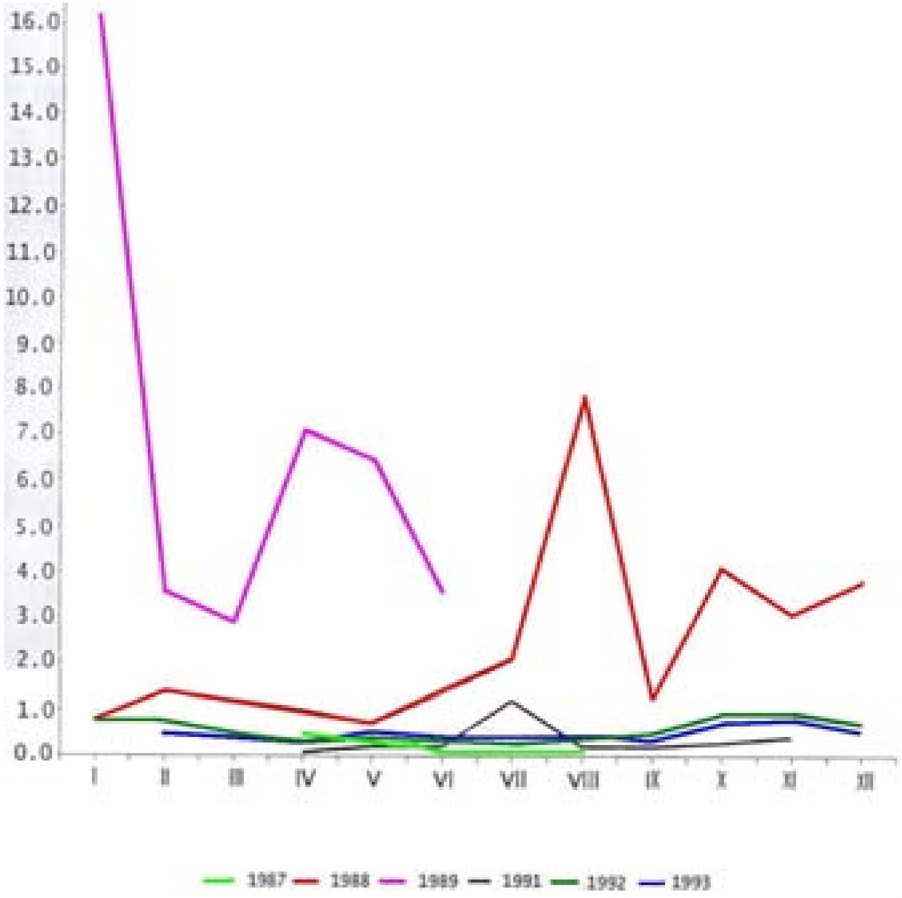

FIG. 4. Annualized effective dose from exposure to radon in Yerevan

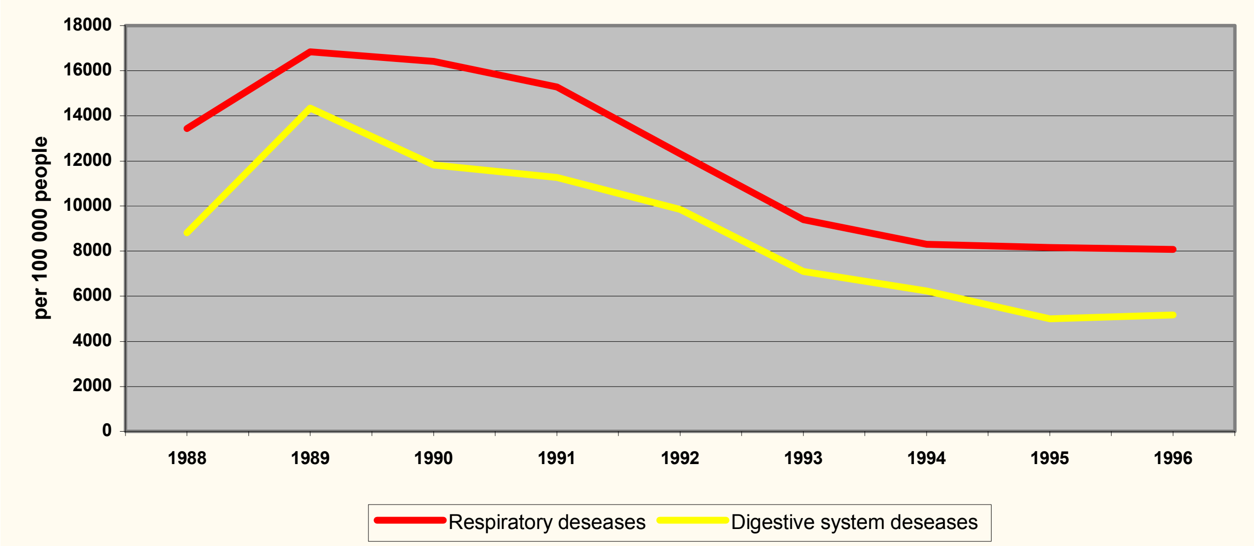

FIG. 5. Morbidity of adults and teenagers by types of disease

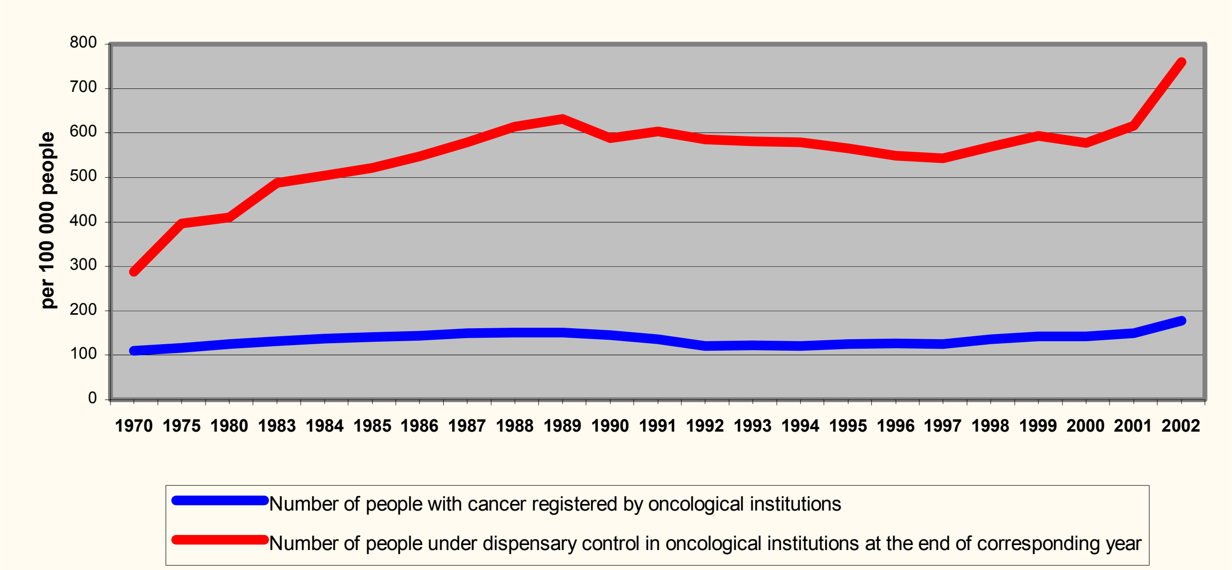

FIG. 6. Malignant cancer morbidity

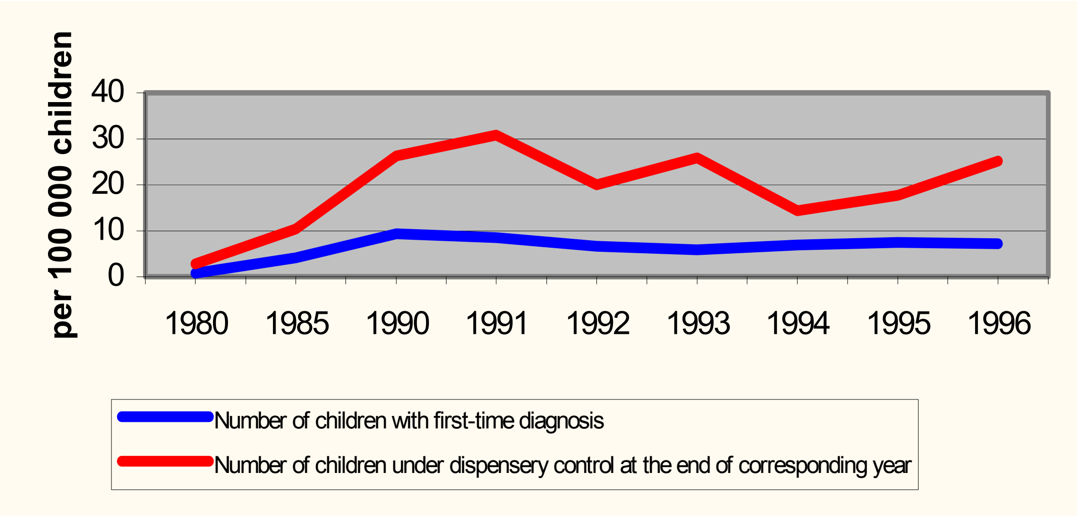

FIG. 7. Morbidity, malignant cancer in children age 0–14

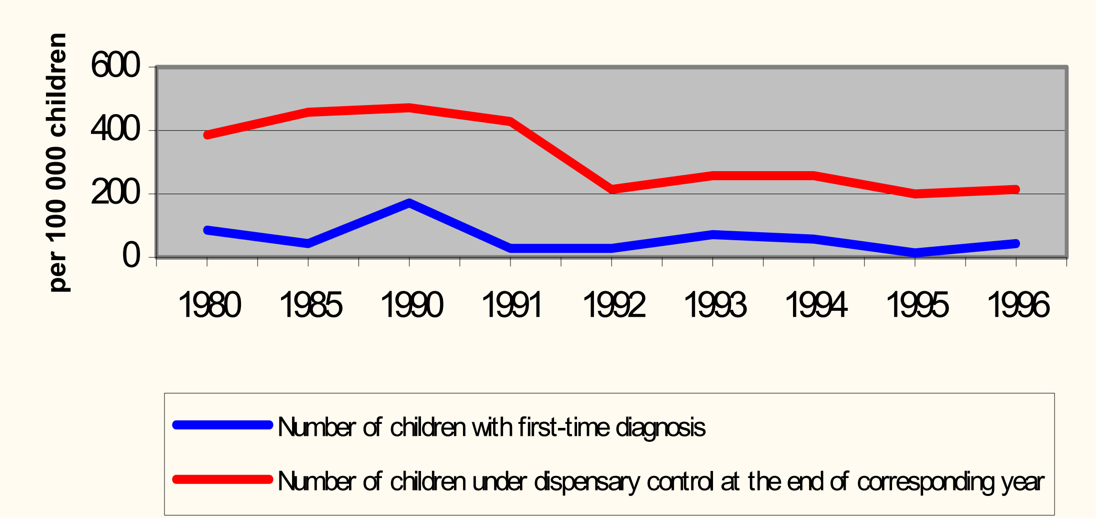

FIG. 8. Morbidity, mental disorders in children age 0–14

The results obtained challenge existing notions about natural radiation sources and their exposure mechanisms, and suggest that all epicenters of earthquakes and the surrounding areas under their influence in seismically active regions should be considered as ‘hot spots’ with respect to radon.

At the same time a series of questions connected with the radiation problem conditioned by earthquakes need to be resolved and confirmed by means of examples in other seismically active regions, requiring joint efforts of investigators in different countries. The author of this paper has developed a programme of investigations on this matter, which may be discussed with those who are interested in the problem.

It is quite evident that alongside existing aspects of investigations connected with earthquakes it is necessary to develop a new aspect: earthquake and ecology of man. This aspect should be aimed at the study of phenomena influenced by earthquakes and their effect on man (radiation, ionized air, electromagnetic fields, ultrasound, etc.).

4. CONCLUSIONS

As a result of the work performed, the following preliminary conclusions can be drawn.

- In seismically active regions with unstable conditions of the earth crust, a major source of radon is not simply the soil itself, but also the soil as a component of the engineering and geological properties of the ground that has been built upon or is in the process of being built upon. The composition and the physical and mechanical properties of soils, the level of groundwater, the availability of small breaks and zones of micro-penetrability all play an important role. The combined effect of these factors determines the level of radon in dwellings.
- Radon in the air of dwellings and other closed buildings does not just accumulate there, but also changes its concentration significantly on the eve of the earthquake. That is why the monitoring of indoor radon may be used as a component of a system for predicting seismic activity.
- The significant increase in radon concentration in dwellings is characterized also by a prolonged period of high concentration after the earthquake before stabilization of the unstable seismically active condition of the area. This increases by many times the risk of cancer associated with alpha radiation (radon).

The hazard from natural radiation arising from an earthquake exists for all urban areas of seismically active regions, and it requires the coordination of investigations in different countries according to clearly planned programmes. A new problem — radiation safety of the population in earthquakes — should be delineated.

ROUND TABLE DISCUSSION

NOTES ON THE ROUND TABLE DISCUSSION

The Conference was concluded with a Round Table Discussion, led by a three-member panel, on a number of common topics and observations arising during the course of the different sessions. Although the items addressed were of a general nature, and although the time available was very restricted, it was possible to reach a more or less general consensus among the participants. This can be used as an input for a more thorough discussion on these items in future.

Panel members: J. Skowronek (Poland, Chairman of NORM IV)

D.G. Wymer (IAEA, Vienna)

A. Poffijn (University of Ghent, Belgium)

TOPIC 1: APPROPRIATE TERMINOLOGY

In the past, different terms have been proposed and used for materials with elevated or enhanced concentrations of radionuclides of natural origin, and for the activity associated with such materials. The most commonly used are:

- NORM: naturally occurring radioactive material;
- TENORM: technologically enhanced naturally occurring radioactive material;
- TENR: technologically enhanced natural radioactivity;
- ENOR: enhanced naturally occurring radioactivity.

These terms reflect the fact that radioactivity is only a natural feature of such materials and not exploited itself, contrary to the situation with fissile materials and materials comprising or containing artificial radionuclides.

While many countries have brought natural sources of radiation into the scope of their general regulations on radiation, other countries have implemented specific regulations, often addressing particular types of material rather than natural sources in general. Internationally, during the last few years, several regulatory initiatives have been undertaken with respect to such material. An important example is that of the European Community, which developed and adopted the Council Directive 96/29 Euratom — which includes radiation protection issues related to natural sources of radiation — to harmonize the national regulations of EU Member States. This Directive is risk-based, and uses the recommendations contained in ICRP Publication 60 as a basis. It lays down criteria for the assessment and selection of hazardous areas, and requirements for monitoring and for the optimization of protection measures. The Directive gives examples of work activities within which the presence of natural radiation sources may lead to a significant increase in the exposure of workers or of members of the public that cannot be disregarded from the radiation protection point of view.

From November 2001 to December 2004, a project ‘New approach to assessment and reduction of health risk and environmental impact originating from TENORM according to requirements of EU Directive 96/29’, known by the acronym TENORMHARM, was carried out within the 5th Framework Programme of the European Commission. Participants from Central Europe — Czech Republic, Hungary, Poland, Slovenia (nowadays EU Member States) and Romania — as well as the EU countries Germany and Belgium joined the project. In this project, the term TENORM was used to describe the following materials:

(a) **Materials (products, by-products, residues, waste)** with enhanced concentrations of radionuclides of natural origin, which result from technological processes in non-nuclear industries. The processing of raw material, such as chemical separation, metallurgical smelting or physical screening, had enhanced the concentration of individual or several radionuclides of natural origin.

(b) **Raw materials** or **waste rock** with elevated concentrations of radionuclides of natural origin, which are not processed as mentioned under (a) but are heaped up or reused, e.g. as construction material or for backfilling of mines.

(c) **Waste (sludge)** with enhanced concentrations of radionuclides of natural origin arising from the treatment of drinking water or waste water (e.g. surface water, pit water, seepage water).

(d) Accumulations of radionuclides of natural origin in **environmental media** such as river bed or bank sediments, soils or sewage sludge arising from discharges to surface water, seepage water or groundwater of radionuclides of natural origin other than ^{222}Rn or ^{220}Rn (in suspended solids or dissolved) from mining or industrial processes.

The final report of the project was issued in February 2005, and can be used as a guide for organizations and scientists investigating issues associated with exposure to natural sources.

The papers presented in the conference used a wide variety of terms to refer to material containing radionuclides of natural origin. The definition of such terms was not always clear, and consistency between them was lacking.

Question:

Do we need all the terms NORM, TENORM, ENOR, NOR, etc?

Comments:

- There is no clear definition of what is meant by ‘technologically enhanced’. It obviously applies to materials in which the activity concentrations have been increased by orders of magnitude, e.g. some scales, but what about materials in which the concentrations have only been increased by, say, 50%?
- The processing of a mineral does not always increase activity concentrations — it can also decrease them. So material does not automatically become TENORM just because it has been processed.
- The radiological risk associated with natural raw materials depends on many factors, not just activity concentration, so it is not always meaningful in terms of radiation protection to distinguish between material with non-enhanced concentrations (NORM) and material with enhanced concentrations (TENORM) — some ‘non-enhanced’ materials can actually present a greater radiological hazard than some ‘enhanced’ materials.
- The terms NORM and TENORM are not good descriptors because, strictly speaking, the term ‘naturally occurring’ should refer to the radionuclides in the material, not the material itself.
- NOR was suggested as being more appropriate, since it covered most situations, not only ‘materials’. However, it is not in common use.
- The IAEA only uses the general term NORM in its safety-related publications;
- In the US, the term TENORM is widespread;
- The EU has not discussed the issue;

- The use of a single, common term would be preferred;
- Attention should be paid to the public's perception of 'technologically enhanced' in the term TENORM.

Conclusion:

A single, universal term is needed for denoting material containing (only) naturally occurring radionuclides *and requiring consideration from a radiation protection point of view*. NORM is the most general and commonly used term, although as a descriptor it is not technically the most accurate.

TOPIC 2: MEASUREMENT AND ANALYSIS

Measurements of radionuclides in different matrices are often the most important measures for analysing the radiation risk. Nevertheless, the definition of measurement values and detection limits as well as of monitoring installations should not be made only on the basis of a dose criterion or of specific dose contributions. It should comprise also such activity and concentration levels that — although being insignificant radiologically, chemically or toxically — may nevertheless show an identifiable trend that can lead to limits or recommended values being exceeded if no countermeasures are taken.

In the EU, for example, while the Council Directive 96/29 Euratom sets an effective dose limit of 1 mSv/a for the general public, in the case of radionuclides in drinking water Council Directive 98/83/EC (the 'EU Drinking Water Directive') sets an annual dose limit 0.1 mSv. One example of such an approach can be found in the recommendations of the German Commission on Radiological Protection (SSK) '*Radiation Protection Principles for Storage, Use and Clearance of Contaminated Materials, Buildings, Areas and Waste Rock Heaps from Uranium Mining and Milling*', in which the additional real or potential radiation exposure from ore mining and milling legacies may not exceed 1 mSv/a. To this end, exposure pathways must be addressed when the dose contribution is $\geq$0.1 mSv/a.

A different approach has been chosen in Poland, where a monitoring and control system for underground coal mines has been implemented. Due to the entry into force of regulatory Acts in the form of the Geological and Mining Law, and the Decree of the Ministry of Industry, the monitoring of and protection against natural radiation is obligatory in all Polish underground mines. This duty is strictly supervised by local offices of the State Mining Authority in cooperation with other governmental agencies. Monitoring and mitigation measures are obligatory not only for active mines but also for mines used for other purposes such as museums and balneotherapy spas. Such a solution is unique in non-uranium mining; it seems to be the only complete system of radiological protection in the coal industry. This system ensures not only the assessment of miners' exposure but, due to the fact that results can be obtained quickly, provides the necessary data for formulating preventive measures.

The radiometric analysis of NORM is widely based on the application of gamma spectrometry as a very reliable method for the detection of radionuclides of natural origin. Additionally, it is possible to use the same calibration for solid materials as well as for liquids. Other measurement techniques are used if necessary (mainly for radon monitoring). For instance, in the Polish mining industry the following parameters should be monitored in underground workings:

- Concentrations of short-lived radon progeny in mine atmosphere;
- Gamma dose rates;
- Concentrations of ^{226}Ra and ^{228}Ra in mine water;

- Concentrations of ^{226}Ra and ^{228}Ra in mine sediments.

On the other hand, the application of the dose coefficients from Council Directive 29/96 Euratom to the EU Drinking Water Directive may lead to a situation where methods with very low detection limits are needed for monitoring of specific radionuclides (for instance ^{227}Ac). Therefore, the development of appropriate measurement methods for NORM is an important issue.

A significant number of presentations in the conference dealt with the making of measurements, in some cases down to background levels, but the purpose of such measurements was perhaps not always as clear as it should be.

Questions:

- Do we know in all cases why we are making measurements?
- Do we really need to measure to such very low levels, when these are probably not important in terms of the radiological hazard?
- Is radiation protection or scientific endeavour the true objective?

Comments:

- It is important to make measurements in situations where there are significant differences from natural background;
- For monitoring purposes, the objective should be to find measurement techniques that are simple and inexpensive, but give good results;
- A capability of measuring down to very low levels may be required at the beginning of an investigation, when one does not know what to expect. In the later phases, the required level of measurement sensitivity may be less.

Conclusions:

- **Cost is an important factor in many measurements;**
- **Quality assurance is essential;**
- **There are different objectives in making measurements, and each has its own specific requirements in terms of sensitivity, cost etc.**

TOPIC 3: MODELLING VERSUS MEASUREMENT

One of the conclusions reached during the investigations carried out within the TENORMHARM project was that, in the majority of investigated cases of industrial activities involving NORM, the risks to workers and members of public could not be reliably assessed automatically by applying standardized factors, assumptions and exposure scenarios. There is no universal method for risk evaluation applicable to all possible situations. Each particular type of occurrence of NORM determines some unique scenario of exposure. For this purpose, only realistic pathways should be considered, and methodologies for dose calculations need to be prepared. In each case the assessment should be done based on direct measurements of particular risk factors. Only in this way can all the influencing features be considered, e.g. particular work conditions, source geometries, attenuation, personal protective equipment.

Moreover, the consequences of NORM occurrence can be assessed from different points of view. Sometimes the public perception of NORM is as a plentiful source of very serious effects far more detrimental and harmful than direct exposure to radiation. Risk caused by

NORM is a subject where the enforcement of the ALARA principle can become very complex and multidimensional.

In the case of the EU regulatory system, it can be seen that very often it contains a lot of detail concerning subjects that are not significant in the context of radiation risk. On the other hand, in many cases the Council Directive 96/29 Euratom does not cover all possible sources of radiation hazard. The results achieved within the TENORMHARM project on establishing the effects of NORM occurrence in industry and the environment have provided sufficient reliable data to enable the EU to compile in an official document a list of branches of industry that need to be considered from the point of view NORM occurrence. The project has shown the complex problems concerning natural radioactivity in industrial activities.

The presentations at the NORM IV conference indicated that the radiological data now becoming available for NORM activities are tending to be based more and more on measurements rather than on modelling exercises (as was largely the case in the past). However, considerable modelling work is still being done.

Question:

In ongoing radiological investigations of NORM activities, where should we be putting the effort — measurements or modelling?

Comments:

- Development of knowledge based on reliable measurements is the preferred way to go. However, modelling still has a role to play in situations where measurements are not feasible;
- Modelling is a very important tool for sensitivity analysis and selection of the optimum solution;
- There is a danger in relying too much on modelling, because modelling results are only as good as the assumptions used, and big discrepancies between modelling results and actual measurements are starting to become evident in some cases.

Conclusions:

- **Modelling and measurement each have their specific merits;**
- **The choice between modelling and measurements should be made on the basis of what is required — measurements are the best approach where reliability of the result is important, but modelling offers more flexibility in its ability to investigate options;**
- **Rely on simple models.**

SUMMARY

The lively discussion during the Round Table panel discussion showed the importance of the status of occurrence of natural radionuclides in different branches of industry, in environmental protection and for the assessment of the impact on general public. On the other hand, some particular NORM issues must be clarified or defined properly; therefore further investigations and development of regulatory instruments are necessary.

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S. Simopoulos	Greek Atomic Energy Commission, Greece
J. Skowronek	Central Mining Institute, Poland
S. Sterliński	Central Laboratory for Radiological Protection, Poland
J. van der Steen	Nuclear Research and Consultancy Group, Netherlands
R. Wiegers	IBR Consult BV, Netherlands
D.G. Wymer	International Atomic Energy Agency

LIST OF PARTICIPANTS

Beddow, H.	University of Reading, United Kingdom
Briquet, C.	Comissão Nacional de Energia Nuclear, Brazil
Colombo, G.	ENI SpA, Italy
Costa, E.	Universitat Autónoma de Barcelona, Spain
de Clerck, T.	University of Ghent, Belgium
Degrange, J.-P.	Centre d'étude sur l'Evaluation de la Protection dans le domaine Nucléaire, France
Döring, J.	Bundesamt für Strahlenschutz, Germany
Efremenko, V.	International Atomic Energy Agency
Faanhof, A.	South African Nuclear Energy Corporation, South Africa
Gellermann, R.	HGN Hydrogeologie GmbH, Germany
Gerler, J.	Bundesamt für Strahlenschutz, Germany
Gorjanacz, Z.	Veszprem University, Hungary
Grabowska, S.	Institute of Nuclear Physics, Polish Academy of Sciences, Poland
Henrich, E.	Commission of the European Communities, Belgium
Isajenko, K.	Central Laboratory for Radiological Protection, Poland
Jankowski, J.	Nofer Institute of Occupational Medicine, Poland
Janssen, R.	Röntgen Technische Dienst BV, Netherlands
Jernstrom, J.	JRC, Germany
Jovanovic, P.	Institute of Occupational Safety, Slovenia
Kapała, J.	Białystock Academy of Medicine, Poland
Karpínska, M.	Białystock Academy of Medicine, Poland
Kies, A.	University of Luxembourg, Luxembourg
Kłos, B.	Uniwersytet Śląski, Poland
Komosa, A.	Maria Curie-Sklodowska University, Poland
Kossir, A.	CERPHOS, Morocco
Kozak, K.	Institute of Nuclear Physics, Polish Academy of Sciences, Poland
Krizman, M.	Ministry of Environment, Slovenia
Leveque, C.	Canberra, United States of America
Limanovica, I.	Radiation Safety Centre, Latvia
Lizurek, G.	Uniwersytet Śląski, Poland
Lopes, I.	Nuclear and Technological Institute, Portugal
Mamont-Cieśla, K.	Central Laboratory for Radiological Protection, Poland
Manjón, G.	Universidad de Sevilla, Spain
Maseko, N	South African Nuclear Energy Corporation, South Africa
Mazur, J.	Institute of Nuclear Physics, Polish Academy of Sciences, Poland
Moravanska, H.	Nuclear Research Institute Rez, Czech Republic
Mrabet, T.	IMPHOS, Morocco
Müller, W.	Siempelkamp Nukleartechnik GmbH, Germany
Nguyen Dinh, C.	AGH University of Science and Technology, Poland

Oatway, W.B.	National Radiological Protection Board, United Kingdom
Olszewski, M.	Politechnika Łódzka, Poland
Organo, C.	Radiological Protection Institute of Ireland, Ireland
Pietrzak-Flis	Central Laboratory for Radiological Protection, Poland
Piller, G.	Bundesamt für Gesundheit, Switzerland
Poffijn, A.	University of Ghent, Belgium
Popescu, M.	National Research and Development Institute for Metals and Radioactive Resources, Romania
Przylibski, T.A.	Politechnika Wrocławska, Poland
Quade, U.	Siempelkamp Nukleartechnik GmbH, Germany
Rădulescu, C.	National Research and Development Institute for Metals and Radioactive Resources, Romania
Reszka, M.	Maria Curie-Sklodowska University, Poland
Risica, S.	Istituto Superiore di Sanità, Italy
Rojc, J.	Zirovsky Vrh Mine, Slovenia
Rolle, R.	Göttingen, Germany
Ryan, T.P.	Commission of the European Communities, Belgium
Schönhofer, F.	National Metrology Institute, Austria
Soderman, A.-L.	Swedish Radiation Protection Authority, Sweden
Soh, K.G.	International Fertilizer Association, France
Solatie, D.	Radiation and Nuclear Safety Authority, Finland
Stawarz, O.	Central Laboratory for Radiological Protection, Poland
Sterliński, S.	Central Laboratory for Radiological Protection, Poland
van Cauteren, J.	Controlatom, Belgium
van Velzen, L.P.M.	Nuclear Research and Consultancy Group, Netherlands
van der Westhuizen, A.J.	NOSA International, South Africa
Varhegyi, A.	Mecsek, Hungary
Vesterbacka, P.	Radiation and Nuclear Safety Authority, Finland
Wallberg, P.	Swedish Radiation Protection Authority, Sweden
Weiss, D.	Gesellschaft für Anlagen- und Reaktorsicherheit mbH, Germany
Wiegand, J.	Essen-Duisberg University, Germany
Wiegers, R.	IBR Consult BV, Netherlands
Wymer, D.G.	International Atomic Energy Agency
Zalkalne, A.	Radiation Safety Centre, Latvia
Zampieri, C.	Regional Agency for the Environmental Protection of Veneto, Italy
Zenata, I.	State Office for Nuclear Safety, Czech Republic