IAEA-TECDOC-1271

Technologically enhanced natural radiation (TENR II)

Proceedings of an International Symposium
held in Rio de Janeiro, Brazil, 12–17 September 1999

INTERNATIONAL ATOMIC ENERGY AGENCY

February 2002

The originating Section of this publication in the IAEA was:

Radiation Safety Section
International Atomic Energy Agency
Wagramer Strasse 5
P.O. Box 100
A-1400 Vienna, Austria

TECHNOLOGICALLY ENHANCED NATURAL RADIATION (TENR II)
IAEA, VIENNA, 2002
IAEA-TECDOC-1271
ISSN 1011–4289

Printed by the IAEA in Austria
February 2002

FOREWORD

Natural radiation is ubiquitous. In recent decades, there has been a developing interest in fully documenting exposure of human beings to radiation of natural origin. Radiation experts have recognized that natural sources of radiation can cause exposure of members of the general public and workers to levels that warrant consideration of whether controls should be applied.

The second International Symposium on Technologically Enhanced Natural Radiation (TENR II) was held in Rio de Janeiro from 12 to 17 September 1999. The objective of the symposium was to provide a forum for the international exchange of information on the scientific and technical aspects of those components of exposure to natural radiation that warrant consideration. These components were examined under the headings: the technological enhancement of natural radiation in mining and non-nuclear industries; radon indoors and outdoors; mobility and transfer of natural radionuclides; natural radiation and health effects; analytical techniques and methodologies; the remediation of contaminated sites; and regulatory and legal aspects.

The symposium found that exposures to natural sources of radiation should be considered from the point of view of their amenability to control. This approach is reflected in the International Basic Safety Standards for Protection against Ionizing Radiation and for the Safety of Radiation Sources (BSS) and the associated IAEA documents on occupational exposure and rehabilitation of contaminated lands. The concepts of exclusion and intervention are particularly relevant to the amenability to control of natural sources of radiation. Indeed, the BSS specify that any exposure whose magnitude is essentially unamenable to control through the requirements of the BSS is out of the scope of the BSS. The BSS further indicate that protective or remedial actions shall be undertaken whenever they are justified in terms of the benefit to be obtained.

Following their deliberations, the participants of the symposium found that these concepts of exclusion and intervention needed to be further developed for regulatory purposes, preferably in a quantitative form (e.g. through the establishment of activity concentrations).

It is expected that the papers presented will serve as useful guidance for scientists involved in the research of natural radiation as well as for regulators charged with the task of developing national standards in this area.

The symposium organizers are grateful to the following sponsoring institutions: the International Atomic Energy Agency (IAEA); the Institute of Radiation Protection and Dosimetry (IRD/CNEN); the Brazilian Society of Nuclear Biosciences (SBBN) and the Research Support Foundation of Rio de Janeiro (FAPERJ).

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SUMMARY

Technical contributions presented during the symposium revealed that wastes generated in mines and mills other than those which produce uranium may contain elevated concentrations of natural radionuclides. Accordingly, the final deposition of these wastes should take into account appropriate management strategies to avoid undue exposures. Methods of examination of the potential release of radionuclides from these wastes may include: (i) sequential extraction approaches of various kinds; (ii) analysis of wastes fluids, groundwater and associated soils, and (iii) geochemical modelling. For example, a study concerning a phosphogypsum stack in Florida revealed that while the fluids within the stack contained significant quantities of dissolved radionuclides, various removal mechanisms appeared to prevent large-scale migration of radionuclides to the underlying aquifer.

It has also been demonstrated that the pumping of mine drainage has the potential to mobilize large quantities of radionuclides and transport them into the environment. This was observed in coal mines in Poland where the enhancement of radium concentrations in river waters, bottom sediments and vegetation affected by the mines was observed. Another important aspect was that the precipitation of radium from radium-bearing waters leads to the formation of radioactive sediment (with ^{226}Ra concentrations as high as 400 000 Bq/kg) that have to be properly managed. Acid mine drainage, caused by the oxidation of sulphidic minerals, also has the potential to mobilize important levels of radionuclides, mainly uranium. Uranium-238 activity concentrations up to 100 Bq/L have been reported.

Regarding occupational aspects, a survey of six mines in Brazil revealed that the doses to the workers in the mines were low enough not to require a routine individual bioassay program for the control of internal contamination. It is generally reported that workers are exposed to airborne particles in the inhaled and respirable fractions of the aerosol. However, it was demonstrated that the thorium concentrations in samples of faeces from workers of a niobium mine indicated that the element was being mainly incorporated by ingestion. Another contribution showed that the average thorium concentration in faeces of investigated workers of a mineral sand industry (monazite) was 3.6 times higher than the average value found for local inhabitants. Inhabitants of this region are exposed to thorium through ingestion. A study that included the analysis of completely prepared meals basically composed of local products performed in conjunction with the examination of faeces and urine samples from local volunteers revealed urine to faeces ratios for thorium higher than that predicted by the ICRP models. It was concluded that the chemical form of an ingested element may affect its absorption. As a result it was pointed out that the use of standard parameters in dose assessments may lead to an underestimation of the internal radiation dose to the population.

Several contributions discussed the exposure of workers to ^{222}Rn in non-uranium mines. Radon-222 concentrations up to 20 kBq/m^3 were measured in a copper mine when no forced ventilation was provided. Results of this type are frequently observed and reported in the literature and it is usually pointed out that there is a need for national co-ordinated investigations in underground non-uranium mines. A survey of this type was reported in Germany. It was shown that the median radon concentration in the country amounts 40 Bq/m^3 in dwellings and about 14 Bq/m^3 outdoors. Only 1% of the houses in Germany had an indoor radon value of more than 250 Bq/m^3; however, radon concentrations of more than 10 kBq/m^3 were found in some high radon areas. A similar survey was reported for Poland. These measurements were done in two stages. As a first step a screening was carried out by means of short term methods of radon measurement, such as through the use of activated charcoal canisters or grab sampling to find places with elevated radon risks. In a second stage, a long term investigation took place in locations selected during the screening campaign. The available monitoring results and experiences with protective measures will be used to propose reasonable ways of implementing regulations. The experience of research in Germany on occupational exposure assessment to radon progeny reveals that workplaces with exposure conditions similar to dwellings should not be included in the radiation protection system until a national policy concerning radon exposure of the public is established. Accordingly, for workplaces to be controlled, a graded system of workplace and individual monitoring is recommended.

There was concern expressed at the symposium on the need for the interpretation of the application of radiation protection principles to materials containing naturally occurring radioactive materials, especially following the publication of the International Basic Safety Standards for the Protection Against Ionizing Radiation and the Safety of Radiation Sources (IAEA Safety Series No. 115). The predominant impression was that further clarity on the application of the BSS would be highly desirable.

It was pointed out that the legislative radiation protection framework is usually complex and confusing in different nations when dealing with the exposure to natural sources of radiation. The assumptions used in modelling this exposure are not entirely correct and the results of the theoretical risk assessment do not correspond with data available at the national and industrial levels. Available information can contribute significantly to a better understanding of the risk. However, this information is fragmented, with various parties possessing incomplete data. A significant issue was the clear need for co-operation between regulatory authorities and industries. Towards this end, participants from industry who were present at the symposium and representatives of the regulatory sector proposed the creation of the Natural Material Radiation Control Initiative (NMRCI). The plan of action of this organization would be aimed at developing a Safety Report addressing (i) exposures of the workforce and general public to enhanced concentrations of naturally occurring radioactive materials and (ii) the international trade in commodities containing such materials. The Safety Report would provide information on the methods acceptable for national regulatory authorities and industries to meet the requirements of the BSS for the safety of materials containing an enhanced concentration of naturally occurring radionuclides, as well as quantitative assessments. As far as is practicable, the assessments would be carried out on the basis of data collected from industries and national regulatory agencies (not on probabilistic assumptions). It was expected that such a report would provide the methodology to quantitatively apply the principles of justification and optimization to potential exposures.

Tenorm legislation — theory and practice

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Abstract. Processing of minerals often increases concentrations of naturally occurring radioactive materials (NORM) in mineral concentrates, products and waste streams. This so-called TENORM (Technologically Enhanced Naturally Occurring Radioactive Materials) phenomenon can result in usually very small increases of radiation exposures to workers and the public. However, proposed international radiation protection standards are likely to bring the TENORM issue into the realm of regulatory concern. Verbatim adoption by the national legislation's of the radiation protection standards like those proposed in the IAEA's 1996 Basic Safety Standards (BSS) would present enormous practical problems. Many industries and industrial practices would, for the first time, become subjected to the provisions of radiation protection legislation. Consequently, registration, licensing, occupational and environmental monitoring, statutory reporting, appointment of appropriately qualified staff, new approaches to the management of minerals and waste labeled as "radioactive", etc. would be required. This would be mirrored by corresponding demands on the regulatory authorities, needing to provide an increased radiation protection regulatory control. In response to new Australian and other national radiation protection legislation that have incorporated the BSS criteria, this paper illustrates their impact on a number of industries that historically have not been considered as dealing with radioactive materials. The paper also proposes a number of initiatives that could be considered. Nationally, those initiatives should aim at adopting radiation protection legislation that is commensurate with the nature of the minerals industry operations, national circumstances, conditions and interests without compromising rational radiation protection practices. Otherwise, non-judicious application of the BSS would result in major diversions of resources from well recognized occupational health and safety issues towards the less important end of the OH&S risk spectrum throughout the minerals industries worldwide.

1. Introduction

This presentation is a synopsis of the large and detailed report on this topic, which is available on the "World Collection of Radiation Links" Internet site [1]. The following text was prepared especially for the verbal presentation.

1AEA Basic Safety Standards [2] propose that a single practice can be exempted from regulatory control if it contributes to individual doses of no more than 10 microSv per year.

For each individual radionuclide there are two exemption levels: the first one is a concentration in Becquerels per gram (Bq/g), the second one — a Total Activity of a given nuclide present on the premises. Even if concentrations of 'common' NORM elements uranium or thorium are below the exemption limit of I Bq/g, the material could become 'regulated' due to the existence of the 'total activity' limit. These exemption values are [lot necessarily applicable for mining and minerals processing. The main aim of this presentation is to attract the attention of national regulatory agencies to the fact that IAEA Basic Safety Standards must not be adopted verbatim, without prior assessment of health, economic and legal aspects of the TENORM issue, particularly in the mining and minerals processing industries.

It is appropriate to discuss if these Standards prescribe appropriate control measures for the Technological Enhancement of Natural Radioactivity.

2. Legislative inconsistencies

There are several inconsistencies in the current and proposed radiation protection legislation.

2.1. Action levels for the exposure to radon

The action levels proposed for radon in IAEA BSS are associated with an annual exposure of about 3–5 mSv for a member of the public and 6 mSv for an employee. These values are extremely high when compared to 0.01 mSv/year "exemption" limit for the exposure of a member of the public proposed in the same document for 'other than radon' radiation exposure. The explanation is that practices and work activities are planned and are *adding* to the radiation exposure of a person; radon exposure *is natural,* and if one is going to decrease it, it will be an *intervention.*

Radon exposure limits of 3–5 mSv/year and the simultaneous promotion of the 'exemption limit of 0.01 mSv/year' coupled with the differences between 'nuclear' and 'non-nuclear'. 'normal practice' and 'intervention', 'work activity' and 'practice' are only complicating the application of radiation protection principles, which is already complicated sufficiently enough.

If international and national regulatory bodies are to be truly consistent we should have two options: Either use the exemption limit of 0.01 mSv/year for radon exposures for members of the public, which leads to the ridiculous situation when almost everybody on this planet would be 'well above the threshold' with an obvious result that the Earth is too hostile for us and we should move somewhere else, or to recognize that there is no point whatsoever in regulating radiation exposure at levels practically indistinguishable from natural background.

2.2. Artificial separation of 'nuclear' and 'non-nuclear' activities

There is no difference between radiation dose of 3 mSv received by a uranium miner and a dose of 3 mSv for an operator of a tin smelter. The argument that in the case of uranium mining and processing "radiation is beneficial for the product" and in 'other' mining "radiation is an unwanted impurity" is, from the general radiation protection point of view, irrelevant. Extracted uranium concentrate is the same naturally occurring radioactive material, with its uranium concentration being technologically enhanced.

Let us consider the following example: Both radium–226 ions that were washed off from the pile of fertilizer on a farm into a stream nearby and radium–226 ions that were discharged from a 'nuclear facility' upstream into the same river are exactly the same. However, in the first instance radium in water is the result of a 'work activity' and in the second one is the result of a 'practice'. Therefore, radium ions from a 'nuclear installation' are gaining some special magic powers to harm a farmer much more than the ones from the fertilizer.

2.3. Application of legislation to consumer products

In some legislative proposals specific exemptions are being made for 'consumer goods' and 'retail products' containing NORM. Raw materials and semi-products are not, however, included in these proposals. Let us consider the possibility of the same material being ‘radioactive' and 'non-radioactive' on different stages of processing:

Mining and concentrating: The separation of the mineral zircon from mineral sands ore is achieved by purely physical means (gravimetric, electrostatic and electromagnetic separation). Therefore, the product ready for shipping is in exactly the same chemical and physical form as found in the natural environment. The specific activity of zircon (due to natural thorium and uranium content) is typically around 4 Bq/g. Therefore, the material is currently not considered 'radioactive', but would be classified as such in accordance with IAEA 1996 BSS.

Transport: The special provision for 'natural' material in IAEA Transport Safety Regulations STA [31 raises the exemption level by a factor of ten. There are, however, two potential problems, which are yet to be solved. Firstly, different methods are currently used to calculate specific activity due to the differences in including daughter radionuclides in the calculations. An operator or an appropriate authority could potentially classify zircon as 'radioactive material' due to the simple 'mix-up' of numbers. Secondly, due to the differences between possible definitions of a 'natural material' the transport of zircon could also become the transport of 'radioactive' material in some countries.

Processing: Let us take, for example, a zircon 'micronising' operation, where grains of the mineral (150–200 microns in diameter) are milled to produce the product called 'zircon flour' with a fineness of about 3 microns. The chemical properties of the material do not change during the processing. Due to the potential differences in the interpretation of the term 'natural' and the fact that small 'zircon flour' particles could be more easily inhaled than mineral grains, the following situation may result: A zircon mill will be receiving a 'non-radioactive' raw material from which it will be producing a 'radioactive' product for further applications in other industries.

Manufacture of a 'consumer product': Zircon flour is used as an opacifier In ceramic glazes. An interesting situation, which is directly opposite to the one described above may result: A facility manufacturing ceramic tiles will be receiving a 'radioactive' material which will be used in the production of 'non-radioactive' 'consumer products'.

3. Possible outcomes from adopting IAEA BSS verbatim

Let us estimate what effect would be caused by the verbatim adoption of IAEA Basic Safety Standards in a country without a thorough investigation of potential health, economic and legal consequences. Such a country would have an immediate need for:

(a) sufficient amount of suitably qualified and experienced radiation protection specialists in order to ensure that all materials which will be classified as 'radioactive' are being handled in accordance with new legislation at the place where they are produced, transported, stored and processed;

(b) a significant increase in the number of personnel in 'radiation protection' branches of the government to deal with 'newly appeared' work activities, including licensing, approvals, review of statutory reports, site inspections, verification monitoring and so on;

(c) numerous 'low level radioactive waste' storage and disposal facilities for millions of tons of waste which will be generated each year and will require appropriate disposal.

Another item which will require immediate attention is the 'saleability' of the locally mined and processed minerals, semi and final products on the international markets. The 'radioactive content' of a product could become a decisive factor in market negotiations. It would be comparatively difficult to sell products that contain NORM in concentrations higher than, say, a 'world average'.

Thus, the TENORM issue ceases to be theoretical. An established mining or mineral processing industry in a given region or country could simply cease to exist due to the perceived risks of radiation exposure from TENORM.

4. Practical suggestions

The study of national and international radiation protection legislation, which is presented in full on the Internet site mentioned earlier, lead to the following practical suggestions may be considered by radiation protection professionals, appropriate authorities and potentially affected industries.

4.1. Radiation protection professionals

It is expected that the demand for radiation protection professionals will increase because it number of industries where natural radioactivity is technologically enhanced will require radiation monitoring programs, authorizations, notifications and so on. It is likely that the appointment of a 'Radiation Protection Officer' will be required at many facilities. Therefore, mutual recognition of radiation protection education and experience between different countries will be very desirable. The proposal put forward by the German–Swiss Radiation Protection Association [4] deserves attention from other radiation protection societies.

Suggestion 1: Regional and international programs relevant to the mutual recognition of radiation protection education and experience, eventually leading to the signing of some international agreements should be considered by national radiation protection societies and IRPA.

Only about 15% of the human exposure to ionizing radiation come from man–made sources. The remaining 85% of the annual dose is the result of the exposure to 'natural' radiation, but this fact is generally unknown to the public.

Suggestion 2: Different ways of communicating information about natural radiation directly to the general public should be examined.

Suggestion 3: Public education initiatives such as Science Teachers' Workshop Program by the Baltimore–Washington Chapter [5] of the Health Physics Society should be encouraged and expanded.

Suggestion 4: The liaison between radiation protection societies and other professional bodies (such as engineering institutions, environmental protection groups and societies, medical associations and unions of journalists) should be encouraged.

Suggestion 5: Biased reports in mass media should be vehemently opposed and not left to 'die by themselves', as it is often the case.

The concept of a 'controllable dose' proposed by ICRP Chairman R. Clarke [6] is so far the most convenient solution for eliminating the inconsistencies in radiation protection.

Suggestion 6: The 'controllable dose' concept should be discussed and, hopefully, results of the discussion implemented in practice. The simplification of the protection philosophy, associated with this concept, represents obvious benefits for radiation protection.

There are many radiation protection Journals and Bulletins dedicated to the exposure to the man–made sources of ionizing radiation. Surprisingly, there is not a one solely dedicated to the NORM/TENORM issues.

Suggestion 7: Publication of a dedicated TENORM Journal should be considered in order to provide an opportunity for researchers to communicate their findings and solutions.

Suggestion 8: A special TENORM e-mail exchange list has been created on the Internet [7]. Informal instant communications between researchers iii different countries are now possible.

4.2. National regulatory authorities

National regulatory authorities may consider the following suggestions regarding an adoption of IAEA BSS.

Suggestion 9: The magnitude of potential problems associated with the local TENORM industries must be assessed by an appropriate authority.

Suggestion 10: The creation of a separate task force at IAEA and within national government departments dedicated solely to NORM and TENORM should be considered.

Suggestion 11: After the draft of the regulations has been completed, the assessment of its possible economical impact and legal implications both for a regulatory authority and for affected parts of the local industry should be made. It is suggested that this process is carried out in co-operation with all industries that may become 'regulated' and different industry committees (such as, for example, a chamber of mines), and other government bodies (departments of environmental protection, minerals and energy, resources and development and so on).

Suggestion 12: If, after the consultations with the industry and the public, the decision is made to adopt 1AEA Basic Safety Standards in full, different methods of a 'gradual' adoption of the legislation could be considered. The degree of the regulatory control should be proportional to the potential exposure of the member of the public.

4.3. TENORM industries

The following suggestions may be taken on board by TENORM industries.

Suggestion 13: The potential problems associated with TENORM within an industry should be identified and solutions should be found before the local regulations will come into force. Studies carried out in other countries should be taken into account, as it is quite possible that problems, which seem to be impossible to solve by the local industry, were already rectified some time ago in another country.

Suggestion 14: The potential implications of radiation protection legislation should be communicated within an industry and to appropriate authorities. Workshops, seminars and conferences on TENORM must address not only studies of radiation exposure but also potential economic and legal consequences of bringing natural radioactivity under regulatory control.

Suggestion 15: Co-operation with appropriate authorities in the development of relevant radiation protection regulations should be an aim for industries, which are sometimes just a passive target for the already promulgated legislation.

Suggestion 16: National and international co-operation between producers and downstream processors of NORM–containing products should be encouraged.

The general public is mainly not aware of the presence of naturally occurring radioactive materials in the surrounding environment. Biased reports by different 'interest groups' in mass media could severely damage the sound reputation many TENORM industries enjoy in regards to the safety in the workplace and the preservation of the environment.

Suggestion 17: Industries should be proactive in communications with the general public and try to open a dialogue with the 'interest groups'. The creation of 'media watch' and 'public consultation' groups for TENORM industries could be suggested.

Suggestion 18: The co-operation between TENORM industries internationally will result in obvious benefits. For example, if there are several committees dealing with radiation protection in a given TENORM industry, the creation of a working group that will coordinate the activities of these committees will be very beneficial for an industry in all countries. Similar guidelines would be streamlined to the practicable extent and the identical research activities would be evenly distributed between experts in different counties.

In some industries, for example in the phosphate industry, the co-operation is very well developed; in others, such as in the mineral sands mining and processing industry, the co-operation is only rudimentary.

Some of the suggestions above could be very practical, other ones possibly would be described as 'out of phase with reality'.

5. Conclusion

The main conclusion made on the basis of the information presented above is:

International Atomic Energy Agency Basic Safety Standards should not be adopted into a national radiation protection legislation verbatim, without a thorough investigation of health, economic and legal implications for the many industries where natural radioactivity is technologically enhanced.

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Environmental impact of coal mining on the natural environment in Poland

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Abstract. Saline waters occurring in underground coal mines in Poland often contain natural radioactive isotopes, mainly ^{226}Ra from uranium series and ^{228}Ra from thorium series. Approximately 40% of total amount of radium remains underground in a 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. Technical measures as spontaneous precipitation of radium in gobs, decreasing of amounts of water inflows into underground working etc. have been undertaken in several coal mines and as the result total amount of radium released to the surface waters diminished of about 60% during last 5-6 years. Mine waters can cause a severe impact on the natural environment, mainly due to its salinity. But also the enhancement of radium concentration in river waters, bottom sediments and vegetation is observed. Sometimes radium concentration in rivers exceeds 0.7 kBq/m^3, which is due to Polish law a permissible level for waste waters. The extended investigations were performed in all coal mines and on this basis the radium balance in effluents has been calculated. Measurements done in the vicinity of mine water's settling ponds and in rivers gave us an opportunity to survey radium behaviour in river waters and the range of contamination. Solid waste materials with enhanced natural radioactivity have been produced in huge amounts in power and coal industries in Poland. There are two main sources of these waste products. As a result of combustion of coal in power plants low radioactive waste materials are produced, with ^{226}Ra concentration seldom exceeding few hundreds of Bq/kg. Different situation is observed in coal mines, where as a result of precipitation of radium from radium-bearing waters radioactive deposits are formed. Sometimes natural radioactivity of such materials is very high, in case of scaling from coal mines radium concentration may reach 400 000 Bq/kg - similar activity as for 3% uranium ore. Therefore maintenance of solid waste with technologically enhanced natural radioactivity (TENR) is also a very important subject.

Enhanced natural radioactivity

The occurrence of the natural radioactivity in uranium mines became a known phenomenon early on. In other types of mines (as coal or phosphate ones) enhanced levels of natural radioactivity have been observed, but unfortunately this phenomenon is not known as well.

The enhanced levels of gamma radiation in Polish coal mines have been discovered by Saldan in early 60's [1], but regular investigations have been started in 70's by Tomza and Lebecka [2], concerning mainly radium-bearing waters and radioactive deposits. In one case in a coal mine in Poland the radium concentration (^{226}Ra) in such scale reached 400 kBq/kg, which corresponds to an activity of 3% U ore. Similar problem in Ruhr Basin was reported by Gans [3], which found high radium concentration in waste waters from coal mines. Natural radioactivity enhanced by effluents from phosphate industry has been investigated in Brazil by Paschoa and Nobrega [4]. Recently very high radium concentrations have been found in the USA in brine sludge - a mineral waste water produced by oil and gas industry. As a result of radium precipitation from such waters in pipes etc. high radioactive scales are formed. Problem of radioactive contamination causing by such materials (called NORM - naturally occurring radioactive materials) is presently investigated [5]. Similar situation is observed in

Romania [13] in oil industry, which causes the contamination of the natural environment. Some reports from coal industry [11] give a suggestion, that similar situation - occurrence of radium-bearing saline waters - could takes place also in coal mines in United States. In fact, the consensus from many presentations at the Natural Radiation Environment Meeting in Montreal, June 1995 seems to be that in most mines and deep wells waters contain enhanced natural radioactivity.

The Upper Silesian Coal Basin (USCB) is located in southern part of Poland and there are of about 50 underground coal mines. Total outflow of water from these mines is of about 800 000 m^3/day. The salinity of these brines if far higher than that of the ocean water. The total amount of salt (total dissolved solids - TDS) carried with mine waters to the rivers is about 10 000 tonnes/day. The dominating ions in these brines are Cl^- and Na^+ with concentrations up to 70 g/l and 40 g/l accordingly, but these waters contain also usually several grams per litre of Ca^{2+} and Mg^{2+} and significant amounts of other ions [2]. Waters with high radium concentration occur mainly in the southern and central part of the coal basin, where coal seams are overlaid by a thick layer of impermeable clays [1]. Saline waters occurring in coal mines in Upper Silesia cause severe damages to the natural environment. It is mainly an effect of their high salinity, sometimes higher than 200 g/l, but additionally, these waters often have high radium concentration, reaching 390 kBq/m^3 [8].

Investigation done by Tomza and Lebecka [2] showed that concentration of radium in water is correlated with it’s salinity. As the salinity of mine waters is usually increasing with the depth, waters with higher radium concentration occur in deeper horizons. Later two different types of radium-bearing water were found in coal mines [8]. One type (type A) of water contains radium and barium, but no sulphate ions, whilst in another type of water (type B) there is no barium but radium and sulphate ions. From waters type A radium is easily co-precipitated with barium as sulphates when mixed with other natural waters containing sulphate ions. In case of radium-bearing waters type B, there is no carrier for radium, therefore precipitation does not occur. Further investigation [12] showed that radium bearing waters released from coal mines sometimes cause widespread contamination of small and larger rivers in their vicinity. This contamination is caused by radium present in an ionic form in water as well as by radium present in suspended matter and in deposits. Radioactive deposits are formed particularly by co-precipitation of barium and radium as sulphates from radium-bearing waters type A [2]. This process results in diminishing of the total activity released into rivers because part of radium remains in underground mine workings as deposits. Precipitation of barium and radium sulphates in underground mine workings takes place either spontaneously or as a result of applied purification technologies which are aimed to reduce the radium concentration in waste waters below the permissible level [9].

In the past the highest concentration of ^{226}Ra in discharge waters from a single coal mine in USCB was as high as 25 kBq/m^3 [8]. **According to Polish regulations discharge waters with radium ^{226}Ra concentration over 0.7 kBq/m^3 should be treated as a liquid radioactive waste** [9]. Such waters were released from ten out of sixty six underground hard coal mines in Poland, in which radium-bearing waters were dumped from settlement ponds to the natural environment. Waters type A were discharged from 7 coal mines (now from 3 collieries). The total activity of ^{226}Ra released with these waters is of about 30 MBq per day. Although waters type B have been discharged also from only 3 mines, but the total output of ^{226}Ra is higher than in waters type A - approximately 200 MBq per day [10]. The occurrence of the enhanced natural radioactivity in Polish coal mines causes the radiation hazard for mining crews. In the mining industry in Poland, monitoring of the radioactivity of mine waters, precipitates as well as gamma doses is obligatory since 1989.

Monitoring of radioactive contamination caused by effluents and tailings from coal mines must also be provided since 1986 [9]. Due to these regulations the following measurements must be done in mine's vicinity:
I. The concentration of ^{226}Ra and ^{228}Ra in effluent from the settlement pond, in river above and below the discharge point, in water supplies nearby discharge point.
II. The concentrations of natural radionuclides in solid samples, dumped onto the piles.

Such complex monitoring system gives an opportunity to obtain a complete picture of the influence of a certain mine on the underground and surface employees as well as on inhabitants of adjoining areas.

Applied methods and instrumentation

(A) Measurements of radium isotopes and ^{210}Pb in waters

Radioactive waters from coal mines contain mainly radium isotopes - ^{226}Ra from uranium series and ^{228}Ra from thorium series. A method of chemical separation of radium, developed by Goldin [6], have been modified for liquid scintillation counting [7, 8]. In this method, radium is co-precipitated with barium in form of sulphates and this precipitate is mixed with liquid gelling scintillator. The measurements of prepared samples have been performed by means of a low background liquid scintillation spectrometer QUANTULUS (Wallac Oy, Finland). This counter is equipped in feature of alpha/beta separation and anti-coincidence guard, which enables measurements of ^{226}Ra concentration as low as 3 Bq/m^3 and simultaneous measurements of ^{228}Ra (LLD = 30 Bq/m^3) and ^{224}Ra (LLD = 50 Bq/m^3). In addition, this method enables a simultaneous preparation of ^{210}Pb, which can be measured in LS spectrometer from 20 Bq/m^3.

(B) Measurements of gamma emitting natural isotopes in solid samples

Solid samples (radioactive deposits from settlement ponds, river beds but also soils, solid wastes, ashes) contain mainly isotopes from uranium and thorium series, ^{40}K and sometimes ^{137}Cs (as a result of Chernobyl disaster). For the measurements a gamma spectrometry system have been used - it contains HPGe detector (45%, PGT), multichannel analyser built-in computer (CANBERRA) and software for spectrum analysis GENIE-PC (CANBERRA). This instrumentation enables measurements of ^{226}Ra concentration (as low as 1 Bq/kg), ^{228}Ra and ^{224}Ra, ^{40}K and other natural and artificial isotopes [14].

Investigations of the contamination of the natural environment, caused by coal mining industry

The assessment of the total activity of radium released from coal mines in Upper Silesia with waste water was done basing on:

- results of determination of radium isotopes in waters released by all coal mines;
- data on amount of water released by individual mines.

We have also made an estimation of total activity of radium which remains in underground workings in a form of deposit precipitated out of radium-bearing waters either due to unintended mixing of natural waters of different chemical composition or due to purification of radium-bearing waters. This estimation has been done basing on:

- results of determination of radium isotopes in original waters inflowing to the underground mine workings from the rocks;
- rough estimation of the amounts of water inflows from different sources or parts of mines;
- calculated value of the total activity of radium pumped out from underground mine workings with waste waters by individual mines.

Analysis of inflows of radium-bearing waters into underground workings

Concentration of radium isotopes in original water samples from different coal mines varies in a very wide range - from 0 to 110 kBq/m^3 for ^{226}Ra and from 0 to 70 kBq/m^3 for ^{228}Ra [10]. Waters with radium concentration above 1.0 kBq/m^3 were found in 43 out of 65 coal mines in Upper Silesian Coal Basin. The highest concentrations of radium were measured in highly mineralised waters from deeper levels in radium-bearing waters type A. The ratio of ^{226}Ra to ^{228}Ra in radium-bearing waters type A was in average of about 2:1. In opposite in radium-bearing waters type B there were more ^{228}Ra than ^{226}Ra, the ratio ^{226}Ra: ^{228}Ra was from 1:2 up to 1:3. Concentration of ^{226}Ra in these waters reached 20 kBq/m^3, while concentration of ^{228}Ra reached 32 kBq/m^3. These values justify the statement that Upper Silesian radium-bearing waters belong to the waters with highest known radium concentration.

Original waters flowing into mine workings from the rocks from different aquifers are collected in gutters in underground galleries, brought together from different parts of the mine, clarified and pumped out to the surface. Radium concentration in these mixed waters was lower than in original water and did not exceed 25 kBq/m^3 of ^{226}Ra and 14 kBq/m^3 of ^{228}Ra [10].

Basing on the results of measurements of radium concentration in the original waters 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 mines and to different mines were calculated. This results were compared with values obtained using radium concentrations in mixed waters taken from the drainage system (from gutters) from different parts of mines and corresponding flow rates obtained from the mines. The difference is indicating the activity of radium remaining in underground mine workings due to spontaneous precipitation of radium and barium sulphates or due to applied purification of water. The calculated activity of radium remaining in underground mine workings as deposits in all Upper Silesian coal mines is 425 MBq/day of ^{226}Ra and 300 MBq/day of ^{228}Ra. These values can not be considered as very accurate, since the uncertainty of measurements of flow rates of small inflows is rather large. The approximate amount of ^{226}Ra in **water inflows in coal mines** in USCB have been calculated as high as 650 MBq/day (i.e. 230 GBq per year) while for ^{228}Ra this value is of about 700 MBq/day or 255 GBq per year (see fig.1.). Although radium concentrations in waters type B are usually lower than in waters type A the total inflows to mines where radium-bearing waters type B occur are much higher. As a result the total activity of radium carried with water type B is higher. The highest values for a single mine (with waters type B) are: 78 MBq per day of ^{226}Ra and 145 MBq per day of ^{228}Ra.

In comparison corresponding values of 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.

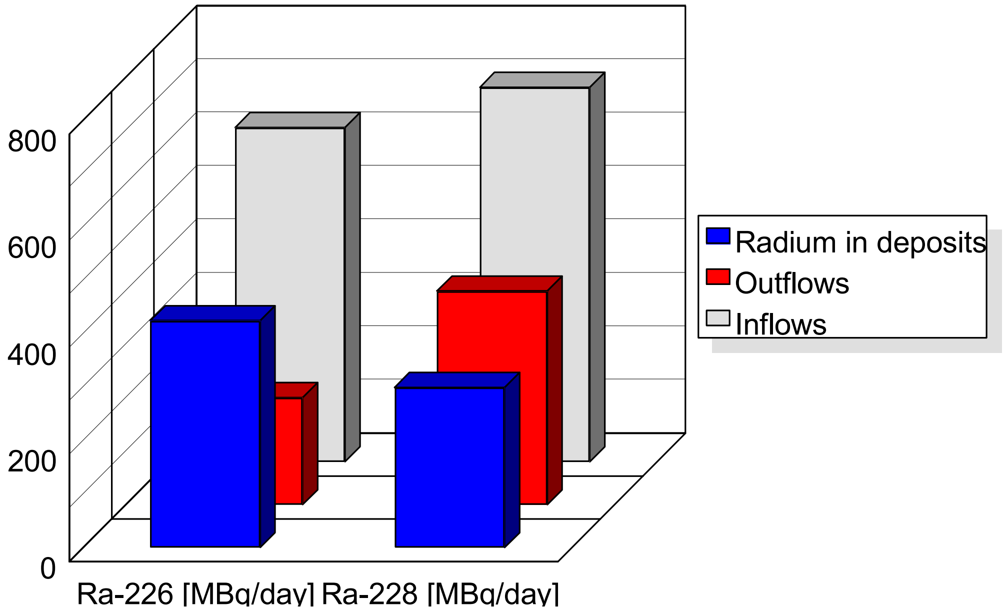

FIG. 1. Radium balance in coal mines.

Analysis of outflows from coal mines

Much more accurate are the results of calculations of the total activities of radium present in water pumped out from individual mines. These values were calculated basing on the radium concentration determined in these waters and on data of amount of water provided by mines.

Samples of discharged waters were taken from settlement ponds. We found that the amount of radium ^{226}Ra, **released with saline waters** to the rivers is approximately equal 225 MBq per day (75 GBq/year) and for ^{228}Ra - 400 MBq/day (145 GBq per year).

In outflows from settlement ponds in 87 % mines ^{226}Ra concentration exceeds 0.008 kBq/m^3, in 25% ^{226}Ra concentration is higher than 0.1 kBq/m^3 and in 8 % exceeds permissible level - i.e. 0.7 kBq/m^3 [9].

In rivers enhanced concentrations of radium can be observed many kilometres down from the discharge points. This is mainly true for radium-bearing waters type B, because out of these waters radium is not easily precipitated. The highest value of ^{226}Ra concentration was as high as 1.3 kBq/m^3 - it was found in a small stream near it's conjunction with Vistula river.

Enhanced radium concentrations are mainly observed in the Vistula river, into which most of the radium is discharged with B type waters - approximately 180 MBq of ^{226}Ra and 375 MBq of ^{228}Ra per day. Concentration of ^{226}Ra (0.035 kBq/m^3) was observed in Vistula in Cracow - 70 km downstream from Upper Silesia. The concentration of ^{226}Ra in Vistula river is shown on fig.2a and 2b. Bars show the concentrations of radium in discharge waters from mines. Some of these waters are not discharged directly to Vistula river, but to it's tributaries. In this case bars are located in places of conjunction of these rivers. The influences of singular inflows can be seen very clearly. Moreover, waters from first mine are A type and the difference of radium behaviour (fast precipitation) in comparison with other 3 mines (waters

B type) is very evident. Different situation was observed in the vicinity of Oder river, where in coal mines occur mainly waters type A. The amount of radium discharged into this river is much lower - 20 MBq per day of ^{226}Ra and 10 MBg/day of ^{228}Ra. As a result concentrations of radium in Oder ***are below 0.1 kBq/m^3.***

Concentrations of radium isotopes in some rivers in Upper Silesia are clearly enhanced as compared with natural levels. In comparison with data from other locations, concentrations of radium isotopes in rivers in USCB are significantly higher. Enhanced concentrations of radium in river waters in Upper Silesia are caused solely by the influence of mine waters.

Due to release of radium-bearing mine waters from coal mines there is a contamination of river waters. As a result radium concentration in some small rivers exceeds permissible level for radioactive wastes. Therefore development and application of purification methods is justified and further efforts should be done to reduce the contamination of rivers, particularly of Vistula River and it’s tributaries.

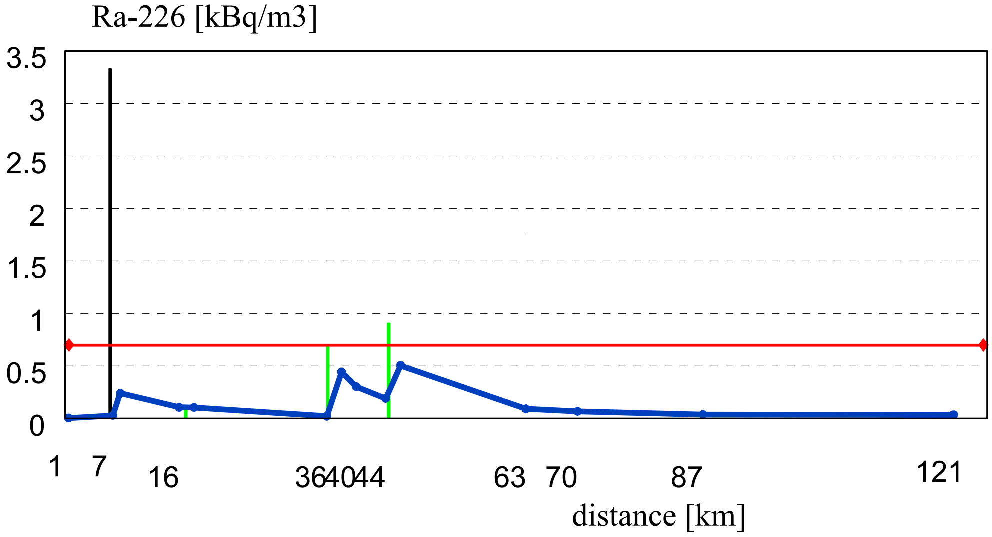

FIG. 2a. Radium in Vistula — during hot summer.

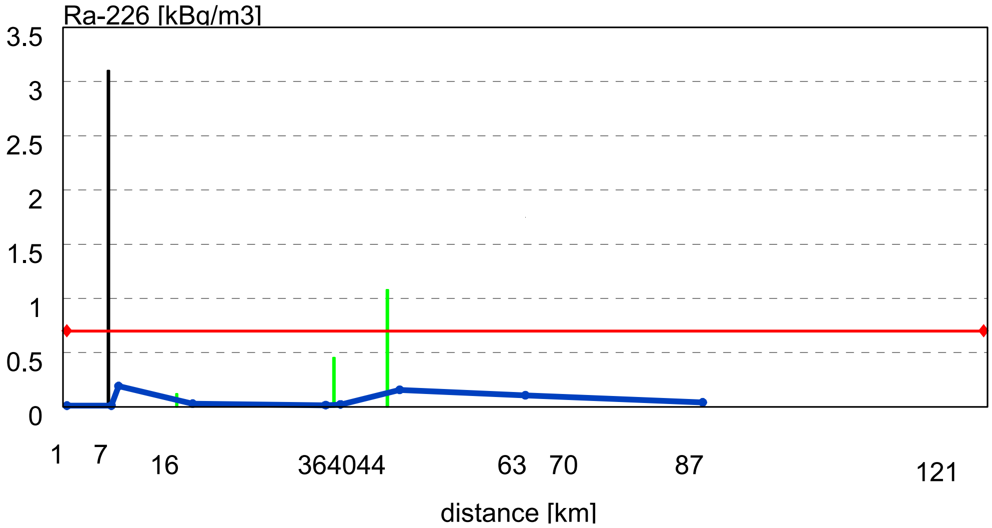

FIG. 2b. Radium in Vistula - during autumn and winter.

It can bee seen that in Cracow, which is 80 km downstream from the last point of mine waters discharge, radium content is about 0.04 kBq/m^3 of ^{226}Ra, while the average value for other Polish rivers is only 0.004 kBq/m^3 [16].

In one of small tributaries of Vistula, in Gostynka river concentrations of radium isotopes from 0.006 kBq/m^3 above discharge point to 0.635 kBq/m^3 (^{226}Ra) and from 0.01 kBq/m^3 to 0.99 kBq/m^3 (^{226}Ra) were found. The values of radium concentration in water samples from settling pond Bojszowy, from which mine waters were discharged into that river, varied from 2.397 to 4.236 kBq/m^3 for ^{226}Ra and from 3.51 to 7.01 kBq/m^3 for ^{228}Ra. Due to Polish regulations waters from the reservoir and from Gostynka should be treated as a waste with enhanced natural radioactivity. Therefore implementation of the purification methods in coal mines is so important.

Natural radioisotopes in bottom sediments

Enhancement of concentrations of natural isotopes in bottom sediments takes place in different places and under different conditions. First of all the level of the enrichment of radium isotopes in sediments depends on the type of saline water. Therefore three different sites were chosen for the investigations.

First site was a large settling pond into which waters type A were dumped in the past (before 1990). At that time ^{226}Ra concentration reached 21 kBq/m^3, while ^{228}Ra - 12 kBq/m^3 [17]. Co-precipitation of radium and barium caused a severe problems on that area. But now the radium content in mine waters released into that pond is below 0.1 kBq/m^3 [18]. That is the main reason, that the concentrations of radium isotopes in bottom sediments are not very high.

The second site is a small river, into which waters type B are released from one of coal mines. Maximum concentration of ^{226}Ra was as high as 2 kBq/m^3, while the maximum of ^{226}Ra was of about 4 kBq/m^3 [19].

As a third site a large settling pond with waters type B was chosen. Concentration of ^{226}Ra may reach 4 kBq/m^3, while concentration of ^{228}Ra is even higher - up to 7 kBq/m^3 [7]. The main process of the contamination is the sorption of radium isotopes on bottom sediments, therefore radium concentration in it is lower than in the first case.

Several samples of bottom sediments were taken from all sites. For each sample gamma spectrometric analysis was made. Also soil samples were collected at the banks of reservoirs and rivers. . In most cases a strong disequilibrium in ^{226}Ra/^{210}Po and ^{228}Ra/^{224}Ra sub-series can be observed.

The impact of bottom sediments on the contamination of the river's banks is usually negligible. Only in places where due to the flooding of river banks or as a result dredging and removal of bottom sediments, contamination took place, we can observe the increase of gamma dose rates.

It is clear, that concentrations of natural radionuclides in soils in the vicinity of reservoirs are typical for the earth crust [15]. Though, concentrations of radium isotopes in bottom sediments in settling ponds and in rivers are enhanced. This is clearly the result of deposition or sorption of radium from radium-bearing waters. We observe these phenomena in ponds and rivers as well.

Table 1. Concentrations of natural radioisotopes in bottom sediments from different investigation sites

Sampling place	^{226}Ra [Bq/kg]	^{228}Ra [Bq/kg]	^{224}Ra [Bq/kg]	^{210}Pb [Bq/kg]
Jankowice settling pond	350 - 4400	215 - 2400	190 - 2250	210 - 3400
Golawiecki river	70 - 543	163 -1229	89 - 531	12-86
Bojszowy reservoir	295 - 950	417 -1750	306 - 889	90 - 522

Conclusions

- The underground mining of coal causes sometimes a significant enhancement of the natural radioactivity in the environment. It is mainly a result of the release of radium-bearing waste waters from coal mines as well as a storage on the surface solid waste products with enhanced natural radioactivity. This phenomenon is observed not only in the Upper Silesian Coal Basin (USCB) but also in Germany and in other countries.
- In Upper Silesia the annual release of radium with mine waters to the natural environment can be assessed as of about 75 GBq of ^{226}Ra and approximately 145 GBq of ^{228}Ra.
- We found, that different types of radium-bearing waters (A and B) have the different impact on the natural environment. Not only the range of the transport and contamination of river waters is bigger in case of brines type B but also a possibilities of a further migration of radium are different. Probably radium adsorbed on bottom sediment from waters type B is far more mobile than radium precipitated in a form of a barium and radium sulphates from waters type A. This problem needs further investigations.
- As a result of the monitoring of the contamination of the natural environment we can draw conclusions concerning methods of ground reclamation and methods of the control of the radioactive contamination:
  - a complete investigation of the range and a level of the contamination must be done before the ground reclamation;
  - the method of the reclamation must be adequate to the range and level of the contamination and must diminish the possible impact on the inhabitants of the adjacent lands;
  - during and after the reclamation a continuous monitoring must be performed to assure the achievement of the desired parameters of the radiation level and to avoid any possibilities of spread of the sediments along the transportation routes;
  - after the reclamation measurements of the gamma radiation and radon concentration must be done.

Due to the fact, that the problem of the radioactive contamination of the natural environment is only partly regulated by Polish law, a certain actions must be undertaken to solve this problem.

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Contamination of settling ponds of coal mines caused by natural radionuclides

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ABSTRACT

As a result of a discharge of the radium-bearing waters from coal mines into settlement ponds and later into rivers a significant increase of radium concentration in bottom sediments can be observed. Sometimes also a contamination of river banks, soils and vegetation occurs. Mine waters contain mainly radium isotopes i.e. ^{226}Ra from uranium series and ^{228}Ra from thorium series. Due to chemical properties of such brines, these waters contain usually no uranium, no thorium and rather seldom elevated concentration of other isotopes as lead (^{210}Pb) and polonium (^{210}Po). The deposition or adsorption of radium on bottom sediments may take place on a distance of several kilometres from the discharge points. After a deposition or adsorption of radium isotopes the built-up of the activity of their progeny begins. Therefore concentrations of radium isotopes are higher than the decay products. We are able to measure the disequilibrium in ^{226}Ra decay chain as well as in ^{228}Ra decay chain, which shows the approximate age of the deposit.

The paper describes results of investigation of sediments with enhanced natural radioactivity occurring in settlement ponds, where mine waters have been dumped. The results of measurements show that these deposits contain mainly ^{226}Ra and ^{228}Ra and their progeny. Influence of bottom sediments with enhanced radium concentration on the natural environment in the vicinity of settlement ponds was studied on the example of two different water reservoirs where radium-bearing mine waters type A and B are released. The results show clearly enhanced radioactivity of bottom sediments and water in the settling ponds and in the rivers, but no evident enhancement was found in the adjacent land. Both coal mines are located in the drainage area of Vistula river, and bottom sediments with enhanced radium concentrations were found in Vistula up to 70 km downstream from the discharge point.

INTRODUCTION

Very often human activity, connected with an exploitation of mineral resources, leads to the contamination of the natural environment. Sometimes natural radionuclides are being released or concentrated in a form of waste material. In Poland the main source of waste and by-products with enhanced concentration of natural radionuclides is power industry, based on the coal exploitation and combustion. In hard coal mining industry 50 million tons 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 roughly by several km^2 per year [1].

Additional component of the radiation contamination of the natural environment, different than ordinarily joined with this kind of industry, is caused by underground coal exploitation. In many of coal mines, located in Upper Silesian Coal Basin waters with enhanced radium content occur [2]. Sometimes in radium-bearing brines barium ions are also present, in concentrations up to 2 g/l. Such waters were classified as radium-bearing waters type A. Contrary, in other waters (called B type) no barium can be found but radium and sulphate ions are present.

The presence of barium in waters is the most important factor for the further behaviour of radium isotopes in mine galleries or on the surface. From waters type A radium and barium always co-precipitate as sulphates, when such waters are mixed with any water, containing sulphate ions. As the result of the precipitation of barium sulphate, deposits with highly enhanced radium concentrations, which may sometimes reach 400 kBq/kg, are formed [2,3]. In comparison, average radium content in soil is equal 25 Bq/kg [4].

In case of another type of radium-bearing waters (type B), no precipitation occurs due to the lack of the barium carrier. From such waters radium is removed in a slow process of sorption on bottom sediments in gauntons 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 as for waters type A. But we can observe enhanced concentration of radium isotopes in river waters or in bottom sediments on a long distances downstream from the discharge points.

In Laboratory of Radiometry in the Central Mining Institute, routine measurements of radium concentration in mine waters as well as in waters, discharged into the river from settling ponds of coal mines have been performed since several years [5]. Such monitoring is obligatory for all mines in Poland [14]. Therefore, our database consists of several thousands results of radium concentration in water. On this basis the balance of radium in underground mines and in their vicinity was prepared [8]. Results of this assessment are different for two radium isotopes - ^{226}Ra and ^{228}Ra. In case of ^{226}Ra of about 70% out of 625 MBq/day remains in underground galleries, while only 225 MBq per day is released into surface waters. For ^{228}Ra situation is opposite – only 40% out of 700 MBq/day remains underground but 400 MBq is discharged daily into settling ponds and rivers.

Co-precipitation of radium and barium as sulphates and sorption of radium on bottom sediments take places also in small brooks and rivers [7].

Contamination of the natural environment in Upper Silesia

Investigations of the contamination of the natural environment in Upper Silesia region have been started in early 70's. Since 1986 our Laboratory performs routine monitoring of the pollution, caused by mining, on the basis of the Decree of Ministry of Mining and Energy [14]. Due to that act, mine's management are obliged to ensure such monitoring. Possible sources of contamination are radium-bearing waters as a primary source and deposits with enhanced radium content as the secondary source.

As mentioned above, radium behaviour is connected with barium content in brines. If barium ions are present in radium-bearing waters, than deposits of radium and barium sulphates always precipitate out, when such waters have been mixed with waters, containing sulphate ions. Usually such processes occur in underground galleries, only in a very few cases on the surface. Therefore discharge of radium-bearing waters type B leads to severe pollution of settling ponds and river, but on a short distance from the mine. Quite opposite situation can be observed in cases, when waters type B are discharge into settling ponds and later to river. We can observe only slight enhancement of the natural level of radiation but the distance from the source, where contamination happen, is typically quite large, sometimes few tens of kilometres.

As a result of all these processes, of about 70% of ^{226}Ra remains underground in deposits and only 225 MBq per day is discharged with water into natural environment. Corresponding values for ^{228}Ra are as follows: only 40% activity of this isotope remains in underground galleries, but 450 MBq/day is dumped onto surface. It is due to the fact, that the ratio ^{228}Ra: ^{226}Ra is higher in waters type B, without barium. Waters type B occur in mines located in the area in the vicinity of Vistula river, so enhanced radium concentrations can be observed in small tributaries of this biggest Polish river.

Applied methods of measurements

The reliability of the results in measurements of natural and artificial radioactivity is the most important problem. The method to ensure the quality of such measurements is the implementation of the internal quality assurance system in radiometric laboratory. In our case, such system was implemented in early 90's.

Laboratory of Radiometry of the Central Mining Institute has the accreditation granted by Polish Centre of Research and Certification [9]. The scope of certification is as follows:

- Measurements of ^{226}Ra and ^{228}Ra in waters and aqueous solutions
- Measurements of ^{210}Pb in water
- Measurements of gamma radionuclides in solid samples
- Measurements of gamma doses and dose-rates
- Measurements of potential alpha energy concentration (PAEC) of short lived radon progeny
- Calibration of portable instruments for measurements of PAEC.

For the purpose of this work we applied high resolution gamma spectrometry for measurements of natural radionuclides in solid samples (^{226}Ra, ^{228}Ra, ^{224}Ra, ^{40}K) and liquid scintillation counting for measurements of radium isotopes (^{226}Ra and ^{228}Ra) in water.

Monitoring of contamination of settling ponds on the surface

The best example of radium behaviour in correlation with type of radium-bearing waters is the analysis of waters and deposits from different settling ponds, into which waters from coal mines are discharged. The main task of such pond is to settle the mechanical suspension, but additionally deposition of radium takes place there. In this paper results of investigations, performed within the period 1995-1999 are described.

Two big settling ponds were chosen for the comparison. Into the first one, named ***Rontok***, waters type A are discharged. The second reservoir, ***Bojszowy***, is used as a settling pond for waters type B.

1. Rontok Reservoir

The exploitation of that pond has been started in 1977. During this period of about 72 million cubic meters of saline waters were dumped into the reservoir from "SILESIA" Coal Mine. The concentration of the suspension varied from 0.3 to 2.4 g/dcm^3. The total amount of the suspension, deposited in the pond, was calculated as 100 000 m^3 (of about 150 000 tons). Information of the settling pond are presented in table 1.

Waters type A were discharged into the pond during whole period (with radium and barium ions). The activity ratio between two radium isotopes ^{226}Ra: ^{228}Ra was of about 2:1. Previously the daily discharge of water was at the level 10 000 m^3, but since 1998 the amount of water is much smaller, only 5 600 m^3/day. Inflows of groundwater with content of sulphate ions are small but numerous, therefore precipitation of $BaSO_4$ + $RaSO_4$ occur in the pond. In deposits concentration of radium isotopes is clearly enhanced. From the pond waters are dumped directly into Vistula river.

The process of co-precipitation of radium and barium in the pond is now less intensive, because of the two reasons – lower radium content in waters during recent years in comparison with previous period (now ~ 2.5 kBq/m^3 of ^{226}Ra but up to 15 kBq/m^3 before). Another reason is a decrease of water inflow into pond by factor two. It means, that the total amount of radium in waste water, dumped into pond, is lower several times as for instance 4-5 years ago.

Table 1.
Characteristics of two settling ponds

	Bojszowy	*Rontok*
Type of radium-bearing waters	B	A
Area [ha]	16	36
Volume [m^3]	400	440
Flow rate [m^3/day]	33000 in 1999 - 26000	9200 since 1998 - 5600
^{226}Ra in discharge waters [kBq/m^3]	2.0 - 3.9	2.3
^{228}Ra in discharge waters [kBq/m^3]	3.9 – 7.0	2.4
TDS :	48 (max 55)	40 (max 58)
Cl ions	35.9	25
SO_4^{2}- [kg/m^3]	2.1	2.5
Total amount of water dumped into the pond: [million m^3]	227	73
Exploitation period	19 years (since 1980)	23 years (since 1976)

1. Bojszowy Reservoir

Second settling pond is **Bojszowy Reservoir**, into which saline, radium-bearing waters from two mines are released. Inflow from "Czeczott" Coal Mine is of about 15 000 m^3/day and from another mine "Piast" the discharge is even bigger - roughly 20 000 m^3/day. In both cases the type of water is the same (B type) – no barium only radium and sulphate ions. The activity ratio between ^{226}Ra: ^{228}Ra is 1:2, quite opposite in comparison with Rontok. Due to the lack of barium, no precipitation of radium in the pond can be observed. Nevertheless, measurements of radium content in bottom sediments showed enhanced concentration of radium isotopes up to several hundred Bq/kg as a result of the sorption of radium.

The exploitation of the pond have been started in 1980, and till now of about 227 million m^3 of waters were discharged into reservoir. From the pond waters are released into small river Gostynka, a tributary of Vistula river.

2. Results of investigations

In case of both settling ponds the problem of the contamination is rather a delicate subject. Local communities asked for investigations to check the levels of the pollution.

Another reason was the preparation to the purification of radium-bearing waters in "PIAST" Mine. We wanted to know, how the purification would affect the radium balance in the river waters. Measurements of radium isotopes in waters from settling ponds and rivers were done – upstream and downstream from the discharge points. Monitoring of natural radionuclides in bottom sediments from ponds and rivers was performed, also contamination of soils in the vicinity of both reservoirs have been checked.

Rontok Reservoir - Radium-bearing waters

In fall and winter of 1998 radium concentrations were measured in water samples, taken from the inflow to the pond. Average values of radium content were as follows:

- Ra-226 – 2.27 kBq/m^3, Ra-228 – 2.37 kBq/m^3.

The assessment of radium balance in the inflow to ***Rontok*** gave the result approximately 9.5 GBq/year. But before 1998 amount of water, discharged from the mine to the reservoir, was of about two times higher (10 000 m^3/day). Also average radium concentrations were slightly different: for ^{226}Ra – 3.20 kBq/m^3 and for ^{228}Ra – 1.43 kBq/m^3. During the period 1988 to 1999 40 samples taken from the inflow to the settling pond were analysed and results are shown in table 2.

Table 2. Results of radium concentration in inflows to Rontok

Rontok	Radium concentration	
	^{226}Ra	^{228}Ra
	[kBq/m^3]	[kBq/m^3]
Average	3.21	1.43
Median	1.76	1.35
max	**14.20**	**3.38**
min	0.56	0.40

On this basis the assessment of radium balance gives the annual release of radium isotopes at level 10.7 GBq for ^{226}Ra and 4.8 GBq for ^{228}Ra. Taking into consideration the whole period of exploitation of the pond we can calculate the amount of radium, discharged into the pond with saline waters as 240 GBq for isotope ^{226}Ra and 110 GBq for ^{228}Ra.

But analysis of the results of radium concentrations in water samples, taken from the outflow from the pond to Vistula river, leads to a very strange conclusions (see table 3).

Table 3. Results of radium monitoring in outflows from Rontok

Rontok	Radium concentration	
	^{226}Ra	^{228}Ra
	[kBq/m^3]	[kBq/m^3]
Average	**4.77**	**2.03**
median	**4.78**	**1.38**
max	**10.54**	**5.01**
min	**0.89**	**0.55**

It can be seen, that average values of radium concentration in outflows are higher than corresponding values for inflows (table 2). It means that temporal variations of radium content in inflows are very high, while at the outflow radium concentrations are more stable. The results of radium concentrations in waters from the pond (table 4) support that conclusions. For instance, maximum value of ^{226}Ra concentration was found in the reservoir - 20 kBq/m^3. The main reason of such situation is de-watering of deeper horizons (where waters with higher radium concentrations occur) during nights, because the cost of energy is lower.

Table 4. Radium concentration in water samples from Rontok

Rontok	Radium concentrations	
	^{226}Ra [kBq/m^3]	^{228}Ra [kBq/m^3]
Average	**6.81**	**1.65**
median	**6.88**	**1.73**
max	**20.46**	**2.60**
min	**0.18**	**0.23**

Release of radium-bearing waters from Rontok leads to the increase of radium concentration in Vistula. In table 5 results of radium analysis of samples from Vistula are shown – for the period between 1988 –1999.

Table 5. Radium concentration in Vistula upstream and downstream from the discharge point from Rontok

Radium content in Vistula	*upstream [kBq/m^3]*		*downstream [kBq/m^3]*	
	^{226}Ra	^{228}Ra	^{226}Ra	^{228}Ra
Average	0.011	0.011	0.246	0.099
median	0.01	0.01	0.207	0.06
max	0.05	0.05	0.787	0.6
min	<0.003	<0.003	0.04	0.01

Bottom sediments in Rontok

Monitoring of the contamination of bottom sediments in Rontok and soil in adjacent area was done. Sampling of scales from the bottom of the pond was done in a grid 50x50 meters. Also the thickness of the layer of sediments was measured in each sampling point. After drying, samples were measured and concentrations of the natural radionuclides have been calculated. The same procedure was applied for soils samples. On this basis a map of the radium isotopes concentrations was prepared. Accordingly to the plans of mine management a restoration of the area, where **Rontok** is located, will be done within few years. Therefore investigations of the pollution is so important

Table 6. Radium in bottom sediments from Rontok

Rontok	Radium in sediments	
	^{226}Ra [Bq/kg]	^{228}Ra [Bq/kg]
Average	5105	1407
median	1191	593
max	49151	6388
min	67	62

We found maximum values of radium content in sediments near the outlet of the pipeline, transporting waters from the mine to the settling pond. The total activity of radium isotopes ($^{226}Ra+^{228}Ra$) reached there 55 kBq/kg. In average, radium content was much lower, and the distribution of radium at the bottom of the pond is very non-uniform. In some places radium concentration in sediments was at level of typical radium concentration in earth crust, as can be seen in table 6.

Table 7. Assessment of the amount of deposits in Rontok and total radium activity in deposits

Area of the pond [m^2]	**Volume of deposits [m^3]**	**Amount of water [m^3]**	**Total activity of ^{226}Ra [Bq]**	**Total activity of ^{228}Ra [Bq]**	**Amount of radium in the pond $^{226}Ra+^{228}Ra$ [Bq]**
360000	113107	262084	240×10^9	74×10^9	314×10^9

For of about 35 - 40% of the area of the pond, concentrations of radium isotopes are lower than 350 Bq/kg for Ra-226 and 230 Bq/kg for Ra-228. These levels are our proposal as the maximum permissible concentrations, below which no remedial action is needed [13]. In contrary, in the southern-east part of the pond, near the inlet to the pond, the thickness of deposit's layer is approximately 1.2 m and the maximum concentrations of radium were found. Taking into account all these data, we were able to assess the total amount of deposits in the settling pond and a balance of radium isotopes in deposits – see table 7.

Bojszowy Reservoir

Radium-bearing waters.

Waters, released from two coal mines into Bojszowy reservoir, are type B and ^{228}Ra concentrations are higher than that of ^{226}Ra. Average values of radium concentrations in inflows from Piast Mine were equal for ^{226}Ra ca. 4.1 kBq/m^3, while for ^{228}Ra of about 7.2 kBq/m^3. Corresponding values for inflows from Czeczott Mine were lower and equal – 3.2 kBq/m^3 for ^{226}Ra and 4.9 kBq/m^3 for ^{228}Ra. That are average values for the period of last two years.

Assessment of radium balance ($^{226}Ra + ^{228}Ra$) in inflows to Bojszowy settling pond gives us the annual activity of about 124 GBq. It is more than the half of the total amount of radium, released with waters from all coal mines in Poland (55%) [10]. We calculated average radium concentrations in waters discharged to the pond as 3.6 kBq/m^3 for ^{226}Ra and respectively 6.2 kBq/m^3 for ^{228}Ra.

Sampling of waters from reservoir was done in 1996. The grid was similar as in case of Rontok settling pond – it means 50x50 meters. In the same places samples of bottom sediments were taken. Results of analysis of radium concentrations in water samples are shown in table 8.

Table 8. Radium concentration in water samples from Bojszowy

Bojszowy	**Radium concentrations**	
	^{226}Ra [kBq/m^3]	^{228}Ra [kBq/m^3]
Average	**3,45**	**6.95**
Median	**3.34**	**6.76**
Max	**5.21**	**8.32**
min	**2.12**	**4.67**

It can be seen, that distribution of radium in water in Bojszowy is more uniform as in Rontok settling pond. The main reasons of such situation seem to be more stable radium content in inflows and type of the water, from which radium is removed only on a way of sorption.

The average radium concentration in outflows from the settling pond were similar to the values at inflow - 3.5 kBq/m^3 for ^{226}Ra and 6.0 kBq/m^3 for ^{228}Ra. It means that only small amount of radium is deposited at the bottom. Moreover, total concentration of radium isotopes in waters, released to Gostynka is of about 10 kBq/m^3, more than 10 times exceeds a permissible level for waste water (0.7 kBq/m^3 [11]). The significant improve of that situation would be seen very soon, due to the implementation of the technology of underground purification of mine's waters from radium in Piast Colliery.

Comparing results of radium analysis of inflows and outflows from the Bojszowy reservoir to Gostynka river, we calculated that only 2.9 % of ^{226}Ra and 3.3% of ^{228}Ra activities remain in the pond and caused the enhancement of radium concentrations in bottom sediments.

More than 95% of radium is dumped with saline waters into Gostynka. Therefore the influence of such discharge is good visible. Upstream the discharge point the concentration of radium isotopes in Gostynka is very low, below 0.1 kBq/m^3 – which value is typical for groundwater and river waters in Poland [12]. Downstream from the discharge point we observed a rapid increase of radium content. Usually during winter and spring, when water flow in the river is higher, concentration of radium didn't exceed value 0.7 kBq/m^3. But during summers concentrations of ^{226}Ra in Gostynce vary in range 0.5 - 0.7 kBq/m^3, and in case of ^{228}Ra concentrations are higher – of about 1.0 – 1.3 kBq/m^3. Total activity of radium isotopes in water in Gostynka reaches even 1.5 - 2.0 kBq/m^3 [8]. Additionally, a portion of radium (several percent) is adsorbed on bottom sediments in Gostynka, but main part of radium is transported with water to Vistula. In this big river radium concentration decreases as a result of dilution and further adsorption [6].

Bottom sediments.

Sampling of bottom sediments have been done in these sites, where water samples were taken. Boreholes were drilled in the bottom of settling pond and cores of sediments were collected and analysed by means of gamma spectrometry. We found in sediments from Bojszowy radium ^{226}Ra concentrations in range 95 - 950 Bq/kg, and respectively for ^{228}Ra from 124 up to 1705 Bq/kg [7]. Characteristic for these samples is the fact, that almost in all cases activities of ^{228}Ra and ^{224}Ra were close to equilibrium and very often concentration of ^{226}Ra was only slightly lower than ^{228}Ra content. It means, that such scales are relatively old ones, at least few years. It means also, that the adsorption in such places is very slow. Only in a very few places, far from the banks, we found “young” deposits. Results of measurements are shown in table 9.

Table 9. Radium in bottom sediments from Bojszowy.

Bojszowy	Radium concentration	
	^{226}Ra	^{228}Ra
	[Bq/kg]	[Bq/kg]
Average	414	627
Median	406	628
Max	950	1705
min	95	124

On the basis of performed measurements the balance of radium in deposits in the settling pond was done (see table 10). For that assessment the assumption was made, that the distribution of radium isotopes in bottom sediments is uniform. Therefore we used the average concentrations of both radium isotopes for our calculations.

Results of these considerations are as follows. The total activity of ^{226}Ra, accumulated in bottom sediments during 19 years of exploitation of Bojszowy reservoir, is equal ca. 66 GBq, and the corresponding value for ^{228}Ra – 100 GBq. The annual rate of deposition is of about 3.5 GBq for ^{226}Ra and 5.8 GBq/year in case of ^{228}Ra. It is only 7% of the annual discharge of radium with waters into the settling pond. Our earlier calculations gave us lower rate of deposition [7] – of about 4 % per year, but such assessment is not very accurate, accordingly to big uncertainties of all parameters, which have been taken into account.

Table 10. Assessment of the amount of deposits in Bojszowy and total radium activity in deposits

Area of the pond [m^2]	**Volume of deposits [m^3]**	**Amount of water [m^3]**	**Total activity of ^{226}Ra [Bq]**	**Total activity of ^{228}Ra [Bq]**	**Amount of radium in the pond ^{226}Ra+ ^{228}Ra [Bq]**
160000	240000	262084	66×10^9	100×10^9	166×10^9

The comparison of radium deposition is both settling ponds

Mentioned above results of analyses and assessments can be used to description of radium behaviour in the settling ponds and rivers in correlation with chemical composition of radium-bearing waters. Comparison of the results is shown in table 11.

In case of Bojszowy Reservoir, the rate of deposition of radium is very low, only of about 4 -7% of the total activity is adsorbed at pond’s bed per year. The distribution of radium in sediments is rather uniform, therefore calculation of radium balance in sediments was relatively easy. On the other hand at least 90% of radium is dumped into Gostynka river and later to Vistula, leads to the contamination of river’s water on the long distance from the discharge point.

Table 11. Radium balance in Bojszowy and Rontok settling ponds

Settling pond	**Area [m^2]**	**Volume of deposits [m^3]**	**Total amount of radium discharged into pond [GBq]**	**Amount of radium deposited in the pond [GBq]**	**Ratio Rd %**
Bojszowy	160 000	240 000	2356	166	4-7
Rontok	360 000	113107	350 [**] 810[***]	314	90[**] 39[***]

[*] → total activity of $^{226}Ra+^{228}Ra$

[**] → assessment made on a basis of measurements of radium concentration in inflows to the pond

[***] → assessment made on a basis of measurements of radium concentration in outflows to Vistula and amount of radium, deposited in the pond.

Rd is a ratio of radium activity deposited in the pond to total amount of radium discharged to the certain pond

In case of Rontok settling pond situation is quite different. The rate of deposition is much higher, because of different type of water – type A with elevated barium content. Also assessment of deposition rate of radium was difficult. Calculations made in two different ways gave different results. Taking into account measurements of radium concentration in inflows we obtained the value of about 350 GBq for whole period of exploitation. Another method of calculations, based on balance of radium in deposits and measurements of radium concentrations in outflows gave result almost three times higher – 810 GBq. It means, that the average concentration of radium isotopes in waters released to the pond during whole period of exploitation was roughly 10 kBq/m^3. In this case the deposition rate is of about 39 %, and this result is more reasonable in comparison with 90%, calculated for the first approach. But for waters type A the deposition rate strongly depends on the amount of groundwater inflow, and the balance of sulphate ions in such inflows.

CONCLUSIONS

- Significant amount of radium, released with mine water into settling ponds on the surface, is transported to rivers. This way of the contamination of the natural environment is very important in the catchment area of Vistula river, the Polish biggest river.
- The behaviour of radium strongly depends on the presence of barium ions in water. Barium acts as a carrier for radium, therefore from radium-bearing waters type A radium co-precipitated out with barium as sulphates. Very often the precipitation takes place in underground galleries and sometimes in settling ponds on the surface. Only small portion of radium is finally dumped into rivers. In case of waters type B, radium is removed in slow process of adsorption on bottom sediments. At least 90% of radium is discharged into rivers with such brines and enhanced radium concentration in water can be found few tens kilometres downstream from the discharge points.
- In particular settling ponds significant amounts of radium isotopes have been accumulated during its exploitation. It leads to the increase of gamma dose rates in the vicinity of such ponds and to the contamination of the banks of such reservoirs.
- Till now regulations concerning mining industry are applied for such reservoirs and dose equivalent limit for miners is much higher than for the general public. Problems may appear

after closing of the mines, because local authorities would have to maintain ground reclamation or removal of deposits with enhanced natural radioactivity. Moreover, much lower dose limit - 1 mSv per year is applicable for inhabitants.

- Very important is also social aspect of that problem. For local societies the contamination of the natural environment in the close vicinity of their homes is treated as a real threat.

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Purification of mine water of radium — the implementation of the technology in a coal mine

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Abstract

In underground coal mines in the Upper Silesian Coal Basin there are inflows of highly mineralised waters containing radium isotopes. These waters cause radioactive pollution of the natural environment in mining areas. Therefore cleaning of saline waters of radium is very important. Two types of radium-bearing waters 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 waters of Ba^{2+} and Ra^{2+} ions was developed and implemented in two coal mines. As the result of used technology, based on application of phosphogypsum as the cleaning agent, a significant decrease of radium discharge was achieved - daily of about 120 MBq of ^{226}Ra and 80 MBq of ^{228}Ra.

Another type of radium waters 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 discharged waters to main rivers. Different method of purification from radium must be applied for such waters. Laboratory and field experiments were performed, and a cleaning method was chosen. For purification of saline waters - waste products from other industrial processes are applied. The method of purification have been applied in full technical scale in coal mine with very good results - of about 6 m^3/min of radium-bearing waters is cleaned. Whole this process takes place in underground old workings without any contact of mining crew with radioactive deposits, which are produced during the process. As a result radium amount released to the natural environment was significantly diminished - approximately of about 90 MBq of ^{226}Ra per day and 150 MBq of ^{228}Ra.

Introduction – Occurrence of radium-bearing waters in Polish coal mines

In coal mines, located in 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 radium concentration may reach 400 kBq/m^3. Therefore the assessment of the balance of radium isotopes in inflows showed, that amount of ^{226}Ra was of about 725 MBq per day, while the corresponding value for ^{228}Ra was roughly 700 MBq per day [5]. We found, that only 40% of radium remained in the underground galleries and gutters, while 60% were transported with waters to the settling ponds on the surface and later to rivers [6,7,8]. It was an important source of the contamination of the natural environment in the vicinity of coal mines.

The phenomenon of the radioactivity of saline waters from coal mines in Poland was discovered in 60's [2]. Later, investigations performed by Tomza and Lebecka showed, that radium concentration in water was correlated with the salinity [3]. Moreover, two types of brine were distinguished in coal mines. In waters type A ions of barium and radium are present, while in waters type B only radium ions and sulphate occur, but no barium [5]. From waters type A radium is very easily precipitated out with barium carrier as sulphates after mixing with waters rich in sulphate ions. In waters type B there is no carrier for radium, therefore precipitation of radium scales doesn't happen. Further investigations showed, that discharge of radium-bearing waters from coal mines caused in many cases contamination of the natural environment in the vicinity of these mines, especially small brooks and rivers. The highest levels of contamination were always connected with release of waters type A and precipitation of deposits with enhanced radium content. Such process occurs sometimes in underground galleries and sometimes on the surface in settling pond and small rivers, leading to the contamination of river's beds. Also purification of radium-bearing waters is based on the same process. In case of waters type B only a slow adsorption occurs, therefore the level of contamination is much smaller in comparison with waters type A.

In the past, the highest concentration of ^{226}Ra in discharge waters from coal mines in Upper Silesia was of about 25 kBq/m^3 [6]. **But due to the Polish regulations, waters in which radium content ^{226}Ra is higher than 0.7 kBq/m^3 should be treated as a waste material with enhanced radioactivity** [1]. In Poland, at the beginning of 90's in 10 out of 66 mines such waters were released into the rivers. Waters type A were discharged from seven collieries, and waters type B from 3 mines. As a result of application of purification methods, at present waters type A are dumped into rivers from two mines. The total activity of ^{226}Ra in these waters is only 30 MBq per day. The same number of mines (3) are sources of waters type B, but the amount of radium in such waters is much higher – for ^{226}Ra is of about 200 MBq [8]. Additionally, concentrations of another radium isotope, ^{228}Ra, are higher than that of ^{226}Ra, therefore the charge of that isotope in discharge waters is slightly higher than 300 MBq per day.

The difference between two types of radium-bearing can be explained on the example of two coal mines – Krupinski and Piast.

In Krupinski Colliery waters type A are present, and the maximum radium concentration of ^{226}Ra was as high as 100 kBq/m^3. In the past the coal mine released of about 150 MBq/day of both radium isotopes into the pipeline, collecting also salty waters from 11 other mines. The scaling of radium and barium sulphates in the pipeline caused severe problems with the exploitation of the pipeline. During several years, roughly 20 000 tons of deposits were formed inside pipes, and the average concentration of ^{226}Ra was 30 kBq/kg [9]. It was a first case, when the purification of mine waters from radium and barium was highly desirable. Investigations were undertaken in our laboratory and chosen method of cleaning was applied in the Krupinski Mine in 1990 [12]. Since that time, only 3 MBq out of 150 MBq is released on the surface due to the underground purification.

In Piast mine waters type B are present, in which maximum concentration of ^{226}Ra is as high as 12 kBq/m^3. Waters from the mine are released to the Vistula river, through Bojszowy reservoir and small river Gostynka. The assessment of radium balance in the mine gave the following results. Only small portion of radium remains underground, more than 99% is pumped out on the surface – of about 90 MBq/d ^{226}Ra and 150 MBq/day ^{228}Ra.

Piast Colliery together with two other mines - Czeczott and Ziemowit – are the main source of the contamination of waters in Vistula River. We found enhanced levels of radium 100 km downstream from the discharge points of mentioned above mines, close to Cracow [13].

Results of the investigations of the contamination of natural environment in the vicinity of coal mines forced us to think about the possibility of cleaning the mine waters from radium. At first we tried to design the method of purification for waters type A, which was relatively simple [12]. Such technology of radium removal have been implemented in two collieries – Krupinski (1990) and 1-Maja (1991).

As the effect of the undertaken measures, the amount of radium pumped out on the surface decreased significantly – more than 45% of the previous value during period 1990 - 1995 [13].

Removal of radium from waters type B

Investigations on possibilities to purify radium-bearing waters type B were started in Laboratory of Radiometry in the Central Mining Institute in late 80's. It was connected with two important factors. First of all, the Decree of the President of Polish Atomic Energy Agency, concerning waste products with enhanced radioactivity was issued in 1989 [1]. Due to this act, it is forbidden to release to the natural environment waters, in which ^{226}Ra concentration exceeds level 0.7 kBq/m^3. On the basis of the Decree, in the local authority (Voivodship) in Katowice a commitment was issued, that Piast Colliery was obliged to make efforts to diminish as low as possible concentrations of natural radionuclides (radium isotopes) in waters, discharged into rivers. Moreover, long-term release of radium-bearing waters caused in certain places a significant contamination of settling ponds and small rivers, so the ecological aspect of the possibility of radium removal from mine waters was also important.

Laboratory and field investigations on radium removal from mine waters were supported by Polish Committee of Scientific Research [4]. Results, obtained during tests (also in underground galleries), gave a basis to design the purification station in Piast Colliery [10]. In 1996 in Piast Mine the construction of the station have been started. Expenses were partly covered by National Fund of Environmental Protection and Water Resources. Construction of the installation was finished at the end of 1998 and the start-up of the implementation began [14].

As the sorbent, used for removal of radium, barium chloride was chosen. During laboratory and field test capabilities of this agent have been proved. Unfortunately, there are some limitations in use of that chemical. First of all, barium chloride is poisonous and the training of the mining crew had to be done to avoid any possibilities of intoxication. Moreover, we had to check the background of radiation level before implementation of the purification method in underground galleries as well as on the surface. Some other organising and research activities were completed.

And finally, during the period March – June 1999 the start-up of the purification installation, designed for removal of radium from saline waters have been done in Piast Colliery. It is a unique, first underground installation, built in a coal mine in a full technical scale. This installation is located at the depth 650 meters beneath the surface. Now the system is working in a routine way, therefore it is possible to purify 6 m^3/min. of underground saline waters from radium. Implementation of the purification method in Piast Mine have been carried out by Central Mining Institute in co-operation with certain services from the colliery.

This work is just the first step of the purification of radium bearing waters in Piast Colliery, because till now only waters from the deepest horizon (650 meters) are a subject of radium removal. As the next stage the purification of waters from level 500 meters will be done. Later, the radium removal method will be implemented in two other collieries – Ziemowit and Czeczott. It should solve the problem of the radioactive contamination of the natural environment, caused by underground mining in Upper Silesia.

Hydrogeological situation in Piast Mine

In the overburden the most important layer is an impermeable, thick clay stratum. Therefore there is no hydraulic contact of mine working with the surface and no inflows of meteoric waters. Therefore water inflows into underground galleries of Piast Colliery are mainly due to the aquifers in carboniferous rocks. That are old waters, with high salinity. In 1998 at the level 500 meters the total inflow of brines was of about 5.7 m^3/min, and at the deeper horizon 650 m - 6.1 m^3/min.

The mineralization of the water varies in a very wide range. For instance, in shafts inflows of potable water are presents, while in other places inflows of waters with salinity close to the saturation, occur. The average concentration of Cl^- in brines from level 500 meters is approximately 40 g/dm^3, while in saline waters from level 650 meters the corresponding value is ca. 75 g/dm^3.

The average and maximum concentrations of radium isotopes in waters from Piast Mine are as follows:

^{226}Ra -	average concentration	6.3 kBq/m^3	maximum	12.4 kBq/m^3
^{228}Ra -	average concentration	10.2 kBq/m^3	maximum	19.3 kBq/m^3

THE DESCRIPTION OF THE PURIFICATION SYSTEM

The whole system is located in the central part of Piast Mine, in the vicinity of main shafts, at the depth 650 meters. This area was chosen by geological service accordingly to the following facts. First of all several development heading were driven in that area, moreover the structure of coal seams was too complicated for the exploitation. Additionally, the coal quality from that seem was low and numerous inflows of salty waters were found. Therefore the exploitation of coal in the area was stopped. Very convenient is also the fact, that existing galleries in chosen area are sublevel to the main galleries at the horizon, so no water hazard 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 cleaning agent. Water from the eastern part of the mine (3.5 m^3/min) is pumped to the purification station through the pipeline with length 1500 meters, but water from the western part flows along gutters and the flow rate is a bit smaller – 2.6 m^3/min.

In the chamber of the purification station an automatic sorbent's feeder was installed. Water flows in the gutter under the feeder, and the sorbent is fed into the water. In the gauton several wards are built to make the water flow more turbulent. Under such conditions, the mixing of the sorbent with water is better and the dissolving of barium chloride is faster as well as the consecutive co-precipitation of radium with barium carrier as sulphates. Water is removed from the chamber through the pipeline with length 600 meters and diameter ϕ 600 to the system of settling galleries. That are five parallel galleries with length ca. 1050 meters each and a cross section is equal roughly 11.8 m^2. In these galleries the sedimentation of radium/barium deposits and of mechanical suspension takes place.

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

From the settling galleries water flows out to the main water galleries near the exhausting shaft and is pumped out to the surface, to Bojszowy reservoir and finally discharged to Gostynka river.

THE START-UP OF THE PURIFICATION SYSTEM IN PIAST MINE

The purification of mine waters have been started in Piast Colliery in May 1999. As the settling galleries were full of waters with enhanced radium concentration, so the feed of sorbent during first ten days were done continuously, with the dose rate of about 100 grams per m^3. The volume of the settling galleries was assessed as 80000 m^3, and we supposed to obtain results at the outflow from the system after 6-8 days, because the daily inflow is approximately 10000 m^3.

The monitoring of radium content in water was done in several points of the system. Water samples were taken from the inflow (before purification), another sampling point was located at the outflow from the system. Moreover, samples of water pumped out on the surface and from the Bojszowy reservoir were taken from time to time.

On fig.1 preliminary results of purification during the period 5th of May – 19th of July are shown. The curve, describing radium concentration in outflow water, can be divided into few sections. Since 5th of May till 11th of May radium concentration in water was stable. But later, within few hours, we observed a rapid drop of the concentration of radium isotopes from ~ 15 kBq/m^3 to the value of about 3 kBq/m^3. Later on, it was a kind of stabilisation at that level until 19th of May. On this day the concentration of radium isotopes ($^{226}Ra+^{228}Ra$)

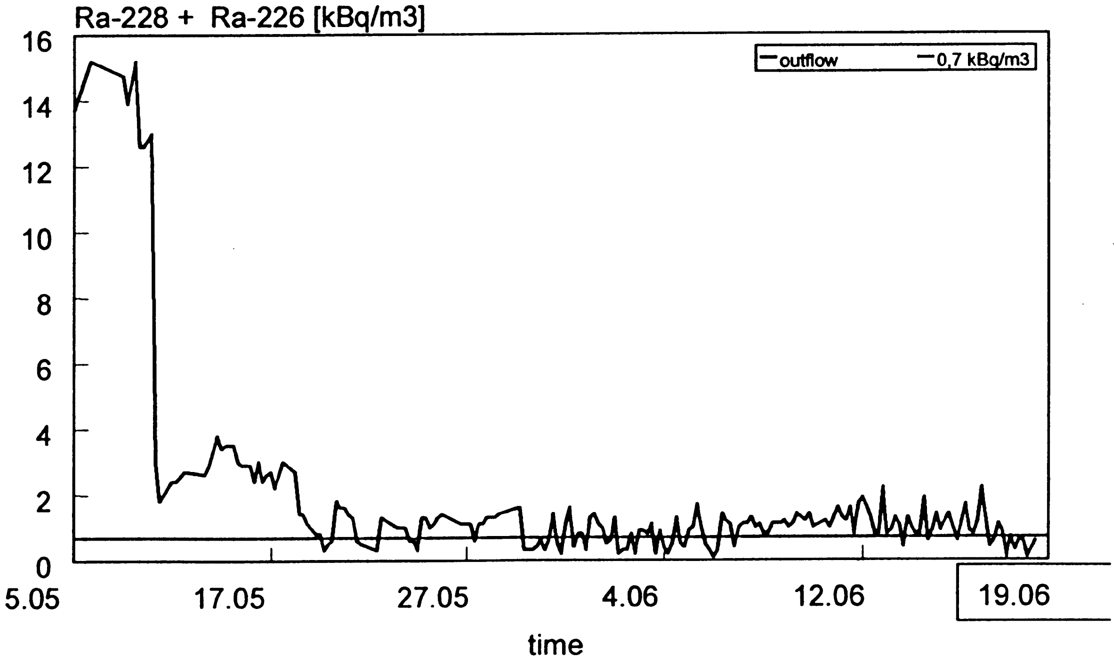

Fig.1. Results of the purification of waters in Piast Mine

decreased first time below 0.7 kBq/m^3. But during whole this period the feeder was working continuously and the dosage was two time higher as was planned (100 g/m^3 in comparison with planned 50 g/m^3).

Unfortunately, some problems with engine of the feeder caused the break of the feeding of the sorbent between 18th and 20th May. After reparation of the feeder the semi-continuous mode of dosage have been started, because we tried to reach the planned value of dosage. Probably both reasons caused the following effects - we observed variations of radium concentration at the outflow. During the period 19th of May until 19th of June we measured radium concentration in waters from the outflow in a range 0.2 - 1.5 kBq/m^3, and the average concentration was calculated as 0.7 - 0.9 kBq/m^3.

Concentrations of radium isotopes in water (^{226}Ra and ^{228}Ra) were measured by means of liquid scintillation counting, preceded by chemical separation of radium [11]. On fig.1. can be clearly seen, that in a very short time results of purification were excellent. Finally, after one month and a half, the radium content in water outflow from the purification system was below permissible value 0.7 kBq/m^3. We would like to emphasise the fact, that the efficiency of purification is better than 95%. As the result of the application of the method of radium removal from mine waters in that particular case, in Piast Colliery, amounts of radium pumped out onto the surface, decreased significantly.

THE EFFECTS OF THE PURIFICATION FOR THE NATURAL ENVIRONMENT

The influence of the purification on the radioactivity of discharged waters

We started to measure radium concentration in waters, released from Piast Mine into Gostynka, several years ago [7]. Also contamination in the vicinity of Bojszowy reservoir and of the river's bed was investigated [15]. During this period we gathered a lot of data, which gave the basis for the assessment of the effects of purification. On fig.2. results of measurements of radium concentration in waters from different sampling points are shown. We measured radium content in waters from main water galleries at level 650 meters, in discharge waters from Piast Mine to settling pond on the surface as well as in waters, released from settling pond into Gostynka river.

During the start-up of the purification, the effect of radium removal was significant. In cumulative waters from the horizon 650 meters concentration of radium isotopes ^{226}Ra+^{228}Ra decreased from 15 kBq/m^3 down to the value 1.5 kBq/m^3. Later on the decrease of radium content was even bigger – below 0.7 kBq/m^3. It means, that the amount of radium, pumped onto the surface from that horizon is more than ten time lower as before purification.

Fig.2. Effects of the purification - decrease of radium concentration in water

Such significant decrease of radium concentration in waters from level 650 meters caused similar effects in the waters from settling pond on the surface. On the surface the result of radium removal isn't so big, because waters from horizon 500 meters are not a subject of purification yet. The assessment of the radium balance showed, that the amount of radium released into the pond was lower of about 65% in comparison with previous values. Of course, the same pattern we observed at the outflow from the pond, but slightly retarded due to the retention time in the pond, roughly 8-9 days.

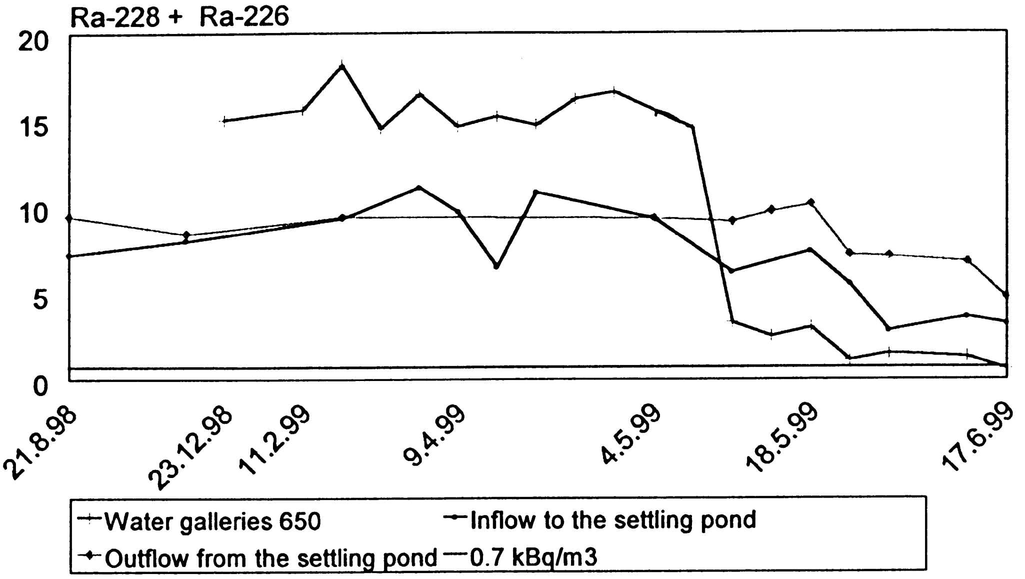

Fig.2. Piast Mine - effect of purification for the environment

Nonetheless, the radioactive contamination of waters, discharged into Vistula river was significantly diminished as a result of the implementation of the purification method. Calculations, made on the basis of obtained results of measurements, leads to the conclusion, that the total amount of ^{226}Ra, released through Gostynka to Vistula river is 60 MBq/day lower as before, while corresponding value for ^{228}Ra is equal 90 MBq/day. **The decrease of discharge of both radium isotopes from Piast Colliery into natural environment with saline waters is of about 150 MBq per day.**

SUMMARY

The purification station in Piast Colliery is a unique, first underground installation for the removal of radium isotopes from saline waters. Therefore no experiences, concerning construction, exploitation and management, have been known.

Implementation of the method of purification of radium bearing waters in 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. Also the proper organisation of the transport of poisonous sorbent from the surface to the chamber in case of operating coal mine was very important. On the other hand, observations and experience gathered during the implementation of the method will be fruitful in the future, for the planning and improvement of similar systems in other coal mines.

During start-up of the installation in Piast Colliery good results of purification were reached after very short time. The most important effect of the purification is almost complete removal of radium from cumulative waters at level 650 meters – the effectiveness of the method is over 95%. Till the end of June 1999, the concentration of radium isotopes in outflow from the system decreased below 0.7 kBq/m^3. Of course, sometimes we found higher values of radium in these waters, but such variability at the very previous stage of implementation was predicted. We think, that in the future the average value of radium concentration will be even lower.

The ecological effect of the purification is also important. On the surface, at the inflow of saline waters into the settling pond as well as at the outflow from that pond, concentrations of radium isotopes are approximately 60-65% lower as in the previous period, before purification. It corresponds to the decrease of about 60 MBq for ^{226}Ra and 90 MBq for isotope ^{228}Ra of daily release from Piast Mine. It means, that the total amount of radium, discharged into Gostynka and Vistula is much lower, by value150 MBq/day.

To achieve the complete purification of mine waters in Piast Colliery, removal of radium isotopes from waters at level 500 meters must be done. We would like to use for this purpose the existing installation in the nearest future, at first for waters with highest concentrations of radium, later on for all radium-bearing waters from that horizon.

Full ecological effect would be reached in case of purification of radium-bearing waters type B from two other coal mines – Czeczott and Ziemowit. We are going to purify all these waters in Piast Mine, therefore the underground system of water transport must be build at first. Moreover, several additional settling galleries must be excavate. But the purification of saline waters from all these mines will solve the problem of the contamination of small tributaries of Vistula river. Laboratory experiments and field tests in Czeczott and Ziemowit mines proved the possibility of application of the same method of purification.

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Acid mine drainage as an important mechanism of natural radiation enhancement in mining areas

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Abstract. Acid mine drainage (AMD) is a world wide problem that occur whenever sulfidic material is present in association to the mined ore. The acidic waters generated by the process of sulfide minerals oxidation can mobilize important amounts of pollutants and cause significant environmental impacts. The composition of the drainage will depend, on a very large extent, on the mineralogy of the rocks. The purpose of this paper is to demonstrate that acid mine drainage has the potential to enhance the natural levels of environmental radioactivity. The paper revises some strategies to be used in the diagnostic of the problem. General mathematical formulations that can assist on the prediction of the duration of the problem, and the definition of the size of the oxidizing zones in a waste dump are given. A study case on a waste dump of the Poços de Caldas Uranium Mining Site, Brazil is also presented.

1. INTRODUCTION

In several mining sites around the world, the presence of oxidising sulfides in waste rock and in the tailings is the cause of most important potential environmental problem. Oxidation products can include hydrogen sulfide, partially oxidized oxianions, such as thiosulphate and polythionates, iron sulfate in solution, elemental sulfur, various jarosite compounds, sulfuric acid, and heavy metals [1]. Radionuclides are recognized as being of concern when uranium ore is mined. Several works have reported the occurrence of acid mine drainage in uranium mining site [1,2,3]. Two of the most famous mining sites to present this problem are the Rum Jungle Mining Site in Australia and the Poços de Caldas Mining Site in Brazil. However, the presence of radioisotopes in acid mine drainage may also be of relevance in non-uranium mining sites, specially when uranium occurs in higher concentrations than the average concentration generally found in the crust. Any acid formed from pyrite oxidation will, to some extent, react with other gangue minerals within the solid sample. The basic reaction to be considered is:

$\mathbf{FeS_2 + 7/O_2 + H_2O \Leftrightarrow FeSO_4 + H_2SO_4}$ (equation 1)

The composition of the resulting solution will be dependent on the other minerals present in the rock (or tailings). Some examples are:

- $CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$ (calcite dissolution)
- $CaMg(CO_3) + 2H_2SO_4 \rightarrow CaSO_4 + MgSO_4 + 2\ H_2O + 2CO_2$ (dolomite dissolution)
- $Kal[AlSi_3O_{10}](OH)_2 + H^+ + 3/2\ H_2O \rightarrow K^+ + Al_2Si_2O_5(OH)_4\ (s)$ (muscovite dissolution)
- $KalSi_3O_8(s) + H^+ + 9/2\ H_2O \rightarrow K^+ + 2\ H_4SiO_4 + ½\ Al_2Si_2O_5(OH)_4\ (s)$ (K-feldspar dissolution)

The rate of dissolution of the minerals and, ultimately, the composition of the drainage will be controlled by a series of kinetic and equilibrium reactions.

There are other points to be considered. These waters can not be released into the open environment because of the low pH. Treatment of these waters generally involves their neutralization with lime, aiming to increase the pH to something around 7.0. Due to the amount of pollutants present in the drainage, a highly contaminated sludge will be formed. This material will need to be disposed off with some care because it may pose undue health risks to the members of the general public.

2. PREDICTING THE OCCURRENCE OF ACID MINE DRAINAGE

It has already been demonstrated that acid mine drainage may mobilize and introduce in the environment significant amount of radionuclides. The first step to be achieved then is to predict the occurrence of acid mine drainage and assess the load of pollutants involved on the process.

The first step in assessing the acid forming potential of a mining site is to carry out an acid-base account on various samples. In essence, this involves static laboratory procedures that evaluate the balance between acid generation processes (oxidation of sulfide minerals) and acid neutralizing processes (dissolution of alkaline carbonates, displacement of exchangeable bases, and weathering of silicates). The values arising from the acid-base account are referred to as maximum potential acidity (MPA) and acid neutralizing capacity (ANC), respectively. The difference between the MPA and ANC values is referred to as the net acid producing potential (NAPP). The following procedures are suggested in order to investigate the potential for acid generation [4]:

- pH and electrical conductivity (EC): measured on water extract (1:2, solid:water) after 24 hours;
- Total sulfur content of solids;
- Acid neutralizing capacity (ANC) of solids: determined by the addition of acid to a known weight of sample, then tritation with NaOH to determine the amount of residual acid;
- Net Acid Producing Potential (NAPP) of solids: calculated from the total sulfur and ANC results;
- Net Acid Generation (NAG) of solids: determined by the hydrogen peroxide oxidation method;
- Kinetic (or monitored) net acid generation (NAG) tests: determined by the hydrogen peroxide oxidation method with reaction kinetic monitored by continuous recording of pH and temperature. After reaction, the NAG liquor is filtered (0.45 um), being sub-samples analyzed for acidity, multi-elements, and radionuclides;
- Multi-element composition of solid: determined directly using a combination of ICP-mass spectroscopy (ICP-MS), ICP-optical spectroscopy (OES), atomic absorption spectrometry (AAS) and radiochemical analysis.

3. THE GLOBAL OXIDATION RATE (GOR) AND THE INTRINSIC OXIDATION RATE (IOR)

The Global Oxygen Consumption Rate (GOR) in a waste rock dump can be equated to the oxygen flux through the surface of the dump if the gas transport can be considered one-dimensional. The total oxidation rate, in units of $kg(O_2)s^{-1}$, can be found by integrating the GOR over the total surface area of the dump. An additional step is the evaluation of the Intrinsic Oxidation Rate (IOR). The IOR is simply the rate of consumption of oxygen by the material in the waste under the conditions that apply to that material. The most practical units to use are $kg(O_2)m^{-3}.s^{-1}$. The IOR depends on a number of parameters such as temperature, particle size distribution, physical form of pyrite, Eh, pH, Fe3+/Fe2+ ratio and the bacterial ecology and numbers. The GOR can be related to IOR by means of equation 2 [5].

GOR = IOR * L (equation 2)
Where, L is the average height of the dump.
Ideally, oxidation is initially confined to an upper discreet zone in the dump. There would be no oxidation below this region because oxygen entering from above is consumed by this upper zone of sulphidic material. The extent of this region may be calculated by means of equation 3 [5]:

$\mathbf{X = (2*D*C_o/IOR)^{1/2}}$ (equation 3)
Where X = extent of the region of oxygen consumption (m), D = diffusion coefficient of O_2 in the dump ($m^2.s^{-1}$), and C_o = oxygen density in air ($kg.m^{-3}$).
The time that would be necessary for the whole oxidation of the pyritic material in the dump can be calculated by means of equation 4 [5]:

$\mathbf{T = (E*d_{rs}*L^2)/(2*C_o*D)}$ (equation 4)
Where, E = mass of oxygen used per mass of sulfur consumed, and d_{rs} = bulk sulfur density.
The time involved on the duration of acid mine drainage generation may vary. However, it is likely to be about hundreds of years. This implies on the fact that if the problem is detected and, in the case that it already exists in a determined site, permanent remedial actions will have to be adopted.

4. A STUDY CASE ON THE URANIUM MINING SITE OF POÇOS DE CALDAS AND IMPLICATIONS TO OTHER NON-URANIUM MINING SITES

Mining operations at the mining site of Poços de Caldas (Brazil), gave rise to two major waste rock piles – WRP 4 and 8. The first will be object of this study since all the drainage from the pile is collected in a holding pond. Table 1 shows the average concentrations of some pollutants in the drainage from WRP-4.

Table 1. Average, Maximum and Minimum Concentrations of Pollutants in the Acid Drainage of WRP-4 (n=21)

Pollutant	Mean	Minimum	Maximum
^{226}Ra (Bq/L)	0.29	0.14	0.58
^{238}U (Bq/L)	175	71	315
Al (mg/L)	96	61	161
F (mg/L)	99	5.1	167
Mn (mg/L)	75	6.6	105
pH	3.30	2.9	3.7

The most significant observation that can be made from the values in Table 1 is the disequilibrium between ^{226}Ra and ^{238}U giving a Ra/U ratio of 0.0017. This can be explained by the fact that radium (co) precipitates with Ca/$BaSO_4$ formed in the process of the gangue dissolution. Table 2 shows the result from a column leaching experiment carried out with rocks from WRP-4. A pilot column 1 m high and 0.5 m in internal diameter was filled with rock collected in the waste rock deposit area. Distilled water was introduced at the top of the column at a rate intended to reproduce the local rainfall records. Water samples were collected daily and analyzed for the relevant natural radionuclides. Three sub-samples of the material in the column were taken for total analysis of radionuclides before and after the leaching process. The solid material was homogenized and submitted to total digestion in Teflon containers with a mixture of HNO_3/HF/$HClO_4$.

Table 2. Radionuclide Activity Concentration in the Solid Material in the Column Before and After the Leaching Experiment

Sample	^{238}U	^{234}U	^{230}Th	^{226}Ra	^{210}Pb	^{210}Po
Before	4,203	4,090	4,066	5,845	5,120	6,600
After	1,633	1,570	2,273	4,660	4,223	5,236
Ratio	0.38	0.38	0.55	0.79	0.82	0.79

The results show clearly that uranium isotopes are leached at the same extent, while ^{230}Th occupies an intermediate position and Ra, Pb and Po are leached in a lesser extent. It can also be observed that disequilibrium already exists in the rock before the leaching experiment and is reflected in the WRP drainage

It is reported by the mining operator that 8.9×10^5 m^{-3} of acidic waters are pumped annually from the holding pond that collects the drainage from WRP-4. The average sulfate concentration in the drainage is 1,010 mg/L. It can be estimated that 9.0×10^5 $kg(SO_4)a^{-1}$ are produced as a result of pyrite oxidation in the WRP. The oxygen consumption rate can be readily related to a sulfate generation rate by means of equation 1. The GOR in the waste rock pile can be equated to the oxygen flux through the surface of the pile if the gas transport can be considered one-dimensional. As a result, the total oxidation rate can be found by integrating the GOR over the total surface of the dump (56.9×10^4 m^2). For the present case the GOR can be assumed as equal to 2.9×10^{-8} $kg(O_2)m^{-2}.s^{-1}$. The IOR can be calculated by means of equation 2. A value equal to 1.3×10^{-9} $kg(O_2)m^{-3}.s^{-1}$ is obtained. This value is a typical low rate one, generally found in waste rock dumps [5]. The oxidizing region can be estimated by means of equation 3. The calculate value of X is 45 m. Taking into account that the pile height is about 90 m, two oxidizing regions may be imposed to the system. The time that would be necessary for the whole oxidation of the pyritic material in the dump can be calculated by means of equation 4. It can be pointed out that more than 1,000 years will be necessary for the consumption of all the pyritic material in the dump. This is quite a long time and will impose the application of permanent remedial actions.

Presently, the acid drainage is treated with lime. Table 3 shows the results of radioisotope concentrations in the sludge, resulting from the neutralization of acid waste rock drainage.

Table 3. Radioisotope Activity Concentrations in the Sludge of the Poços de Caldas Uranium Mining Site Acid Waste Rock Treatment (Bq/kg)

^{238}U	^{226}Ra	^{210}Pb	^{232}Th	^{228}Ra
14,350 +/- 7,875	370 +/- 245	384 +/- 671	371 +/- 444	579 +/- 1,877

The uranium concentration is two orders of magnitude higher than the other radionuclides and shows a correlation with the disequilibrium reported for the acid drainage itself as reported in table1.

The origin of the water collected in the holding pond (and subsequently pumped to the treatment unit) is the rainfall infiltration through the dump and the water infiltration through the toe of the dump (the dump is placed in an ancient river course). It has been demonstrated that it will take more than 1,000 years for the pyritic material in the dump be fully oxidized. Since the drainage collected in the holding pond is maintained basically by natural processes, there is no reason to believe that the water balance will be changed in the future. It can be estimated that 12 t/year of ^{238}U and 2.44 x 10^{10} Bq/year of ^{226}Ra will be produced annually by the chemical treatment of these drainage. Taking into account that this treatment is being undertaken for more 10 years, it can be estimated that, at least, 120 t $^{238}{}_{U}$ and 2.4 x 10^{11} Bq$^{226}{}_{Ra}$ have already been produced as a consequence of the treatment of acid drainage from the WRP-4. These figures correspond respectively to 34% and 5% of the total amount of ^{238}U and ^{226}Ra deposited at the tailings dam of Poços de Caldas Mining Site. If a tailings dam deserve a lot of attention in terms of commissioning and closeout strategies in terms of radiation protection issues, there is no reason to accept that a different approach shall be used for the proper management of this sludge.

In two mining sites investigated in the project reported in [6], a gold and a coal mining site, ^{238}U uranium concentrations in the acid mine drainage from both installations were respectively equal to 30 and 100 Bq/L. The last value is quite similar to the average ^{238}U concentration observed in the acid drainage of the uranium mining site of Poços de Caldas. The explanation for that may rely on the fact that, despite the higher ^{238}U concentrations in the waste rock of Poços de Caldas Mining Site, it may occur in a less mobile state in comparison to what is observed in the Pyritic Waste Piles of the coal mine. Moreover, pyrite concentration in the spoils from the coal mine is about 20% while in the Poços de Caldas waste rock piles the average pyrite concentration is ten times lower (say 2%). The conclusion on this issue is that sludge from non-uranium mining sites may have significant amounts of radionuclides. As a result, it is mandatory that this material needs to be disposed off with care. Moreover, in some cases, as it happens in the Gold Mining Site of Jacobina (countryside of Brazil), the lack of a regular water supply (the mining site is located at a very dry region with precipitation records bellow 500 mm/year) makes the inhabitants use any available water. Thus, direct consumption of water with elevated levels of radionuclide concentrations shall not be disregarded at all.

5. REMEDIATION AND OVERALL STARTEGY TO DEAL WITH THE PROBLEM

It has been demonstrated above that, acid mine drainage may lead to the enhancement of natural radiation in the environment. It has also been reported some general actions that may be used to predict the occurrence of acid drainage resulting from mining operations; to predict the extension of oxidizing regions in waste rock piles and to estimate the duration of the process. These strategies are useful in predicting the occurrence of the problem and are very helpful in the planning of the overall management strategies. However, the remediation of existing sites needs also to be addressed.

In a general way, it can be considered that a dump already formed has an inert cover (maybe a capping layer) over it. Figure 1 summarizes a series of process occurring in the waste dump environment. Initially, oxygen will diffuse through the capping layer and react with the uppermost layer of rock. Oxygen penetration into the rock will depend on the thickness of the cap, the values of the diffusion coefficients and the intrinsic reaction rate. It can be assumed that an oxidation zone will be established; above the top of the zone there will be no reactive sulfur and below the zone the oxygen concentration will be zero. Within the zone, oxidation will proceed at uniform rate until sulfur is consumed, which will happen at the same time at all points in the zone. The oxygen will then diffuse through this newly created inert zone and establish a new oxidation zone, taking a negligible time to reach a new equilibrium. As this process repeat itself the inert or depleted layer will increase in thickness, being a sum of a series of former oxidation zones.

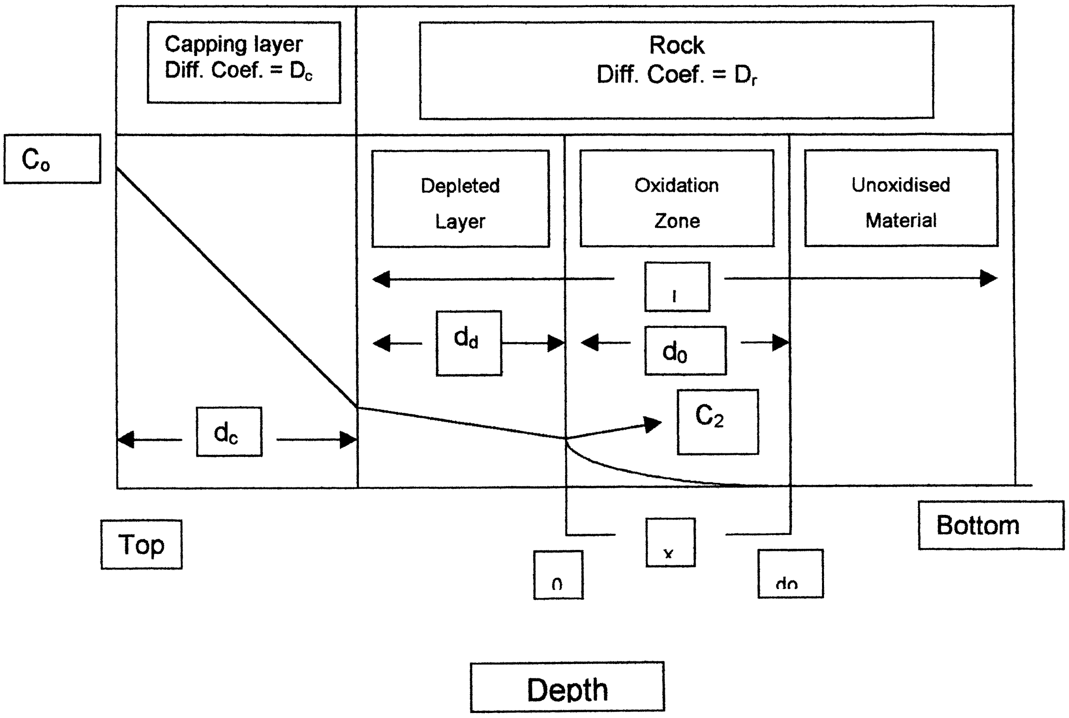

Figure 1. Schematic representation of the oxidation process in a waste rock dump.

A general strategy in the permanent remediation of a waste rock dump is the covering with a material presenting a low oxygen diffusion coefficient. It is reported that the reduction factor will depend much more on the properties of the covering layer than on the properties of the dump forming material (this include the IOR). The practical problem to be solved is to design an appropriate cover and guarantee the cover integrity along the time.

A cover of an inert material of X_c thickness and oxygen diffusion coefficient D_c generates the equation 5 [5]:

$$\mathbf{GOR = (2C_0D^*IOR)^{1/2}\,((a + n)^{1/2} - (a + n-1)^{1/2})} \text{ (equation 5).}$$

Where $a = (X_c/D_c)^2\,((IOR^*D)/2C_0)$.

This equation has been applied to the WRP-4 of the Poços de Caldas Uranium Mining Site. The composition of the drainage was simulated for three different cover thickness (0,5; 1,0 and 2,0 m) of varying oxygen diffusion coefficients (1.0×10^{-8}; 1.0×10^{-9} and 1.0×10^{-10} $m^2.s^{-1}$). The obtained results are shown in table 4. It can be seen that the best option relies between the options 4 and 5. From this stage on there will be no gain of effectiveness of the remediation applied.

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Review of Electret ion chamber technology for measuring technologically enhanced natural radioactivity

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Abstract. Electret ion chamber (EIC) is a passive integrating ionization chamber used extensively for measuring technologically enhanced radioactivity. Commercially available electret ion chambers called [1]E-PERM® (Electret-Passive Environmental Radiation Monitors) electret ion chambers are relatively new and are in use only from the past 10 years. The EIC consists of a stable electret (electrically charged Teflon disc) mounted inside an electrically conducting chamber. The electret serves both as a source of the electric field and as a sensor. The ions produced inside the chamber are collected by the electret. The reduction in charge of the electret is related to total ionization during the period of exposure. This charge reduction is measured using a battery operated electret reader. Using appropriate calibration factors and the exposure time, the desired parameters such as radon concentration in air is calculated. These low cost monitors require neither power nor battery and several hundreds of these can be used simultaneously and serviced by one reader. These monitors do not provide on line readings, but provide an average value over a period of time. The EICs have been used for measuring: (a) indoor and outdoor radon, (b) thoron, (c) dissolved radon and radium in water, (d) environmental gamma, (e) radon emanating radon concentration in soil samples and in pipes, (f) radon flux from surfaces and building materials. The purpose of this paper is to describe these methods and give selected reference to the related publications for more detailed reading.

1. INTRODUCTION

Electret ion chambers (EIC), commercially available under trade name E-PERM ®, are extensively used for characterizing technologically enhanced radiation. Such applications include:

(a) Indoor and outdoor radon
(b) Thoron
(c) Dissolved radon and radium in water
(d) Environmental gamma
(e) Radon emanating radon concentration in soil samples and in pipes
(f) Radon flux from surfaces and building materials

These are extensively used because of several practical advantages. The purpose of this paper is to describe these methods and give selected references to the related publications for more detailed reading.

2. ELECTRET ION CHAMBERS-HOW DO THESE WORK?

Electret ion chambers (1) consists of a stable electret (electrically charged Teflon® disc) mounted inside an electrically conducting chamber. The electret serves both as a source of the electric field and as a sensor. The ions produced inside the chamber by radiation are collected by the electret. The reduction in charge of the electret is related to total ionization

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[1] E-PERM® is a trade name for the Electret Ion Chambers manufactured by Rad Elec Inc., 5714-C Industry Lane, Frederick, MD 21704 USA

during the period of exposure. This charge reduction is measured using a battery operated electret reader. Using appropriate calibration factors and the exposure time, the desired parameters such as airborne radon concentration in air is calculated using hand held pocket computer with suitable software. **Figure 1** gives a photograph of electret, chambers and the electret reader. The scientific bases for the performance EIC are:

(1) The change in charge on the surface of the electret is caused only by the collection of ions and no other processes
(2) The change in charge on the surface of the electret after the collection of ions is permanent
(3) The charge on the surface of the electret is measured by a non-destructive method.

Figure 1. Components of electret ion chambers. Electret, chamber and reader.

These features make the EIC, a true integrating device. These low cost monitors require neither power nor battery and several hundreds of these can be used simultaneously and serviced by one reader. Normally encountered temperatures, humidities and mechanical shocks do not affect the performance of these monitors, making them robust for field use. Further, the method is purely a physical method and does not depend upon the chemical absorption of gases being measured or does it involve chemical processing.

Basic portable EIC System consists of:
(1) Several electrets
(2) Several chambers
(3) One electret voltage reader
(4) Data analysis tool

The electret is used and reused until the surface voltage falls too low (less than 200 volts) to collect the ions produced in the volume of the chamber. This feature provides multiple use of the same electret.

The data sets needed for analyzing the results are:

(1) The initial reading of the electret
(2) The final reading of the electret
(3) The exposure time

3. INDOOR AND OUTDOOR RADON IN AIR

Most popular application of EIC device is in measuring indoor and outdoor radon concentration (2,3).

A typical radon monitor has a mechanical arrangement, shown in **Figure 2**, for opening and closing the electret from outside the monitor chamber. This feature allows flexibility of reading the electret in the laboratory. Following steps need to be done for making a measurements:

Take initial reading of the electret in the laboratory
Load the electret into the chamber
Turn the E-PERM to off position
Transport E-PERM to the place of measurement
Turn the E-PERM to on position
Continue exposure for desired length of time
Turn the E-PERM to off position
Transport to the laboratory
Unscrew the electret and take final reading of the electret
Electret can be left inside the chamber in off position or screwed back into the storage cap.
Use the data, initial reading, final reading, and exposure time for calculating radon concentration.

For certain chambers which do not have on-off mechanism, electret has to be loaded and unloaded at the place of exposure.

Corrections are applied for gamma background. If the gamma background is not known corrections are applied using 100 nGy/h as the background.

These have some similarity with alpha track (AT) detectors. In alpha track detectors, alpha particles from radon hit the special plastic and create a defect that will become visible when chemically processed. The number of tracks formed in the plastic over a time is related to integrated radon concentration over that period. In EIC, ions produced by alpha particles from radon are collected by electrets. The change in charge of the electret over a time is related to the integrated radon concentration over that time. Unlike alpha track detectors, no chemical processing is needed for EIC. Change in charge can be read rapidly, in seconds. Being a non-destructive mode of analysis, it is possible to take intermediate readings and continue the measurement. This is a distinct advantage over AT radon monitors.

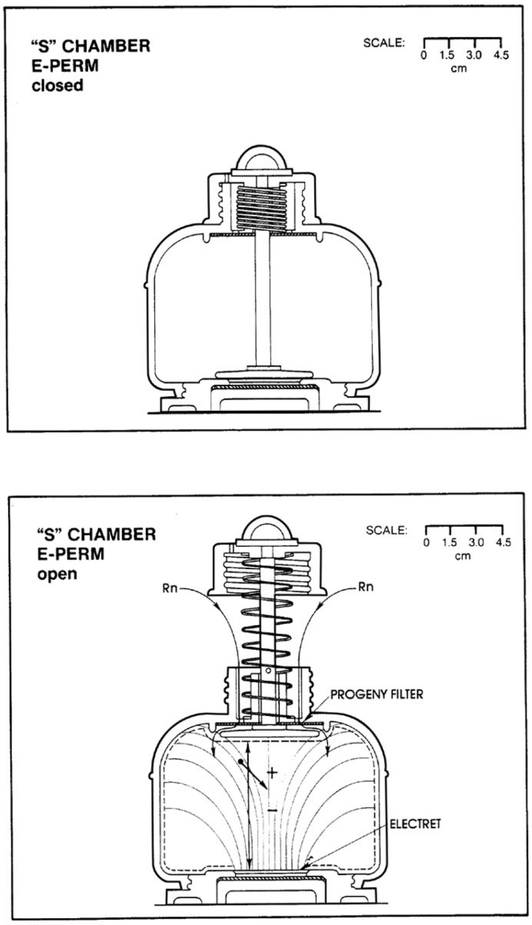

Figure 2. Radon Monitor with on/off mechanism. In closed position, ions do not reach electret. In open position ions discharge electrets.

The sensitivity is controlled by using electrets of different sensitivities and also by using chambers of different volume. Using different combination it is possible to measure radon concentrations ranging from 50 Bq m^{-3} to 3 million Bq m^{-3}.

These monitors are widely used and have performed well in the national and international inter-comparison exercise (4).

These have sufficient sensitivity to measure ambient radon concentration, provided the E-PERM is exposed for sufficient exposure period. United States Environmental Protection Agency used SST (S chamber with short-term electret) E-PERMs for their National Ambient Radon Project (5,6), and made 3-monthly average measurements.

4. THORON IN AIR

E-PERM® passive integrating electret ionization chamber for measuring radon in air has a restricted filtered passive access to radon (^{222}Rn). Area to volume ratio of access is designed to allow sufficient delay to decay ^{220}Rn effectively and respond only to radon (^{222}Rn) and not to thoron (^{220}Rn). A modified unit called thoron monitor, with unrestricted access to radon and thoron responds to both radon and thoron. Radon monitor and thoron monitor when used side by side allows measurement of both radon and thoron concentration in air. Such monitors were calibrated in a well-characterized thoron test chamber maintained by Canadian Mining Institute (CANMET). More details of this and the equations to be used for computing both radon and thoron concentrations are given by Kotrappa **(7). Figure 3** gives schematic of such chambers. These performed well in recent inter-comparison exercise at US Department of Energy thoron tests.

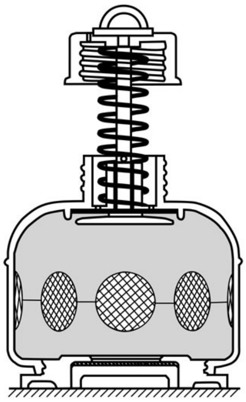

Figure 3. Thoron monitor.

5. DISSOLVED RADON IN WATER

This method belongs to the general class of “de-emanation method” of measuring dissolved radon in water. A small water sample is placed in the bottom of a glass jar. An E-PERM® is suspended in the air phase above the water. The lid of the flask is closed and sealed to make it radon-tight. Radon reaches equilibrium between the water and air phase. At the end of the desired exposure period, the flask is opened and the E-PERM® removed. The average radon concentration in the air phase is calculated using the standard E-PERM® procedure. A calculation using this air concentration in conjunction with the other parameters gives the radon concentration of the water. Kotrappa and Jester (8) give details on the theoretical basis for this method. Paper also evaluates the results of the measurements done with electret ion chambers and with liquid scintillation method on the same samples. **Figure 4** gives a schematic of the measurement arrangement.

For measuring very low levels of radon in water, slightly different method is used. The detector is immersed in the body of the water, after sealing it in a thin polyethethelene bag (9). Equilibrium gets established between radon in water and in air phase of the detector. Measuring radon concentration and using appropriate partition coefficients, it is possible to calculate the radon concentration in water.

6. DISSOLVED RADIUM (^{226} Ra) IN WATER

The arrangement used for measuring radon in water can also be used for a quantitative measurement of radium in water. Using equations that take into account build up and decay of radon emanated from radium in the sample, the integrated average radon concentration as measured by E-PERM radon monitor over a time is used to calculate the radium concentration in water. The immersion method increases the sensitivity by a factor of five from 5 pCi/L(0.18 Bq/L) to (0.036 Bq/L) (9).

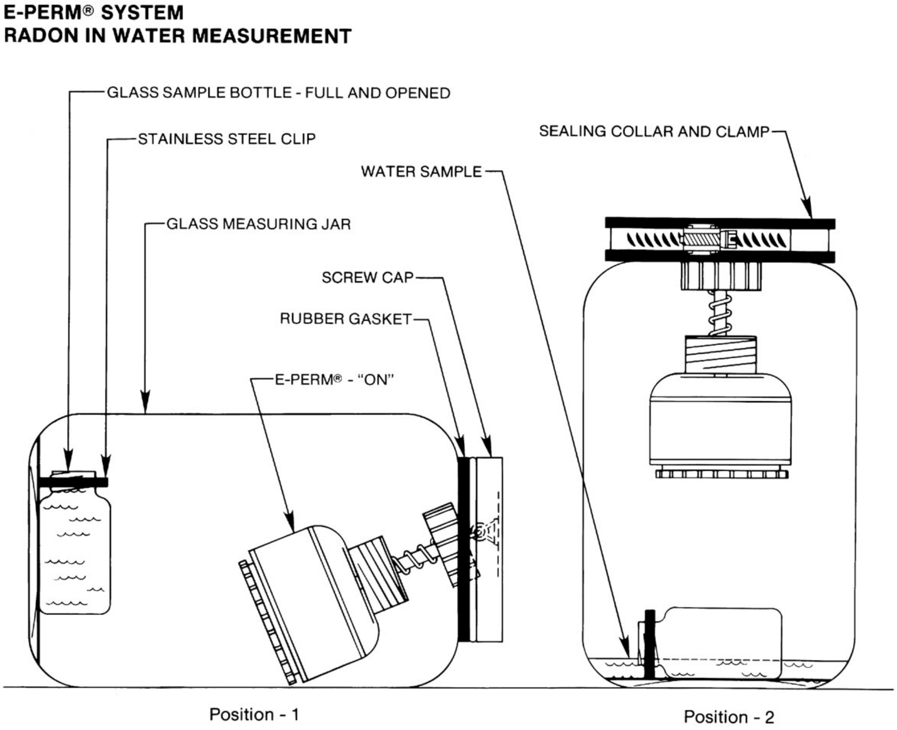

Figure 4. Schematic for measuring radon in water.

7. RADON EMANATING RADIUM CONCENTRATION IN SOIL AND RADIUM IN PIPES

By taking a sample of soil or other materials in the place of water in the arrangements used for measuring radon in water, it is possible to calculate radon-emanating radium in soil sample. Using equations that take into account build up and decay of radon emanated from radium in the sample, the integrated average radon concentration as measured by E-PERM radon monitor over a time is used to calculate the radon emanating radium concentration in the sample. Several investigators have successfully used this method (10, 11). Figure 5 gives schematic of the arrangement. Same principle can be used for measuring radium inside the pipes. Enclose an E-PERM inside the pipe, seal both ends of the pipe, and expose the detector for a known period. The data on the radon concentration, the exposure time and the volume of the pipe is used to calculate radon emanating radium concentration. If emanation coefficient is known, it is possible to calculate gross radium concentration.

8. E-PERM® RADON MONITORS FOR MEASURING UNDISTURBED RADON FLUX

The measurement of radon flux from the ground or other surfaces is useful for determining the (a) radon emanating potential of a building site, (b) to meet the regulatory requirements for uranium mill tailings or phosphate tailings or gypsum stacks, and to determine the radon flux from test materials such as bricks and other surfaces.

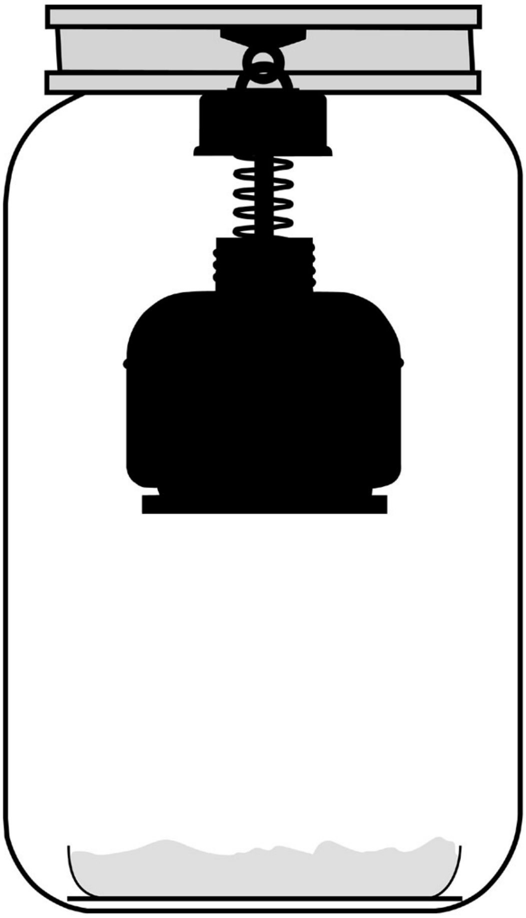

Figure 5. Schematic for measuring radium in soil sample.

8.1.Passive method

A large, one-liter hemisphere with a large, carbon coated Tyvek$^{(R)}$ diffusion window, allows radon to get into the chamber volume. Filtered outlets vent the chamber so that it will not accumulate radon (Figure 6). When the E-PERM® flux monitor is placed on radon emanating surface, the radon enters through the Tyvek® barrier and exits through the vents. The semi-equilibrium radon concentration established inside the chamber is representative of dynamic flux from the surface. Because of the equilibrium between the ground and outside environment through vents, the flux emanation from the ground is not disturbed. The electret discharge rate of the electret is a measure of the radon flux. E-PERM® flux monitors are calibrated on the well-characterized radon flux beds at CANMET (Canada). These flux beds consist of ^{226}Ra bearing material (well-characterized uranium tailings) 5.5 cm thick and 5 meter in diameter. The bed is precisely characterized by CANMET* to provide a radon flux of 7.7 pCi m^{-2} sec^{-1} (0.285 Bq m^{-2} sec^{-1}).

Details of the methods are described in a published papers (12,13) describe the comparative evaluation of the flux measured by electret ion chamber method and by other base line technologies that uses large area charcoal detector method on the same measurement area.

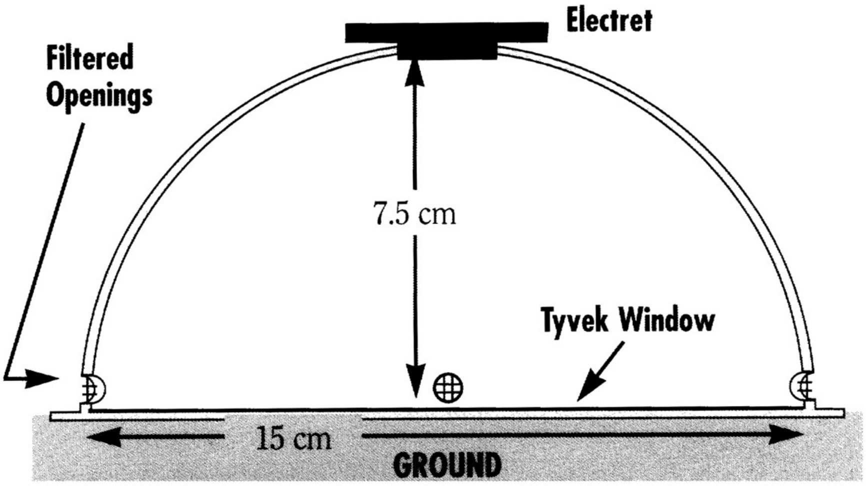

Figure 6. Schematic of passive radon flux monitor.

8.2. Dynamic method

A rectangular enclosure is placed on the ground where radon flux has to be measured. Establish a steady known air flow. Quickly, a steady radon concentration is reached inside the enclosure that depends upon the radon flux, flow rate and the area of ground in the enclosure. By measuring the radon concentration inside the enclosure using E-PERMs it is possible to calculate radon flux from first principles.

9. ENVIRONMENTAL GAMMA

The EICs are ionization chambers and respond to any ionizing radiation including gamma radiation. The radon monitors can be used as gamma monitors, if sealed inside a radon leak tight bags, such as Mylar bags, which prevent the entry of radon into the sensitive volume of the chamber. The E-PERM is made of materials that are near tissue equivalent and therefore do not have energy dependence. It makes correct gamma measurements irrespective of the energy of the gamma radiation. Once it is calibrated properly using a standard source of any particular energy such as Cs-137, it can be used for a true measurement of gamma radiation of any energy or a combination of different energies.

Even though the respective national authorities have published an average level of natural gamma radiation, there can be some isolated spots of higher dose rates, from the technologically enhanced sources such as those from granites and refractory materials used in the construction of buildings. Other sources could be the storage yards of pipes and other accessories used in mining/petroleum industry. Another source could be an operating Nuclear Power Plant or other nuclear facility.

These are usable wherever TLD (thermo-luminescent dosimeters), but provide a tissue equivalent and energy independent response. These are widely used for perimeter monitoring of nuclear facilities (14,15).

10. DISCUSSIONS AND CONCLUSIONS

The E-PERM® Electret ion chamber technology is an integrated method providing capability of measuring several diverse technologically enhanced sources of radiation. It is important to note that you use the same sensors and same reader, whether you are measuring radioactive gases or radiation. This unified approach saves money and training needed. It is not surprising that this is one of the most popular methods for indoors and workplace radon monitoring in USA and in several other countries in Europe. The E-PERM System manual (16) gives exhaustive description of all the applications in one place.

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GE detectors calibration procedure at IRD/CNEN for in situ measurement

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Abstract. A methodology for germanium detector's gamma spectrum unfolding has been established and implemented at the Institute for Radioprotection and Dosimetry — IRD (CNEN/Brazil) for environmental gamma fluency determination and, consequently, the energy distribution of the air kerma. It consists of calibration procedure and a computer code for data handling. A calibrated germanium detector was taken to outdoors large radioactive concrete sources of 3 m diameter at IRD, with known radiation fields for validation.

1. INTRODUCTION

Rapid methods for the determination of radioactivity in the environment are needed, specially after an accidental release of radionuclides or surveys over large areas. Gamma ray spectrometry, which is done *in situ*, is such a method, based on measurement of the spectral distribution of the photon fluence rate [1].

It is shown in the ICRP report 51 [2], that the effective dose and, consequently, the risk, varies with both the geometry and the energy of irradiation. When it is necessary to find ways to establish the energy distribution of the radiation field, gamma spectrometry using a high purity germanium detector is the only way to determine the spectra of a radiation field with high resolution. It enables the determination of the various radionuclides which contribute to the gamma dose.

Due to the various modes of gamma rays interaction and the various material surrounding the detector, even a monoenergetic gamma ray bean can lead to a complex detector's response function.

For fluence spectra determination, it is necessary to discard the area of the spectrum which represents partial photon interaction in the active and non active detector's volume and it's associated material. This is called "spectrum unfolding". The unfolding method used for the calculation is the matrix inversion described by Miller [3].

The detectors response can be determined either by measuring standard point sources, covering the energy range of interest, or by using Monte Carlo techniques to simulate both the detector and the radiation field [4,5,6,7,8,9,10]. The Electron Gamma Shower 4 (EGS4) computer code provides means to simulate gamma ray detectors and has been used for this work [11].

2. DESCRIPTION OF THE METHODOLOGY

2.1. Unfolding method

The direct result of a measurement with a germanium detector is a pulse-height distribution which represents the spectral distribution of energy deposition events in its active volume. The relation of the pulse height distribution and the photon fluence are described by the response function $R_V(E)$ of the detector. In general the response function $R_V(E)$ can be expressed as an integral:

$$R_V(E) = \int D_{E'}(E).G_V(E').dE' \tag{1}$$

where $R_V(E)$ is the probability of a photon with energy E originates a pulse of height V (response function), $D_{E'}(E)$ is the probability of a photon of energy E would deposit an energy E' in the detector crystal and $G_V(E')$ is a combination of efficiency, statistics and processing of data.

The procedure for spectrum unfolding is based on the photon fluency in energy and pulse height distribution relation given by:

$$MV = \int_0^{\infty} R_V(E).\Phi(E).dE \tag{2}$$

where M_V is the pulse height distribution and (E) is the gamma flux.

Equation (2) can be expressed as discrete energy bins as:

$$Mi = \sum_{j=1}^{n} R_{ij}.\Phi_j \qquad i = 1,2,3,\ldots,n \tag{3}$$

Using the matrix inversion method, it comes to:

$$\Phi j = \sum_{i=1}^{n} (R^{-1})_{ij}.M_{iV} \qquad j = 1,2,3,\ldots,n \tag{4}$$

2.2. Response function determination

Although the shape of the continuum is a function of the incident photon energy, it does not vary significantly for germanium detectors [3]. Starting from a monoenergetic source, the shape of the continuum can be determined by applying two step functions fit, one for the region below the Compton edge, and another for the region between the Compton edge and the incident photon energy. The two step functions represent the fractional contribution of the continuum in each band. It has been called f factors [4].

The count due to the continuum is correlated to the counts due to the total absorption events by the ratio of the total efficiency and the photopeak efficiency. This quantity is called r factors [4]. The total efficiency can be determined by shadow shield experiments.

2.3. Unfolding procedure

The spectrum from natural environmental radiation, after removal of the cosmic contribution, is divided in 10 keV bands, the unfolding starts from the highest energy band, which corresponds to the 2614 keV energy peak due to ^{208}Tl, because there is no contribution of partial absorption events from higher energies [4].

The continuum count due to the first band is calculated using the r factors. The contribution of this continuum in each region of the spectra is calculated using the f factors. The spectra can be cleaned out of this contribution by subtraction.

This procedure can be expressed by:

$$N_j^{esp} = N_j^{tot}.(r_j - 1) \qquad (5)$$

$$N' = N_i - N_j^{\exp}.f$$

where j and i are relative to the 10 keV and continuum bands respectively, N_j^{esp} is the continuum counts due to the partial absorption events of photons with energy relative to band j N_j^{tot} counts due to the total absorption events of photons with energy relative to band j, N_j and N_j’ counts in band i before and after subtraction of the partial absorption events.

2.4. Fluence determination and dose calculation

After the unfolding procedure, the fluence can be determined by the equation:

$$\Phi j = \frac{N'_j}{\varepsilon_j.t} \qquad (6)$$

where N'_j is the fluence, ε_j is the detection efficiency and t is the counting time.

Once the fluence is known, the dose, kerma or exposure can be calculated in function of the energy by using the proper equation. A subroutine calculates the gamma exposure rate in 10 keV intervals.

A computer code has been developed for computational gamma spectra analysis to calculate the contribution of the partial absorption events of the gamma rays (Compton effect) in the active and non-active regions of a germanium detector previously calibrated. The resulting total absorption spectrum is then converted to fluence distribution in function of the energy for the photons reaching the detector, which is then used to calculate the exposure rate or kerma in air in function of the energy [12].

3. CALIBRATION SET UP

The detector’s calibration measurements are done in a low scattering building at IRD, its dimensions are 7 m wide, 18 m long and 6 m tall, wooden walls with no ceiling and the roof is made of asbestos. The set up was mounted on a wooden mezzanine at 2.2 m above the floor and away from the walls, minimizing scattering even further.

In order to account for the scattering on the surroundings, the shadow shield technique is used to determine the spectrum due to the incident photons coming directly from the source, by counting with and without the shadow shield and subtracting one spectrum from the other. The position for the shadow shield, where there is a minimum scattering striking the detector, has been determined to be half way between the source and the detector. It is then possible to determine the total to photopeak efficiency ratio and the spectrum shape.

The racks for the components; source, shadow shield and detector; are made of polyethylene, also to minimize scattering. The racks are aligned by a rail system.

The point sources, shown in Table I, used for the detector’s calibration are positioned 1m away from de detector, to achieve a almost parallel flux and to minimize the influence of the effective detector’s center due to the energy of the incident photon.

The spectrum shape is determined by measuring the ^{54}Mn because of the single line emission; the photopeak efficiency curve is determined by measuring the ^{210}Pb, ^{241}Am, ^{109}Cd, ^{152}Eu, ^{137}Cs, ^{54}Mn and ^{88}Y to cover the hole range of energy of interest; the total to photopeak efficiency ratio curve is determined by measuring the ^{203}Hg, ^{113}Sn, ^{137}Cs e ^{54}Mn, and ^{60}Co sources because the curve is better determined with single line emitters; and ^{152}Eu is used for angular efficiency dependence because a single source provides.

Table I: Point gamma sources used for the detector's calibration

Isotope	Energy (keV)
^{210}Pb	46.5
^{241}Am	59,54
^{109}Cd	88,03
^{139}Ce	165,85
^{203}Hg	279,20
^{113}Sn	391
^{152}Eu	several
^{137}Cs	661,66
^{54}Mn	834,84
^{60}Co	1173,24; 1332,5
^{88}Y	1936

4. DETECTOR'S SIMULATION

This work used a portable p-type coaxial Ge detector of 5.55 cm diameter and 3.94 cm high with a relative efficiency of 20% when compared to the efficiency of a 7.6 X 7.6 cm NaI(Tl) crystal for the 1.33 MeV energy at 25 cm distance and a dead layer of 600 μm, according to the manufacturer, no information about the central well was given.

Based on the information available, it was developed a subroutine describing the detector structure, in great detail, and the photon source was implemented as point source, in order to reproduce the experimental calibration. The subroutine runs with the EGS4 computer code. Figure 1 shows a schematic representation of the simulated detector.

It was observed a important disagreement between the experimental results and the results obtained by simulation, for full absorption peak efficiency, when using the manufacture's data. However, the crystal outer surface can be considered to consist of a dead layer on the surface where no charge collection occurs and an underlying transition layer of increasing charge collection [13]. It was necessary to determine the real thickness of the transition layer and also determine the dimension of the inner crystal well.

It is possible to complete the information about the crystal by using two point sources: ^{241}Am, low energy emitter of 60 keV photons, and ^{137}Cs, middle energy emitter of 662 keV photons.

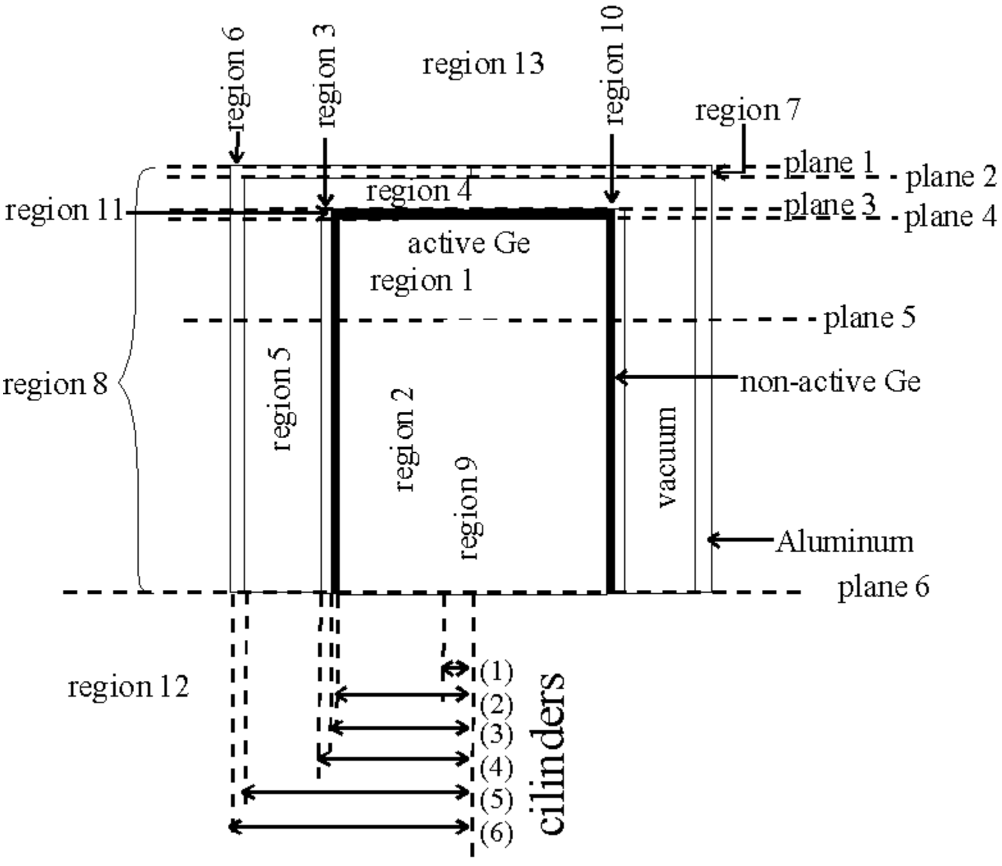

Figure 1. Schematic representation of the simulated germanium detector.

The ^{241}Am source is used for the determination of the inactive layer in the crystal. The well known source is first counted at a known distance from the front of the detector and the counting geometry is then simulated. Comparing both results, measured and simulated, and the thickness of the inactive layer is adjusted, in the simulation, to better match both results. The interactive process goes until the best agreement can be achieved. The same procedure is done for the side wall of the crystal.

The ^{137}Cs source is used for the determination of the dimensions of the inner well. The well known source is first counted at a known distance from the front of the detector and the counting geometry is then simulated. Comparing both results, measured and simulated, and the dimensions of the well is adjusted, in the simulation, to better match both results. The interactive process goes until the best agreement can be achieved. The same procedure is done for the side wall of the crystal.

At the end of the cycle, it starts all over again, each time a better refinement of the dimensions can be achieved, until the difference of the measured and simulated results are as closes as possible. For this work, the difference between the experimental and simulated results was under 3%.

5. VALIDATION

There is a radiometric calibration system at IRD consisting of eight radioactive concrete sources to simulate rock outcrops. The sources are of cylindrical shape with 3 m diameter and 0.5 m thickness weighing about 7.5 tons each. Uranium, thorium and potassium ores were added to the concrete under conditions to achieve perfect homogenization. 104 samples were taken and analysed by 8 laboratories. In addition, in situ radiometric grade determination were performed with calibrated instruments making for 2100 measurements. The sources are guaranteed to be homogene and well characterized [14]. There is also a 4 m diameter water pond for cosmic ray determination. The exposure rate due to the pads on contact have been calculate based on the potassium, uranium and thorium concentrations.

It is possible to simulate a gamma flux similar to the normally found in the environment with this calibration system.

The detector calibration methodology has been verified at the pads. Four pads were chosen: one pad made of potassium ore (pad K1), one made of thorium ore (pad Th1), one made of uranium ore (pad U1) and one made of a mixture of uranium and thorium ores (pad UTh1).

6. RESULTS

A 20% relative efficiency HPGe portable detector (EG&G ORTEC) has been calibrated both experimentally, at the setup described before, and theoretically, by simulation using Monte Carlo calculation. The intrinsic efficiency calibration curve for this detector is shown in Figure 2 and the total to peak efficiency ratio curve is shown in Figure 3, both results, experimentally and by simulation using Monte Carlo calculation, are presented.

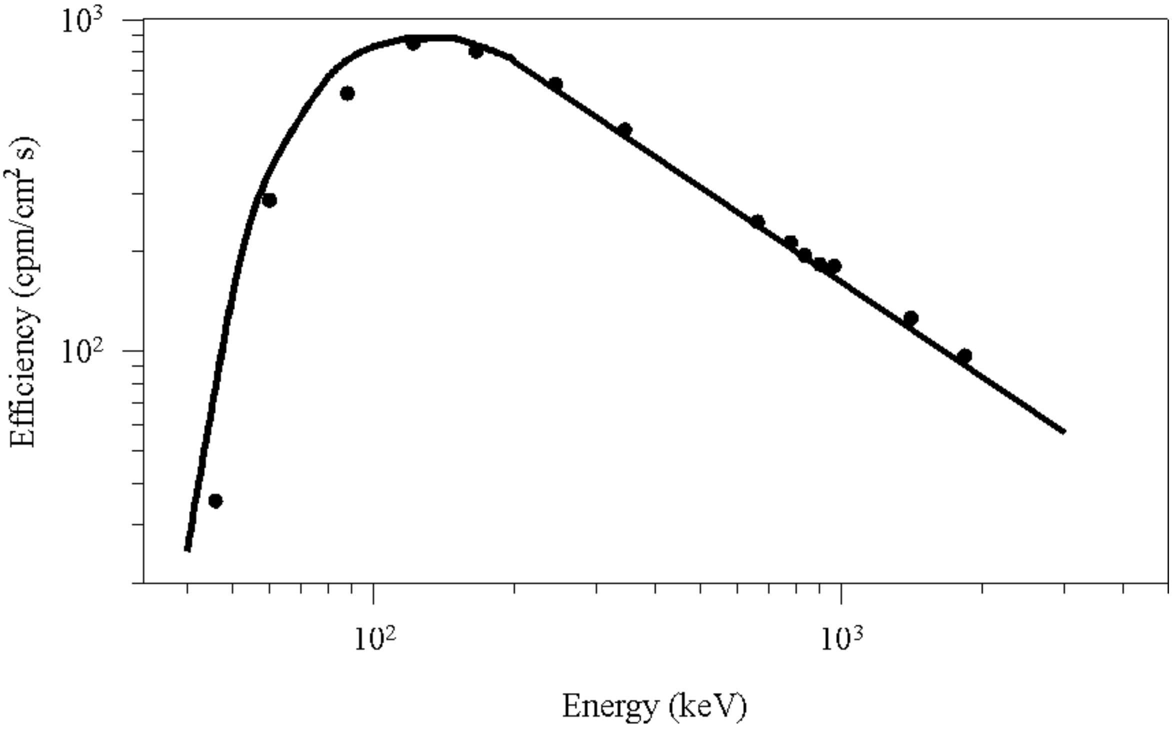

Figure 2. Intrinsic efficiency calibration curve for a 20% relative efficiency HPGe detector for point sources at 1m distance.

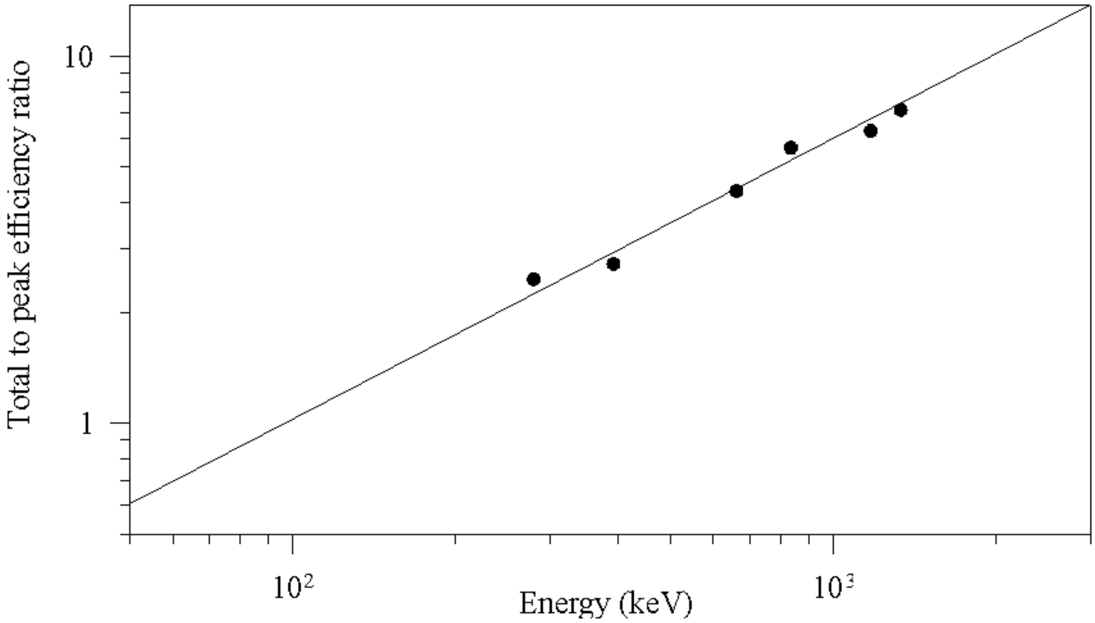

Figure 3. Total to peak efficiency ratio calibration curve for a 20% relative efficiency HPGe detector for point sources at 1m distance.

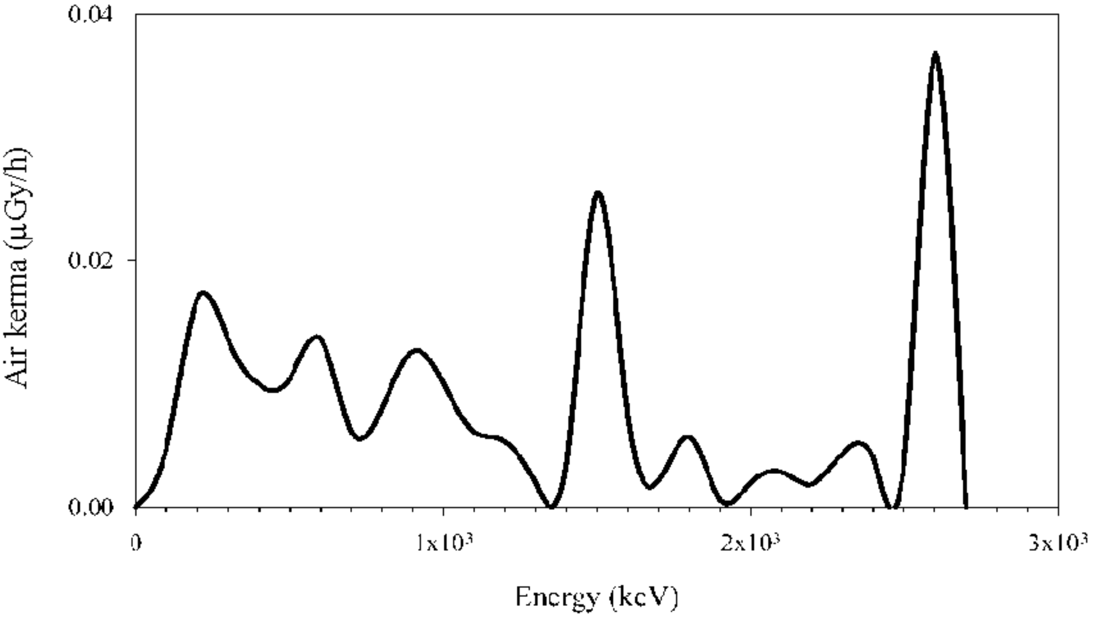

Figure 4. Plot of the variation of the air kerma rate in function of the energy, determined by gamma spectroscopy for the UTh1 pad, made of a mixture of uranium and thorium ores, for 100 keV intervals.

Table II shows the reference values of the total air kerma at the pad's surface and results determined by gamma spectroscopy. The results from gamma spectroscopy were determined for 10 keV intervals and added up.

Figure 4 shows the air kerma in function of the energy, determined by gamma spectroscopy for the UTh1 pad. Each point was determined for 100 keV intervals.

Table II: Reference and determined by gamma spectroscopy values for the exposure rate on the pads at contact.

Pad id.	Reference (μGy/h)	Measured (μGy/h)	Ratio (measured/reference)
K1	0,113 ± 0,005	0,111 ± 0,005	0,98
Th1	0,534 ± 0,028	0,515 ± 0,018	0,96
U1	0,324 ± 0,017	0,312 ± 0,008	0,96
UTh1	0,208 ± 0,009	0,209 ± 0,006	1,00

7. CONCLUSION

Ge detectors calibration procedures for *in situ* air kerma, in function of the energy, measurements are being proposed, both experimentally and by simulation.

The calibration parameters obtained experimentally and by simulation are in very good agreement, the maximum deviation is less than 5% for the total air kerma rate.

The methodology for determining the detector's parameter, dead layer plus transition zone and inner well dimensions, proved to be effective, specially for the low energy region where the surface of the detector plays an important role in the efficiency.

The spectral stripping method introduced by Miller (1984) is useful for the determination of the energy distribution of the incident gamma flux by gamma spectrometry, it is possible to identify and account for the contribution of each radionuclides present.

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Field methods for the rapid analysis of naturally occurring radioactive material in solids

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Abstract. In the remediation of land contaminated with ^{226}Ra and the shipment of solids, the concentration of ^{226}Ra is required. Techniques have been developed for the rapid field analysis of samples of solids. Samples in a fixed geometry are counted for 5 minutes utilizing a 5 cm x 5 cm NaI detector and a single channel analyzer. Techniques are presented for the survey of drums with a micro-R meter to determine whether or not the drum is exempt from shipping requirements and if not the technique can be used to establish the shipping class. Examples of the use of each technique are presented.

1. INTRODUCTION

When minerals are extracted from the earth's crust usually trace quantities of naturally occurring radioactive materials (NORM) are also extracted. In many cases the radionuclides of concern are ^{226}Ra and to a lessor degree ^{228}Ra. As a result of past and in some cases current practices large quantities of equipment and land have been contaminated with radium. Concentrations are such that equipment and land must be decontaminated prior to its release for uncontrolled use. Usually waste is placed into containers, commonly 55 gallon drums, and shipped for disposal. Techniques which can assay ^{226}Ra concentrations in the field allow for rapid decision making regarding remediation and/or decontamination. Similar techniques to determine regulatory shipping class are beneficial. This paper presents techniques for accomplishing both.

2. METHOD

2.1. Assaying of waste

Although Radium-226 emits gamma it is not very abundant (~4%) and is low energy (~186 keV). The daughters of ^{226}Ra emit numerous gamma rays of various energies. One of the predominant photon energies is 609 keV emitted by ^{214}Bi. Due to the radiological characteristic of the ^{226}Ra series, the activity of ^{214}Bi will usually be equal to the activity of ^{226}Ra. Thus, if one can measure the ^{214}Bi concentration in a sample, one can assume that there is an equal amount of ^{226}Ra present. Bismuth-214 can be measured with a NaI detector connected to single channel analyzer (SCA). Obviously a multichannel analyzer would be better, but they are much more expensive and probably would not hold up as well under field conditions. The detection system consist of a 5 cm x 5 cm sodium iodide detector (Ludlum model 44-10) connected to a single channel analyzer (Ludlum model 2200). The SCA was set up with a window width of 30 keV ranging from 594 keV to 624 keV. After calibrating the detection system by counting a standard of known concentration in a fixed geometry, one can assay waste samples. A count time of 5 minutes was selected. A longer counting time will increase the sensitivity. A typical calibration constant is 18 counts per 5 minutes per 37 mBq of ^{226}Ra per gram of sample. Background of the detection system is in the order of 150 counts per 5 minutes. Using these parameters a Lower Limit of Detection of 122 mBq/g is derived. This assumes a sample weight of 1400 grams. Typically the final answer is adjusted by the ratio of sample weight in grams divided by 1400 grams. It should be noted that this technique was developed using a 1 liter sample container; however, any type sample container can be used as long as the system is calibrated with a standard in the same geometry.

This technique has been used for several years to determine when an area of contaminated soil has been decontaminated to about 185 mBq/g ^{226}Ra. **NOTE:** Neither the regulators nor the authors believe that this technique is adequate to detect 185 mBq/g ^{226}Ra with a significant degree of accuracy. In Louisiana, oilfield waste that contains no more than 1110 mBq/g ^{226}Ra can be disposed of in sites designated as non-hazardous oilfield waste disposal sites. This technique is routinely used to determine ^{226}Ra concentrations in such waste.

2.2. Determination of Shipping Class

Depending on the concentration of NORM, shipments may be exempt from packaging and shipping requirements or may be shipped as either Limited Quantity or Low Specific Activity Materials (LSA). In 1995, the U.S. Department of Transportation published some revisions to shipping regulations (USA Federal Register Vol. 60, No.188, September 28, 1995). One of the revisions was the establishment of three Low Specific Activity (LSA) material classes: LSA-I, LSA-II, and LSA-III. Shipments fall in each of these classes as a function of radionuclide concentration (referred to as A_1 and A_2 values).

2.2.1. Derivation of A_2 Values

$$A_2 = \frac{1}{\sum \frac{(f_i)}{A_2(i)}}$$

USA 49 CFR 173.433 gives the procedure to follow when determining the A_2 values for mixtures of radionuclides. The formula is straight forward when there are A_2 values for all of the radionuclides. Where:

f_i is the fraction of the activity from the ith radionuclide

$A_2(i)$ is the A_2 value for the ith radionuclide.

Table I contains the A_2 values for some of the members of the ^{226}Ra and ^{228}Ra decay chains. Note that several of the members of the decay chain do not have listed A_2 values. In a case such as this 49 CFR 173.433 specifies that the A_2 value for the parent of daughters which do not have A_2 values and which have half lives of no greater than 10 days, the daughters can be ignored when calculating A_2. In the case of the ^{226}Ra chain ^{222}Rn is the parent of the daughters through ^{214}Po, thus, ^{218}Po, ^{214}Pb, ^{214}Bi, and ^{214}Pb may be ignored. Radium-228 is the parent of ^{220}Rn and ^{216}Po, and ^{212}Bi is the parent of ^{212}Po and ^{208}Tl. These daughter radionuclides may be ignored.

The calculation of the A_2 for ^{226}Ra which has aged 5 years since it was removed from the production formation is as follows:

Assuming unit activity of ^{226}Ra and ^{222}Rn, the grow in of ^{210}Pb, ^{210}Bi, and ^{210}Po after 5 years is 0.143 fraction of the parent (this derived from the serial decay equation “Bateman equation”). The total activity for A_2 determination is:

$$1 + 1 + 0.143 + 0.143 + 0.143 = 2.43$$

thus the fraction of activity by radionuclide is each radionuclide activity divided by 2.43.

$$A_2 = \frac{1}{\frac{0.42}{20.0\ \text{GBq}} + \frac{0.42}{4.0\ \text{GBq}} + \frac{0.053}{9.0\ \text{GBq}} + \frac{0.053}{500.0\ \text{GBq}} + \frac{0.053}{20.0\ \text{GBq}}} = 7.5\ \text{GBq}$$

Table II presents A_2 values for various ages of ^{226}Ra and various ^{228}Ra activity fractions. Table III shows similar values for the Bq of ^{226}Ra in an A_2 quantity.

Table I. A_2 Values for Members of the ^{226}Ra, and ^{228}Ra Decay Chains

Decay Chain Member	A_2 GBq	Decay Chain Member	A_2 GBq
^{226}Ra	20.0	^{228}Ra	40.0
^{222}Rn	4.0	^{228}Ac	400.0
^{218}Po	N.L	^{228}Th	0.4
^{214}Pb	N.L.	^{224}Ra	60.0
^{214}Bi	N.L.	^{220}Rn	N.L.
^{214}Po	N.L.	^{216}Po	N.L.
^{210}Pb	9.0	^{212}Pb	300.0
^{210}Bi	500.0	^{212}Bi	300.0
^{210}Po	20.0	^{212}Po	N.L.
		^{208}Tl	N.L.

N.L. Not Listed

2.2.2. Exempt, Limited Quantity, LSA-I, LSA-II and LSA-III Classifications

USA 49 CFR Part 173.435 includes a table of “A_1” and “A_2” values. Due to the form of the waste, only A_2 values are of importance. The regulations refer to these values or fractions of these values when classifying shipments. The classifications are as follows:

Exempt,material where the concentration is less than 74 Bq/g
Limited Quantity,the quantity of material is less than 10^{-3} A_2 and the radiation reading at the package surface does not exceed 5 microSv/hr
LSA-I,material where the concentration is less than 10^{-6} A_2 /g
LSA-II,material where the concentration is equal to or greater than 10^{-6} A_2 /g and less than 10^{-4} A_2 /g
LSA-III,material where the concentration is equal to or greater than 10^{-4} A_2 /g and less than 2×10^{-3} A_2 /g

Table II. A_2 values for various ages of ^{226}Ra and Activity Concentrations of ^{228}Ra and Daughters

	^{226}Ra Decay Time								
Activity Percent ^{228}Ra	0 years	5 years	10 years	15 years	20 years	30 years	40 years	50 years	60 years
	GBq of the Mixture Equivalent to A_2								
0	20.0	7.5	8.1	8.6	9.0	9.5	9.9	10.1	10.3
10	4.6	5.1	5.5	5.9	6.1	6.6	6.8	7.1	7.2
20	3.7	4.1	4.4	4.6	4.8	5.1	5.4	5.5	5.6
30	3.3	3.6	3.8	3.9	4.1	4.3	4.4	4.6	4.7
40	3.0	3.2	3.3	3.5	3.6	3.7	3.8	4.0	4.0
50	2.8	2.9	3.1	3.1	3.2	3.3	3.4	3.5	3.6

Table III. Curies of ^{226}Ra in an A_2 Quantity

	^{226}Ra Decay Time								
Activity Percent ^{228}Ra	0 years	5 years	10 years	15 years	20 years	30 years	40 years	50 years	60 years
	GBq of ^{226}Ra								
0	20.0	3.1	2.9	2.8	2.7	2.5	2.4	2.3	2.3
10	1.7	1.6	1.6	1.6	1.5	1.5	1.4	1.4	1.4
20	1.1	1.0	1.0	1.0	1.0	1.0	1.0	0.9	0.9
30	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
40	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
50	0.4	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3

2.2.3. Determination of NORM Transportation Class

In order to determine the transportation class for NORM, one must know the radionuclide concentration. For the exempt class, the limit of 74 Bq/g is for all radionuclides in the shipment, i.e., the total of ^{226}Ra, ^{228}Ra, and their daughters that have half-lives greater than 10 days.

Due to the radiological characteristics of ^{226}Ra and its daughters, all the components of the chain through ^{214}Pb are in secular equilibrium (the same number of atoms of each radionuclide decay per unit of time). However, the three remaining members of the chain ^{210}Pb, ^{210}Bi, and ^{210}Po will grow in very slowly. These three members will have only half of the activity as the other members of the chain after about 22 years have elapsed from the time the ^{226}Ra was initially removed from the earth's crust. Because of this, it is not possible to know the activity make-up of NORM without a detailed radiochemical analysis. Consequently, if a waste generator does not have a good estimate on the age of the waste, it will always be prudent to assume that the waste is very old. This ensures that one will not underestimate the total activity of the waste. Table IV lists ^{226}Ra concentrations which are equivalent to 74 Bq/g for ages of ^{226}Ra ranging from initial deposit (essentially an impossible situation) to 50 years since removal from the earth's crust versus percent of total activity from ^{228}Ra. Once a value of ^{226}Ra is determined and the relative activity of ^{228}Ra is known or assumed, referring to Table III, one can determine if the shipment is exempt. For example, assuming that the ^{226}Ra is 40 years old and that 20 percent of the activity is from ^{228}Ra, one can refer to Table III under Column 40 Years and Activity Percent 20. The table value is 9.0 Bq/g of ^{226}Ra. Typically, the waste will likely be between 5 and 30 years old and the most commonly reported ratio of ^{226}Ra/^{228}Ra is 3 to 1. Consequently, ^{228}Ra activity accounts for 30% of the materials activity. This information can be used to predict when the NORM will meet or exceed the 74 Bq/g limit for DOT shipping purposes. If the material being shipped is not exempt, then one can determine the proper shipping category per DOT requirements using the predicted activity and the A_2 values listed in Table II and Table III.

Table IV. ^{226}Ra Activity Equivalent to a Total NORM Activity of 2,000 pCi/g

	^{226}Ra decay time								
Activity Percent ^{228}Ra	Initial* deposit	30 days	5 years	10 years	15 years	20 years	30 years	40 years	50 years
	exemption concentration Bq/g ^{226}Ra								
0	74.0	12.3	11.5	10.9	10.4	10.0	9.5	9.1	8.9
10	66.6	11.7	11.1	10.5	10.1	9.8	9.3	9.0	8.8
20	59.2	11.2	10.7	10.2	9.9	9.6	9.2	8.9	8.7
30	51.8	10.7	10.3	9.9	9.6	**9.4**	9.1	8.8	8.7
40	44.4	10.3	9.9	9.6	9.4	9.2	8.9	8.7	8.6
50	37.0	9.9	9.6	9.4	9.2	9.0	8.8	8.7	**8.5**

*Freshly formed NORM scale will include only ^{226}Ra and ^{228}Ra. Their daughters will grow in as the scale ages. All removed scale has aged since it was first formed.

Table IV highlights two ^{226}Ra limits, one being very conservative, the other follows more typical waste compositions. The conservative approach assumes 50 year old waste with a 1/1 ratio of ^{226}Ra/^{228}Ra (this would be highly unusual because of the short half-life of ^{228}Ra). Using these assumptions, anytime one predicts a ^{226}Ra concentration in excess of 8.5 Bq/g the total activity will exceed the DOT exempt level for radioactive material. The typical scale limit assumes 20 year old scale and a 3/1 ratio of ^{226}Ra/^{228}Ra. Under these assumptions, any predicted ^{226}Ra concentration exceeding 9.4 Bq/g would not be exempt.

If one knows the concentration of ^{226}Ra and ^{228}Ra and the lapse time since the waste was formed, Table IV can also be used to determine if a material is exempt. For example, assume that the ^{226}Ra concentration is 10.0 Bq/g and the ^{228}Ra concentration is 2.0 Bq/g. The activity percent attributed to ^{228}Ra is 17% [55 ¸ (270 + 55)]. To be conservative, from Table III select the next higher table value for the activity percent of ^{228}Ra (20% for this example). If the material was no older than 10 years, it is exempt (measured ^{226}Ra 10.0 Bq/g vs. table value of 10.2 Bq/g) where as if the material was 15 years old, it would not be exempt (measured ^{226}Ra 10.0 Bq/g vs. table value of 9.9 Bq/g).

2.3. Field Technique To Determine The Shipping Class Of NORM In 55-Gallon Drums

2.3.1. General

By calibrating a radiation survey meter against 55-gallon drums of known ^{226}Ra concentration, one can draw a curve of meter response versus ^{226}Ra concentration.

2.3.2. Instrumentation

Although there are several manufacturers of micro-R meters, the industry standard is either a Ludlum model 3 connected to a Ludlum model 44-2 detector or a Ludlum model 19. In either case, the sensitive component is a 2.5 cm x 2.5 cm NaI (Tl) detector.

2.3.3. Correction for ^{228}Ra Content

As indicated above, one must know or assume a ^{228}Ra concentration. This is necessary so that the reading taken with the survey instrument can be correct for the ^{228}Ra contribution. Table V is a listing of the fraction of gamma reading attributed to ^{228}Ra as a function of ^{228}Ra activity percent.

Table V. Correction Factors for ^{228}Ra Activity

Activity Percent ^{228}Ra	Percent of total Reading Attributable to ^{226}Ra
0%	100%
10%	87.1%
20%	74.2%
30%	**62.7%**
40%	51.9%
50%	41.8%

2.3.4. Determine ^{226}Ra Concentration in a Drum of NORM

(1) With the sensitive volume of the instrument one inch from the drum, take three readings (15 cm down from top of the drum, midway down the drum, and 15 cms up from the bottom of the drum in a vertical line up the side of the drum).

(2) Repeat the measurements on the opposite side.

(3) Average the readings

  (a) If all of the readings are within 10 percent of the average, the average may be used to determine ^{226}Ra concentration.

  (b) If any reading varies from the average by more than 10 percent take additional reading 90 degrees off from the original set.

(4) Average the set of 12 readings, and use the average to determine ^{226}Ra concentration.

(5) Correct the reading for ^{228}Ra by multiplying the observed reading by the appropriate Table V value.

Comparative assessment of the European and Latin American scenarios for NORM/TENORM exposure

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Abstract. The geological formation of the areas of high natural radioactivity are usually associated with mineral ores commercially important. As a consequence, extracting industries are installed in or near those areas. Several industrial products and byproducts can be obtained from thorium, uranium and potassium rich mineral ores, for example: niobium concentrate from pyrochlore; monazite, ilmenite, rutile and zirconite concentrates from monazite sands; phosphate fertilizers from apatite; tin and lead from cassiterite; gold and copper form a variety of thorium and uranium rich mineral matrices. Other industries like oil- and natural gas production and processing, production of thoriated tungsten lamps, welding, gas mantles and pigments produce non-negligible amounts of wastes containing technologically enhanced naturally occurring radioactive materials (TENORM). In addition, quite frequently unknown amounts of natural radionuclides end up embedded in a variety of consumer products. Thus, naturally occurring radioactive materials (NORM) as well as TENORM in consumer products and/or industrial wastes may be of importance as far as human exposures are concerned. This work will present a comparative assessment of the radiological significance of different NORM/TENORM exposure scenarios in Europe and Latin America.

1. INTRODUCTION

In the scientific community it has been known for about 25 years that workers in the natural gas- and oil industry can be exposed to technologically enhanced levels of natural radioactivity (TENR), although they are not a priori classified as occupationally exposed persons [1–3].

At the regulatory level the International Commission on Radiological Protection (ICRP) recognized in 1991 the need for regulatory control over TENR-sources. It recommended that the full system of radiation protection (adherent to the principles of justification, limitation and optimization) should apply for workers if the TENR-exposure scenario results in average annual doses exceeding 1 mSv [4]. Subsequently these recommendations have been adopted internationally as reflected e.g. in the recommendations by the International Atomic Energy Agency (IAEA) on radiation safety and the safety of radiation sources [5].

In Europe the EURATOM Radiation Protection Basic Safety Standards – EURATOM BSS – recommends in Item VII [6]:

- It is the responsibility of the Member State to identify all those work places where handling of material with increased TENR could occur.
- In such cases appropriate measures should be taken in terms of monitoring and/or reduction of the TENR-induced radiation exposure.
- The limit for mandatory action is set at 1 mSv/a.

- The activity concentration of naturally occurring radioactive material in waste of the non-nuclear industry should not exceed 500 Bq/g.
- If the limit of 500 Bq/g is exceeded a Member State can exempt this type of activity only if the individual annual dose of 10 μSv, respectively the collective dose of 1 man-Sv is not exceeded.
- Alternatively the results of an optimization process have to demonstrate that the exemption is indeed the optimum solution in terms of radiation protection.

Those industrial processes in Member States which could be of concern of Item VII of the EURATOM BSS were identified in Radiation Protection 88 [7]. Quite recently, the reference levels for workplaces processing materials with enhanced levels of naturally occurring radionuclides, which included the oil and gas extraction industry, were the subject of Radiation Protection 95 [8]. The Group of Experts established under the EURATOM Treaty identified the most likely pathways through which exposures to TENR occur, and proposed a four band system with marker points between each two of them for regulatory control above the limit at 1mSv/a. As far as regulatory control is concerned, the band structure is the following: band 1 (no need to consider regulatory control – equivalent to a band below an exemption level); band 2 (lower level of regulation); band 3 (higher level of regulation); and band 4 (process should not be permitted without a full individual assessment).

Taking into account the identified pathways for each case, screening and reference levels were derived to indicate the likely level of regulation for the radionuclides important for the relevant industry. Thus, for example, if the derived screening and reference level put the industrial process in band 1 there is no need for regulatory control. However, if the derived level would place the industrial process higher than in band 1, control measures would be applied, or the process should receive individual assessment prior to deciding which control measures to adopt [8].

In Brazil, there is not yet any established procedure as far as TENR is concerned. The TENR levels are still regulated through dose limits which are non-specific. There is, however, a broad regulatory legislation which can be applied, in principle, to any industry, including the extraction industries.

The increasing public awareness of environmental issues is putting pressure on the Brazilian legal system to solve complex environmental problems resulting from the application of inadequate laws which ignore long term implications to the environment [9]. The lack of clear cut national guidelines concerning the disposal of accumulated TENR wastes has already engendered ridiculous judicial battles in the courts of justice between environmentalists and the monazite industry in Brazil.

2. TENR-EXPOSURE SCENARIOS IN THE OIL- AND GAS INDUSTRY

2.1. Source terms

In Europe the recycling industry is being increasingly supplied with metal originating from the dismantling of installations in the oil- and gas industry. Such material is frequently contaminated by natural radioactive nuclides from the U- and Th-decay series, such as ^{238}U, ^{235}U, ^{232}Th, ^{234}Th, ^{226}Ra, ^{228}Ra and ^{210}Pb. The contamination of the equipment results mainly from :

- Solid radium (^{226}Ra) contained in scale deposited on the inner surface of pipes, vessels and tanks.

- Gaseous radon (^{222}Rn) concentrated in ethane and propane fractions due to the fact that the boiling point of Rn lies in between that of propane and ethane. Elevated Rn-activity concentration have been measured at several such sites of processing plants [10].
- Short lived Rn-decay products (Rn-d) deposited on internal surfaces of various equipment components. The radioactive decay results in a radioactive contamination by the long lived radioactive lead-isotope ^{210}Pb (T ½ = 22.3 a) and the growth of the alpha-emitting polonium isotope ^{210}Po (T ½ = 138d).

The association of TENR and petroleum genesis have already been proposed, to the extent of that should be a correlation between the age of oil and those of ^{238}U and ^{232}Th found in the organic materials from which petroleum is originated and TENR produced in the oil and gas industries [11]. Experimental work to confirm such association is still to be done.

Until recently there was a legal monopoly to extract oil in the whole territory of Brazil exercised by a government owned company. Such monopoly made this company the largest Brazilian industrial and commercial enterprise. As one of the unwanted consequences of such concentration of commercial and, to a considerable degree, political power, the Brazilian environmental regulatory agencies were unable to enforce non-specific regulations concerning TENR to such a powerful company. However, many thousands of cubic meters of TENR wastes and pipes with radioactive scales have been accumulated by the Brazilian oil extraction industry throughout the years. The current meeting may help State and Federal regulatory agencies to draft more specific regulations concerning TENR applicable to the Brazilian oil extraction industry. Such regulations are becoming even more urgent in view of the fact that end of the monopoly of the oil industry enables other companies to extract oil and gas in the Brazilian territory.

There are also large oil and gas extraction industries in other Latin American countries, such as Argentina, Bolivia, Ecuador, Mexico, and Venezuela. However, unlike the European Union Member States, Brazil and these other Latin American countries have not yet made any effort to discuss, propose and finally adopt a common regulatory structure concerning TENR, which may be applicable to the extraction industries, including the oil and gas industry.

By and large, the size of the TENR source terms in the Latin American oil- and gas producing countries are either unknown, or at least poorly identified. Joint efforts ought to be made to improve the current dissatisfactory situation.

2.2. Exposure pathways

Radiation exposure of workers in the oil- and gas industry can occur under the following conditions:

- Gas samples taken near well-heads show an average Rn-concentration of 0.5 Bq/L [12].
- In Germany almost 30 million tons of brines are raised to the surface annually as an unwanted by-product [12]. Increased exposure to external gamma radiation can occur in the vicinity of vessels and tanks filled with brines.
- Maintenance operations on scale-contaminated process equipment can generate undesirably high dust levels in the breathing area of workers [13]. Such operations occur e.g. during sand-blasting of the inside of tanks, opening of valves for repair purposes, brushing of surfaces or grinding of metal. Scales contain the following radionuclides (maximum value in Bq/g): ^{226}Ra (1000), ^{210}Pb (72), ^{228}Ra(360), ^{228}Th (360). The range of typical values in brines and scale is shown in Table I.

Table. I. Range of typical activity concentration values for ^{226}Ra in brines and scale from the gas- and oil industry [14].

	^{226}Ra
brines	7.6 – 286 [Bq/l]
scale on equipment	202 – 1000 [Bq/kg]

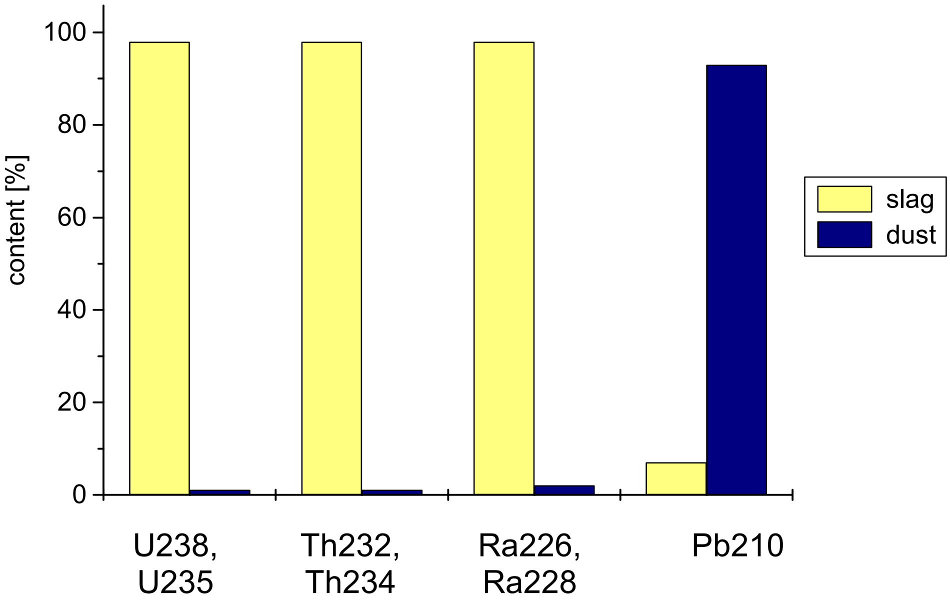

Figure 1. Nuclide distribution in slag and filter-dust after melting of TENR-contaminated metal during commercial recycling processes.

Furthermore the disposal of large amounts of contaminated wastes resulting from the various stages at processing plants can pose an environmental problem due to its content of long lived radionuclides (e.g. T ½ ^{226}Ra = 1600 a).

Finally the recycling of TENR-contaminated metal can pose a contamination problem for the operator of such a recycling plant. During the process of melting down ^{226}Ra and its decay products concentrate mainly in the resulting slag, whilst ^{210}Pb (gaseous at operating temperatures ~ 1400 C°) can be found predominantly in the dust filtration system of the exit-air [15](see Figure 1).

The Group of Experts of EURATOM considered the most likely pathways through which exposures to humans might occur as the following: inhalation of radon; ingestion of dirt and dust; skin contamination [8]. Taking into account such exposure pathways, and the effective dose limits at point marks between the four bands mentioned in section 1, this Group of Experts estimated screening concentration levels for ^{226}Ra plus progeny for oil and gas removal, scales in pipes, and sludge to be between 30 and 300 Bq/g. Thus, for concentrations below 30 Bq/g there would be no need to consider regulatory control, and above 300 Bq/g individual assessment would be necessary prior to deciding which control measures to take.

Advantage may be taken from exposure pathways observed in the studies of natural radioactive areas. In particular, the highest concentrations of ^{226}Ra, ^{228}Ra, and $^{228\text{Th}}$ in food and water samples from selected Brazilian areas of high natural radioactivity have been published [16]. Environmental behavior rather than laboratory conditions may be useful to establish TENR pathways, starting from the source-term until the exposure of man.

2.3. Resulting Doses

On the one hand, according to the recent compilation of data in UNSCEAR, the absorbed dose rate in air, including cosmic and terrestrial radiation, range from 0.02 to 30 μ Gy/h in areas of high natural radiation background [17]. On the other hand, in the thorium rich areas of Brazil external exposure radiation levels were reported to range from 0.3 to to 18 μ Sv/h [16], which is somewhat consistent with the exposure which would be obtained from worldwide UNSCEAR data. Moreover, the concentration of radionuclides from the uranium and thorium series in foods and drinking water throughout the world has also been compiled by UNSCEAR [17]. The age weighted annual intake effective dose from ingestion of uranium and thorium series radionuclides was estimated to be 160 μSv. These doses resulting from exposure to naturally occurring radioactive materials should be taken into due account when estimating the relative importance of TENR due to any particular anthropomorphic activity.

The National Academy of Sciences — National Research Council (NAS-NRC) of the United States published recently a report with the results of an investigation to assess, among other issues, whether there is relevant scientific information that has not been used in the developments of guidelines to NORM [18]. Among the conclusions and recommendations of the NAS-NRC report it is worth mentioning the following:

"*1. The committee concludes that background radiation levels of NORM are highly relevant to regulation of TENORM because the radionuclides being regulated as TENORM are identical with those in nature. Arguments concerning small differences in the target regulatory level at small fractions of the natural background tend to pale into insignificance in comparison with natural background levels and their local and regional variations.*
2. Considering only external photon exposure, the committee notes that EPA (Environmental Protection Agency)'s proposed 0.15 mSv (15 mrem) standard is equivalent to an incremental increase in the concentration of radium-226 in soil of about the usual natural background level of 0.0 4 Bq/g (1 pCi/g). In view of the ubiquitousness of ^{226}*Ra in soil and the substantial local variation of natural background, it is likely to be difficult to implement a 0.15 mSv (15 mrem) soil-cleanup standard for radium, particularly when the contamination is only marginally above the local background. That is especially the case if potential exposures to indoor radon are included in complying wth the standard.*
3. As a practical matter, the implications of existing levels and the variability of natural radionuclide concentrations and doses received by humans should receive careful consideration in the regulation of TENORM."

3. CONCLUSIONS

1. The impact on society (occupationally exposed persons and members of the public) can only be estimated (Fig.2). Due to the lack of an adequate international database this estimate is associated with large uncertainties. Using the currently available data [19] it can be shown that the global impact from a one-year operation of the oil industry is equivalent to about 30 years of operation by the gas industry.

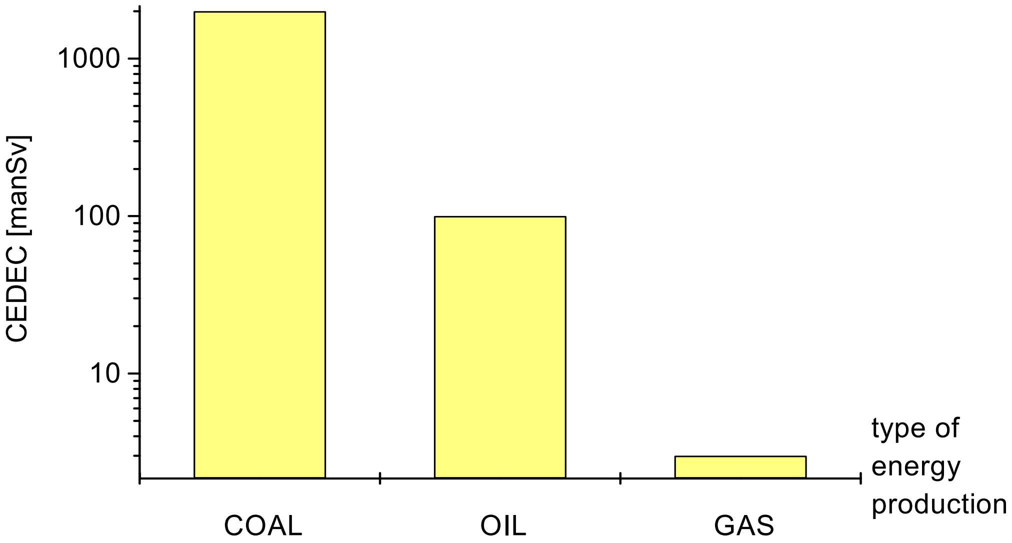

Figure 2. Collective effective dose equivalent commitment (CEDEC) for one year of world practice.

2. However, it is considerably less than the radiological impact from the coal industry (CEDEC: approx. 92 000 manSv).
3. A common basis for the international regulation of TENORM, taking into proper account natural background levels and their local and regional variation, should be found to establish a regulatory structure acceptable throughout the world, as it is the case with the IAEA BSS, and to a lesser extent the proposed EURATOM BSS.

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Adopted levels and derived limits for Ra-226 and the decision making processes concerning TENORM releases

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Abstract. A fraction of a primary dose limit can be, in general, agreed upon as a dose related level to be adopted in decision-making processes. In the case of TENORM releases, fractions of primary dose levels for ^{226}Ra, ^{228}Ra, and ^{210}Po may be of particular importance to establish adopted levels and derived limits to guide decision making processes. Thus, for example, a registration level for ^{226}Ra could be adopted at the highest portion of the natural background variation. Above such level, intervention and remedial action levels could also be adopted. All those levels would be fractions of the primary level, but translated in terms of derived limits expressed in practical units. Derived limits would then be calculated by using environmental models. In such approach "critical groups" would have to be carefully defined and identified. In addition, the size of a critical group would be chosen to be used in environmental modeling. Site specific environmental models and parameters are desirable, though unavailable, or very difficult to obtain, in most cases. Thus, mathematical models and parameters of more generic nature are often used. A sensitive parametric analysis can make a ranking of the parameters used in a model, allowing one to choose how important each parameter will be for the model output. The paper will point out that when using the adopted levels and derived limits, as suggested above, the uncertainties and importance of the parameters entering an environmental model can make the difference for decision makers to take the right or wrong decision, as far as radiological protection is concerned.

1. INTRODUCTION

The International Commission on Radiological Protection (ICRP) was created in 1928 by independent scientists to gather the most updated scientific information at any given time in order to publish sets of recommendations concerning radiation protection. Such sets of recommendations end up being followed, to a large extent, by national and international bodies whose objectives and responsibilities were to protect workers and the general public from potential deleterious effects of ionizing radiation. As time passed, the ICRP underwent several transformations in both, structure and composition. After the World War II, the ICRP received worldwide recognition as an important international independent organization, much needed as the world was entering into the nuclear age. As a consequence, the ICRP published a large number of technical documents that became respected guidelines for radiation protection throughout the world. In the United States of America, the field of radiation protection developed somewhat differently because of the experience accumulated in the Manhattan Project [1–2]. However, many American investigators in radiation protection have been giving their contribution to ICRP development since its inception.

The National Committee on Radiological Protection (NCRP) was formed in the United States with the objective of developing recommendations on radiation protection. The NCRP succeeded in 1946 the National Committee on Radiation Protection and Measurements, which had been created in 1929 as the Advisory Committee on X ray and Radium Protection. The NCRP is na advisory independent organization without authority to establish or enforce any requirements for radiation protection. However, the NCRP recommendations are highly influential in the development and guidances for radiation protection in the United States, and even in other countries. As far as NORM and TENORM are concerned, the NCRP has published a number of reports [3–9].

Recently the National Academy of Sciences – National Research Council (NAS-NRC) of the United States published an authoritative report which examined the guidelines for exposures to TENORM [10]. The relationships among risk, dose, exposure, and concentration of radionuclides in environmental media were discussed in this NAS-NRC report. Figure 1 illustrates such relationships [10]. A concept underline in Figure 1 is taht a measure of risk due to exposure to radiation may be cancer mortality, or in some cases cancer incidence (morbidity), however, in many environmental-radiation assessments the end point of the calculations is dose rather than cancer risk. When such is the case an assessment of risk corresponding to given concentrations of radionuclides in the environment can be used, or vice versa.

This paper deals with adopted levels and derived limits, expressed in practical units, as surrogates for risks and doses used in the standards used for radiation protection.

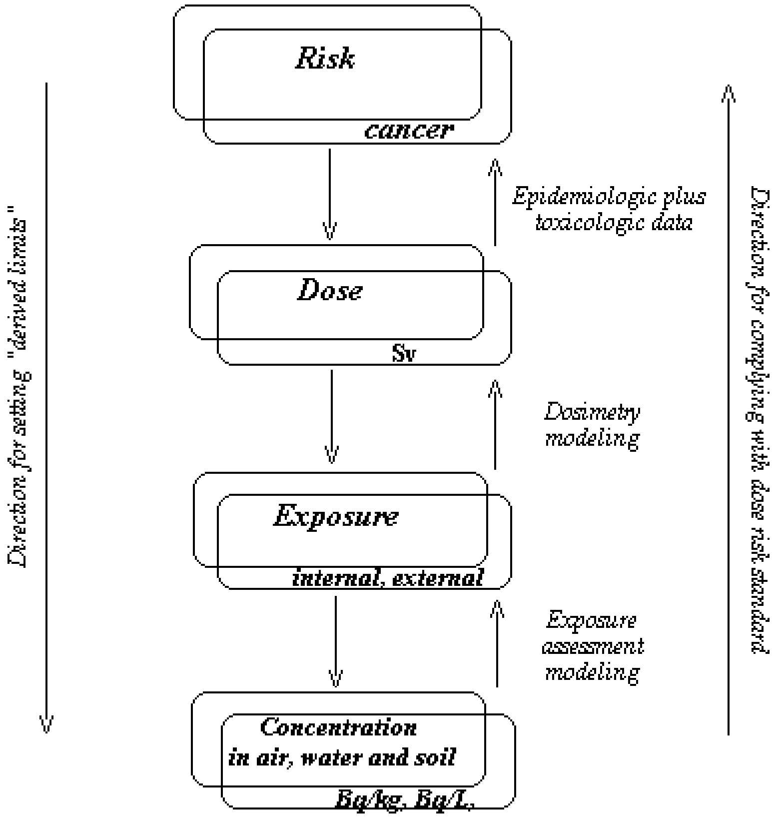

Figure 1. Relationships among risk, dose, exposure, and concentration of radionuclides in environmental media. Adapted from ref. [10].

2. RISK ASSESSMENT

The subject of *risk assessment* has been part of an intense debate following the publication, in 1977, of the recommendations made by the International Commission on Radiological Protection (ICRP) in its Publication 26 [11].

Here it is worth mentioning that many investigators in the field of radiation protection, as well as a large number of officials from national authorities throughout the world failed to perceive promptly that the intense debate on *risk assessment* that followed the set of recommendations published by the ICRP in 1977 was in reality a consequence of an evolution of concepts. At that time the ICRP recognized that, for purposes of regulation and monitoring, the quantity called radiation dose was difficult to determine directly; accordingly, it suggested simplified models establishing interrelationships for radiation doses, environmental quantities and parameters, and planned releases of radionuclides into the environment [12]. The ICRP recommended also derived and secondary limits, explained in detail in ICRP Publication 30 Part 1 [13]. The metabolic data and models used in the ICRP Publication 30 were essentially those of an adult person with anatomical and physiological characteristics of the Reference Man [14].

The system of *risk assessment* and dose limitation devised by the ICRP Publication 26 is to be used within the framework of *risks* versus benefit and cost-effectiveness. This is essentially a system of dose reductions. The key phrase was already written in paragraph 52 of ICRP Publication 9 [15]: "*As any exposure may involve some degree of risk, the Commission recommends that any unnecessary exposure be avoided, and that all dose be kept as low as is readily achievable, economic and social considerations being taken into account.*"

Not withstanding, the concepts associated with *risk* had already been used for many years in the previous ICRP recommendations. As early as 1959, the ICRP Publication 2 introduced a dose limitation system based on a fraction of the maximum permissible concentration (MPC); this system contrasted the concept of acceptable *risk* to the individual and society with the benefits which might be derived from activities involving exposure to radiation [16]. ICRP Publication 9 explicated that any exposure to radiation[1] might carry *risks* of somatic and genetic effects [15]. Paragraph 34 of ICRP Publication 9 explains that the permissible radiation dose must limit *risk* to an acceptable level, and suggests that such a dose might also be called an **acceptable dose** [15]. In addition, Paragraph 74 of Publication 9 states that at very low levels of *risk*, such as those associated with the dose limits for members of the public, only minor consequences to the health of those exposed (or their progeny) may occur if the dose limits are exceeded [15]. The concept of maximum permissible dose (MPD) was introduced to quantify a degree of risk associated with a limit of radiation dose at which the assumed risk could be considered acceptable to the individual and to society in relation to the benefit derived from activities involving exposure to radiation. These earlier concepts associated with *risk* were somewhat related with the United Nations Scientific Committee on the Effects of the Atomic Radiation (UNSCEAR) Reports [17–18].

The Publication 8 of the ICRP had already moved closer to UNSCEAR position by considering useful to estimate *risks* for radiation protection purposes [19]. Three types of *risks* were considered in the ICRP Publication 8 [19]: somatic *risks* to the exposed generation, genetic *risks* to the first generation offspring of exposed persons, and genetic *risks* to later generations. Absolute *risks* were expressed as [19]: "*the number of disabilities expected per unit dose of radiation in the lifetime of a million members of a population or as the number of disabilities per year in such population.*" Orders of risk were also used in such a way that a *risk* of death or injury would be defined as a *fifth order risk* if in a total population of 10^6 persons, 10 to 100 deaths (or injuries) would be expected. Relative *risks* were considered when the *risk* associated with an effect supposedly caused by 1 rad could be compared with the *risk* of a similar effect caused by natural causes [19]. Tentative estimates of genetic *risks* proved to contain too high uncertainties to be taken quantitatively into account. The genetic *risks* which might be associated with low level ^{226}Ra releases from the front end of the nuclear fuel cycle, for example, could not be estimated with any degree of certainty based on the concepts of *risk* used in the ICRP Publication 8.

The ICRP Publication 9 established that the MPD for occupational exposure should be regarded as upper limits and the annual dose limits for members of the public should be one-

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[1] The word **radiation** as used in the ICRP Publication 9 and in the context of this work refers only to **ionizing radiation**, and is used interchangeably.

tenth of the corresponding MPD for workers. The MPD concept gave rise to the maximum permissible concentrations in air $(MPC)_a$ and in water $(MPC)_w$. The dose limitation system introduced by the ICRP in 1959 was based on a 5 rem (50 mSv) 30 years genetic dose limit, which through models and calculations led to MPCs in air and water [16]. Both, the $(MPC)_a$ and $(MPC)_w$ can be derived from a power function or an exponention model. The $(MPC)_w$ values for ^{226}Ra, for example, were derived based on the assumption that the maximum permissible burden to bone (the critical organ for ^{226}Ra) was 0.1 μCi (3.7×10^3 Bq), which could be obtained by consuming 1.1 L of water in working day periods of 8 hours, corresponding to one half of the water consumed in 24 hours. Such maximum permissible body burden to bone supposedly would carry "*no effect*" as far as bone tumors were concerned. It was observed that there was a built in risk factor in recommendations made on the basis of comparisons with ^{226}Ra body burdens, because $(MPC)_w$ values for ^{226}Ra concealed a degree of *risk* assumed to be acceptable [20].

3. RADIATION PROTECTION GUIDE (RPG) AND NORM/TENORM

The cumulative wastes from surface uranium mining in the United States from 1950 to 1977 amounted to about 1.7×10^3 Gt [21]. This fact was one of the main reasons why the Public Law 95-604 was enacted. As a practical consequence to this law the U. S. Department of Energy (USDOE) established the uranium mill tailings remedial actions [22]. Later on, in 1983, the United States Environmental Protection Agency (USEPA) issued a report to the United States Congress that presented a generic assessment of the general impacts of the uranium industry in the United States [23]. However, at that time *risk* assessments for the ^{226}Ra releases were not available. The USEPA position became clearer with the final decisions on the "National Emission Standards for Hazards Air Pollutants (NESHAPs) under section 112 of the Clean Air Act (CAA) for emissions of radionuclides from the following sources category: DOE facilities, Licensees of the Nuclear Regulatory Commission and Non-DOE Federal Facilities, Uranium Fuel Cycle Facilities, Elemental Phosphorous Plant, Coal Fired Boilers, High level Nuclear Waste Disposal Facilities, Phosphogypsum Stacks, Underground and Surface Uranium Mines, and the operation and disposal of Uranium Mill Tailings Piles" [24]. In this USEPA document, the *safe or acceptable level of risk* is tentatively explained taking into account the Natural Resources Defense Council, Inc.(NRDC)v.EPA decision 824 F.2d at 1146 (1987) − better known as the *Vinyl Chloride Decision* − at the District of Columbia Circuit [24]. In a later publication the USEPA specifies that the non-threshold model (for the dose-response curve) is used to assume "*an estimated risk to an average member of the U.S. population of* $5x10^{-2}$ *fatal cancers per sievert (*$5x10^{-4}$ *fatal cancers per rem) delivered at low dose rates*" [25]. The same document also says that the *risk per sievert* of severe mental retardation from doses to a fetus is estimated to be at least one order of magnitude greater than that of fatal cancer to the general population. The risk of inducing severe hereditary effects is of the order of 10^{-2} *per sievert* (10^{-4} *per rem*) [24]. USEPA tried, to the extent possible, to harmonize its guidance with the knowledge of the effects of ionizing radiation on humans, taking into proper account the scientific data gathered throughout many years by the BEIR Committee of the National Academy of Science−National Research Council on health risks of low levels of ionizing radiation [26–28]. In addition, the USEPA document considered the UNSCEAR reports published from 1977 to 1988 [29–31]. This USEPA's radiation protection guidance constituted a review of the of earlier guidances to Federal agencies on the protection of workers and the general public from radiation (25 FR 4402 and 25 FR 9057).

Table I. Recommendations proposed in the USEPA radiation protection guidance. Adapted from ref. [25].

NUMBER	PROPOSED RECOMMENDATION
1	There should be no exposure of the general public to ionizing radiation unless it is justified by the expectation of an overall benefit from the activity causing the exposure.
2	A sustainable effort should be made to ensure that doses to individuals and to populations are maintained as low as reasonably achievable. This includes consideration of economic and societal factors, and apply to radiation exposure that may occur now or in the foreseeable future.
3	The combined radiation doses incurred in any single year from all sources of exposure should not normally exceed 1mSv (100mrem) effective dose equivalent to an individual.
4	Authorized limits for sources should be established to ensure that individual and collective doses in current and future populations satisfy the objectives of the Radiation Protection Guide.
5	Risks associated with exposure of the general public to radiation that may occur due to Federal agency decisions and the policies upon which these actions are based should be made public as part of the decision process.
6	Assessments and records appropriate to the origin and magnitude of expected doses and the exposed population be performed and maintained to demonstrate conformance with requirements which implement these recommendations.
7	Exceptions to Recommendation 3 for planned exposure to radiation should be made only for highly unusual circumstances, and only when requirements which implement these recommendations.

The ICRP recommendations of 1977, in Publication 26 [11], and 1990, in Publication 60 [32], as well as NCRP Report No. 116 [9] were also considered relevant to the USEPA guidance. The USEPA guideline proposed to change the "*Radiation Protection Guide (RPG) limiting the average genetic dose to members of the U.S. population to 5 rems (50 mSv) in 30 years and the annual whole body dose to 500 mrem (5 mSv) dose equivalent be replaced by a single RPG of 1 mSv (100 mrem) effective dose equivalent received by or committed in a single year to any individual from all sources combined; doses from individual sources normally be limited to a fraction of the RPG; and increased emphasis be given to the principle that all exposure should be maintained as low as reasonably achievable, within the RPG*" [24]. USEPA's 1994 recommendations are summarized in Table I.

The application of the USEPA's RPGs to NORM/TENORM, however, pose a number of problems. The natural radiation background presents significant spatial and temporal variations. There is not a well defined baseline of exposures from natural sources of radiation against which exposure due to TENORM can be compared. The latter has been addressed recently by UNSCEAR [33].

4. UNSCEAR, IAEA AND THE NORM ISSUE

Although there is a concealed degree of *risk* assumed to be acceptable in the $(MPC)_w$ values for ^{226}Ra, the last UNSCEAR Report does not address the risk issue. However, the 1997 UNSCEAR Report calculated the effective doses resulting from intake of natural radionuclides in air, food and water from measured concentrations in the body or estimated from concentrations in intake materials. The worldwide average committed dose from annual intakes was estimated to be 0.23 mSv, being 0.17 mSv due to ^{40}K and 0.06 mSv from radionuclides of the ^{238}U and ^{232}Th series, excluding radon and its decay products. The UNSCEAR estimations of the average annual effective dose to adults from natural sources are reproduced in Table II.

Table II. UNSCEAR estimations on the average annual effective dose to adults from natural sources of ionizing radiation. Taken from ref. [33].

Component of exposure	Annual effective dose (mSv)	
	Normal	Elevated
Cosmic rays	0.38	2.0
Cosmogenic radionuclides	0.01	0.01
Terrestrial radiation: external	0.46	4.3
Terrestrial radiation: internal*	0.23	0.6
Terrestrial radiation: internal**		
Inhalation of Rn-222	1.2	10
Inhalation of Rn-220	0.07	0.1
Ingestion of Rn-222	0.005	0.1
Total	2.4	----

* Exposure excluding radon

** Exposure from radon and its decay products

It is interesting to notice that, taking into account the data presented in Table II, the average annual effective dose from external exposure to terrestrial radionuclides is double than that due to internal exposure. These two modes of exposure represent about 29% of the total exposure, radon inhalation is responsible for 50%, cosmic radiation accounts for 16%, while all other modes of exposure contribute with less than 5% of the total annual effective dose. When one does not consider high exposure to cosmic rays, in areas of high natural background the main doses are due to inhalation of radon, and external and internal exposures to terrestrial radiation. These latter modes of exposures are the most likely way that NORM/TENORM will incur doses to humans.

The UNSCEAR evaluated the internal doses from ingestion of uranium and thorium-series radionuclides, taking into account a fractional population distribution of 0.05, 0.3 and 0.65, respectively for infants, children and adults. The UNSCEAR annual effective doses form ingestion of uranium and thorium-series radionuclides are summarized in Table III.

Table III. Annual effective doses from ingestion of uranium and thorium-series radionuclides. Taken from ref. [33].

Radionuclide	Annual effective dose (μSv)			
	Infants	Children	Adults	Age-weighted
^{238}U	0.23	0.26	0.25	0.25
^{234}U	0.25	0.28	0.28	0.28
^{230}Th	0.42	0.50	0.64	0.59
^{226}Ra	7.6	12	6.3	8.0
^{210}Pb	54	49	25	34
^{210}Po	227	114	75	95
^{232}Th	0.26	0.32	0.38	0.36
^{228}Ra	33	42	10	21
^{228}Th	0.38	0.28	0.22	0.24
^{235}U	0.011	0.012	0.012	0.011
TOTAL	320	220	120	160

The age-weighted total value of 160 μSv reported in Table III is more than three times higher than the 52 μSv derived in the earlier UNSCEAR Report [34]. The total annual effective dose from inhalation (≈ 10 μSv) and ingestion of terrestrial radionuclides is about 340 μSv, of which 170 μSv is from ^{40}K [33]. It is not clear, however, whether those effective doses from natural radionuclides can be used as representatives or not. Further data are necessary to establish a dose baseline due to the intake of natural radionuclides. Such baseline becomes more important as TENORM may reach the foodchains.

The ICRP Publication 26 reviewed critically the former concept of genetic dose limit of 5 rem (50 mSv) in 30 years from all sources of radiation additional to the dose from natural radiation background and from medical procedures [11]. The revision made in the ICRP Publication 26 was made under the following assuption [11]: "*continuance of the former genetic dose limit could be regarded as suggesting that acceptability of a higher population exposure than is either necessary or probable, and a higher risk than is justified by any present or easily envisaged future development*."

The International Atomic Energy Agency (IAEA) adopted principles based on the system of dose limitations recommended by the ICRP Publication 26, stressing that cost-benefit analysis, quantitative assessment, and value judgements should support decision making processes [35–37]. However, the IAEA recommendations did not address the issue of naturally occurring radioactive materials (NORM).

5. CURRENT BASIC SAFETY STANDARDS (BSS) AND NORM

A number of well respected international organizations — the Food and Agriculture Organization (FAO), the International Atomic Energy Agency (IAEA), the International Labour Organization (ILO), the Nuclear Energy Agency of the Organization for Economic Co-operation and Development (OECD/NEA), the Pan American Health Organization (PAHO) and the World Health Organization (WHO) — recently sponsored the International Basic Safety Standards for Protection against Ionizing Radiation and for the Safety of Radiation Sources (BSS) [38]. The BSS was approved by the IAEA's Board of Governors in September 1994. The NORM issue was not specifically contemplated in the BSS, however, exempt activity concentrations and exempt activities of radionuclides were established based on the following general principles [38–39]:

> "(a) the *radiation risks* to individuals caused by the *exempted practice* or *source* be sufficiently low as to be of no regulatory concern;
>
> (b) the collective radiological impact of the *exempted practice* or *source* be sufficiently low as not to warrant regulatory control under the prevailing circumstances; and
>
> (c) the *exempted practices* and *sources* be inherently safe, with no appreciable likelihood of scenarios that could lead to a failure to meet the criteria in (a) and (b)."

Table IV lists the exempt activitiy concentrations established in the BSS for ^{222}Rn (plus ^{218}Po, ^{214}Pb, ^{214}Bi, ^{214}Po), ^{224}Ra (plus ^{220}Rn, ^{216}Po, ^{212}Pb, ^{208}Tl -36%-, ^{212}Po -64%), ^{226}Ra (plus ^{222}Rn, ^{218}Po, ^{214}Pb, ^{214}Bi, ^{214}Po, ^{210}Pb, ^{210}Po, ^{210}Pb), ^{228}Ra (plus ^{228}Ac), ^{228}Th (plus ^{224}Ra, ^{220}Rn, ^{216}Po, ^{212}Pb, ^{208}Tl -36%-, ^{212}Po -64%), Th-nat (including ^{232}Th and progeny), ^{230}U (plus ^{226}Ra, ^{222}Rn, ^{218}Po, ^{214}Po), and U-nat (including the ^{238}U progeny), which are the most relevant radionuclides in the case of NORM releases, and activity concentrations found in some selected extractive industries [38].

It would be helpful to be able to establish easy to measure limits, so industries that deal with NORM or have TENORM as byproducts could benefit from these practical limits. Derived limits for ^{226}Ra releases will be presented here for illustration purposes only.

6. SECONDARY AND DERIVED LIMITS FOR RA-226 RELEASES

One must bear in mind that a primary dose limit is established based on an amount of effective dose which is not supposed to be exceeded. The ICRP defined, for practical purposes, secondary, derived and authorized limits which were since then adopted by the IAEA and EU [37;46–48].

Metabolic and environmental modeling are necessary to make possible inter-comparison involving measurable quantities instead of effective dose. Thus, for example, the use of metabolic and environmental models in association with a derived limit (DL) for ^{226}Ra releases allows a direct comparison with measurable and/or estimated ^{226}Ra concentrations in environmental and biological media due to actual or potential releases of this radionuclide into the environment.

Derived limits for ^{226}Ra, as well as for any other radionuclide, should be based on the annual limit of intake (ALI). The ALI for ^{226}Ra is 7×10^4 Bq/yr (1.9 μCi/yr). This ALI shall not be exceeded ever, and is to be used for the control of occupational exposure. However, for adult members of the public a ^{226}Ra ALI of 7×10^3 Bq/yr (0.19 μCi/yr) has been suggested as appropriate, and was actually adopted by the EU to be used by the Member States in theirs radiation protection programs [47]. It is interesting to notice here that this EU ALI is about twice the maximum permissible body burden adopted by the ICRP much earlier [16].

Table IV. Exempt activity concentrations for the most relevant radionuclides (plus their progeny) in the case of NORM releases, as established in the Basic Safety Standards and activity concentrations found in selected extractive industries.

RADIONUCLIDE	ACTIVITY CONCENTRATION (kBq/kg)	
	Exempt [39]*	Extractive industries
Rn-222	10	
Ra-224	10	
Ra-226	10	2.7 [40] – 658 [41]
Ra-228	10	368 [42]
Th-228	1	1.1 [40] – 200 [41]
Th-natural	1	0.7 [43–45] – 111 [40]
U-230	10	
U-natural	1	3 [43–45] – 30 [40]

* The reference numbers are indicated between brackets.

A ^{226}Ra DL has been suggested for a manioc growing Brazilian region where thorium and uranium rich pyrochlore and apatite [49]. However, practical applications of DLs for ^{226}Ra releases in more general terms can also be used, as well as for other radionuclides.

DLs for ^{226}Ra releases can be linked to primary or secondary limits, like an ALI, with an accuracy which will depend on the realism and adequacy of the environmental model used in the derivation. Thus, environmental modeling is essential for calculating DLs for ^{226}Ra releases.

Generic models and parameters can be used in the preliminary assessment of environmental transfer of radionuclides from routine releases. Thus, a generic derived limit (GDL) either for ^{226}Ra releases from a specific source or for ^{226}Ra concentrations in environmental or biological media can be easily calculated based on generic models and parameters for this radionuclide.

Potential *critical groups* must be defined or identified for the application of a GDL for ^{226}Ra or any other radionuclide. The concept of *critical group* was introduced to circumvent the lack of precision in the definition of the expression "*members of the public*," frequently used in the ICRP publications. On the one hand, "*members of the public*" imply large differences in age, size, metabolism, customs, and environmental variations in the places of working and living. On the other hand, *critical groups* must be small enough to be relatively homogeneous with respect to those characteristics that can affect the doses received; like age, diet, and behavior [11;35;37]. An homogeneity requirement establishes that, in general, the maximum to minimum ratio within a critical group do not exceed an order of magnitude. *Critical groups* may be either identified among existing members of the general population, or defined as a group of persons; in either case a critical group is expected to be exposed to a higher dose level than that received by the general population. A typical size of a *critical group* is up to a few tens of persons, mostly to restrict habit surveys. However, when large populations are uniformly exposed, the size of the *critical group* can be considerably larger. The size, as well as the identification or definition of *critical groups* are relevant aspects to be considered in environmental modeling concerning ^{226}Ra or any other radionuclide releases into the environment.

In addition to *critical groups*, environmental modeling requires the use of *critical pathways* for a critical radionuclide. In the case of ^{226}Ra releases into the environment, the relative importance of ^{226}Ra vis-a-vis ^{210}Po as the critical radionuclide should be considered in some pathways, because the latter may be also an important contributor to internal dose levels under certain circumstances [50].

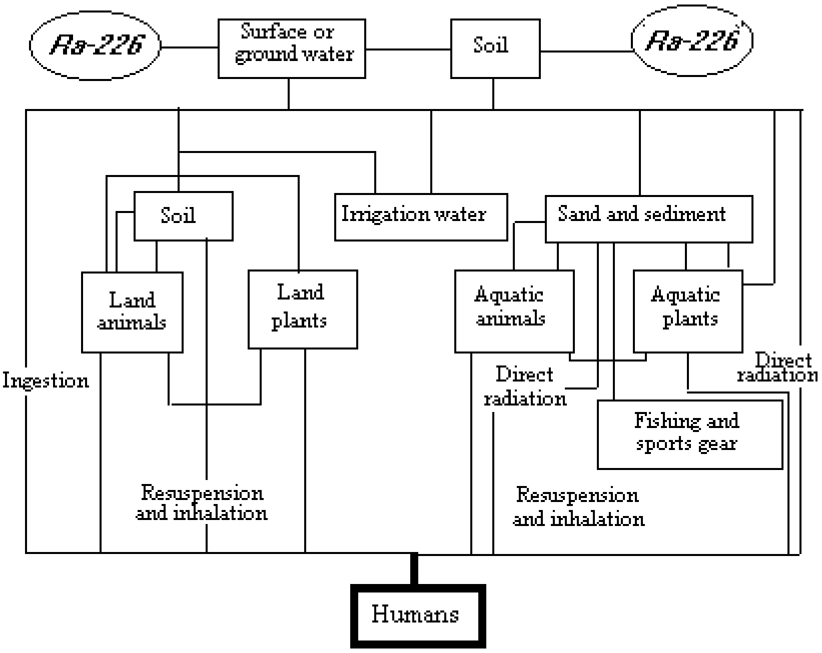

Figure 2. Selected pathways for ^{226}Ra through soil and surface or ground water. Adapted from ref. [12].

Critical pathways to be considered for ^{226}Ra releases will be essentially terrestrial or aquatic, because air is usually an unimportant pathway for ^{226}Ra intake. Simplified pathways for ^{226}Ra released into ground and surface waters, and in soils are presented in Figure 2. One must observe, however, that the direct radiation exposure pathway is only important when the *critical group* is located near the site of ^{226}Ra releases or is living near surface soils or sediments that accumulated high ^{226}Ra concentrations. Direct radiation might be considered a *critical pathway* when, for example, TENORM bearing tailings are inadvertently used as construction material or are not isolated from a *critical group*. In such cases, however, radon rather than ^{226}Ra should be considered the critical radionuclide.

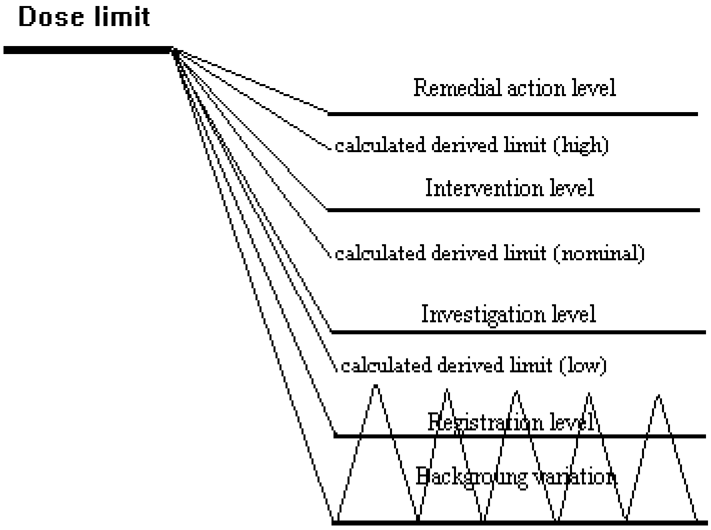

Figure 3. Schematic representation of calculated derived limits (low, nominal and high) — in accordance with parameters used — plus registration, investigation, and remedial action levels in comparison with the natural radiation background variation.

Table V. Selected derived limits (DLs) for ^{226}Ra

DERIVED LIMIT FOR	PRACTICAL UNITS*
Water	Bq/L
Pasture or soils	Bq/kg
Rate of discharge	Bq/year
Air	Bq/m^3

* Not necessarily SI units.

The basic conditions for an useful DL are the following:

1. be comparable with measurable quantities. Thus, for ^{226}Ra one can expect, for example, to determine DLs with units in accordance with Table V.
2. be related with the ALI for ^{226}Ra. That means 7 x 10^3 Bq/yr (0.19 μCi/yr) for adult members of the public;
3. be chosen in such a way that once not exceeded, the dose limit will not be exceeded also.

It is well recognized that the physical descriptions of the critical pathways followed by ^{226}Ra from the source of release until will reach humans, and the appropriate values for parameters used in generic environmental models may differ considerably of site specific environmental models and parameters.

Site specific models and parameters are desirable in most cases, but by and large, they are unavailable and are very difficult to obtain. As a consequence, mathematical models and parameters of more generic nature are often used.

Concerning the uncertainties of radio-ecological assessment models it has been observed the following [51]:

"*(i) there is a need to distinguish between research and assessment models, mainly regarding the objectives for developing and applying such models;*
(ii) limits specifying the applicability of the results of modeling should be clearly indicated when using deterministic models for decision making; and
(iii) the introduction of further complexities in a model does not necessarily assure any improvement in the predictions."

When the calculated doses approach dose limits, that means, whenever doses predicted by models are less than about one order of magnitude below the relevant dose limit, the model structure, its parameters and all associated values should be re-evaluated. The criterion to decide to re-evaluate a model is a matter to debate.

Figure 3 suggests a sequence of dose related levels that can be useful in decision making processes. Once a primary dose limit is established, fractions of this primary limit can be agreed upon. Thus, for example, a registration level would be established at the highest portion of the background variation. Above this registration level investigation, intervention and remedial action levels would also be established. All those levels could be established in terms of fractions of the primary dose, but translated in terms of derived limits expressed in practical units, as in Table V. The derived limits would be calculated by using environmental models. A sensitive parametric analysis can make a ranking of the parameters used in the model, allowing one to choose how important each parameter can be in the model output.

A detailed discussion on the uncertainties involved in radiological models, as well as an application of ranking parameters, based on sensitive analysis of an environmental model can be found in the literature [51–52]. When using adopted levels and derived limits as those suggested in Figure 3, the uncertainties and importance of the parameters entering an environmental model can make the difference for decision makers to adopt a right or wrong decision concerning radiological protection.

7. CONCLUDING REMARKS

1. A brief review of the concept of *risk* as used in radiation protection was presented, taking into consideration its evolution since the earlier uses.
2. The adoption of secondary levels of dose and derived limits for ^{226}Ra releases have been proposed and illustrated.
3. Attention has been called in regarding the need of parametric analysis to rank parameters entering the models used to obtain the derived limits.

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TENORM wastes and the potential alpha radiation dose to aquatic biota

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Abstract. In the years seventies release-rates and derived limits for releasing radionuclides into the environment were adopted for each particular radionuclide and for a number of pathways. The release-rate limit adopted for alpha emitters was 10^{15} Bq.y^{-1} for a single site, but limited to 10^{14} Bq.y^{-1} for ^{226}Ra and supported ^{210} Po. In addition, to meet the requirements of the London Convention, a derived limit should be expressed in terms of concentration, which for alpha emitters was 10^{10} Bq.t^{-1}, but limited to 10^{14} Bq.t^{-1} for ^{226}Ra and supported ^{210} Po, assuming an upper limit to the mass dumping rate of 10^{5} t per year at a single dumping site. New data on the radioactivity in the marine environment and biota, including plankton, indicated a potential alpha radiation dose to these aquatic organisms due to the release of technologically enhanced naturally occurring radioactive materials (TENORM) wastes. At the highest accumulation of ^{239} Pu in the zooplankton *Gammarus* in Thule, Greenland, due to an accidental release associated with military activities, the dose rate reached about 0.14 μGy.h^{-1}. Such dose rate was similar to that received by the phytoplankton *Chaetoceros* and *Rhizosolenia* from Agulhas current, Africa, due to naturally occurring radioactive materials (NORM) supposedly enhanced for almost one century of gold mining at first, and subsequently because of heap-leaching uranium extraction from the tailings left behind by earlier gold miners. The paper will discuss the alpha radiation dose to aquatic biota, in general, and to plankton, in particular, due to potential releases of TENORM wastes in the aquatic environment.

1. INTRODUCTION

The Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matters of 1972, better known as the London Convention, and the Multilateral Consultation and Surveillance Mechanism for the Sea Dumping of Radioactive Wastes of 1977 under the Organization for Economic Co-operation and Development (OECD) are the two main international agreements dealing with the dumping of radioactive wastes into the oceans. The original version of the London Convention prohibited, *inter-alia*, dumping into the sea high level radioactive wastes. The low level radioactive wastes, however, could be dumped into the sea under special permits. The London Convention has given to the International Atomic Energy Agency (IAEA) the responsibility for defining what kinds of high-level radioactive wastes which are unsuitable for dumping into the oceans and to make a series of recommendations for dumping of other radioactive wastes and for keeping the subject under permanent review [1–4]. By 1993, taking into account strong opposition of the world public opinion, the London Convention prohibited the dumping of all kinds of radioactive wastes into the sea.

Later on, the IAEA – Marine Environment Laboratoty (MEL) have established the Global Marine Radioactivity Database (GLOMARD) to store all data available on marine radioactivity in seawater, sediments and biota [5]. More recently, the IAEA-MEL started examining the real or potential radiological consequences of the radioactivity in the marine environment and biota. To do so, the IAEA-MEL started organizing studies of sources of radioactivity in the marine environment, and their relative contributions to the overall dose assessment from marine radioactivity, an effort better known as the MARDOS project [6].

It is well recognized today that at present there is not yet sufficient knowledge of oceanic processes to allow the construction of a comprehensive model to describe the behavior of radionuclides extant or released into the oceans. However, for some time now the IAEA has issued principles for establishing limits for the release of radioactive materials into the environment [7–8]. The approach adopted by the IAEA in issuing such principles is to evaluate environmental capacity and establishing limits within which quantities of radioactive wastes can be controlled. This approach is known as the critical pathways approach.

The derived limits for releasing radionuclides into the environment through various pathways are based on ICRP Publication 29 [9]. Release-rate limits were derived for each particular radionuclide and for a number of pathways. A selection was made to include those pathways which were known to exist at the time plus some others which might become important in the then foreseeable future.

The release-rate limit for alpha emitters was 10^5 Ci/year ($\approx 10^{15}$ Bq/year) for a single site, but limited to 10^4 Ci/year ($\approx 10^{14}$ Bq/year) for ^{226}Ra and supported ^{210}Po [4]. However, to meet the earlier requirements of the London Convention it was necessary to express the derived limits in terms of concentration, which meant – 1 Ci/t ($\approx 10^{10}$ Bq/t) for alpha emitters, but limited to 10^{-1} Ci/t ($\approx 10^9$ Bq/t) for ^{226}Ra and supported ^{210}Po, assuming an upper limit to the mass dumping rate of 10^5 t per year at a single dumping site [2, 10].

The levels of radioactivity in the marine environment had already lead some few investigators to pay attention to the biological availability of radionuclides and the resulting internal doses to marine organisms [11–15]. An important conclusion was that ^{137}Cs would be in the long term the major contributor to the total dose rate for all groups of organisms, but in the case of phytoplankton ^{239}Pu could be of some importance [12]. Thus, it was reasonable to hypothesize that the alpha emitters from technologically-enhanced naturally occurring radioactive materials (TENORM) could be of certain importance for the alpha radiation dose to aquatic biota, mostly because of the bioaccumulation factors for plankton, algae, invertebrates and macrophytes.

2. BIOACCUMULATION OF SELECTED ALPHA EMITTERS

Databases concerning the bioaccumulation (relative concentrations) in aquatic biota for selected alpha emitters, such as ^{239,240}Pu, ^{238}U, and ^{226}Ra have been summarized [16]. There are, however, a number of uncertainties in the determination of bioaccumulation factors for any radionuclide — *radionuclide concentration, at equilibrium, in the organism divided by the concentration in the water* — mostly due to conversion factors for wet weight and dry weight, which vary from species to species. In any case, the reported values indicate that the orders of magnitude of bioaccumulation factors for aquatic biota range for several orders of magnitude, as shown in Table I.

Taking into account the orders of magnitude presented in Table I, one can claim that potentially high alpha radiation dose may be received by phyto- and zoo-plankton, algae, invertebrates, macrophytes. Only the cases of phyto- and zoo-plankton will be discussed here for purposes of illustrating the alpha radiation doses for organisms with high bioaccumulation of alpha emitters. On the one hand, it is know that part of alpha energy internally emitted in plankton may be dissipated in the surrounding water [12]. On the other hand, it is also known that for many species the range of the alpha particles emitted by naturally occurring radionuclides, and artificially produced actinides are of the same order of the linear dimensions of plankton [14–15].

Table I. Ranges of bioaccumulation factors for ^{239,240}Pu, ^{238}U, and ^{226}Ra in freshwater biota. Adapted from ref. [16]

BIOTA	**BIOACCUMULATION FACTOR**			
	Pu-239,240		U-238 and Ra-226	
	Low	High	Low	High
Piscivorous	10^{-1}	10^{0}	10^{-1}	
Planktivorous	10^{-1}	10^{1}	10^{-1}	10^{0}
Omnivorous	10^{-1}	10^{1}	10^{-1}	10^{2}
Benthic	10^{-1}	10^{2}	10^{0}	10^{2}
Zooplankton	10^{2}		10^{2}	
Phytoplankton	10^{2}	10^{4}	10^{1}	10^{3}
Algae	10^{3}		10^{1}	10^{3}
Invertebrates	10^{2}	10^{3}	10^{0}	10^{3}
Macrophytes	10^{2}	10^{4}	10^{1}	10^{3}

3. DOSE TO PLANKTON

The radionuclides produced in the nuclear fuel cycle enter the aquatic environment in a variety of pathways. Among the radionuclides thus produced one should include the technologically enhanced concentrations of natural alpha emitters in the pre-reactor phase, and the transuranic alpha emitters in the post-reactor phase of the nuclear fuel cycle. Ratios of plankton dose rates of the orders of 10 for fallout/natural background, and 10^3 for waste disposal at Windscale/natural background have been estimated [17]. However, specific comparisons between internal dose rates from man-made and natural alpha emitters have been scarcely reported [12–15]. Considering that the bioaccumutation factors reported in Table I are likely to occur also in the marine biota, it is reasonable to expect that TENORM concentrations in the marine environment may result in high annual alpha radiation doses to such biota, and particularly in plankton.

Table II presents, for illustration purposes only, the range of absorbed dose rates due to internally incorporated ^{226}Ra in plankton. Two interesting aspects are worth mentioning here concerning the 1.6×10^{-1} μGy.h^{-1} absorbed dose rate that appears in Table II. Firstly, the ^{226}Ra average activity concentration corresponding to this high dose rate can be traced back to seven phytoplankton samples taken from fifteen plankton samples collected in the Walvis Bay area [18]. According to oral historic accounts – to the best of my knowledge still not supported by any available publication – it was quite likely that the ^{226}Ra concentrations in Walvis Bay had been enhanced throughout almost one century due to gold mining at first, and subsequently as a consequence of heap-leaching uranium extrative activities from the gold mining tailings. Secondly, the 1.6×10^{-1} μGy.h^{-1} absorbed dose rate received by the phytoplankton from Agulhas current in west coast of Africa is of the same order of the 1.4×10^{-1} μGy.h^{-1} absorbed dose rate received from ^{239}Pu accumulated at one time by the zooplankton *Gammarus* from Thule, Greenland, due to an accidental release associated with military activities [15]. However, it has been pointed out that the plutonium concentrations in aquatic organisms living near the accident area have decreased considerably with time [19].

Table II. Absorbed dose rates from internally incorporated ^{226}Ra in plankton

DOSE RATE (Gy.h^{-1})		**REFERENCE**
Low	High	
6.1×10^{-4}	2.0×10^{-3}	[12]
2.0×10^{-4}	1.6×10^{-1} *	[15]

* This high dose rate is estimated from ^{226}Ra incorporated in the phytoplankton ***Chaetoceros*** and ***Rhizosolenia*** from Agulhas Current, in the coast of Namibia.

Here it is worth mentioning that the alpha dose rates to plankton are given throughout this work in grays rather than in sieverts, because the radiobiological consequences, if any, of relatively high alpha radiation dose rates to plankton remain unclear. Thus, to apply any modifying factor to obtain an equivalent dose appears to be awkward at the time of this writing. Further research is necessary to clarify whether there are or there are not any biological effects due to high annual alpha radiation doses to plankton.

4. CONCLUDING REMARKS

1. There is an increasing interest in learning more about the relative contribution to the overall dose assessment from marine radioactivity, but the knowledge on the alpha radiation dose to plankton, algae, invertebrates, and macrophytes is meager.
2. The marine organisms mentioned in remark (1) above are likely to have bioaccumulation factors significantly higher than other marine organisms.
3. TENORM alpha emitters could contribute to a high alpha radiation dose for plankton, algae, invertebrates, and macrophytes.
4. Life long continuous exposure of phytoplankton to absorbed dose rates of the order of 0.16μGy.h^{-1} due to incorporation of ^{226}Ra, may result in absorbed doses as high as 1.4 mGy.y^{-1}, without the knowledge which such high dose will have as far as radiobiological consequences are concerned.
5. Apparently, dose rates to plankton can be enhanced either by continuous internal exposure to TENORM or by acute accidental exposure to man-made alpha emitters; the first case will result in a much higher long term dose.

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^{226}Ra bioavailability to plants at *urgeiriça* uranium mill tailings

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Abstract. Large amounts of solid wastes (tailings) resulting from the exploitation and treatment of uranium ore at the *Urgeiriça* mine (north of Portugal) have been accumulated in dams (tailing ponds). To reduce the dispersion of natural radionuclides into the environment some dams were revegetated with eucalyptus (*Eucalyptus globolus*) and pines (*Pinus pinea*). Besides, some shrubs (*Cytisus s.p.*) are growing at some of the dams. The objective of this study is to determine the ^{226}Ra bioavailability from uranium mill tailings through the quantification of the total and available fraction of radium in the solid wastes and to estimate its transfer to the plants growing on the tailing piles. Plants and solid waste samples were randomly collected at dams. Activity concentration of ^{226}Ra in plants (aerial part and roots) and solid wastes were measured by gamma spectrometry. The exchangeable fraction of radium in solid wastes was quantified using one single step extraction with 1 mol dm^{-3} ammonium acetate (pH=7) or 1 mol dm^{-3} calcium chloride solutions. The results obtained for the ^{226}Ra uptake by plants show that ^{226}Ra concentration ratios for eucalyptus and pines decrease at low ^{226}Ra concentration in the solid wastes and appear relatively constant at higher radium concentrations. For shrubs, the concentration ratios increase at higher ^{226}Ra solid waste concentrations approaching a saturation value. Percentage values of 16.0±8.3 and 12.9±8.9, for the fraction of radium extracted from the solid wastes, using 1 mol dm^{-3} ammonium acetate or calcium chloride solutions respectively, were obtained. The ^{226}Ra concentration ratios determined on the basis of exchangeable radium are one order of magnitude higher than those based on total radium. It can be concluded that, within the standard error values, more consistent ^{226}Ra concentration ratios were obtained when calculated on the basis of available radium than when total radium was considered, for all the dams.

1. INTRODUCTION

A common approach to quantify the availability of soil radionuclides for plant uptake is the ratio between plant activity concentration (Bq kg^{-1}) and total soil activity concentration (Bq kg^{-1}) usually denominated transfer factor or concentration ratio. However, the transfer mechanisms depend on several factors such as: soil types, root development, root system and the plant species. The ion exchange capacity, moisture content, pH, organic matter content and temperature of the soil will influence cation uptake by the roots [1, 2]. Besides, the uptake of an element depends on various soil and plant factors – like composition and concentration of the soil solution, replenishment capacity of the soil, speciation of the element and interelationships of the different species, the soil solution acting as an intermediary phase. The activity of an element in the soil solution rather than its total concentration in the soil determines its short term bioavailability and toxicity [3]. So, in order to evaluate the transfer of radionuclides in soil-plant systems the fraction of soil contamination available for root uptake will be considered. To quantify this fraction single and sequential extraction methods have been used [4, 5, 6]. One mol dm^{-3} ammonium acetate (pH=7) solution has been widely used to estimate “exchangeable” ion concentration in soils [7, 8]. Other authors (Marple cited in [9] and [10]) referred calcium chloride extractions as a good method to estimate the bioavailability of metals, since Ca^{2+} is often the dominant cation competing for soil adsorption complex sites in mineral soils.

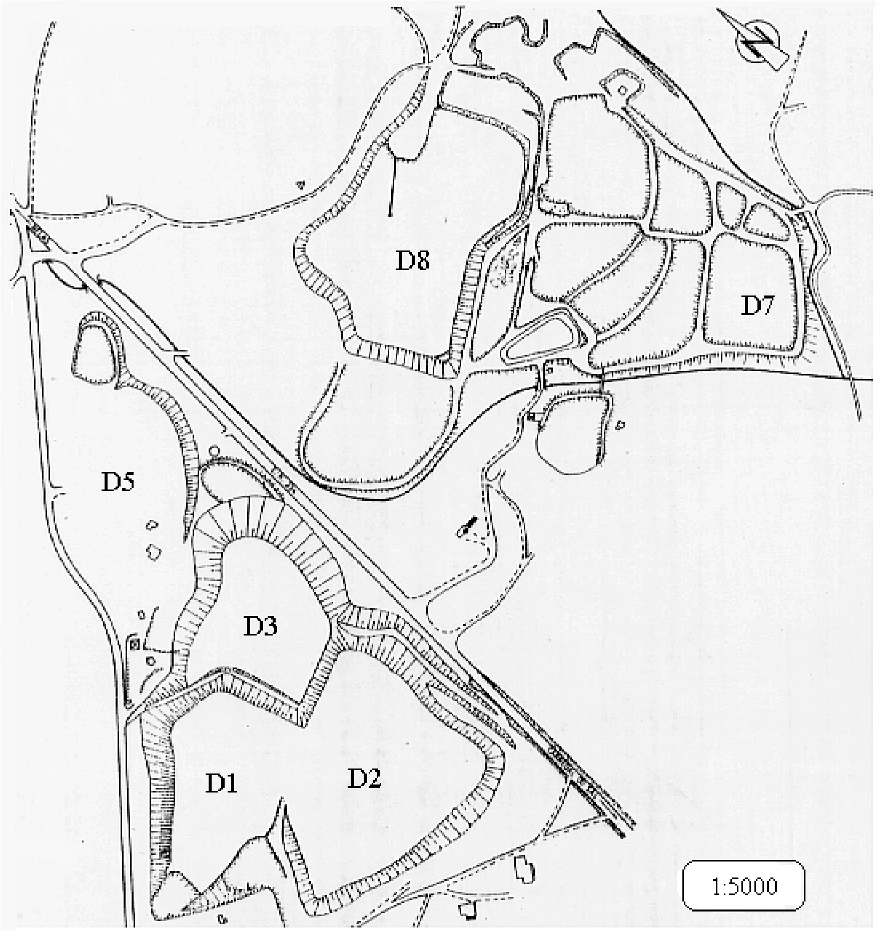

Fig.1. Map of the area studied. D1 to D8 correspond to the sampling sites (dams).

The main goal of this study is to evaluate the radium bioavailability from uranium mill tailings through the quantification of the total and available fraction of radium in the solid wastes and to estimate its transfer to plants growing on the tailing piles.

2. MATERIALS AND METHODS

2.1. The study area

Urgeiriça uranium mine is located at the north of Portugal near Canas de Senhorim (Viseu). The mine´s exploitation began in 1913 for radium extraction. The activity of the Urgeiriça mine was maintained until 1944, and was then exclusively dedicated to the production of uranium. In 1951, a chemical treatment unit for the production of poor U_3O_8 concentrates was built, which was later on, in 1967, transformed into a modern unit [11]. At present the mine is exhausted, but the facilities are still being used for the treatment of pregnant liquour resulting from the acid leaching of the ore treatment from other mines in the same region. The extensive exploitation and treatment of the uranium ore in the *Urgeiriça* mine, has lead to an accumulation of large amounts of solid wastes (tailings). About $4x10^6$ tons, which are discharged into natural depressions confined by dams (tailings ponds) cover an area of about 11 ha. The studied area is presented in Fig.1. Dams 1 (D1) to 5 (D5) are the oldest and had been abandoned in 1987. The solid wastes are composed mainly by sand and silt particles that resulted from uranium acid leaching, after the ore crushing and grinding processes, and were transported to the dams through hydraulic techniques. The chemical components resulting from the solvent extraction and/or ion exchange separation to concentrate uranium from the leaching solution are also deposited at the dams. So, the chemical composition is complex and variable, depending not only on the nature of the original ore and milling reagents added, but also on climatic conditions and on weathering reactions that occur following disposal. The dam 8 (D8) deposition, the most recent one, started in 1987 and is still in operation. The chemical processing after ore treatment produces large quantities of liquid wastes, the pregnant liquours, resulting from the acid leaching, which are neutralized with CaO and then discharged into the tailing pond (D8) for solid deposition. Dam 7 (D7) was covered with a layer of gravel of about 2 meters depth. To minimize the dispersion of natural radionuclides into the environment, some dams were revegetated with eucalyptus (*Eucalyptus globolus*) and pines (*Pinus pinea*). Besides, some shrubs (*Cytisus s.p.*) are growing spontaneously at some of the dams.

Plants and solid waste samples from the soil area close of the roots of the plants were randomly collected at dams (D1–D8) in period January 96–October 97. Reference samples of plants and solid wastes were also collected from areas within 1 km off the tailing piles.

2.2. Samples preparation and analyses

The plants were removed from the soil and washed to take away adhering soil particles. The roots were separated from the aboveground parts of the plants, air dried and weighted. They were then dried at 110ºC cooled and weighted. The dry sample was ashed at 550ºC for 8 h in a furnace, cooled and weighted.

Solid waste (tailings) and soil reference samples were collected from the soil area close of the plant roots. They were homogenised to obtain a representative sample. The solid waste and soil samples were dried at room temperature and the fraction under 1mm was retained for analysis.

Total ^{226}Ra activity was determined in solid waste, soil and plant samples by gamma spectrometry employing a HpGe p-type detector Silena, with 265 cc active volume, coupled and run through a Silena gammaplus software package. The system has been calibrated, for several geometries, using a standard QCY44 solution provided by Amersham. Solid waste, soil and ashed plant samples were counted in sealed containers, after one month delay to allow equilibrium of ^{226}Ra with its daughters. ^{226}Ra was analysed through its progeny, namely ^{222}Rn gamma emiters daughters.

3. RESULTS AND DISCUSSION

3.1. Dependence of ^{226}Ra concentration ratio on soil concentration

Figure 2 (a) shows the total ^{226}Ra concentration (Bq g^{-1}, dry weight) in the *Pinus pinea* (C_p) versus the total ^{226}Ra concentration (Bq g^{-1}, dry weight) in the solid wastes (C_s) for all the samples. By fitting the data to a function of the form $C_p = aC_s^b$, the following values for the parameters a and b were obtained: a= 0.0356, b= 0.859 with a correlation coefficient of 0.87 for roots and a= 0.017, b= 0.479 with a correlation coefficient of 0.49 for needles. The results indicate that the plant uptake response to the total radium concentration in the solid wastes is a non-linear function, tending however to a linear relationship at higher radium concentrations in the solid wastes, mainly concerning roots. This finding was also referred to by other authors [12] who have studied the calcium, radium, lead and polonium uptake in different plants and soils.

As referred in paragraph 1, the transfer of radionuclides from soil to plant is described by the concentration ratio (C_R) which is defined, in this case, as the ^{226}Ra concentration in the plant C_p (Bq g^{-1}, dry weight) divided by the total ^{226}Ra concentration in the solid wastes C_s (Bq g^{-1}, dry weight). Concentration ratios for *Eucalyptus globolus* (leaves), *Pinus pinea* (needles and roots) and *Cytisus s.p.* (aerial parts and roots) samples were calculated. Figure 2 (b) shows the concentration ratio values for *Pinus pinea* versus the total ^{226}Ra concentration in the solid wastes. It is seen that the concentration ratios decrease at low radium concentrations (< 5 Bq g^{-1}) and appear relatively constant at higher radium concentrations (above about 5 Bq g^{-1}). The results obtained for *Pinus pinea* could be explained considering a dose-response curve approach proposed to plants uptake of essential and non-essential elements [13]. This means that, at low solid waste radium concentrations, radium seems to be an essential element or is mimicking an essential element for pines growth, whereas the almost constant concentration ratio values at high solid waste radium concentrations could indicate that the radium is behaving either as an essential or as a non-essential element.

Some authors [12] reported that the shape of the concentration ratio function at high substrate concentrations will depend on the plant uptake response. If the plant uptake continues to increase linearly with increasing soil concentration, a constant CR will be obtained. On the other hand, if the plant uptake decreases or is constant, with increasing soil concentration, CR decreases. Some authors [2] reported that elements such as Ca, Ra, Pb may act as “accumulator” elements in plants. The term “accumulator” does not infer that the elements are accumulated at a great extent; rather it infers that the uptake response of plants to soil activity is a non-linear function increasing to single or multiple saturation values [14]. According to this hypothesis the non-linear relationship obtained to our data, might reflect that radium is behaving as an “accumulator” element. Besides, as there is no linear relationship between internal contamination and the external levels of radium, the ^{226}Ra plant uptake is not a good indicator of environmental contamination [2].

The experimental data presented in Figure 2 (b) were fitted using a model [15] which takes into account the hyperbolic dependence of the radium concentration in the plant with the concentration in the substrate ($C_p = aC_s^b$) and the concentration ratio values ($C_R = C_p/C_s$.). Consequently, the ^{226}Ra transfer for *Pinus pinea* could be estimated using the following equations: C_R= 0.036 $C_s^{-0.14}$ (roots) and C_R= 0.017 $C_s^{-0.521}$ (needles) (Figure 2 (b)).

The same approach was applied to *Eucalyptus globolus* and *Cytisus s.p.* The equations obtained were: C_R= 0.039 $C_s^{-0.53}$ (*Eucalyptus globolus*, leaves), C_R= 0.107 $C_s^{0.294}$ (*Cytisus s.p,* roots) and C_R= 0.08 $C_s^{0.174}$ (*Cytisus s.p.*, aerial parts). The positive values obtained to parameter b for *Cytisus s.p.* show a different trend, i.e. the concentration ratios increase at higher solid waste concentrations approaching a saturation value. This corresponds to an increase of radium uptake by the plant at higher radium concentration in the solid wastes.

The different response to the radium uptake for *Cytisus s.p.* (brushs) when compared with *Pinus pinea* and *Eucalyptus globolus* (trees) may be due to various factors: metabolic rate differences between trees and bushes due to their size and structure; influence of the seasonal variation and the maturity of the plant which should be more significant to *Cytisus s.p.*. It was reported [16] that the trace element content of the whole plant tends to increase with increasing maturity. Besides, different species and different cultivations regulate metal uptake at both the soil/root and root/shoot interfaces at varying degrees.

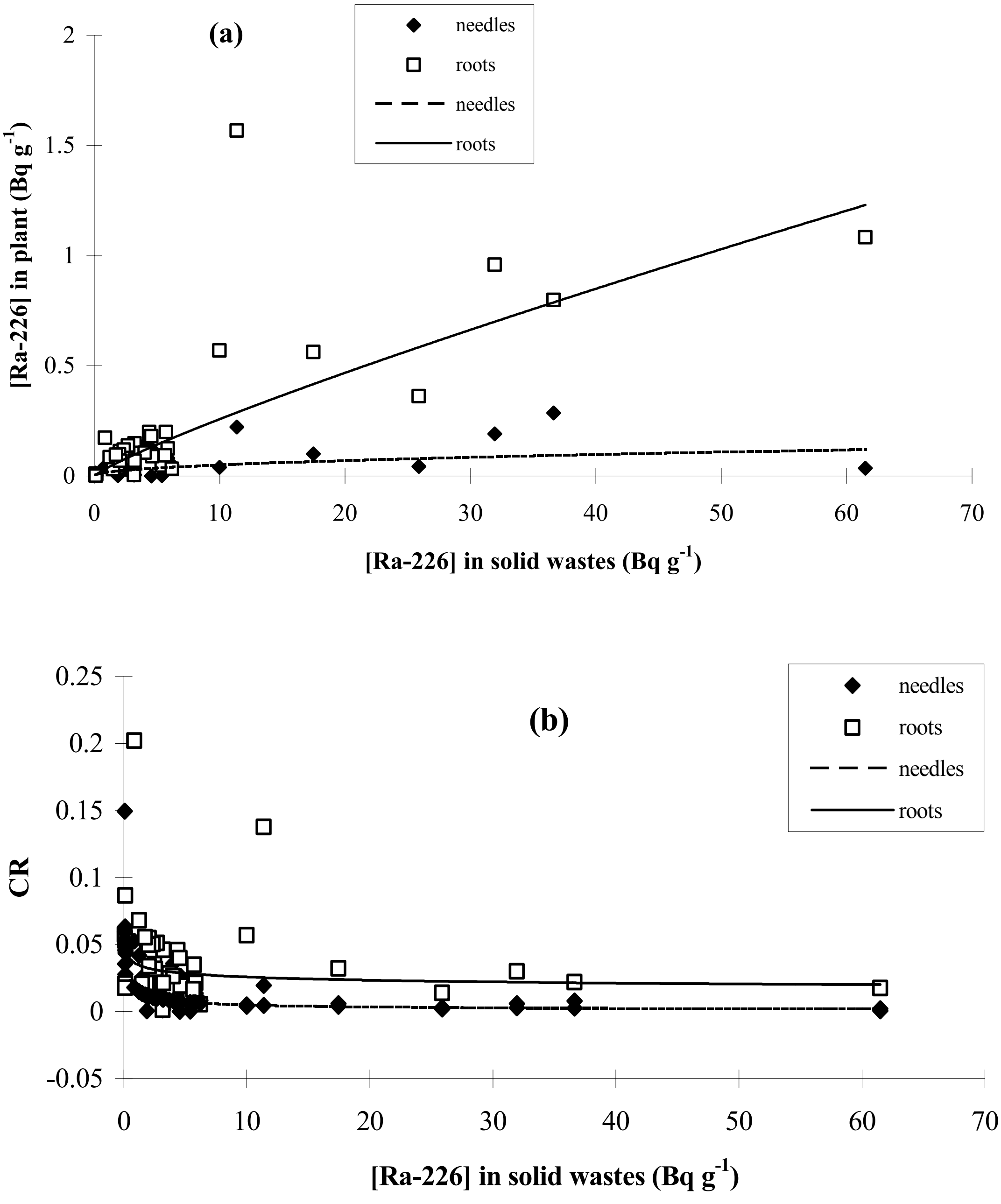

Fig. 2. Radium concentration in Pinus pinea vs. concentration in solid wastes (a) and concentration ratios (CR) in Pinus pinea vs. radium concentration in solid wastes (b).

3.2. Dependence of ^{226}Ra concentration ratio on plant groups and sites

The mean total ^{226}Ra plant to soil concentration ratios for *Pinus pinea*, needles and roots, for the different sampling sites are presented in Figures 3 (a) and (b) respectively. The statistical comparisons of the ^{226}Ra concentration ratios for needles/solid wastes and roots/solid wastes indicate no demonstrable difference between the radium transfer from solid wastes to roots and to needles for the same sampling site (dams). On the other hand, comparison for the different dams, taking into account the standard errors, seems to indicate lower concentration ratio values for D1 to D5 than for D7 and D8. This finding could be due to the different processes that have been used along the years for ore treatment and which had originated wastes with higher radium concentrations in the oldest dams. If, it is taken into account that the uptake mechanisms are identical to the same plant species, higher radium concentrations in the substrate are expected to lead to lower concentration ratio values.

Figures 3 (c) and (d) show the mean total ^{226}Ra concentration ratios for *Cytisus s.p.*, aerial parts and roots, for the sampling sites. It is observed that the mean concentration ratios to the aerial parts are almost constant, except for D2. Comparison among the mean concentration ratios to *Cytisus s.p.* roots suggests significant differences between the dams with a very complex overall pattern. This could however be explained by experimental errors resulting from some soil contamination of the samples which is difficult to avoid, even after the washing procedure was carried out. However, in general, the plants/solid wastes and roots/solid wastes concentration ratios for one single species are in the same order of magnitude. It means that the radium concentration adsorbed by the roots is identical that translocated to the aerial part of the plant.

The observed mean concentration ratios for *Eucalyptus globolus* leaves are shown in Figure 3 (e). As well as with *Pinus pinea*, the statistical analysis revealed a similarity of radium transfer from solid wastes to plant leaves in dams 1 to 5.

For the three groups of plants, important differences between the radium concentration ratios to soils and to solid wastes would be expected due to the different characteristics of the uranium mill tailings when compared with soils. However, only small variations were found, the values obtained for soils being even, within the range of values found for D7 and D8, except in what concerns the *Eucalyptus globolus*. This is in agreement with what we expected for dam 7. Actually, this dam was covered by a gravel layer of about 2 meters and consequently the radium uptake by the roots should not be influenced by the solid wastes.

As referred before, in spite of the natural metabolic differences between these groups of plants, which was confirmed by the different behaviour concerning the radium uptake by plants, values of the same order of magnitude for the mean radium concentration ratios were obtained. It is important to point out that the great variability of the individual mean radium concentration ratios might be caused by the high variability of ^{226}Ra content in the solid wastes and in plants growing at uranium mill sites. Even a single species showed variation from one sampling site to another within the same dam.

The results discussed until now were based on data calculated to total radium concentration ratios. However, to better quantify the uptake mechanisms of radionuclides by plants it is essential to evaluate the fraction of available radionuclide. The fraction of radionuclide soluble in the soil solution, or the fraction extractable to this solution under certain conditions, should be considered as the available fraction. A study to determine the fraction of radium available in these solid waste samples was performed.

3.3. ^{226}Ra extraction from the solid wastes and soils

The "exchangeable" fraction of ^{226}Ra in the solid wastes was extracted, one single step, with 1 mol dm^{-3} ammonium acetate (pH=7) and 1 mol dm^{-3} calcium chloride solutions (S/L=1:8, contact time=1h). The evaluation of extracted ^{226}Ra fraction was carried out by gamma counting of the solid phase, before and after extraction, using a NaI detector (well type) Chrismatec 127SP127 previously calibrated.

Comparative studies of ^{226}Ra extraction with 1 mol dm^{-3} ammonium acetate and calcium chloride solutions, for the solid wastes and soil samples, were performed. It was verified that the average percentage values for ^{226}Ra extracted with ammonium acetate (16.0±8.3) are similar to those obtained for ^{226}Ra extracted with calcium chloride solution (12.9±8.9) for the solid wastes. The low values (< 20%) obtained for "exchangeable" ^{226}Ra indicate that a large fraction of radium is associated with other phases of the substrate, mainly to iron-manganese oxides and organic matter and so in a non-exchangeable phase. This is in agreement with was reported by other authors [9].

The percentage of radium available from the solid wastes, using ammonium acetate (16.0±8.3) is of the same order of magnitude than those proposed in the literature to soil samples. Exchangeable radium percentages of 2.3 to 34.5 [7] and 7.1 to 27.8 [8] for agricultural soils were referred.

3.4. Dependence of ^{226}Ra concentration ratio on exchangeable radium

The ^{226}Ra concentration ratios for *Pinus pinea* (needles and roots), *Cytisus s.p.* (aerial parts and roots) and *Eucalyptus globolus* (leaves) samples were calculated on the basis of the fraction of radium available. The mean exchangeable ^{226}Ra concentration ratios for *Pinus pinea*, needles and roots, for the diferent sampling sites are shown in Figures 4 (a) and (b) respectively. The examination of the data reveals no significant difference (within the standard error values) between the concentration ratios for needles and roots at different sampling sites.

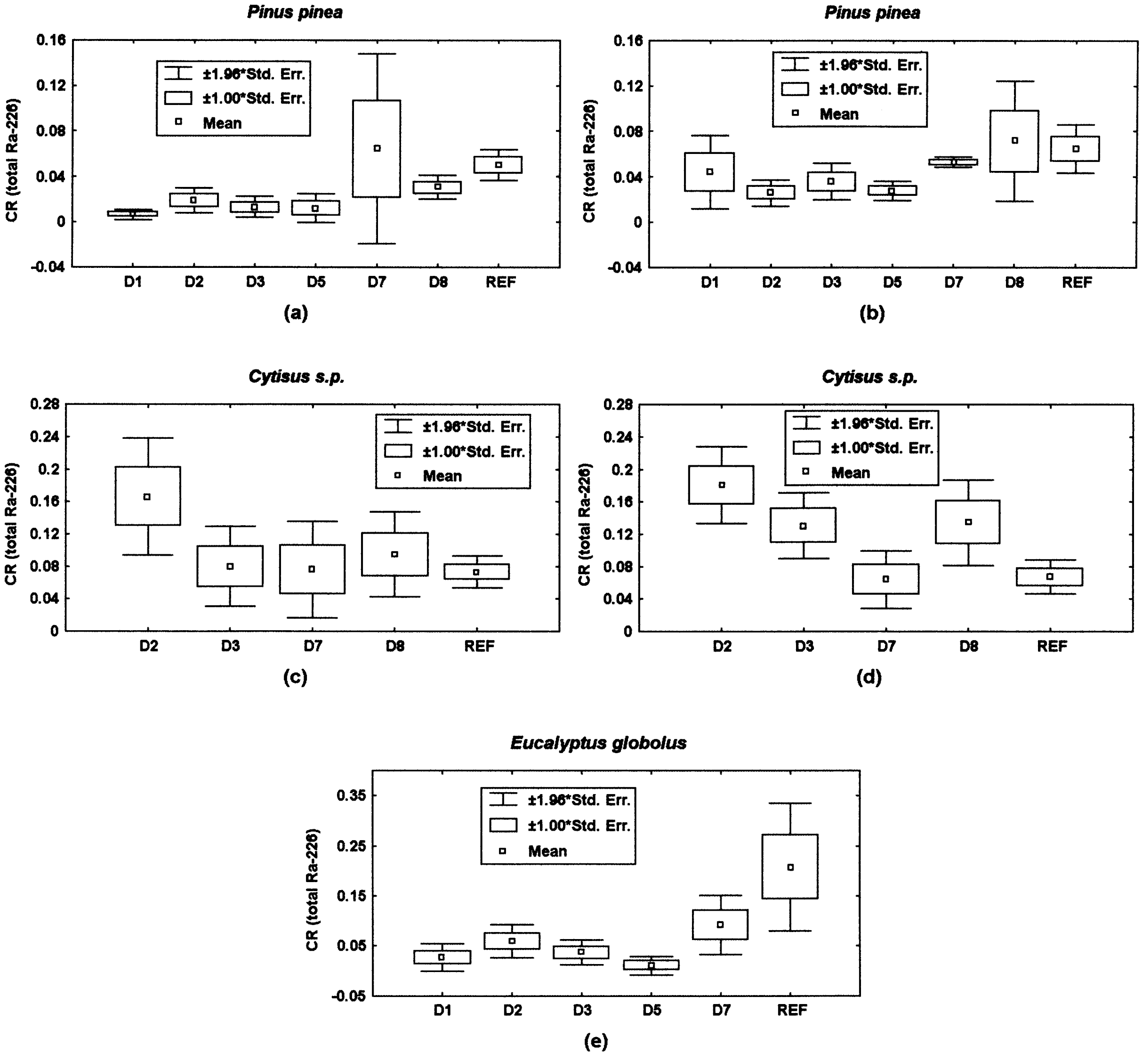

Fig. 3. Concentration ratio for total ^{226}RA vs. sampling sites (D1 to D8 and reference site). (a) Pinus pinea (needles);(b) Pinus pinea (roots); (c) Cytisus s.p. (aerial parts); (d)) Cytisus s.p. (roots); (e) Eucalyptus globolus (leaves).

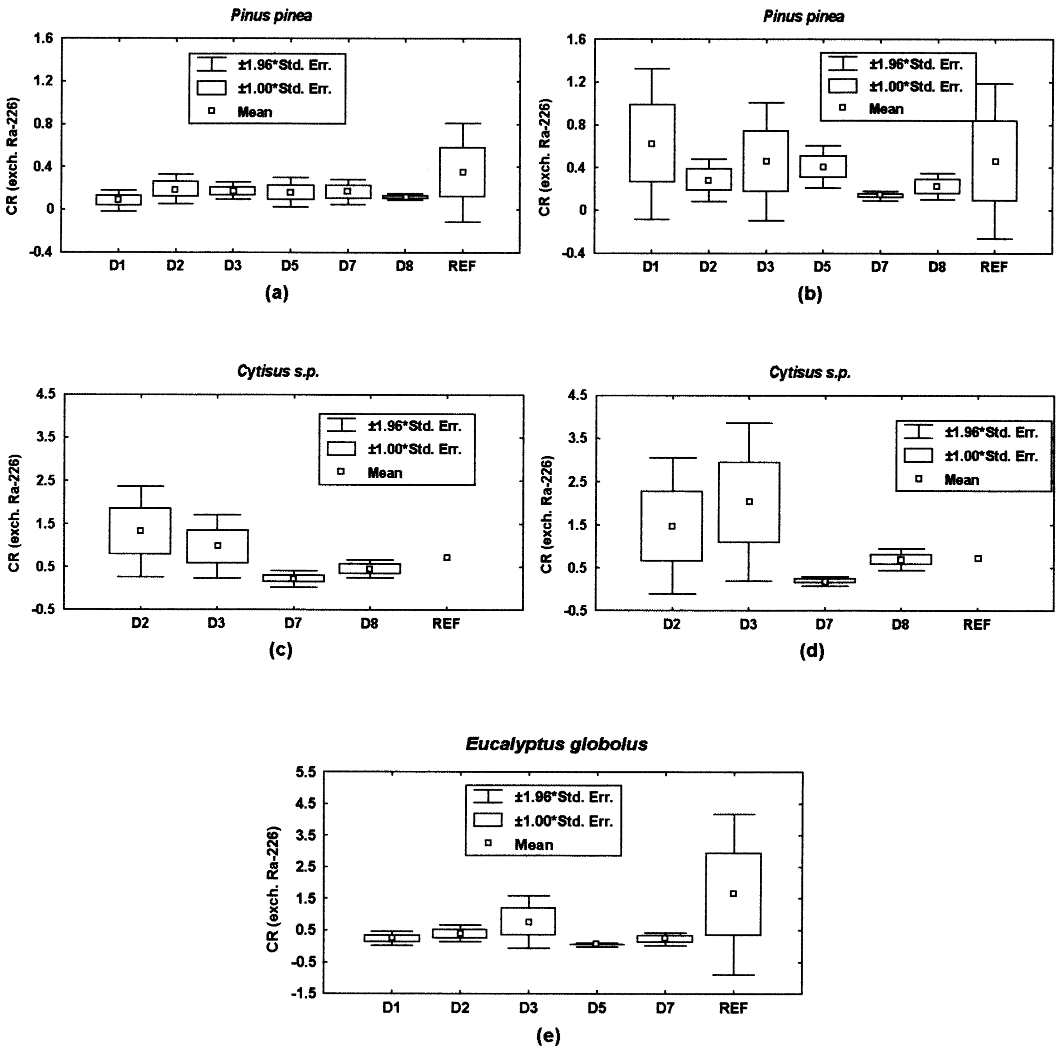

Fig. 4. Concentration ratio for exchangeable ^{226}Ra vs. sampling sites (D1 to D8 and reference site). (a) Pinus pinea (needles);(b) Pinus pinea (roots); (c) Cytisus s.p. (aerial parts); (d)) Cytisus s.p. (roots); (e) Eucalyptus globolus (leaves).

The same trend was followed by *Cytisus s.p.* (Figure 4 (c) and (d)) and *Eucalyptus globolus* (Figure 4 (e)). Some authors [17] reported that controlled experiments carried out with edible plants growing on soil and uranium tailings indicated variation in concentration ratios when calculated on the basis of total radium, while reasonably consistent concentration ratios were obtained when calculated on the basis of the available radium present in the soil or tailings.

Radium-226 concentration ratios calculated on the basis of exchangeable radium are one order of magnitude higher than those based on total radium. Similar results to edible vegetables growing in a region of high natural radioactivity were referred [7].

4. CONCLUSIONS

Different behaviour concerning the ^{226}Ra uptake by the plants was found. For *Pinus pinea* and *Eucalyptus globolus* (trees) ^{226}Ra concentration ratios decrease at low radium concentrations in the solid wastes and appear relatively constant at higher radium concentrations. For *Cytisus s.p. (*shrubs) concentration ratios increase at higher solid waste concentrations approaching a saturation value.

The non-linear functions obtained to describe the plant/solid wastes concentration ratios might indicate that radium is behaving as an "accumulator" element in the plants uptake.

Comparative studies between the total radium concentration ratios on plants groups and sites seem to indicate two different groups of dams D1–D5 and D7–D8 with different characteristics, may be due to the different processes used for ore treatment. However, if the exchangeable radium concentration ratios were considered no significant differences were found among the dams.

The higher radium concentration values obtained with exchangeable radium, by an order of magnitude, could demonstrate a higher radium translocation rate from the solid wastes to the roots and consequently to the whole plants in the presence of available radium.

ACKNOWLEDGEMENTS

We would like to thank Dr. A. Ortins de Bettencourt for his help in reviewing the paper and critical comments. We are grateful to ENU (Empesa Nacional do Urânio) to allow the samples collection at the *Urgeiriça* dams and to Dr. F. Mota for technical assistance.

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Origin of radium in high-mineralised waters

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Abstract. High-mineralised waters are showing frequently high concentrations of ^{226}Ra and ^{228}Ra, which are positively correlated with salinity. The investigated pit water is a high mineralised, reducing NaCl-brine (up to 230 g/l), which contains in coexcidence with Ba (up to 2500 ppm) and Sr, high ^{226}Ra concentrations (up to 63 Bq/l) and ^{228}Ra concentrations (up to 28 Bq/l). Feeding river systems with this water, the contact of the pit water with sulphate bearing surface water results in a precipitation of Ba and Ra as radiobaryte, with ^{226}Ra concentrations up to several tens of kBq/kg. The pit waters originate from a mixture of formation and meteoric waters, older than 20 Ma. High concentrations of mainly Na^+ and Cl^-, but K^+, Ca^{2+} and HCO_3^- as well, are explained by dissolution of Permian salt deposits. Ba^{2+} is enriched by sulphate-reducing bacteria, which destroy detrital baryte. Radium enters the water by leaching and alpha-recoil effect, but a large fraction of it is adsorbed at the surfaces of mineral grains. Mainly Ba^{2+} and Sr^{2+}, but univalent ions like Na^+ and K^+ as well, are desorbing Ra^{2+} from the surface of minerals and take their place. Elution experiments show that beside the ion exchange of the cations, the type and amount of anions control the radium mobilisation. It seems that large anions like NO_3^- are disturbing the hydrate coat around minerals and therefore, enhance the ion exchange process.

1. INTRODUCTION

It's well known that high-mineralised waters or brines very often go along with high radium concentrations, showing a good correlation between salinity and radium concentration [1], [2]. Usually both, ^{226}Ra (^{238}U-series) as well as ^{228}Ra (^{232}Th-series) occur in such waters. The main differences between the two radium-isotopes are: ^{226}Ra has a half-life of 1600 y and before it was formed, 3 alpha-decays occurred; ^{228}Ra has a half-life of 5.7 y and only 1 alpha-decay before it was formed.

Where do you find high-mineralised waters? Partly, bottled mineral water can have a higher salinity, which can result in ^{226}Ra concentrations up to several hundreds of mBq/l [3]. But the waters with high salinity are not drinkable, they occur in the ground at greater depths (hundreds of meters up to several km) and are therefore no longer called ground water but deep water. By exploiting hydrocarbons (oil, gas), deep water is raised unwanted with the hydrocarbons and usually pumped back to the depth immediately. This could not be done in coal mining districts. Here, water had to be pumped up to allow underground or open-pit mining, and the pit water is discharged to the rivers. This study is analysing the origin of radium in high-mineralised pit waters released by hard-coal collieries in the Ruhr district, North Rhine Westphalia, Germany.

2. MEASURING TECHNIQUES

In the investigated area sediments from rivers and soils adjacent to the rivers, as well as pit waters and river waters were sampled and analyzed by using a low level γ-spectroscopy with a HPGE crystal [4]. Additionally, radium concentrations (^{226}Ra, ^{224}Ra) of waters were measured by the standard emanation method [5]. Element concentrations of solid samples are determined by XRF, and for liquid samples ICP-OES was used. The gamma-dose rate is measured with a portable gamma-scintillometer. At each water sampling point, water temperature, pH and conductivity were measured.

3. GEOCHEMISTRY OF THE PIT WATERS

In the state of North Rhine Westphalia hard- and brown-coal mining are very important industries. Brown-coal mining is done in huge open pits, which are up to 400 m deep. Hard-coal mining is done underground, today mainly in the Ruhr district, in depths of up to 1500 m.

The pit waters from brown coal mining are not very high mineralised and reach ^{226}Ra concentrations up to a few hundreds of mBq/l (not published). But the waters from the hard-coal mining of the Ruhr district are brines, high-mineralised, with up to 250 g/l salinity [6]. Such waters can have ^{226}Ra concentrations of 60 Bq/l and ^{228}Ra concentrations of 30 Bq/l [7]. The waters contain no radionuclides staying in the decay series before radium. ^{226}Ra and ^{228}Ra show a mean ratio of 2 : 1 [8]. The knowledge of high amounts of radionuclides in the pit waters is not new, already Patteisky [9] discussed this problem. The same correlation of salinity and radium concentrations can be observed in pit waters from the Silesian coal basin in Poland, where even higher concentrations were detected [10].

The pit waters of the Ruhr district are reducing brines from the NaCl-type. Tab. 1 shows element concentrations and conditions of a typical pit water from a depth of approximately 1000 m. Generally, salinity and of course temperature are increasing with depth. All the deep waters are reducing, except those, where ground water from shallower levels is mixed with the deep water due to anthropogenic disturbance of the aquifer. Beside the dominating Na^+ and Cl^-, the Ba^{2+} concentration should be noticed, which can reach up to 2500 mg/l [6]. Because of the geochemical similarity to Ra^{2+}, the Ba^{2+} concentration gives us a first hind to the radium concentration of the water.

The pit waters are probably formation waters of Cretaceous age mixed with meteoric water older than 20 Ma [6]. High concentrations of mainly Na^+ and Cl^-, but K^+, Ca^{2+} and HCO_3^- as well, are explained by dissolution of Permian evaporite deposits. Ba^{2+} is enriched in the waters by sulphate-reducing bacteria, which destroy detrital baryte.

Table 1. Typical element concentrations and conditions of a pit water from the Ruhr district. All concentrations are given in [mg/l] (compiled after [6]):

Temperature [°C]	PH	Conductivity [µS/cm]	Salinity [g/l]
50	6.5	210 000	230

Na	K	Ca	Mg	Sr	Ba	Cl	SO_4	HCO_3	NO_3	Br
70 000	1 200	9 000	1 500	700	1 500	124 000	< 5	120	20	150

Radium is the first element in the decay series which is significantly soluble under the reducing conditions of deep waters. There are 4 possible processes to get radium from the rock of the aquifer to the water: dissolution of minerals, diffusion, leaching and alpha-recoil effect. The first 2 processes are not very promising. The leaching of minerals in silicate rocks is not adequate to explain higher amounts of radium. The same is true for diffusion, which is much to slow (diffusion distance in minerals $< 1.8 * 10^{-8}$ cm/10^6 y , [11]). Probably, the radium transfer to the water is a mixture of leaching and alpha-recoil effect [2]. Considering the disturbance of the mineral lattice due to alpha-recoil, we have to distinguish ^{226}Ra (after 3 alpha decays) from ^{228}Ra (after 1 alpha decay), Therefore, the former should be more available. When radium enters the water, a large fraction will adsorb on the negatively charged surface of mineral grains. The most probable process to detach them from the mineral surfaces is ion-exchange. If ion-exchange is responsible for the detachment of Ra^{2+}, then one would expect that high-ionic strength waters release more Ra^{2+} to the water than low-ionic strength waters. Mainly bivalent cations like Ba^{2+} and Sr^{2+}, but univalent ions like Na^+ and K^+ as well, are desorbing Ra^{2+} from the surface of the minerals to take their place. Elution experiments, which are still under investigation [12], support this theory. They show that Ba^{2+} is mobilising $^{226}Ra^{2+}$ much better than Na^+ does. In the presence of Cl^- the exchange rate of Ba^{2+} is 4-times better than the one of Na^+ (the results are normalised to the same particle concentration in the water). By taking NO_3^- as the anion, the exchange rate of Ba^{2+} is now 8-times better. This goes parallel with the observation that Ba^{2+} as well as Na^+ are mobilising $^{226}Ra^{2+}$ twice as much in the presence of NO_3^- than in the presence of Cl^-. Looking at the entropy of hydration of ions we find again the factor of 2: Cl^- has a value of +10.2 cal/(K*mol) and NO_3^- has a value of +19.4 cal/(K*mol). Therefore, beside the ion-exchange process, the type and amount of anions has a pronounced influence on the Ra^{2+} mobilisation. Large anions like NO_3^- are disturbing the hydrate coat around minerals stronger. If the hydrate coat is weakened, the ion-exchange process will be enhanced, and therefore more Ra^{2+} will be released to the water.

4. DISCHARGE OF PIT WATERS

What happens when the pit waters are raised? When the mostly reducing waters are discharged to the rivers, it gets in contact with sulphate-bearing oxidising surface water, and as a result Ba^{2+} is precipitated as baryte. Because of the geochemical similarity, Ra^{2+} is co-precipitated and forms together with Ba^{2+} radio-baryte. The solubility product of Ba-Sulphate amounts to $1.0 * 10^{-10}$ mol^2/l^2, Ra-Sulphate with a solubility product of $4.2 * 10^{-11}$ mol^2/l^2 is a bit more insoluble. To verify, under what concentrations Ra^{2+} and Ba^{2+} are precipitating, one has to look at the particle concentration in the water. 1 Bq/l ^{226}Ra is equal to $1.2 * 10^{-13}$ mol/l. So, very high ^{226}Ra activity concentrations go along with a very small number of atoms. If we take 350 Bq/l ^{226}Ra we have a particle concentration of $4.2 * 10^{-11}$ mol/l. Under this very high ^{226}Ra concentration, we need 1 mol/l SO_4^- to precipitate ^{226}Ra with SO_4^-. 1 mol/l SO_4^- is the incredible amount of 100 000 mg/l, which will not be reached in natural waters. On the other hand, 1000 mg/l Ba^{2+} are equal to 0.007 mol/l. Therefore, we can say that Ra^{2+} is only co-precipitated together with Ba^{2+} radio-baryte.

Such precipitation can be seen close to the discharge point of some collieries; they reach ^{226}Ra concentrations up to 32 000 Bq/kg (Tab. 2). Downstream of the discharge point the radium concentrations of the water are decreasing. But the decrease depends very strongly on the radium concentrations of the pit water and the discharge rate, which differs from day to day. Parallel to the decrease of concentrations in the water, a decrease of radium concentrations can be detected in the sediments of the river. Due to floods, radium can even reach the soils adjacent to the riverbanks. Up to 1400 Bq/kg ^{226}Ra are detectable in the overbank deposits (Tab. 2). In comparison to the ^{226}Ra concentrations, the ^{228}Ra concentrations of the overbank deposits are low. This indicates that the radium contamination of the soil samples showing the highest concentrations, happened several years ago (^{228}Ra is partly decayed). Finally, a fraction of the radium in the water is accumulating in sewage sledges formed in clarification plants (Tab. 2), from where it may be dispersed on farmland in order to fertilise the fields.

Table 2. ^{226}Ra and ^{228}Ra concentrations in the environment due to hard coal mining (compiled from [5], [7], [8], [13]:

	^{226}Ra	^{228}Ra
Pit water	< 63 Bq/l	< 28 Bq/l
River water	0.01 – 0.1 Bq/l	0.01 – 0.05 Bq/l
Sediment (discharge point)	< 32 000 Bq/kg	< 15 000 Bq/kg
Sediment (downstream)	< 5 000 Bq/kg	< 2 000 Bq/kg
Overbank deposit	< 1 400 Bq/kg	< 500 Bq/kg
Sewage sledge	500 – 1 400 Bq/kg	< 600 Bq/kg

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Management of roads with abnormal radiation

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Abstract. Several asphalt concrete (AC) roads in Taoyuan County of Taiwan were found radioactively abnormal in 1994. Atomic Energy Council (AEC), the regulatory agency, was asked to take the samples, to perform the radiochemical analysis and dose evaluation as well as to investigate the source of contamination. The cause of high radiation was due to high uranium and thorium concentration slag used in the AC. The dose rate was approximately 1 μSv/hr at the road surface. The maximum annual dose received by pedestrians was estimated at 0.13 mSv (2.5% of annual dose limit of 5 mSv for the public), or approximately 1/15 of the value of annual natural background radiation in the Taiwan area. Consequently, the AEC suggested that there was no need to implement engineering remedy measures to remove the AC surface of the roads. However, upon consideration of socioeconomic condition and public opinion, the local government still decided to remove the contaminated surface of these roads. The AEC helped to formulate the operational procedures for removal and disposal of the AC including the radiation protection program and the disposal site. To date, all the contaminated AC surface of the roads was removed and properly disposed. The contaminated AC roads are a typical example of improper disposal of wastes containing Technologically Enhanced Naturally Occurring Radioactive Materials (TENORM). A new regulation was promulgated by AEC recently to limit the use of slag, coal ash or any other industrial wastes unless its radiation or activity level is below the limit.

1. INTRODUCTION

Atomic Energy Council (AEC), the regulatory agency in Taiwan, found an asphalt concrete (AC) road in Taoyuan County radioactively abnormal in September 1994. Subsequently totally 8 contaminated roads were discovered, which are all located in Taoyuan County. In order to investigate the source of contamination, samples were taken for radiochemical analysis. Results revealed that the contaminating radionuclides were the naturally occurring radioactive materials (NORM) of thorium and uranium series together with potassium-40. According to radiation survey and dose assessment, the radiation doses to nearby residents and pedestrians were low compared to the annual dose limit for the general public or natural background radiation in Taiwan area.

Since the effects of radioactively abnormal roads on nearby residents or pedestrians were well within the safety limit set by AEC, no action was recommended and the roads could be kept for use. But upon consideration of the socioeconomic and psychological factors, especially the falling housing price (The house is the most valuable property of Taiwanese people), the Taoyuan county government decided to remove the contaminated surfaces of all roads. This work has already been completed with the technical assistance of AEC.

TABLE 1. IDENTIFY THE COMPOSITION OF BLACK GLASS-LIKE MATERIAL

Sample		Morphology			Physical properties			Chemical properties (%)									Radioactivities (Bq/kg)			Note
		Shape	Size(mm)	Color	Density	Hardness	Structure	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	P_2O_5	TREO	TiO_2	ZrO_2	^{232}Th	^{238}U	Ratio	
Contamination slag	A (1)	Tube-shaped thin aperture fragment	0.05-9	Black glass-like shining	>2.89	5.5	Amorphous	26.9	-	10.58	16.80	-	0.16	5.57	9.92	1.27	26,745 ±974	9,619 ±187	2.78 ±0.09	$SnO_2$1.04% WO_3 0.42%
	B (2)	Tube-shaped thin aperture fragment	0.05-3	Black glass-like shining	>2.89	5.5	Amorphous	28.9	8.14	11.93	12.18	2.32	0.27	4.34	8.32	1.61	25,650	9,205	2.79	$SnO_2$2.13% $WO_3$0.62%
Heavy sand		Ripple-surface like oval	0.2-0.4	Dark brown	>2.89	-	Polycrystal	3.2	-	51.48	0.28	-	0.68	4.73	16.68	?	20,400	6,940	2.94	
Monazite		Oval pebble	0.15-0.3	Black	4.9-5.3	5-5.5	Monoclinic	25.0	1.30	1.0	0.64	0.66	22.6	45.3	1.5	0.66	28,400-31,585	5,060-5,850	5.86-6.24	
Steel slag	A		-	Gray brown	2.88	-	-	33.46	15.74	0.56	38.81	7.65	-	-	0.52	-	6.6-36	13-161	0.33-0.51	
	B		>30	Dark green shining	>2.89	>5.5	Amorphous	-	-	-	-	-	-	-	-	-	259	337	0.77	
	C	Irregular chunk fragment		Black glass-like shining	>2.89	>5.5	Amorphous	-	-	-	-	-	-	-	-	-	230	155	1.48	
Coal ash	A	granule	-	-	2.07-2.24	-		56-62	20-22	3-7.7	0.5-2	0.4--0.8	-	-	-	-	54-115	72-87	-	
	B	granule	-	-	2.09-2.24	-		55-57	20-35	4-9.3	3-4.1	1.08	-	-	-	-	98-149	72-87	-	
	C	granule	-	-	-	-		46.5	16.5	5.5	24.5	2.5	-	-	-	-	64-170	42-130	-	
Rare earth waste		Cohere granule	0.02-0.7	Yellow brown	-	-	Polycrystal	30.4	-	0.3	-	-	2.12	4.32	1.01	0.13	1,560-26,400	292-9,670	0.71-5.34	RE(OH)3

Note: (1) Taken from contamination roads.

(2) Found from asphalt concrete company.

2. SOURCE OF THE CONTAMINATION

Samples taken from each road were sent to four independent laboratories for analysis [1]. After chemical and physical separation, the radiation was determined from the black-colored glass-like slag contained in the AC. According to SEM and x-ray diffraction analysis, the slag was probably produced from the high temperature steel manufacturing process at more than 1000 degree Celsius. Its physical properties and radioactivity are quite different from ordinary sand, stone, heavy sand, monazite, or coal ash. The results of analysis are shown in Table 1. The total weight of the radioactive slag contained in the AC was estimated at several hundred tons. Therefore, it should be produced by a large factory with higher than normal NORM content in the feed materials. The improper disposal of the wastes, i.e. slag resulted in this incident. After thorough investigation, AEC identified the company produced the AC but was unable to locate the company which produced the slag. It is a typical case of improper disposal of wastes with technologically enhanced naturally occurring radioactive materials (TENORM).

TABLE 2 RADIATION MEASUREMENT AND DOSE ASSESSMENT RESULTS

Road number	Dose rate at 1 meter above ground (μ Sv/h)	Annual dose (μ Sv)		
		Pedestrians walk across the road	Pedestrians walk along the road	nearby residents
1	0.10~0.92	2.6×10^{-3}	1.4×10^{-1}	N/A
2	0.10~0.40	4.6×10^{-4}	9.8×10^{-3}	130.9
3	0.2~1.5	1.1×10^{-2}	1.7	94.5
4	0.3~1.4	9.0×10^{-3}	4.5×10^{-1}	116.3
5	0.6~1.7	6.3×10^{-3}	1.3×10^{-1}	58.2
6	0.4~1.4	4.5×10^{-3}	1.4×10^{-1}	94.5
7	0.2~0.4	5.6×10^{-4}	2.8×10^{-3}	N/A
8	0.2~1.2	1.9×10^{-3}	1.5×10^{-2}	130.9

3. RADIATION DOSE EVALUATION

The radiation dose at the contaminated road surface depends on the slag content in the AC. The average dose rate was about 1μ Sv/hr. A conservative dose assessment for the nearby residents or pedestrians was performed. The results are shown in Table 2. The maximum annual dose received by a resident was about 130μ Sv, or 2.5% of the annual dose limit of 5 mSv for the general public, or 1/15 of the natural background radiation in Taiwan area. Therefore, the AEC recommended to local government not to take action to this radioactive abnormal road. Nevertheless, due to the large psychological impact to the public and the falling land and housing prices, the local government finally made decision to remove the contaminated surface.

4. WASTE DISPOSAL SITE

In Taiwan, there is no low-level radioactive waste final disposal site. It is very difficult to find the private land to bury the removed AC containing NORM. After an exhausting search for a proper place, a freeway roadbed was judged to be the best choice for disposal.

To prevent the public concerns about the NORM contained in the radioactive slag after disposal will be dissolved by rain or groundwater and then migrate to the life chain, a leaching test similar to the solidified radioactive wastes was performed in the laboratory. The experimental results showed that the leaching rate was well below the instrument detection limit.

Considering the airborne particulate problem during the road surface removal process, an air sampling and analysis in a section of abnormal road was performed. The airborne particulate measurement also showed that it was below the instrument detection limit.

5. ROAD REMOVAL PROJECT

The Taoyuan County government had to submit a road removal project, which detailed the removal operations, radiation protection program, quality assurance program, the disposal site after removal, etc. After approval by AEC, the local government then proceeded with removal operations.

After reviewing the international disposal experiences and suggestions from the experts, the AEC demanded shallow land burial after removal. The depth of earth cover shall be more than 50 cm and dose rate after earth cover shall be lower than 0.14μ Gy/hr.

In the actual removal operation, there were two different types of disposal operations. One is the removed AC was transferred and poured into the roadbed of freeway, then mixed with the cement, and later covered with earth. However, this approach encountered difficulties during bad weather. The other is the removed AC was mixed with cement at one to one ratios in the cement company first, and then transferred to the construction site of freeway. The latter type not only accelerated the construction, but also lowered the radiation dose to the workers.

Because the radiation dose rate of contaminated AC was not high and it was later diluted with both non-contaminated AC and cement, the final dose rate of concrete was within the variation range of natural radiation background.

After surveying the disposal site of the newly constructed freeway, the environmental radiation measurement results were within the variation of natural radiation background.

6. NEW REGULATION

The radioactively abnormal roads are a typical example of improper disposal of wastes containing TENORM. Following the international practices, the AEC promulgated a new regulation on the reuse of industrial wastes such as coal ash and slag as construction materials [2]. An equation specified the limit on content of uranium, thorium and potassium is adopted. In addition, the radiation dose rate is set to be lower than 0.4μ Sv/hr. By meeting this regulation, the non-hazardous industrial wastes can be used as building materials. For other applications such as road or runway, the above criteria could be relaxed. Furthermore, the AEC has recommended the construction companies to perform radiation survey before using non-natural sand or stone. With the new regulation, misuse of technologically enhanced naturally occurring radioactive materials can be avoided.

7. CONCLUSIONS

The AEC successfully resolved the removal of radioactively contaminated roads and the disposal of the resultant wastes. In order to prevent the recurrence in the future, the AEC has promulgated the new regulation to limit the NORM content in the industrial wastes to be used as construction materials.

In addition, the AEC will persistently pay attention to the international development and the trend on the use of the technologically enhanced naturally occurring radioactive materials.

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^{222}Rn determination in mineral waters from the Poços de Caldas Plateau in Brazil

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Abstract. It is estimated that 50% of the radioactive effective dose equivalent to man comes from radon and its radioactivity daughters. The main ^{222}Rn sources are the soils, building materials and potable waters. There is an especial interest in spas waters with high natural radioactivity. It's considered that the use of these waters as drinking waters is a significant radiation exposure factor, and it is worthwhile to assess the consequent dose. Such estimation has been made for the Poços de Caldas Plateau, which is a region of high natural radioactivity, from volcanic origin, containing several spas (Águas da Prata, Caldas, Poços de Caldas and Andradas). The ^{222}Rn content was determined in 23 spring waters in Poços de Caldas and neighboring cities. In water sampling, modified Marinelli flasks were used. The determinations were effected with a high resolution gamma ray spectrometer. High concentration variations were observed in the collected mineral waters, the highest values having been found in Fonte Villela's waters, in Águas da Prata town (926 Bq/l); Grande Hotel's in Caldas Town (420 Bq/l) and COLAB's in Poços de Caldas region (289 Bq/l). The annual whole body effective dose equivalent estimate for adult due to water ingestion, using the Crowford – Brown's biokinetic model's adult dose conversion factors, was higher than 1 mSv/year in 61% of the analyzed waters. Key words: ^{222}Rn, spring waters, Poços de Caldas plateau, radioactive dose, natural radioactivity.

Introduction

The Poços de Caldas Plateau is situated in the southwest region of Minas Gerais State, Brazil. It is formed by a volcanic caldera with a diameter of approximately 35 km, with a central depression surrounded by a 300 meters high borderline.

The Plateau has a high natural radioactivity with many radioactive anomalies containing uranium and thorium in association with rare earth, zirconium and molybdenum minerals.

In this region (figure 1) are located the spas of Águas da Prata, Caldas, Poços de Caldas and Andradas, which have many mineral waters springs amply used by local people and tourists. Two of these springs are commercially exploited.

These spring's waters come from prolonged contact with mineral rocks and so it's expected to find radioactive elements dissolved and diffused. Lauria and Godoy (1988) have found low concentration of ^{238}U, ^{234}U, ^{226}Ra, ^{228}Ra, ^{232}Th, ^{230}Th, ^{228}Th in these spring's waters, except for one spring Fonte Villella, with high ^{226}Ra and ^{228}Ra values.

In this paper, ^{222}Rn concentration was determined in 23 mineral water springs in the Poços de Caldas Plateau cities. The sampled springs were the most widely used by the population as drinking water. These waters were collected just at the emergence point.

An estimate for annual effective dose equivalent of adult individual of the public consuming waters has been made.

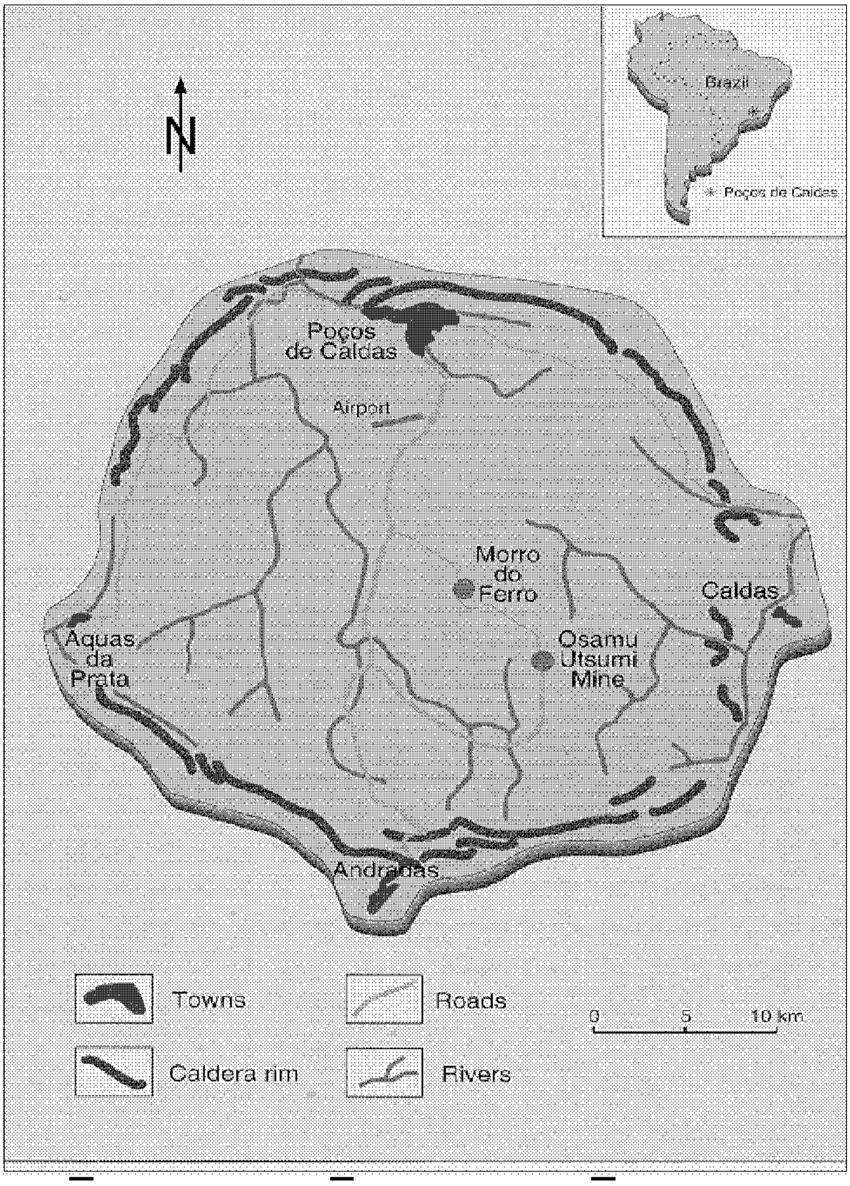

Figure 1. Poços de Caldas Plateau (NAGRA, 1993).

Materials and methods

Sampling

The water samples were collected using modified Marinelli flasks (Figure 2), like those described by Belloni, Cavaioli, Ingrao, Mancini, Notaro, Santaroni, et al (1995) but without the lock valve. In substitution of the lock, a flexible plastic cover with thread and a long staff was made to close the opening. For the other opening a stopper with a long staff, so that when closing the flasks after filling it, there is a small internal pressure, to avoid bubble formation. The sampling was made using a tube placed at the bottom of the flasks, letting the water overflow for a couple minutes. Three samples were taken from each spring.

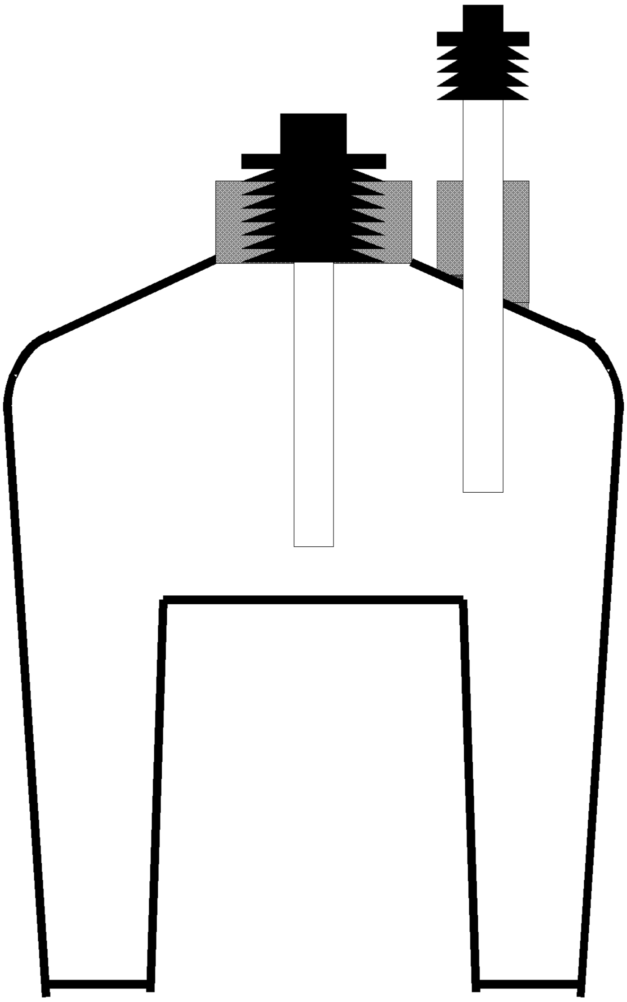

Figure 2. Modified Marinelli flask.

The samples were taken to the laboratory in thermal boxes, to maintain the temperature.

Gamma ray spectrometry

After four hours, to allow radioactive equilibrium of ^{222}Rn and it daughters' ^{214}Pb and ^{214}Bi, the samples were measured at 295, 352 and 609 KeV, in a gamma ray spectrometer model GMX — 4519 from CANBERRA, with relative efficiency of 45%, for 15 minutes.
For the system calibration, an Amershan ^{226}Ra standard solution, diluted to a final activity at 1467.88 Bq/l was used. This solution was placed into a counting flask, sealed and after 30 days (to reach radioactive equilibrium of ^{226}Ra and its daughters) the ^{214}Pb and ^{214}Bi photo peaks were measured.
Using the same geometry, the samples were counted under identical conditions, the results being obtained by direct comparison with the standard solution above mentioned.
The algorithm used to calculate the activity is:
$A_a = A_p \times CPS_a/CPS_p$
Where:
A_a = sample activity;
A_p= standard sample;
CPS_a= counts per second at the photo peak of the sample;

CPS_p = counts per second at the photo peak of the standard;

Dose estimate

The annual whole body effective dose equivalent due to radon ingestion was estimated using Crawford–Brown biokinetics model's adult dose conversion factors (Crawford–Brown, 1990), assuming an individual ingests 2 l of water per day and 1,5 day elapsed between water collection and consumption.

Table: ^{222}Rn concentration in spring waters and estimated of annual effective equivalent dose due radon ingestion

Fountains	**Rn-222** (Bq/l)			**Dose**[a] (mSv/year)
	Poços de Caldas			
Águas Minerais Poços de Caldas 1	**60,50**	±	**2,50**	**0,81**
Águas Minerais Poços de Caldas 2	**27,33**	±	**6,44**	**0,36**
Bianuchi	**150,50**	±	**2,00**	**2,01**
Cibel	**54,67**	±	**3,11**	**0,73**
COLAB	**289,00**	±	**10,0**	**3,86**
Cristo	**39,67**	±	**1,11**	**0,53**
Fraya	**64,50**	±	**0,50**	**0,86**
Monjolinho	**122,67**	±	**4,22**	**1,64**
Morro das Cabras	**152,33**	±	**4,89**	**2,03**
Primavera	**170,50**	±	**1,50**	**2,27**
Quati 1	**180,00**	±	**17,3**	**2,40**
Quati 2	**214,67**	±	**0,80**	**2,87**
Sant'Ana	**86,33**	±	**1,11**	**1,15**
Sinhazinha	**84,00**	±	**4,00**	**1,12**
	Águas da Prata			
Antiga Prata	**53,00**	±	**4,67**	**0,71**
Paiol	**6,00**	±	**1,33**	**0,08**
Radioativa	**88,33**	±	**15,11**	**1,18**
Vilella	**925,67**	±	**38,22**	**12,36**
	Caldas			
Grande Hotel	**417,67**	±	**9,11**	**5,58**
Sebastião Cândido	**79,67**	±	**1,78**	**1,06**
	Andradas			
Rua Cedro	**88,50**	±	**1,50**	**1,18**
Serra	**35,67**	±	**1,11**	**0,48**
Vila Mosconi	**13,67**	±	**0,44**	**0,18**

a – annual whole body effective dose equivalent for adult

Results

The ^{222}Rn activity concentrations in water samples and the annual effective equivalent dose to an adult are presented in table 1. The values are an average of three measurements of three samples collected in the same spring.

The highest value for ^{222}Rn was found in the Villela spring, in Águas da Prata town, in agreement with the highest ^{226}Ra and ^{228}Ra values cited by Lauria and Godoy (1988).

All ^{222}Rn values are higher than 3,7 Bq/l, the limit recommended by US-EPA (Crawford–Brown, 1991), which corresponds to a cancer incidence probability of 10^{-4}. All the same, the values surpass the Brazilian norm reference value of the 0,1 Bq/l (Brazil, 1990).

If the US-EPA recommendation is to be adopted, all spring waters should be treated, or the population be instructed on ^{222}Rn concentration decreasing techniques.

In 14 of these 23 analyzed samples (61%), the estimated effective equivalent dose is higher than 1mSv/year, which is the maximum annual dose for an individual of the public in Brazil.

These results suggest that this region's mineral waters are an important factor in radioactive dose due to natural exposure and so collective dose assessment and cancer risk should be determined.

Another sampling campaign will be conducted in the rainy period, in order to check the ^{222}Rn content variation in the spring waters analyzed.

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Training on NORM: Increasing awareness, reducing occupational dose

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Abstract. Awareness of a risk is the starting point of protection against it. The best way of creating this awareness is by providing training to the persons that run the risk. This also applies to the risks associated with the presence of Naturally Occurring Radioactive Materials (NORM) in oil and gas production installations. Our experience shows that with relatively little effort, and low cost it is possible to provide training on NORM to operational personnel of oil and gas companies. In this way, a reduction of occupational dose and an increased protection of the environment can be achieved. This applies in particular to the less developed countries, where little regulation is in place. The workers themselves form a group that is motivated and eager to learn about these risks.Training of personnel is a valuable tool to make people more conscious of the risks involved with radiation and to safeguard society, instead of a system of permissions and governmental regulations that often is not functioning properly.

1. INTRODUCTION

The oil and gas industry is one of the industries that is faced with the problem of naturally occurring radioactive material (NORM). In this paper we describe the way in which an oil company operating in a less developed country can deal with this problem by drawing up special NORM procedures, and training of its workers.

However, first we give a brief, and therefore simplified, description of the origin of NORM in the oil, and gas industry and illustrate the risks associated with it.

2. ORIGIN OF NORM DEPOSITS IN THE OIL AND GAS INDUSTRY

^{238}U, and ^{232}Th are distributed throughout underground rock formations from which oil and gas are produced. They are part of the matrix of the rock, essentially insoluble in the reservoir fluids (fresh water, salt water, oil, gas or condensate), and therefore immobile. However the radium isotopes ^{226}Ra, and ^{228}Ra which are daughters of respectively ^{238}U, and ^{232}Th are somewhat soluble in water and are therefore mobile. Consequently, radium may be produced with any water.

The concentration of radium that may be present in produced water will depend upon the nature of the formation and the physical and chemical conditions. Radium will be mixed (in very small proportions) with calcium, barium, and some strontium, which are much more abundant and possess similar chemical properties.

As produced fluids move from the reservoir to production facilities at the surface and then through various treatment processes culminate at the surface, the physical and chemical conditions change. This results in significant changes in the ability of the fluids to dissolve radium. If this ability decreases, then radium will precipitate as part of any scale or sludge, either as radium sulphate or radium carbonate.

Another major pathway in which contamination of oil and gas installations occurs is through the diffusion of the radon isotopes ^{220}Rn and ^{222}Rn that are either dissolved in the produced fluids or mixed with natural gas. Radon can be produced either at the surface or in the formation. Gas plants can have very high radiation levels, especially where large volumes of gas are stored or compressed. The most significant radionuclide remaining at the internal

surface of the installation is ^{210}Pb (and it daughter products) originating from ^{222}Rn, which has a relatively long half-life. It is mostly present as a thin lead-film.
Finally, also the transport with reservoir fluids of unsupported ^{210}Pb together with non-radioactive "carrier lead" is observed [1]. With "unsupported" we mean that the ^{210}Pb concentration can neither be explained from ^{226}Ra contributions in NORM deposits, nor from ^{222}Rn concentrations in natural gas.

Thus one can distinguish between deposits containing radium, and deposits containing lead. The activity concentrations in radium deposits in production installations typically range from 1 to 500 Bq/g for ^{226}Ra and from 0 to 300 Bq/g for ^{228}Ra and ^{210}Pb. In well equipment however, ^{226}Ra concentrations up to a few thousands Bq/g were observed.
The activity concentration in lead deposits can be as high as 3,000 Bq/g for ^{210}Pb.
In general scales have a higher activity concentration than sludges.

3. OCCUPATIONAL RISK ASSOCIATED WITH NORM IN O&G PLANTS

Since NORM contains radionuclides from the ^{238}U, and ^{232}Th decay series, it emits α-, β-, and γ radiation, and therefore there is a risk of both external-, and internal radiation exposure.

3.1. External radiation exposure

Significant external dose rates are only observed at the outside of installation parts that are internally contaminated with radium deposits. The 46 keV gamma rays emitted by Pb-210 are not penetrating enough to cause any significant dose rate at the outside of an installation that is internally contaminated with lead deposits.
The dose rate depends on the activity concentration of the radium deposit, its volume, its geometry and on the shielding capability of the walls, but is typically in the order of several µSv/h. Only in some extreme cases dose rates of several tens of µSv/h are observed.

3.2. Internal radiation exposure

Once a process plant is opened for maintenance or inspection, workers are faced with what is than an unsealed radioactive material.
In table I the Dose Conversion Coefficients of ^{226}Ra, ^{228}Ra, and ^{210}Pb for workers as given in the table (C.1) of the Euratom Basic Safety Standards [2] are presented. Please note that these values do take into account the ingrowth of daughter nuclides in all regions of the body following an intake of unit activity of the parent nuclide, but do not take into account any activity of daughter nuclides in the initial intake. The values stated behind ^{226}Ra+, ^{228}Ra+, and ^{210}Pb+ do take into account the activity of daughter nuclides in the initial intake, assuming secular equilibrium.
In table II we have calculated the committed effective dose for inhalation of 1g of aerosols with diameters of 1 µm, and 5 µm respectively or ingestion of 1g of material originating from scales with the maximally observed specific activities in the oil and gas industry.
Table II illustrates that the potential radiation dose due to internal contamination is much higher than the potential radiation dose due to external exposure.
It should be noted that radium possibly is almost as chemically toxic as plutonium which is the most toxic element to man, and therefore there is not only a radiation risk.

Table I. Dose Conversion Coefficients, taken from [2]. The values stated behind ^{226}Ra+,^{210}Pb+, ^{228}Ra+ do assume secular equilibrium between the parent and its daughters in the initial intake.

Radionuclide	DCC$_{inh}$ (Sv/Bq) AMAD 1 μm	DCC$_{inh}$ (Sv/Bq) AMAD 5 μm	DCC$_{ing}$ (Sv/Bq)
^{226}Ra	$3.2 \cdot 10^{-6}$	$2.2 \cdot 10^{-6}$	$2.8 \cdot 10^{-7}$
^{226}Ra+	$3.2 \cdot 10^{-6}$	$2.2 \cdot 10^{-6}$	$2.8 \cdot 10^{-7}$
^{210}Pb	$8.9 \cdot 10^{-7}$	$1.1 \cdot 10^{-6}$	$6.8 \cdot 10^{-7}$
^{210}Pb+	$4.0 \cdot 10^{-6}$	$3.4 \cdot 10^{-6}$	$9.2 \cdot 10^{-7}$
^{228}Ra	$2.6 \cdot 10^{-6}$	$1.7 \cdot 10^{-6}$	$6.7 \cdot 10^{-7}$
^{228}Ra+	$4.5 \cdot 10^{-5}$	$3.6 \cdot 10^{-5}$	$8.1 \cdot 10^{-7}$

Table II. Committed effective doses resulting from inhalation of aerosols or ingestion of material originating from scales contaminated with naturally occurring radionuclides with stated specific activities.

Radionuclide	Specific activity (Bq/g)	Committed effective dose (mSv/g)		
		Inhalation AMAD 1 μm	Inhalation AMAD 5 μm	Ingestion
^{226}Ra+	500	1.6	1.1	0.1
^{210}Pb+	300	1.2	1.0	0.3
^{210}Pb+	3,000	12	10.2	2.8
^{228}Ra+	300	13.5	10.8	0.2

By order of the Dutch Ministry of Social Affairs and Employment an investigation has been done on the exposure of workers in the oil and gas industry to NORM [3]. In this study only materials with a total specific activity above 100 Bq/g were taken into account. Calculations were performed for several scenarios, under the assumption that no special precautions were taken with regard to NORM contamination.

For routinely performed maintenance on components at a production location, the yearly dose was calculated to be 0.03 mSv under normal conditions, and 0.5 mSv under unfavourable conditions.

For revision jobs on components performed by a specialised company on its own location the yearly dose was calculated to be 0.3 mSv under normal conditions, and 7.0 mSv under unfavourable conditions.

It is clear that appropriate safety measures should especially be taken when work is performed on open NORM contaminated installations.

4. NORM PROBLEM OF AN OIL COMPANY IN AFRICA

In 1995 RTD Radiation Protection Services performed a NORM survey for a major oil company in an African country. During this survey NORM contamination was found at various installation parts, that were either still in operation or were supposed to be disposed of as scrap metal, and it became clear that the oil company had a NORM problem.

The Radiation Advisory Committee (RAC) of the oil company reacted to this problem by developing NORM procedures with the aim to implement the policy of the oil company to protect its personnel, the environment and the public against the hazards of exposure to ionising radiation due to its activities.
There are no specific regulations on ionising radiation and radioactive material in the African country were the company operates, let alone regulations on NORM. However, being one of the operational companies of an international group of companies, the oil company has to comply with the group regulations as stated by the group management.
Since the oil company is of Dutch origin, these group regulations are partly based on Dutch regulations and practices. This means for example that material is classified as radioactive material if its total specific activity is higher than 100 Bq/g, as in the Dutch regulations. In the field an action level is set at three times background radiation level for materials that are suspected to be radioactively contaminated, which is the same action level as applied by Dutch oil companies.

4.1. Radiation Protection Supervisors and Radiation Protection Technicians

The oil company uses Radiation Safety Experts of RTD Radiation Protection Services to act as Radiation Protection Advisor (RPA). The task of the RPA is to make policy proposals and, after these have been adopted by the RAC, monitor the implementation of the policy, and to provide expert advice for all matters concerning ionising radiation.
According to the oil company's manual on ionising radiation a Radiation Protection Supervisor (RPS) shall perform measurements and supervise work involving ionising radiation. One of the RPSs is appointed as focal point, and will act as representative on behalf of the RPA, and directly report to the RAC.

Table III. Tasks, and responsibilities of Radiation Protection Supervisors and Radiation Protection Technicians.

The RPS shall:	The RPT shall:
- inspect and supervise work involving ionising radiation - ensure quality assurance of radiation protection - organise the required monitoring and sampling - qualify waste with respect to radioactivity - ensure that radioactive waste and NORM-contaminated equipment is stored, packaged and disposed off in compliance with regulations and procedures	- measure count rates whenever no data are available on installation parts to be opened - register and report the results in compliance with relevant NORM procedures - notify the RPS if count rates exceed the agreed standard, i.e. 3 times background - supervise routine NORM jobs

A RPS can be supported by several Radiation Protection Technicians (RPT), e.g. maintenance operators. A RPT only needs to measure the count rate when a specific part of an installation is opened and report this to the RPS. A RPT will have to follow the instructions given by the RPS.

In table III the tasks and responsibilities of RPSs and RPTs are summarised.

To fulfil his job a RPS shall be trained in basic radiation safety, and specifically in the handling of NORM. The RPS shall have knowledge of the company's manuals and procedures on ionising radiation and NORM. Next to attending a course he should also have gained some experience by assisting a RPS at non-routine jobs with respect to NORM.

A RPT shall be trained in using available radiation monitors to measure NORM. A RPT shall have knowledge of the company's NORM procedures concerning the registration and reporting of measuring results.

5. TRAINING ON NORM

At request of the oil company RTD Radiation Protection Services has developed a NORM training both for Radiation Protection Technicians (RPTs) and Radiation Protection Supervisors (RPSs).

It is important that an independent institute provides the training because in that case the credibility for the employees is larger than when the employer provides the training

5.1. Objective of the training

The main objective of the training is to create a general awareness of the risks of NORM because it means a threat for the workers, the environment , the local population, and in the end the world population (think of the transport of contaminated scrap metal).

Giving these training courses reduces directly the first risk, i.e. the sanity of the workers because these persons are taught in a direct manner how to deal and to handle NORM. It may be expected that the awareness of these risks will diffuse from the directly addressed group of lower and medium level technical employers through the entire company into the society. The workers unions will be very helpful in the process.

In addition to the reduction of risk, more knowledge of the subjects "radioactivity" and "(ionising) radiation" can be reassuring because they often cause agitation amongst non-educated workers.

5.2. Main elements of the course

The training consists of a theoretical and a practical part, and is given "in house" at the production locations. This makes it possible to do practical exercises at the workplaces of the students. Students can directly ask questions concerning their own risk.

Both the RPTs and the RPSs learn how to perform and interpret radiation measurements. In addition, the RPSs learn how to inspect, and supervise work involving NORM independently. They learn about the necessary measures to be taken to protect personnel from getting internally exposed to ionising radiation, and the ways in which dispersal of radioactive material into the environment can be prevented.

The population of students is a mixed population with regard to culture, education, and work experience. Most students have no background in physics, and therefor some of the physical background of radioactivity, and ionising radiation must be treated.

The course consists of the following elements:

- basic atomic and nuclear physics: atoms, molecules, isotopes, radioactive decay;
- ionising radiation: the distinct properties of alpha-, beta- and gamma radiation;
- interaction of ionising radiation with matter, the human body;
- dose and dose rate, annual limits;
- external, and internal radiation exposure, contamination;
- origin of NORM in the oil and gas production;
- detection of NORM (portable monitors)
- interpretation of measurements;
- the specific hazards of NORM;
- protective measures to be taken during work on NORM contaminated installations

6. CONCLUSION

Since NORM is a worldwide problem, and NORM contaminated objects will be transported all over the world, the awareness of the hazards of NORM is of utmost importance. From our experience in the Rotterdam harbour, which is one of the world's biggest trading places for scrap metal, we know that most of the loads of scrap that are intercepted because they show enhanced radiation levels contain NORM contaminated objects.

Unawareness of NORM therefore also leads to a risk for oil companies to be hold liable for the consequences resulting from the transfer of contaminated equipment and scrap metal to other companies and other countries. Such incidents may also result in bad publicity. Increasing the awareness of NORM through training can prevent these unwanted incidents from happening. Training on NORM is relatively inexpensive. Most students are very motivated, because it directly concerns their own daily workplace. Sometimes the students who have been employed by the oil company for a longer period of time can provide valuable information regarding work performed in the past on NORM contaminated installation parts.

NORM training is even more valuable because it creates awareness among the local workers, who in general will have longer contracts than the ex-patriots have, and who are expected to do most of the communication to the local society.

Considering the trend of internationally operating oil companies to make use of local workers as much as possible instead of ex-patriots, it becomes even more important to train this group.

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Disequilibrium implications on dose assessment in the use of NORM as building material

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Abstract. The need of reusing industrial wastes to avoid environmental impact resulting from their deposition and to reduce the management costs, indicates the building industry as an important user of large quantities of industrial wastes, mainly those generated in the ore milling. The industry of phosphate fertilizers is a typical example of this situation. The phosphate rock contains radionuclides of the U and Th decay series. During the chemical attack these radionuclides are distributed in different proportions between the phosphoric acid and the phosphogypsum, depending on the process. Several countries adopt a methodology based on the Ra-226, Th-232 and K-40 content in order to allow the use of materials with natural radionuclides. Dose assessment for the use of phosphogypsum as building material have shown that methodology is not adequate when disequilibrium exists. This paper will present some implications on dose assessment and on the use of that methodology when disequilibrium exists, using two phosphogypsum radionuclides distribution patterns obtained through different milling processes in Brazil.

1. INTRODUCTION

Ore mining and milling industry usually produces large amount of wastes and the use of these wastes is interesting to avoid environmental impact and to reduce the costs of their deposition. In this context the building industry could be important as a user of large quantities of such material.

The industry of phosphate fertilizers is a typical example of this situation. In Brazil there is an increasing interest in use gypsum as building material [1]. Since the natural gypsum deposits are located in the northeast of the country and far from the main market for this material in the southeast, the use of phosphogypsum produced by the fertilizer industry could be economically attractive.

Phosphogypsum is produced during the attack of phosphate rock with sulfuric acid in the production of phosphoric acid. The main chemical reaction for the di-hydrate process may be shown as follows:

$$Ca_{10}F_2(PO_4)_6 + 10\ H_2SO_4 + 20\ H_2O \rightarrow 10\ CaSO_4\,2H_2O + 6\ H_3PO_4 + 2\ HF$$

Phosphate ores contain ^{238}U and ^{232}Th and theirs daughters approximately in radioactive equilibrium, but during the chemical processing the natural radionuclides are fractionated and this equilibrium is disrupted. Then the phosphogypsum contains radionuclides from Uranium and Thorium series originally present in the phosphate rock but in different concentrations than phosphate rock from which it was originated [2].

In Brazil, there is no National regulations limiting the activity concentration of natural radionuclides in building materials The natural radionuclides concentrations in building materials vary in wide range, depending on the origin, geologic history, geochemical characteristics and the chemical processing used in their preparation. To compare the activity concentrations of these radionuclides usually is adopted an index to represent it. This index, called Radium Equivalent Activity, is based on the assumption that 370 Bq/kg of activity concentration of ^{226}Ra in the building material results in absorbed dose rate equal to 1.5 Gy/y to the gonads of a dweller and the same dose rate could be attributed to 260 Bq/kg of ^{232}Th or 4800 Bq/kg of ^{40}K [3, 4].

So the contribution of building materials to the external dose to the gonads can be limited to 1.5mGy/y if the concentrations follow the relation:

$$\frac{A_{Ra}}{370}+\frac{A_{Th}}{260}+\frac{A_K}{4800}\leq 1$$

where: A_{Ra}, A_{Th} and A_K are the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in Bq/kg, respectively . It is important to stress that Radium and Thorium are assumed to be in secular equilibrium with their daughters [5].

Several countries adopt this approach based on the ^{226}Ra, ^{232}Th and ^{40}K content in order to allow the use of materials with natural radionuclides [6]. However this methodology could not be applied when the disequilibrium exists. In the specific case of using phosphogypsum as building material, the chemical process occurred in its generation changes the distribution of activity concentrations initially present in the phosphate rock and the secular equilibrium is disrupted. In this case we should consider that the natural radionuclides from Uranium and Thorium chains present in phosphogypsum will be distributed in the following sub-series, if the exhalation of radon isotopes is not taken in account :

^{238}U series:

^{238}U, ^{234}Th, ^{234}Pa e ^{234}U;
^{230}U;
^{226}Ra, ^{222}Rn, ^{218}Po, ^{214}Pb, ^{214}Bi, and ^{214}Po;
^{210}Pb, ^{210}Bi and ^{210}Po.

^{232}Th series:

^{232}Th;
^{228}Ra and ^{228}Ac;
^{228}Th, ^{224}Ra, ^{220}Rn, ^{216}Po, ^{212}Pb, ^{212}Bi, ^{212}Po and ^{208}Tl.

Due to the half lives of the daughters in each sub-series we could assume that they are in radioactive equilibrium, so the activity concentration of the parent of each sub series could be assumed as the activity of the decay products in the sub-series considered. The effect of the disequilibrium between the sub series will be discussed using as example two different radionuclides distributions pattern obtained for phosphogypsum in Brazil. In this work we did not consider the contribution of ^{40}K to the effective dose due to the use of phosphogypsum, since we are interested on the behavior of Uranium and Thorium series.

2. METHODOLOGY

Samples of fresh phosphogypsum were collected in two different Brazilian fertilizer industries processing phosphate rocks from different mineral deposits. Both companies use the wet process and the mineral processed is apatite from igneous origin. Samples were collected using the operator procedures for process control. The samples were composed on daily base, dried and submitted to radiochemical analysis to determine the activity concentrations of ^{238}U, ^{230}Th, ^{226}Ra, ^{210}Pb, ^{232}Th, ^{228}Ra and ^{228Th} [7]. These radionuclides were selected because they are the long lived radionuclides in the sub-series of the Uranium and Thorium natural radioactive chains. The results are presented in Tables I and II.

The mean concentration values were used as initial activities in the Bateman's equations to evaluate the behavior of these radionuclides in a period of 50 years. The calculations were performed using the algorithm presented by Strenge in 1997 [8].

Table I. Activity concentration of natural radionuclides in phosphogypsum samples of company A

Nuclide	Number of samples	Geometric Mean Bq/kg	Geometric Deviation	Minimum Bq/kg	Maximum Bq/kg
^{238}U	28	18	1.4	6	25
^{230Th}	14	38	1.3	24	53
^{226}Ra	28	91	1.3	52	185
^{210}Pb	14	62	1.3	45	97
^{232}Th	28	39	1.4	24	64
^{228}Ra	28	112	1.5	38	275
^{228Th}	14	84	1.3	53	119

Table II. Activity concentration of natural radionuclides in phosphogypsum samples of company B

Nuclide	Number of samples	Geometric Mean Bq/kg	Geometric Deviation	Minimum Bq/kg	Maximum Bq/kg
^{238}U	30	77	1.2	52	116
^{230Th}	14	184	1.3	110	281
^{226}Ra	30	176	1.8	50	319
^{210}Pb	15	275	1.4	163	513
^{232}Th	29	174	1.3	99	268
^{228}Ra	30	154	2.0	42	384
^{228Th}	14	234	1.3	147	331

Koblinger [9], Stranden [10] and Mustonen [11] have published methods for the calculation of gamma ray exposure originating from building materials. In this paper we use basically the model proposed by Mustonen. The exposure rate at a point in a dwelling may be written as:

$$\dot{X} = K.C.\rho.\frac{1}{4\pi}.\sum_{i} E_i.N(E_i).\mu_c(E_i).\int_{v} \frac{B(E_i,s).e^{-\mu(E_i).s}}{d^2}.dv$$

where:

X = exposure rate (mR/h);
K = constant depending on the units;
C = activity per unity of weight (Bq/kg);
ρ = density of building material (g/cm^3);
E_i = photon energy (MeV)
$N(E_i)$ = number of photons with energy E_i emitted per unit primary disintegration;

$\mu_c(E_i)$ = the linear energy absorption coefficient in air (cm^{-1}) ;
s = the distance the photon travels in the building material (cm);
$B(E_i, s)$ = dose build up factor calculated by Berger's formula;
$\mu(E_i)$ = attenuation coefficient of the building material (cm^2/g);
d = distance from the source point to the middle of the room (cm)

The buildup factors were calculated using the Berger's formula with the data presented in the references [12, 13, 14]. The attenuation coefficients for phosphogypsum were derived from data for concrete using the expression:

$$\mu_{ph} = \frac{\mu_{con} \cdot \rho_{ph}}{\rho_{con}}$$

were $\mu_{ph}, \rho_{ph}, \mu_{con}$ and ρ_{con} are the attenuation coefficient and density for the phosphogypsum and for concrete respectively

The summing were done over all energies of the gamma emitters from the natural series of ^{238}U and ^{232}Th with primary gamma energy greater than 10^{-2} MeV and number of photons emitted per primary disintegration greater than 10^{-3} . The gamma emission of ^{40}K were also considered. All data about gamma emission were taken from ICRP 38 publication. Calculations were performed using the Monte Carlo method to solve the volumetric integral. The effective doses in the middle of the reference room were calculated using a occupation factor of 0.8 and a conversion factor for mR /y to mSv/y from reference [15]. The reference room is a 3 x 4 x 2.8 m^3 room with a window (2 x 1.2 m^2) and a door (0.7 x 2.1 m^2), the walls made of phosphogypsum blocks with 15 cm of thickness and density of 1100 kg/ m^3.

The exposure calculations were performed for each wall and summed up to have the final dose at the point of interest. All results obtained refer to the middle point of the considered room. The method was tested against results obtained by Koblinger, Stranden and Mustonen and the results are presented in Table III.

Table III. Specific exposure rate in the middle of a 4x5x2.8m^3 room made of concrete with a thickness of 20 cm

Reference	Specific Exposure Rate (μ R/h) /(Bq/kg)		
	^{238}U- ^{206}Pb	**^{232}Th- ^{208}Pb**	**^{40}K**
Koblinger (1976)	0.106	0.117	0.00895
	(24)*	(20)	(1)
Stranden (1979)	0.105	0.127	0.00892
	(7)	(7)	(1)
Mustonen (1987)	0.106	0.126	0.00927
	(24)	(20)	(1)
This Work	**0.108**	**0.137**	**0.00929**
	(99)	**(109)**	**(1)**

* Number of photons considered in the calculations.

The behavior in a period of 50 years of effective doses calculated in the middle of the reference room, due the use of phosphogypsum from companies A and B in the walls, are presented in Figures 2 and 3 respectively.

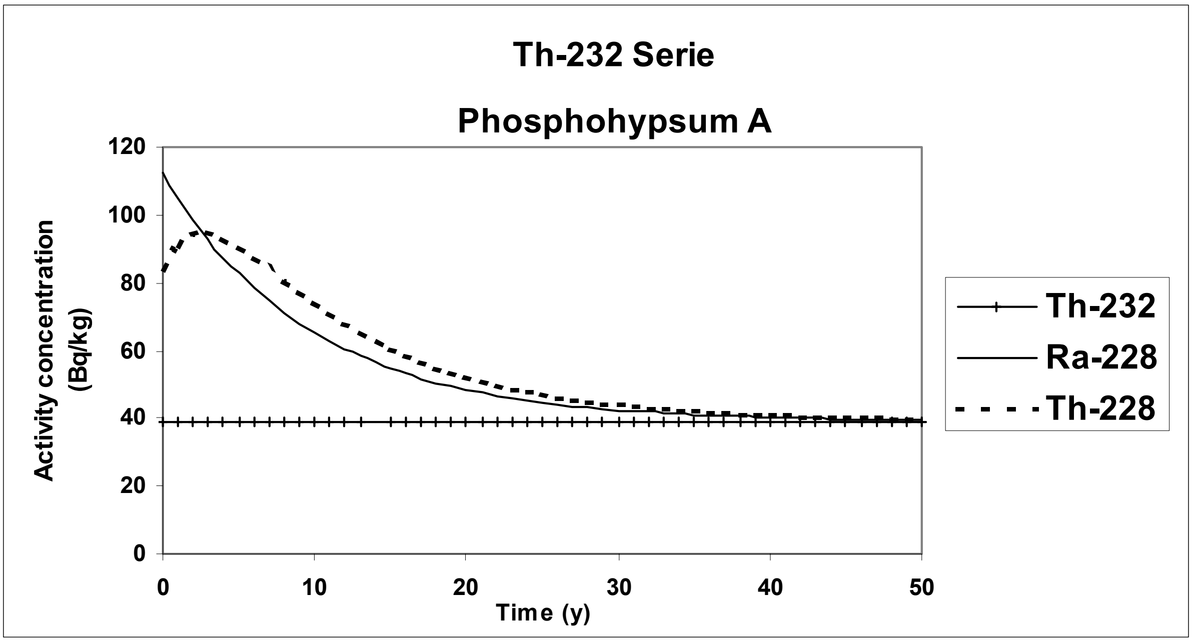

Figure 1. Activity concentration of radionuclides from Thorium series in phosphogypsum A.

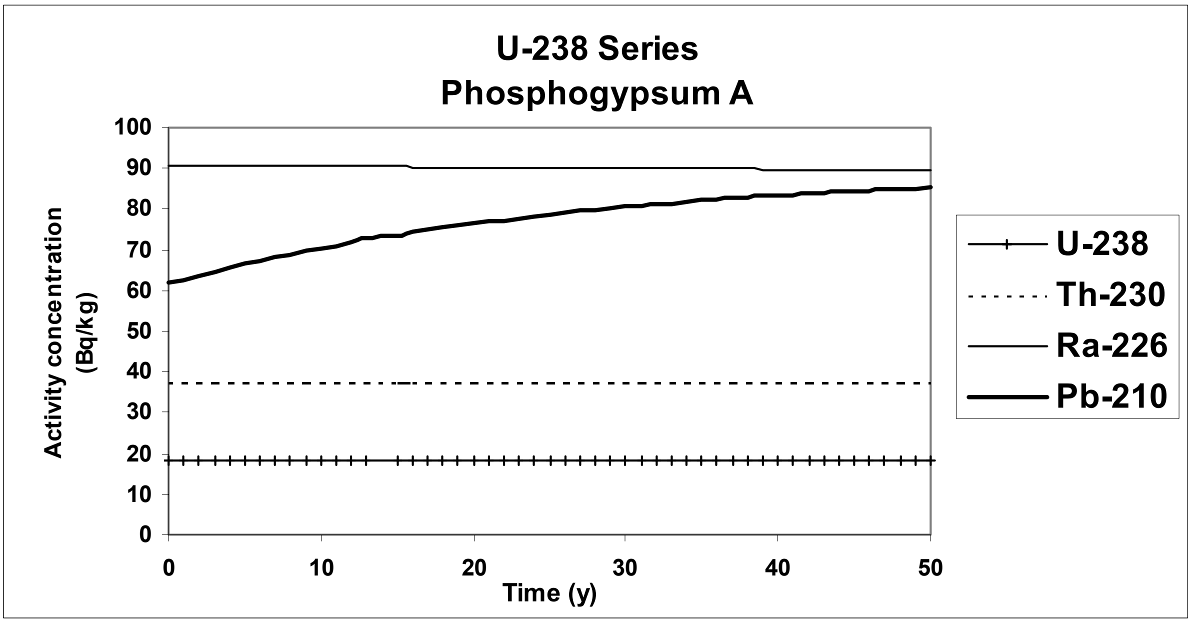

Figure 2. Activity concentration of radionuclides from Uranium series in phosphogypsum A.

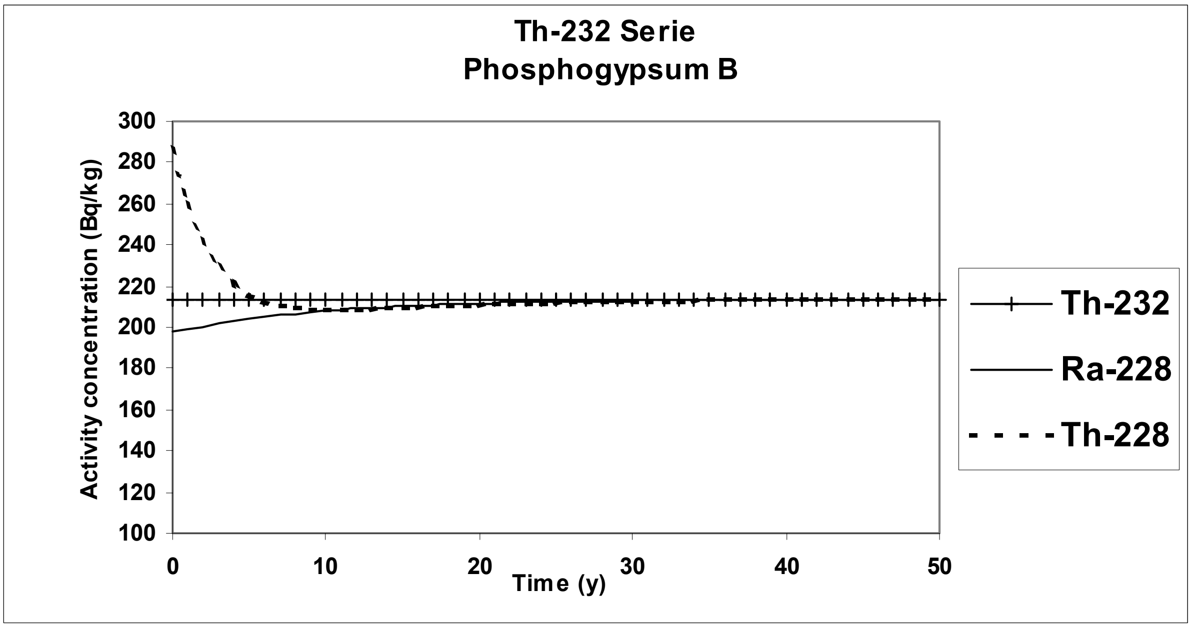

Figure 3. Activity concentration of radionuclides from Thorium series in phosphogypsum B.

3. RESULTS AND DISCUSSION

The activity concentrations found in phosphogypsum samples A could be seen in Table I. We could observe that, as expected from literature, the ^{226}Ra and ^{228}Ra activity concentrations are greater than The ^{238}U and ^{232}Th, respectively. In the samples collected in the company B showed in Table II. The behavior is different since the activity concentrations of ^{232}Th and ^{228}Th are greater than the activity concentration of ^{228}Ra. This behavior is different from the usually reported and could be explained since the thorium is found in this samples associated to a crystalline structure that is not strongly attacked during the chemical processing of phosphate rock.

In the graph presented in Figure 1, we could observe the time behavior of the activity concentrations for thorium series radionuclides in the samples of phosphogypsum A . The transient equilibrium between ^{228}Ra and ^{228}Th will be reached in about 3 years and the secular equilibrium with ^{232}Th in nearly 40 years. In the ^{238}U series we could observe (Figure 2) that, in the considered period, only the variation of the ^{210}Pb concentration is important . It will increase until the equilibrium with ^{226}Ra.

The behavior of the radionuclides of ^{232}Th series in the samples of phosphogypsum B is the same (Figure 3) , but due to the different initial activity concentration ratios, in the first 10 years the concentration of ^{228}Th will decrease until the equilibrium with ^{228}Ra is attained, After that both will increase until the secular equilibrium with ^{232}Th be reached. The behavior of the ^{238}U series is the same (Figure 4) as observed in phosphogypsum A. Except by the fact that in this case the ^{210}Pb activity decrease until the equilibrium with ^{226}Ra.

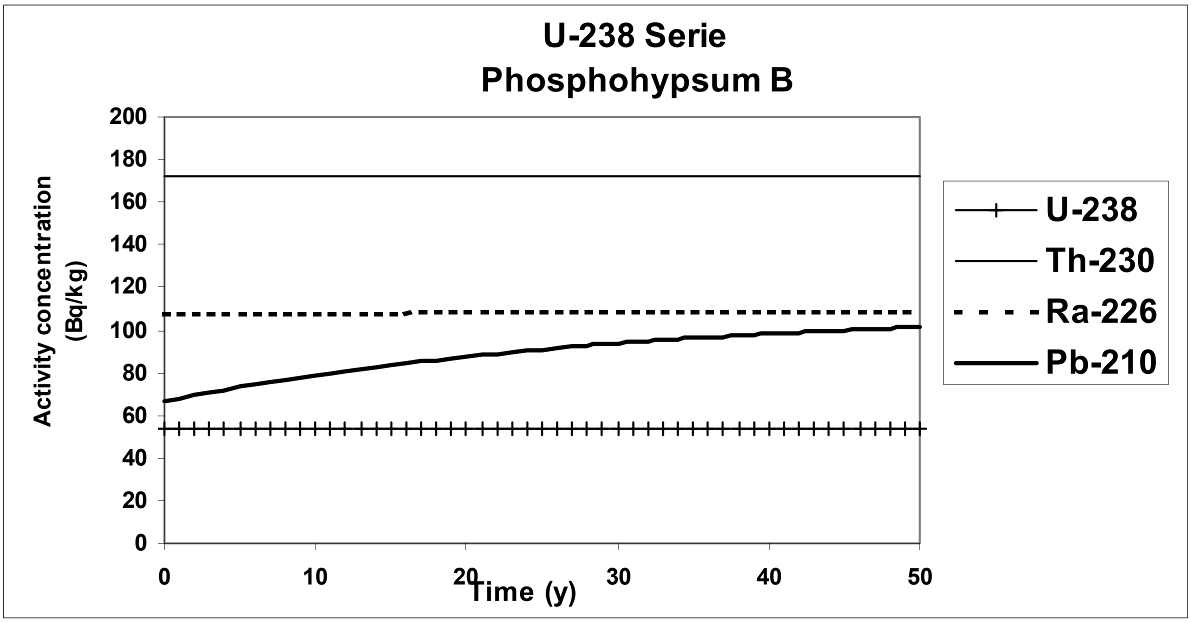

Figure 4. Activity concentration of radionuclides from Uranium series in phosphogypsum B.

Table IV. Specific annual effective dose in the middle of the reference room

Series		^{238}U				^{232}Th	
Sub-series	^{238}U	^{230}Th	^{226}Ra	^{210}Pb	^{232}Th	^{228}Ra	^{228}Th
Specific dose rates	1.23E-5	3.59E-7	1.54E-3	9.82E-7	2.92E-7	8.75E-4	1.25E-3

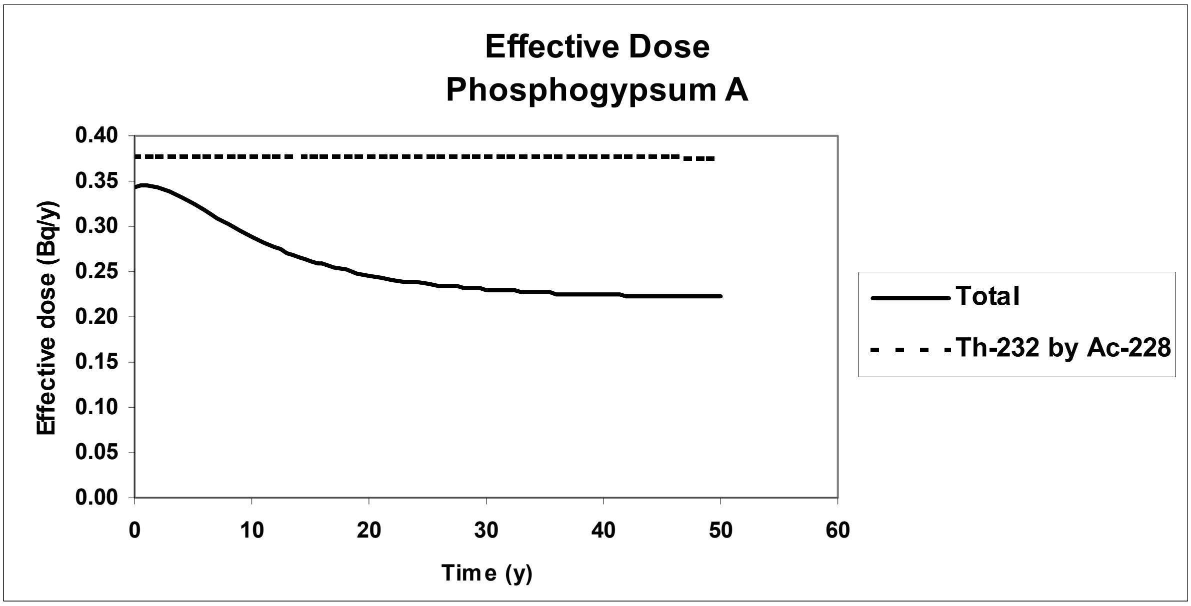

Figure 5. External effective doses due the use of phosphogypsum A in the walls of the reference room.

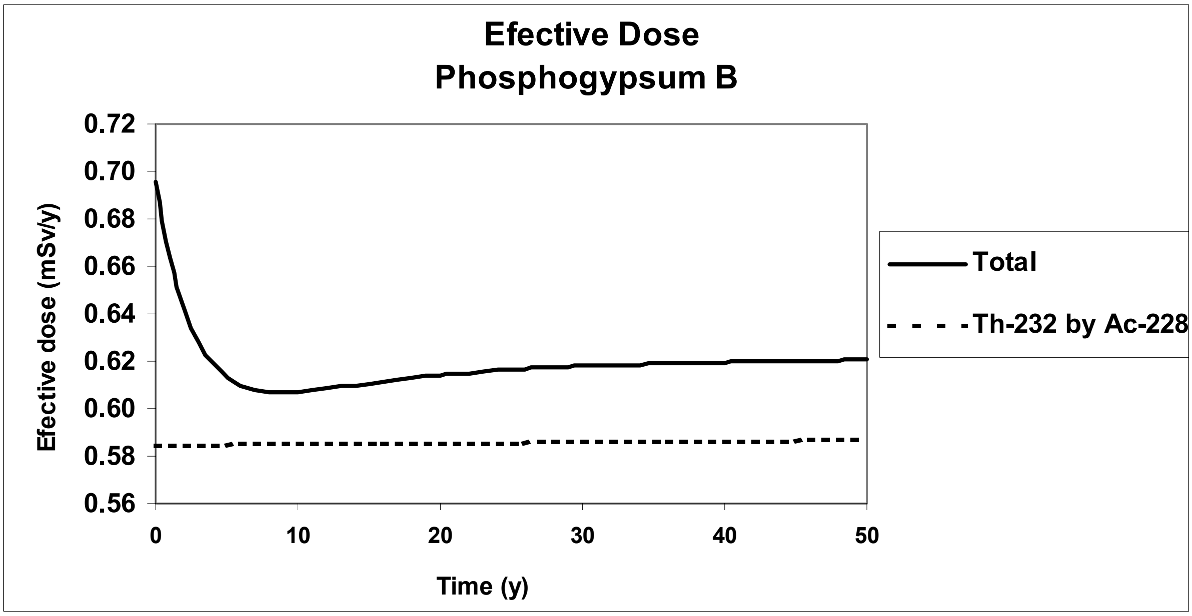

Figure 6. External effective doses due the use of phosphogypsum B in the walls of the reference room.

The application of the methodology for external dose assessment to the reference room results in the specific annual dose factors presented in Table IV. These factors are derived for the location and assumptions presented before. We could observe that in the ^{238}U series the sub series of ^{226}Ra is responsible to the main contribution to the external dose. And the others, could be neglected if the activity concentrations are of same magnitude.

In the Thorium series the external dose is controlled by the activity concentrations of ^{228}Ra and ^{228}Th. As the half life of these radionuclides are short when compared with the period of use of a dwelling, the radioactive disequilibrium could be important in the dose assessment.

It is important observe that most of the measurements of ^{232}Th activity concentration in building materials are done by gamma spectroscopy, using ^{228}Ac lines, and assuming the secular equilibrium. And this activity is used with the purpose to evaluate if the material could be used or not.

The Figure 5 presents the effective dose behavior in a period of 50 years due the use of phosphogypsum A. We could observe that the total dose, considering all thorium sub series, will decrease during the time until be equal to the external dose calculated using the actual ^{232}Th activity concentration. The dashed line represents the dose assessed using the assumption of secular equilibrium and the thorium concentration determined by gamma spectroscopy of ^{238}U ^{228}Ac. So in the case of the phosphogypsum A it will be overestimated.

The resulting doses due to the use of phosphogypsum B could be observed in the graph presented in Figure 6. In this case the effective dose will decrease until the equilibrium ^{228}Ra/^{228}Th is attained, and after, will increase to became equal the dose due the equilibrium of the thorium series. If the activity concentration of ^{232}Th would be determined by gamma spectroscopy using the ^{228}Ac, the annual effective dose will be lower than that evaluated using the actual ^{232}Th activity.

4. CONCLUSIONS

The radioactive disequilibrium of the ^{232}Th series is important during a period of 40 years. In this period the external dose are controlled by activity concentrations of ^{228}Ra and Th-228.

For U-238 series the radioactive disequilibrium is not important and the external doses are controlled by the Ra-226 activity concentration.

The use of equilibrium concentration formulas as a criteria for screening building materials could give rise to errors depending of the chemical process to witch these materials were submitted before.

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Two methods of estimation of radon emission from the mine tailings by NaI-spectrometry

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Abstract. In-situ gamma spectrometry by a portable NaI(Tℓ)- spectrometer gives also useful data for the determination of the emanation coefficient f_r and for the rough estimation of the radon exhalation rate. Two methods were investigated. Variations of the ratio of the radon daughters concentrations to the concentrations of K (or Th) in soil were measured in stable dry and stable wet weather conditions. Alternatively, the ratio of the scattered rays to peak, that was successfully applied to the ^{137}Cs distribution in soil, can be applied also to the estimation of the emanation coefficient f_r. Both methods were tested on several mine tailing and on some types of soil. Results are compared with in-situ Ge-spectrometry as well as with radon-in-soil-gas measurements.

1. INTRODUCTION

The mine tailings of different ores and technological wastes usually represent sources of enhanced natural radioactivity (UNSCEAR, 1992).

In laboratory analysis of samples Ge-spectrometry prevails whereas in-situ the NaI(Tℓ) - spectrometer can be successfully applied due to its simplicity and high efficiency.

The gamma spectra of radon and thoron daughters can be used also for the estimation of the radon exhalation rate.

Two methods were verified. The first one is a modification of the methods that use an uncollimated (Brajnik et.al., 1992) or collimated (Zettwoog, 1993) GeHP detector and measure the ratios of radon daughter lines to the ^{226}Ra (and ^{235}U) line at 186 keV. The saturation value of the ratio is measured in wet conditions or by covering the soil surface with a plastic foil. In the collimated version (Zettwoog, 1993) both the emanation coefficient f_r and the diffusion length z_0 are determined from the energy dependance of the intensity ratios.

By NaI-spectrometry both the version with or without the collimator can be used. Since the 186 keV line lays to low, the ratio of radium (radon) to thorium (thoron) daughters in dry and wet conditions (or uncovered and covered surface conditions) are measured. Pairs like 609 keV/583keV, 1120keV/911keV, 1764 keV/2614keV are most suitable in this respect.

The distribution of gamma-emitters in soil also influences the amount of scattered gamma-rays (Zombori et.al.,1992). Measuring the ratio of the forward scattered gamma rays to the unscattered rays in the peak, the relaxation lenght z_0 of the Chernobyl ^{137}Cs deposit could be measured by NaI - spectrometry (Andjelov & Brajnik 1999).

A reverse situation (with respect to the depth distribution) applies to the radon daughters. Their lines show more scattered gamma rays in comparison to the lines of thorium (thoron) daughters and potassium.

2. MEASUREMENTS AND RESULTS

2.1.Ratio of intensities of gamma lines

In the present measurements we used an uncollimated 3”x 3” NaI($T\ell$) spectrometer equipped with a 256-channel analyser. The detector was calibrated on calibration pads and was used in regional natural radioactivity studies (Andjelov &. Brajnik 1995).

The detector was normally placed 1 m alove the ground. In cases when the saturation was measured by covering the ground with a plastic foil, the detector was placed on the ground.

Previous measurements with a Ge-spectrometer (Brajnik, 1992) showed that the saturation value is reached at 75% - 90%. Therefore a correction factor k = 1.2 ± 0.1 was applied to the emanation coefficient f_r.

In Table 1 the measured emanation coefficients are shown for a few mine tailings.

Table 1

Locations	Type of tailing	Ra-activ. $A[Bq/kg]$	Eman.ratio f_r	Radon flux $\Phi[Bq/m^2.s]$	Ratio $R^* = \frac{\Delta B}{N}$
Žirovski vrh	U-tailing	8800	0.08 ± 0.02	2.9 ± 0.5	1.3 ± 0.1
Velenje lignite mine	Flying ash	300	0.03 ± 0.01	0.032 ± 0.011	1.1 ± 0.2
Koèevje	Coal and ash	650 - 900	0.10 ± 0.02	0.25 ± 0.40	1.2 ± 0.1
Hrastnik brown coal	Flying ash	250	0.08 ± 0.03	0.08 ± 0.03	
Brown soil	Soil – dry – wet	50	0.20 ± 0.05 $0.05^{\dagger} \pm 0.02$	0.04 ± 0.01 ~ 0.01	

†assuming the same z_0 ~ 1 m

*wet conditions

2.2 Ratio of scattered to the peak counts

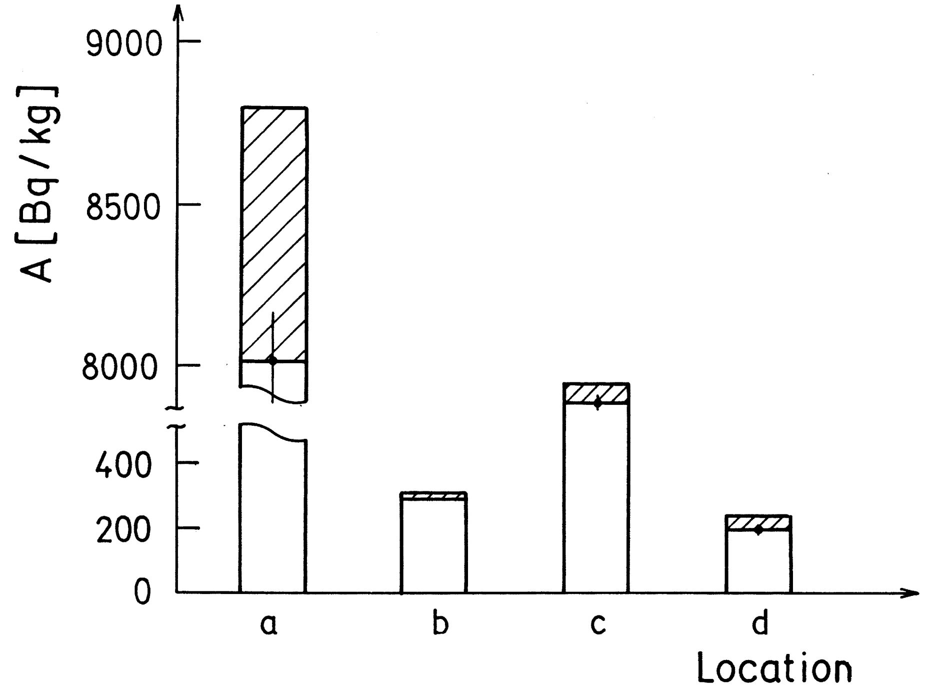
To compare the scattered gamma rays to the unscattered ones the stripped spectra (»pure« U/R_a and (»pure« Th) were used. The stripping factors are calculated according to the intensity of the high energy lines (2614 keV for Th, 1764 keV for U/Ra and 1461 keV for ^{40}K).

Then the ratio R,

$$R = \Delta B/N \tag{1}$$

where Δ^{B} is the difference in counts below and above the peak and N are counts under the peak. Both values are related to the same energy interval $\Delta E_\gamma \sim 2\,\mathrm{FWHM}$.

Further improvements are possible, e.g. to extend the stripping procedure to isolate all the important lines above 609 keV for Ra together with their lower energy continuum.



Locations:
(a) U-tailing Žirovski vrh
(b) Lignite fly-ash tailing Velenje
(c) Brown coal ash and cole dust tailing Koèevje
(d) Brown coal fly-ash tailing Hrastnik – Trbovlje

Figure 1. Specific radioactivity of Ra-daughters in saturated (wet) and unsaturated (dry) conditions.

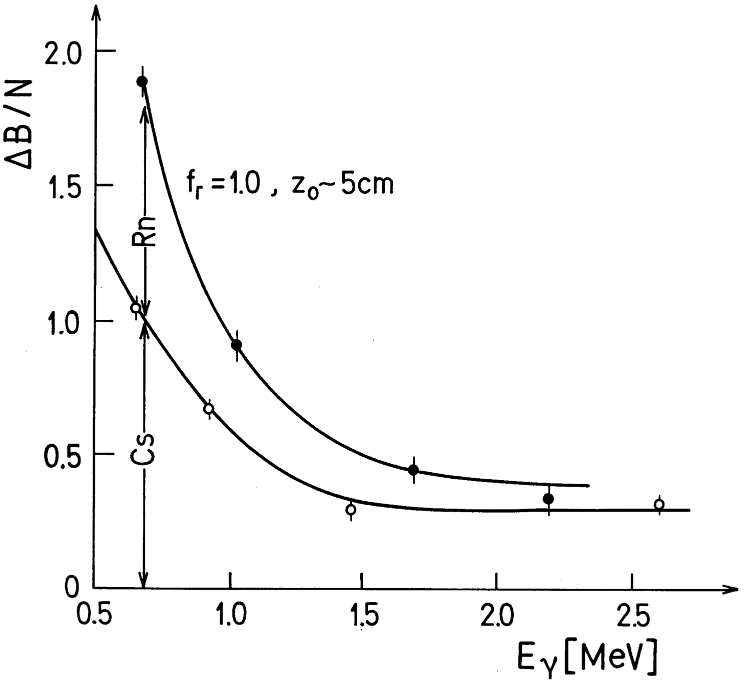


Figure 2. Scattering ratio R=ΔB/N for a homogeneous distribution (lower line) and a surface depleted distribution (upper line).

The measurement of the ratio R is effective when $z_0 \sim z_a$ (up to 10 cm). Therefore this method is complementary to the previous one.

2.3. Some typical results

In Fig. 1 specific radioactivities of daughter lines in wet/dry (or covered/uncovered) conditions are plotted for 4 mine tailings. Since the radon relaxation length is about 1 m and greater than the absorption length ($z_0 >> z_a = 1/\mu$), the emanation coefficient f_r is calculated from the formula

$$f_r = k(1 - A_d / A_w) \qquad (2)$$

where A_d on A_w are specific activities in dry and wet (saturated) conditions and k = 1.2 ± 0.1 is the correction factor.

In Fig. 2 the ratio $R = \Delta B / N$ of the forward scattered gamma rays to the unscattered ones (in the peak), versus energy is plotted. The lower curve represents the value for the uniform distribution. It is calculated from the spectra of thorium and ^{40}K lines.

The upper curve is plotted for z_0 = 5 cm and f_r = 0.5. It is calculated from the formulas for the distribution of ^{137}Cs (Andjelov &. Brajnik, 1999) that are based on the data of Barišiè (1994). The measured data for the brown coal mine tailing are consistent with calculation for a lower value of $f_r \sim 0.2$.

Some results are collected in Table 1 using both methods. The location on the soil was the same as in previous studies with a Ge-detector, that gave slightly higher f_r.

On most of the locations also radon-in-soil-gas concentration was measured. Results were consistent with relations proposed by Yokel and Tanner (1992), assuming a relaxation lenght z_0 = 1 m in dry conditions. Therefore emission estimates from radon-in-soil-gas measurements (Andjelov & Brajnik, 1995) are consistent with values in Table 1.

3. CONCLUSION

The methods described to extract more data from the in-situ gamma spectra are somewhat complementary. The ratio of intensities in unsaturated and saturated conditions is more useful in sandy, podzolian and brown soils and sandy tailings. The measurement of forward scattered gamma rays give useful results in clay, terra rossa and wet or clayed tailings.

Improvements could involve the use of new detectors like CZT on the instrumental side and sequential stripping of all individual lines in the spectrum on analytical side.

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Leaching assessment of radioactive and non-radioactive elements from Brazilian phosphogypsum

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Key Word: Sequential extraction, phosphogypsum, leachability, phosphatic rock, heavy metals, natural radionuclides.

Abstract. Phosphogypsum is a high volume by-product from phosphoric acid industries. Due to presence of certain impurities, mainly naturally-occurring radionuclides, this material has restriction for its use as building material and soil amendment. Then, phosphogypsum currently produced has been stacked near industries. To obtain more detailed information about the physico-chemical availability of heavy metals and radionuclides (Al, Ba, Cr, Fe, Mn, Th, U, Zn, Ra-226, Ra-228, Pb-210) in Brazilian phosphogypsum, three leaching procedures (sequential extraction, toxicity characteristic leaching procedure and soil fertility) were applied in samples from two phosphoric acid industries. Results indicated that the major fraction of heavy metals and radionuclides is associated with phosphogypsum lattice structure.

1. INTRODUCTION

Phosphoric acid, a raw material for phosphate fertilizer manufacture, is produced by chemically processing phosphate rock with sulfuric acid. For every ton of P_20_5 produced about 4–6 tons of phosphogypsum (PG) are generated. Annual Brazilian production of phosphate rock amounted to approximately 4.3 million tons (0.76 millions tons of P_20_5) in 1997, which means 3.1% of world production [1]. Minas Gerais and Goiás states are responsible for 55 and 33%, respectively, of the national phosphate rock production, whereas São Paulo and Minas Gerais produce approximately all Brazilian phosphoric acid. Considering a PG/P_20_5 ratio of 4.3[2], about 3.5 million tons of phosphogypsum per year is being produced in the country. Therefore, many problems associated with subaerial stockpiling may be arisen from such large quantities that have been continuously generated.

Besides being mainly composed of $CaSO_4.2H_2O$, phosphogypsum contains heavy metals and naturally-occurring radionuclides originated from the phosphate rock [3–6]. These constituents have been identified as a potential environmental hazard related to the stockpiling of phosphogypsum and its utilization in soil amendment or as building materials [7–12].

Geochemical processes that control leaching might be understood in evaluating the environmental impact of phosphogypsum. Burnett and Hull [13], investigating Ra-226 behavior in phosphogypsum, verified that there is still an important question to be answered, whether radionuclides are distributed uniformly throughout the lattice structure of phosphogypsum or they are contained in separate, distinct mineral phases. To elucidate this question, it was employed a sequential extraction approach designed originally to evaluate the distribution of transition metals within operationally-defined fractions in soils. It separates the elements in chemical forms likely to be released in solution under various environmental conditions, using different chemical reagents. When applied, sequential extraction separates heavy metals and radionuclides in five fractions: exchangeable, bound to carbonates, phases easily reducible (bound to iron and manganese oxides), bound to organic matter and residual (or lattice-bound) [14].

May and Sweeney [15] used a toxicity characteristic leaching procedure (TCLP) developed by the U. S. Environmental Protection Agency (EPA)[16] to evaluate radium and toxic elements leaching characteristics of Florida phosphogypsum stockpiles. If concentration of some elements in the TCLP extract is greater than EPA maximum concentration of contaminants, the waste possesses a toxicity characteristic. The Brazilian leaching procedure in use is similar to the EPA approach.

For agricultural purposes, phosphogypsum has been widely used as soil amendment in Brazil. Moreover, in soil fertility studies, the nutrients are determined using an extraction procedure with ion-exchange resin [17] in a process that, up to a certain extent, simulates the action of the roots. The method is based on transference of ions in soil solution to mixture of anionic and cationic exchange resin and reextraction of such ions by an appropriated solution.

Sequential extraction, toxicity characteristic leaching procedure and soil fertility methods were used to obtain more detailed information about the physico-chemical availability of heavy metals and naturally-occurring radionuclides (Al, Ba, Cr, Fe, Mn, Th, U, Zn, Ra-226, Ra-228 and Pb-210) in phosphogypsum originated from two major Brazilian phosphoric acid industries.

2. EXPERIMENTAL

Phosphogypsum was randomly sampled on the surface of stacks of two Brazilian phosphoric acid industries and prepared for chemical and radiochemical determinations and leaching procedures.

Table 1: Summary of reagents, temperature and time used for sequential extraction.

2.1.1 Fraction 2.1.2 Desired	Extractive reagent	Temperature (^{0}C)	Time (h)
Exchangeable	1M NH_4OAc pH 7	30	2
Carbonates	1M NaOAc pH 5	30	12
Oxides Fe-Mn	0.1M $NH_2OH.HCl$ 0.01 M HNO_3 pH 2	30	16
Organic matter	30% (vol.) H_2O_2 0.01 HNO_3 2.1.2.1.1 pH 2	85	3
	1M NH_4OAc	30	24
Residual	A	A	A

^{A} Defined by chemical and radiochemical analysis methods.

2.2 Sequential Extraction Procedure

It was used, with a little modification, the well-known procedure proposed by Tessier et al. [14], which separates the fractions of chemical and radioactive species as shown in Table 1.

After each extraction, the slurry was filtered, reweighted and the solution analyzed for heavy metals and radionuclides. This procedure was repeated 3 times for each sample and results are expressed as a mean of obtained values.

2.3 Toxicity Characteristic Leaching Procedure – TCLP

The EPA criterion for toxicity of wastes is based on an extraction procedure that attempts to leach toxic elements present in phosphogypsum similarly to the conditions found in environment [16]. Samples (100g) were stirred 18 hours into a 2 L of extraction fluid 1 (composed by 11.4 mL glacial acetic acid, 128.6 mL 1N sodium hydroxide and diluted to a volume of 2 L of reagent water) and filtered. The toxicity nature of the phosphogypsum is assessed by water-soluble concentration of specific elements in the extract.

2.4 Soil Fertility Method – SFM [17]

Samples (2.5 g) were stirred 16 hour into a 2.5 mL of a mixture of anionic IRA 420 and cationic IRA 120 resins (made by Holm and Haas) and 40 mL of water. The slurry was filtered and washed. The ions extracted by resin were reextracted using a solution of 1M HCl. The procedure was repeated 15 times due to low concentration of available chemical and radioactive species.

In order to evaluate the resin retention efficiency for Ra-226, a test was performed in water solution with known activity of the radionuclide and a value of 98% was found.

2.5 Chemical and Radiochemical Analyses

Chemical species Al, Ba, Cr, Fe, Mn, Zn in phosphogypsum samples and extracts were determined by ICP-AES. Phosphogypsum and residual fraction were dissolved using LiB_4O_7 fusion with a flux-to-sample ratio of 5:1 at a temperature of 900^0C, which permits a total dissolution. U and Th were determined by Arsenazo III spectrophotometry methods. Phosphogypsum and residual fraction samples were prepared using mineral acid (HF, HNO_3 and $HClO_4$). Ra-226, Ra-228 and Pb-210 in the extracts were determined by the ASTM method [18], using a chemical dissolution with LiB_4O_7 fusion. The method consisted on separation of radium and lead water–soluble from solution as $Ba(Ra)S0_4$ and $PbS0_4$. The barium-radium and lead sulfate are selectively dissolved, reprecipitated as $Ba(Ra)S0_4$ and $PbCr0_4$and filtered in 0,45μm membrane. The sample activities were determined using a β detector for Pb-210/Ra-228 and α detector for Ra-226.

2.6 Gamma ray spectrometry

This method was used for determination of Ra-226, Ra-228 and Pb-210 in phosphogypsum bulk and residual fraction obtained from sequential extraction. Samples were packed into plastic container and sealed in order to achieve secular equilibrium between Ra-226 and its daughters Pb-214 and Bi-214. After 30 days, gamma spectrometry was performed using CANBERRA HPGe detector (45% relative efficiency) with beryllium window. Self – absorption correction was done for Pb-210 using the procedure proposed by Cutshall [19].

RESULTS AND DISCUSSION

Table 2 presents the mean values for U, Th, Ra-226, Ra-228 and Pb-210 obtained in bulk phosphogypsum samples from two phosphoric acid industries (A and B). The difference in specific activities may be due to distinct origin of phosphate rocks [3]. Uranium and thorium activity concentrations are smaller than those for radium and lead, since in the processing of phosphate rock they are concentrated in phosphoric acid while Ra and Pb are precipitated in phosphogypsum [8]. Radium and lead activities found in the phosphogypsum samles are higher than normally found in environment.

2.6.1 Table 2. Results of sequential extraction procedure for radioactive elements of two phosphogypsum samples. PG values correspond to the bulk samples.

	3.	Specific Activity [Bq/kg]		4.		Specific Activity [Bq/kg]	
	Fraction	4.1 Sample	Samples B		Fraction	Samples A	Samples B
	1	2.9±0.6	2.3±0.4		1	<0.3	<0.3
	2	2.0±0.6	2.4±0.4		2	<0.3	<0.3
Ra-226	3	1.2±0.7	1.4±0.2	Th	3	<0.3	<0.3
	4	0.8±0.2	1.4±0.2		4	<0.3	<0.3
	5	843±53	360±25		5	167±11	171±13
	PG	889±52	402±24		PG	170±13	189±12
	1	<0.3	<0.3		1	<2.4	<2.4
	2	<0.3	<0.3		2	<2.4	<2.4
Ra-228	3	<0.3	<0.3	U	3	<2.4	<2.4
	4	1.3±0.2	<0.3		4	<2.4	<2.4
	5	202±9.1	224±5.9		5	138±14	101±3.5
	PG	214±5.1	240±7.0		PG	132±9.2	111±9.1
	1	1.2±0.2	<0.5				
	2	<0.5	<0.5				
Pb-210	3	<0.5	2.8±0.4				
	4	2.1±0.2	<0.5				
	5	482±12	171±3.4				
	PG	486±5.6	168±6.3				

Table 3 shows the concentrations of non-radioactive elements Al, Ba, Cr, Fe, Mn and Zn. Except for Ba, heavy metals concentrations in the phosphogypsum samples are of the same order of magnitude as found in typical soil.

Sequential extraction results displayed in Table 2 and 3 indicate that the major part of radionuclides and heavy metals is in the residual fraction (lattice-bound). It is expected that these elements will not be released for a long period of time under the conditions normally found in environment. Such results can also be attributed to the fact that the samples were taken from surfaces of weathered stockpiles, where the more available fraction could be already washed by rainwater. In order to confirm it, investigation on fresh samples and samples from profiles taken from stacks are underway.

TCLP and SFM results in Table 4 corroborate the assumption that radionuclides and heavy metals are bound to lattice of phosphogypsum. Besides, the concentrations found are evidencing that samples do not present toxic characteristics related to heavy metals, as defined by EPA criteria.

Table 3. Results of sequential extraction procedure for non-radioactive elements of two phosphogypsum samples. PG values correspond to the bulk samples.

5.		Concentration [μg/g]		6.		Concentration [μg/g]	
	Fraction	6.1 Samples	Samples B		Fraction	Samples A	Samples B
	1	5.2±0.3	5.6±0.2		1	<1	<1
	2	5.4±0.3	5.8±0.2		2	<1	<1
Al	3	14.4±0.7	8.6±0.3	Fe	3	9.3±0.7	3.5±0.2
	4	5.3±0.3	5.5±0.2		4	1.4±0.1	<1
	5	1631±83	1366±33		5	3346±167	4342±101
	PG	1850±93	1590±80		PG	3580±179	4730±237
	1	<1	<1		1	1.1±0.1	1.42±0.03
	2	<1	<1		2	<1	0.48±0.01
Ba	3	<1	<1	Mn	3	1.5±0.2	2.54±0.03
	4	1.1±0.1	<1		4	<1	0.68±0.02
	5	10662±167	34141±1707		5	83.4±8.7	65.2±6.5
	PG	11200±179	32900±1650		PG	97.8±9.8	79.0±4.0
	1	<1.5	<1.5		1	<0.4	0.18±0.02
	2	<1.5	<1.5		2	5.7±0.6	0.53±0.05
Cr	3	<1.5	<1.5	Zn	3	5.5±0.6	0.68±0.07
	4	<1.5	2.3±0.2		4	<0.4	3.55±0.36
	5	11.9±1.2	12.8±1.3		5	12.7±1.3	24.9±2.5
	PG	15.2±1.5	16.9±1.7		6.1.1.1.1	25.4±2.5	30.2±3.0

Table 4. Radionuclides activities and heavy metals concentrations in phosphogypsum leached by TCLP and SFM procedures. PG values correspond to the bulk samples.

	Specific Activity [Bq/kg]									
	Sample A					Sample B				
	PG	TCLP	%	SFM	%	PG	TCLP	%	SFM	%
U	132±9.2	<0.8	<0.6	<0.9	<0.7	111±9.1	<0.8	<0.7	<0.8	<0.7
Th	170±13	1.6±0.1	0.9	2.2±0.1	1.3	189±11.7	1.7±0.1	0.9	2.8±0.1	1.5
^{226}Ra	889±52	1.5±0.2	0.2	2.1±0.6	0.3	402±24.3	1.2±0.3	0.3	1.6±0.5	0.4
^{228}Ra	214±5.1	<0.3	<0.2	3.1±0.7	1.5	240±7.0	<0.3	<0.2	1.0±0.2	0.4
^{210}Pb	486±5.6	<0.4	<0.1	1.1±0.2	0.2	168±6.3	<0.4	<0.2	0.7±0.3	0.5
	Concentration [μg/g]									
Al	1850±93	16.0±2.0	0.9	14.4±1.5	0.8	1590±79.5	9.2±0.8	0.6	17.8±1.3	1.1
Ba	11200±179	<2	<0.02	<2	<0.02	32900±1650	<2	<0.01	<2	<0.01
Cr	15.2±1.5	<0.6	<3.9	<0.8	<5.3	16.9±1.69	<0.6	<3.6	<0.6	<3.6
Fe	3580±179	1.8±0.3	0.05	6.2±0.8	0.2	4730±236.5	1.1±0.1	0.02	16.8±1.4	0.4
Mn	97.8±9.8	1.3±0.1	1.3	<0.5	<0.5	79.0±3.95	3.2±0.3	4.1	0.9±0.1	1.1
Zn	25.4±2.5	1.9±0.1	7.5	<0.13	<0.5	30.2±2.99	1.0±0.1	3.3	0.2±0.03	0.7

7. CONCLUSIONS

The results of this study indicate that the heavy metals in the phosphogypsum samples analyzed, under conditions normally found in the environment, will not be leached when stockpiled on stacks or utilized as soil amendment. Moreover, heavy metals concentrations in phosphogypsum are lower than normally seen in phosphate fertilizer.

The leachability of radionuclides observed for the phosphogypsum samples is very low. However, specific activities of Ra-226, Ra-228 and Pb-210 are higher than those usually found in the environment, urging detailed studies before using this material. It may be also important to evaluate the environmental behavior of the gaseous radioactive daughter Rn-222, in order to understand the radiological problems associated with phosphogypsum.

ACKNOWLEDGEMENTS

Authors are thankful to CNPq and FAPESP for financial assistance, and to the staff of CENA/USP and CNEN — Laboratório de Poços de Caldas for their valuable contribution to the realization of this work.

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Soil to plant ^{137}Cs transfer factors in *Zea mays* and *Phaseolus vulgaris* in a semi-arid ecosystem from a radioactive waste site

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Abstract. A study of ^{137}Cs in soil, maize plants, (*Zea mays*) and beans (*Phaseolus vulgaris*) has been performed at the confined Storage Centre for Radioactive Waste from México. Under field conditions the site was divided in four zones with different soil contamination characteristics. The plants were grown "in situ" reproducing the local agricultural practices without fertilizers, pesticides or artificial irrigation.The ^{137}Cs determinations were performed using a low background gamma spectrometry system with an HPGe detector. The results indicate that one of the zones had a striking ^{137}Cs contamination in the soil and the uptake by the grown plants showed the highest specific activities at the root. For the edible parts of the plants the amount of ^{137}Cs in the maize grains was one order of magnitude lower than for the beans. The transfer factors ranges for the different parts of the maize plants was from 0.001 in the grain to 0.6 in the root.

Keywords: Maize, beans; soil; ^{137}Cs; transfer factors; semi-arid ecosystem.

1. INTRODUCTION

Soil contamination with ^{137}Cs is causing a long term burden on the food chain. Retrospective analyses of agricultural crops have demostrated that the ecological half-life of ^{137}Cs is in the range of 1.5–3 years. In semi-natural ecosystems ^{137}Cs contamination of their different components is even more persistent than in agricultural systems [1, 2, 3, 4].

Soil to plant transfer is the first step by which ^{137}Cs enters the food chain. This process is highly variable between types of soil and crops. The phytoavailability of ^{137}Cs in soil is traditionally expressed in the so-called transfer factors (TF), defined as the ratio of the ^{137}Cs concentration in the part of the plant to that in the soil. Existing databases of TFs show that values for one crop can vary by more than four orders of magnitude between soil types, climatic conditions and type of studies [5, 6]. From this variability clearly, no average TF can be used for risk assessment in contaminated areas. Since there are no evident correlations between soil characteristics and ^{137}Cs availability, predictions of ^{137}Cs transfer to the food chain are subject to wide errors. However, in general , the availability of ^{137}Cs to crops has been reported to increase with increasing soil organic matter content, decreasing clay content, decreasing soil pH and decreasing exchangeable potassium content [7].

With the aim to study the ^{137}Cs soil to plant transfer, a study was performed in maize plants (*Zea mays*) and beans (*Phaseolus vulgaris*) at the confined Storage Centre for Radioactive Waste (SCRW) from Mexico. The site is located in a semiarid region with a vegetation characteristic of a temperate subhumid zone. Several studies of the transfer of ^{226}Ra and ^{137}Cs to land snails [4, 8] were performed at this site in zones where superficial contamination was observed. In marginal areas of Mexico, that depend on subsistence agriculture and where legume nitrogen fixation is crucial to maintain sustainable agricultural production, the traditional use of the soils include the combination of legume *Phaseolus vulgaris* with cereal *Zea mays* species. These two species are the main basis in the diet of mexican population.

2. EXPERIMENTAL

2.1 Site description

The SCRW site (19º47´39” N; 98º50´04” W) is located in the middle part of the Neovolcanic Mexican belt at an altitude of 2475 m. The local hydrogeology shows superficial tuffs and basalts permeable between 0 and 1 m deep and with scarce permeability from 2 to 5 m. No rivers are present in the zone and soil characteristics reflect very low rock porosity, with minimun water infiltration, except in fractures. No evidence exists of aquifers within 30 Km around the site. In the rainy season (June to October) streams of superficial water are formed following the slope of the ground. The climate is temperate subhumid with average yearly temperatures of 14.4ºC, ranging fron 6 to 32ºC. The mean annual precipitation is 638.5mm. At this site, solid and liquid radioactive waste have been stored for two decades; uranium ore tailing piles also stood for some time before beign buried in specific containers.

Some representative plant species at the site are *Senecio salignus, Opuntia xoconoste, Agave sp.* or *Aristida sp.,* all of them characteristic of semiarid regions. Traditional agriculture is practized at the zone where the farmers adopted the natural process of enriching the soil alternating legumes (beans) with non legume crops (maize). The harvest in the zone is usualy scarce due to the semi-arid soil conditions.

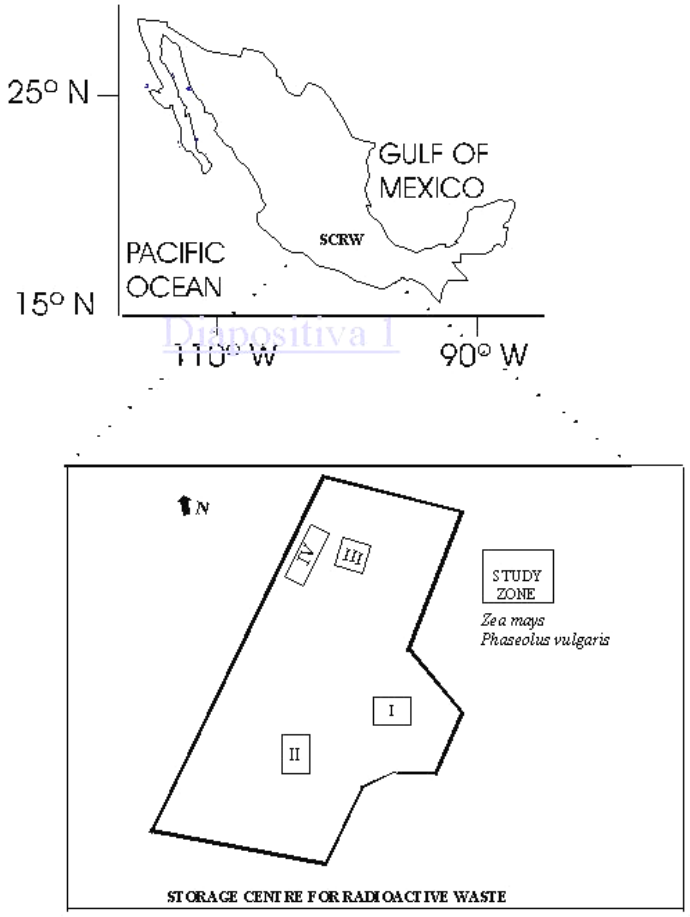

Fig. 1. Location of the site of study. The four zones where Zea mays and Phaseolus vulgaris were grown are also shown.

In the present study *Zea mays* and *Phaseolus vulgaris* have been grown at four zones of the SCRW, from June to October, during four years (Fig 1). The plants were cultivated in 4 fields 20x 30 m, located in zones 1 to 4 in lines separated 50 cm between them. The maize plants in the lines were separated 40 cm between them and the bean plants were grown in between the maize plants, putting one seed each 5 cm. A local contamination in soil with ^{137}Cs ocurred several years ago in zone 1 as a consequence of a broken industrial source.

2.2 Sample treatment

At the four sampling zones, soil samples and the maize and beans plants were collected from July to 0.October during 1991–1994. The samples were yearly harvested except for years when the production was quite deficient probably because the nutrient elements were depleted from the soil and by the lack of external nitrogen and phosphor supply.

In the field the maize samples were separated into root, stem, leaves and grains. Each yearly 4 kg sample was washed to avoid contamination by the soil and dried at 80ºC for 48 h. *Phaseolus vulgaris* only the string beans were sampled and peeled to obtain 4 kg bean grains yearly. These samples were also washed and dried at 80ºC for 48 h. The vegetables dried matter was ground using a Wiley mill. The humidity factor, Hf, was calculated for each sample.

Soil samples of 2.5 kg were sieved to pass a 2-mm sieve and air dried. The Hf for soil samples was 1.1

2.3 Sample analysis

The soil and plant (root, stem, leaves and grains) samples were analysed for ^{137}Cs. The specific activities were determined in a dry weight (d.w.) basis by low background γ-spectrometry with a 29.7% relative efficiency HPGe detector Princeton Gamma Tech., Dusseldorf, model N-IGC 29. The geometry used was a 500 ml Marinelli beaker and the measurement time was around 60 000 s per sample, to achieve a detection limit of 1 Bq.kg^{-1} for ^{137}Cs. The counting errors for the measurements were usualy lower than 10%.

The soil to plant transfer factor (TF) for ^{137}Cs was calculated as the ratio of the ^{137}Cs concentration in the plant (d.w.) to that in the soil (d.w.).

The soil organic matter was determined by the Walkley-Black method. The exchangeable K was determined by atomic absorption spectrophotometry, using a model 5000 Perkin Elmer equipment. The cation exchange capacity (CEC) was measured using silver thiourea as the index cation. Other elemental content were measured by emission spectrography with a Bair Atomic equipment model GX-1 [4].

3. RESULTS AND DISCUSSION

The results from 1991 to 1994 of the yearly average values for ^{137}Cs in soil samples from the four zones are shown in Fig. 2. A striking contamination is evident in zone 1. From 1991 to 1993 the top soil was only slacken in order to be able to cultivate the seeds. By 1993–1994 soil decontamination practices started at the SCRW and the specific acivity in the soil diminished. The chemical composition of the soil show values that are usually found in semi arid regions. The major soil type in the zone of study is Regosol having 25% clay, 46% sand and 28% silt. Some physicochemical parameters are: pH 6; the main organic matter in the clay fraction of the soil 1.5%; the soluble exchangeable potassium, 1.5 ± 0.1 cmol$_c$ kg^{-1}. The nitrogen content was 0.075% and the C/N ratio 20. The cation exchange capacity (CEC) was 27 ± 1.5 cmol$_c$ kg^{-1}. The site soil content of Ca, Mg and K was 39 ± 5, 12 ± 3 and 7.6 ± 0.5 g kg^{-1} [4].

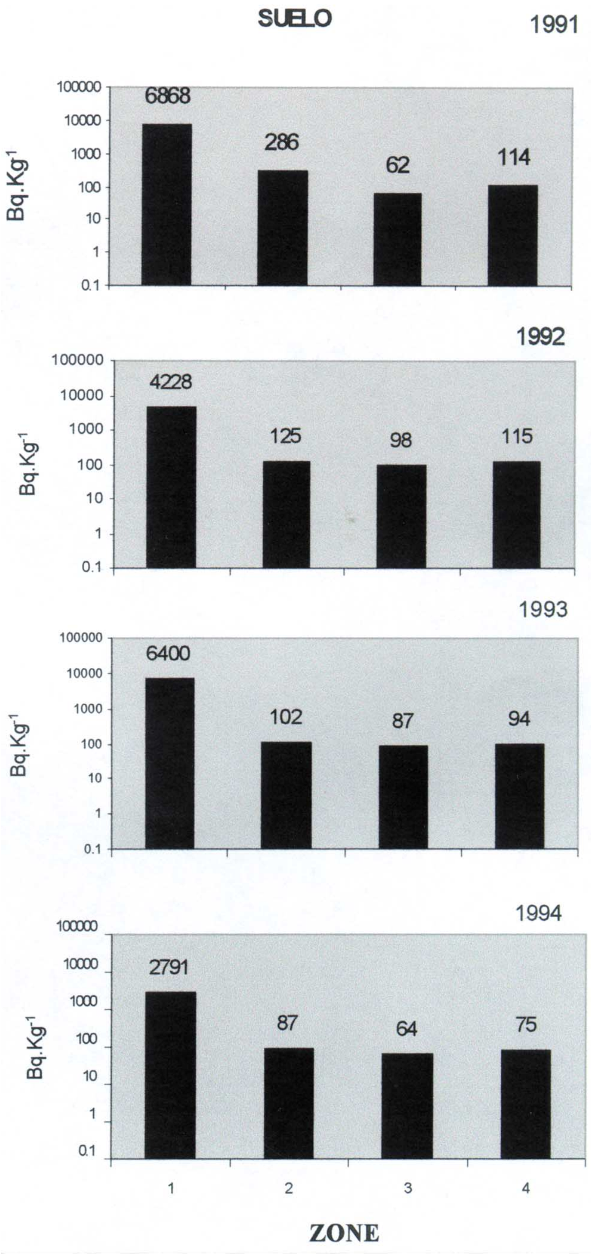

Fig. 2. Yearly average ^{137}Cs values (Bq kg^{-1}) obtained in the soil at the four zones of study from 1991 to 1994. The specific activity in each sample is indicated in the histogram.

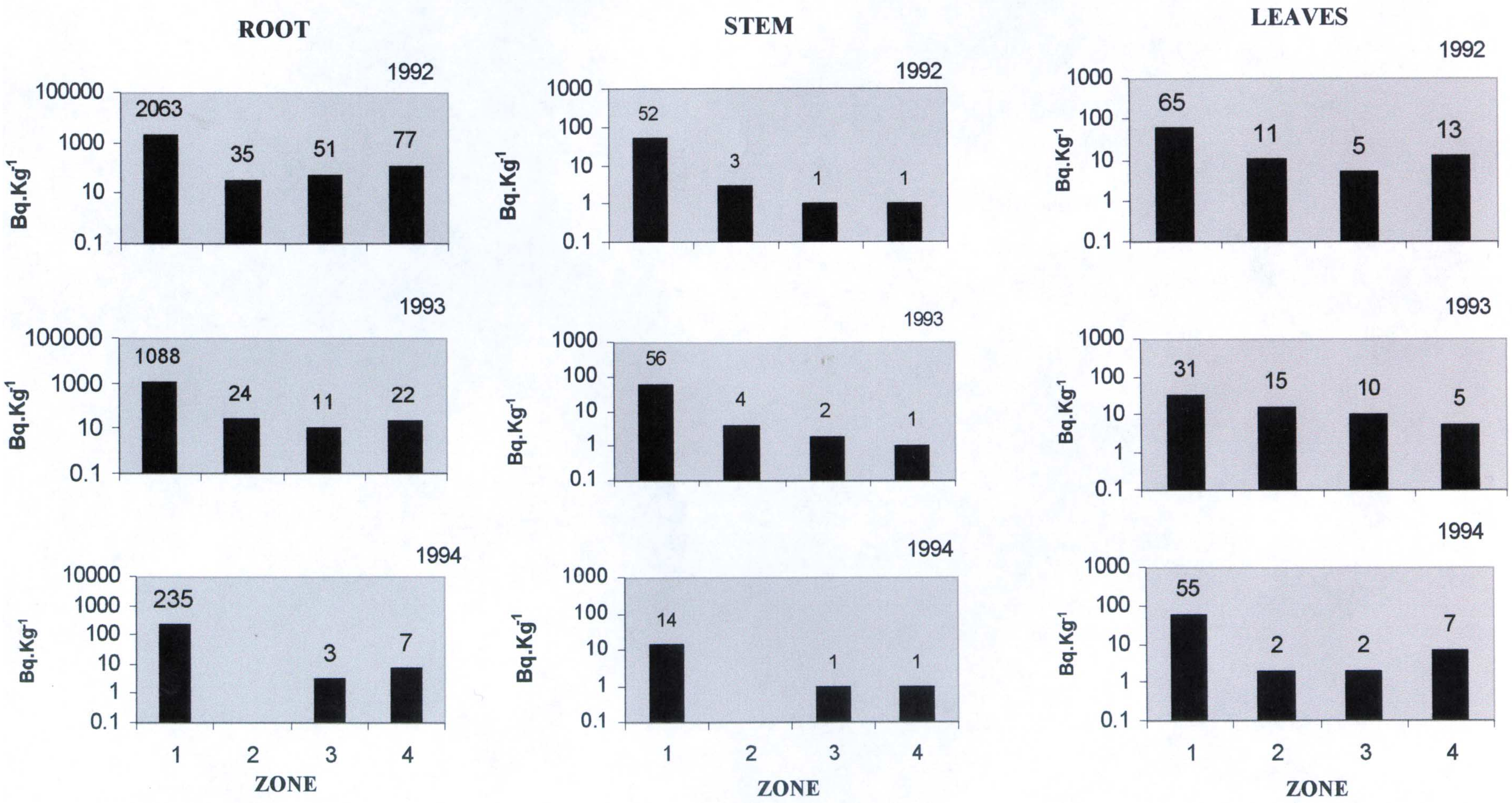

Fig. 3. Yearly average ^{137}Cs values (Bq kg^{-1}) obtained in the root, stem and leaves of Zea mays plants grown at the four zones of study from 1992 to
specific activity in each sample is indicated in the histogram.

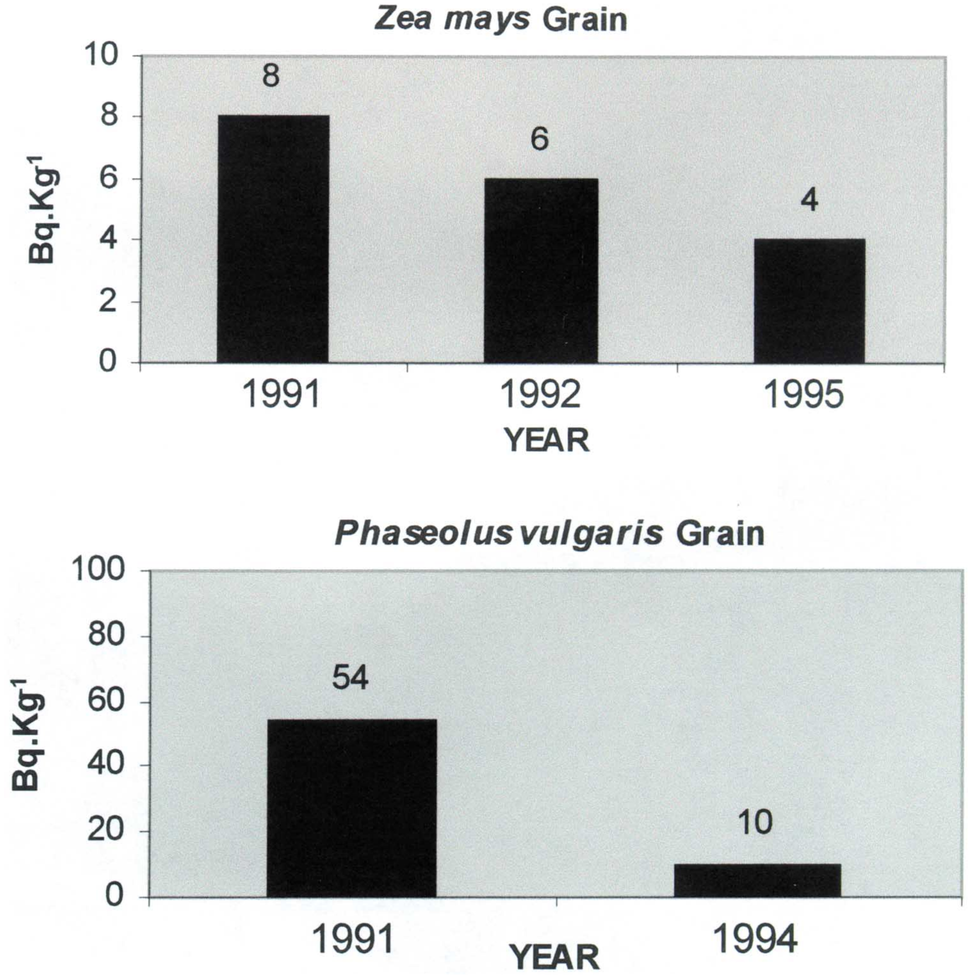

Fig. 4. Yearly average ^{137}Cs values (Bq kg^{-1}) obtained in the grains of Zea mays and Phaseolus vul from zone 1. The specific activity in each sample is indicated in the histogram.

The competition for available soil nitrogen in a semiarid ecosystem can affect the dynamics of the mineralization/immobilization nitrogen cycle which is complex in space and time in field conditions. On the other hand the soil calcium ensures the normal physiological functionning of the root cells.

The transport of a number of important radionuclides can be predicted from the behaviour of chemically analogous nutrient elements. Radiocesium is generally quite soluble and ^{137}Cs uptake in plants vary with the ionic composition in soil solution, with a particular sensitivity to the K^+ concentration. The distribution of a trace constituent between the aqueous and solid phases can be described by the distribution coefficient, K_d (ml g^{-1}), that is inversely proportional to the solution concentration of K (m_k). The m_k value was estimated as $m_k = 1.19$ mM at a K occupancy of approx. 6% of the CEC. The m_k value obtained at the site was larger than reported by Smolders et al. [7] for a Regosol type of soil. However, the value was comparable to the median value for 30 different soil samples reported by these authors.

The specific activities of ^{137}Cs obtained at the yearly samples of the different parts of the maize plant (root, stem and leaves) are shown in Fig. 3. The uptake of ^{137}Cs was higher at zone 1 during all the studied years, with the highest concentrations at the root. It is noticeable that the root specific activities were two orders of magnitude higher in zone 1 as compared with zones 2, 3 and 4. In 1994 the effect of decontamination of the soil was evident since the root specific activity values were one order of magnitude lower than in 1992 for the four zones. In the leaves the specific activity for ^{137}Cs was generaly quite stable along the time and zones. In the stem similar values as for the leaves were obtained at zone 1 while in zones 2, 3 and 4 the activity was very low, but detectable. For the stem and leaves the ^{137}Cs values were two orders of magnitude lower than for the 1992 root sample.

In arid and semiarid ecosystems (potentially unstable systems) the contribution made by a nodulate legume specie to the production of a cereal associated specie, is supported by the input from the nodulated legume when recourse to nitrogen fertilization is not feasible. The role of mycorrhizas in mediating transfer of nitrogenous material via a direct connection of the root systems of legume and no-legume by fungal hyphae, increases the capacity of root nutrients, and ^{137}Cs, due to an increase in the exchange area.

The results of ^{137}Cs activity concentration obtained at the edible parts of the studied plants, maize grains and beans, from zone 1 are shown in Fig 4. The amount of ^{137}Cs incorporated by *Zea mays* grains was one order of magnitude lower than for *Phaseolus vulgaris* beans. However, the incorporation in the time was more stable for *Zea mays* than for *Phaseolus vulgaris*.

The uptake of ^{137}Cs by plants from the majority of agricultural soils is usually much lower than that found for some tropical soils, like our site of study. Part of the ^{137}Cs present in the soil solid phase is not available for exchange with the solution. Root uptake of ^{137}Cs is proportional to its activity in solution and is however significantly reduced by increasing K concentration in solution. This capacity of absorption is attributed to minerals capable of forming a relatively stable structure when saturated with Cs^+, Rb^+, K^+ or NH_4^+ [9].

In Figure 5 the range values of the soil to plant transfer factors (TF) for ^{137}Cs in the *Zea mays* parts and in *Phaseolus vulgaris* beans are shown. The *Phaseolus vulgaris* beans presented a TF range higher than for the *Zea mays* grains. For maize the leaves had a TF range one order of magnitude higher than stem. These parts of the plant are usualy used for cattle forage, being a direct way to human food chain. The highest TF values range were obtained for the roots, being one order of magnitude higher than for stem and two orders of magnitude higher than for grains.

It is worth mentioning that the maize grains in the present experiments were extremely scarce, since no fertilizers were used during the three years experiments. The TF values for the roots agree with those reported by IAEA [10] for tubers. In the cited publication the TFs for root crops, without specifiing the kind of plant are reported as low as 0.04 or 0.01. However the TFs for the grain in the present study showed values one order of magnitude lower than grain cereals reported by IAEA.

Certainly, in field conditions there may be other sources of variability such as heterogeneous ^{137}Cs and K over the root zone, soil solution changes with time, etc. In agreement with Shaw et al. [11], TF values describe equilibrium conditions, a situation which was pointed out being unlikely to exist for most growing plants. They showed the existence of non-linear response of radiocesium TF values and hence uncertainties associated to TF were likely to be caused by the presence of environmentally abundant chemical analogues of Cs as a result of competition for ion binding sites at the root surface. Smolders et al., 1997 indicate that low K solution concentration (m_k) in soil is usually associated with low TFs. The TF values obtained in the present study are slightly superior to that reported for similar soils by the cited authors. In spite of the fact that extensive studies have been reported on the transfer factors for cesium in different agricultural foods, relatively few works have paid close attention to the interaction between legumes and cereal associated plants in semiarid ecosystems. The question of which soil or plant factors control availability of ^{137}Cs is still unresolved.

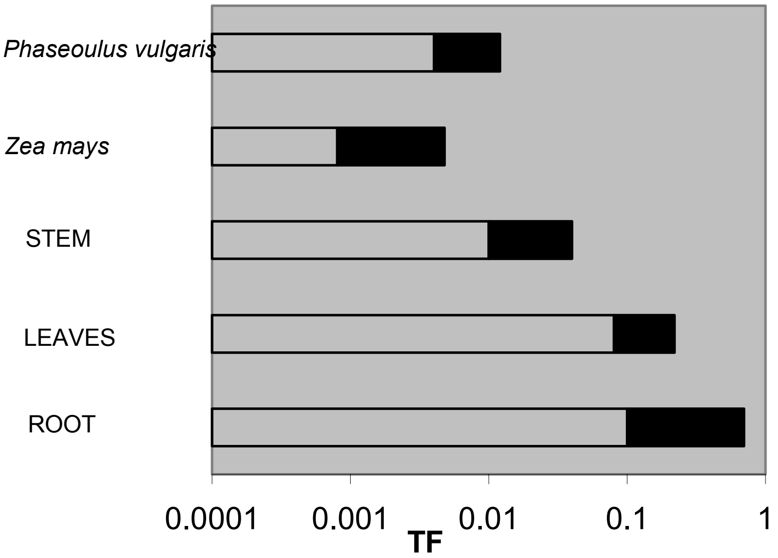

Fig. 5. Range values of the soil to plant transfer factors (TF) for ^{137}Cs in the different Zea mays parts and in Phaseolus vulgaris beans obtained at the SCRW during the period of study.

ACKNOWLEDGEMENTS

The authors acknowledge A. Cervini L., F. Abascal, G. Valentín, S. Alvarado for chemical analysis, monitoring and field support. V.Rojas, E.Quintero, for gamma spectrometry data; V. Huerta for computer support.

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^{222}Rn, ^{226}Ra, and U in drinking water in Hungary

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Abstract. Among radionuclides ingested by drinking water the most important ones are radon, radium and uranium, causing radiation exposure of the lungs, bones, and gastro-intestinal organs, mainly kidneys. For this reason, as a part of the National Environmental Health Program to determine the main risk factors of the Hungarian population from environmental substances, ^{222}Rn, ^{226}Ra, and U concentrations were measured in domestic water supplies. Water samples were taken from all of the 19 Hungarian counties. Three cities were chosen from each county by the criteria of number of the population. Samples were taken from the communal drinking water supplies. Radon was determined by short lived daughter products using scintillation technique after water degassing into Lucas cells. Radium and uranium were determined after chemical separation, by Lucas scintillation method and by liquid scintillation technique. The obtained results were compared to the available literature data. Radioactivity levels were assessed for conformity with the Hungarian standards, WHO guidelines, and used for dose calculations. It was concluded that the radioactivity of the drinking water in Hungary is in the order of magnitude of the worldwide average. The measured radioactivity levels never exceeded the limits of the valid Hungarian standards for annual intake limits and were adequate to WHO guidelines. It was found that public doses from radon, radium, and uranium ingestion by drinking water were 12.7, 8.8, and 7.3 μSv y^{-1}, respectively. Summarizing the results of the survey it was concluded that comparing these doses to the public dose from other natural sources of radiation are negligibly small.

1. INTRODUCTION

It is well known that radioactivity of drinking water is much lower than that of the thermal and mineral underground waters (except some regions of specific geological environment) [1, 2]. However, in spite of the strongly rising contribution of mineral water in the human consumption, share of the traditional tap water is still dominant. From radionuclides in the drinking water the most important ones are:

(i) ^{222}Rn as source of exposure for epithelial cells of the gastro-intestinal tract, and as nuclide causing whole body exposure after dissolution in blood and tissue fluids. Besides, there are some data that during exhalation radon exposure of lungs cannot be neglected.

(ii) ^{226}Ra that accumulated in the mineral fraction of bone tissue.

(iii) U isotopes that mostly act as toxic metals, destroying kidney tissue.

In spite of some preliminary measurements, no comprehensive study of the drinking water radioactivity in Hungary has been done up till now. Despite of the fact that the presented study is not really a representative one, it seems to be a good step forward in this field of research.

2. METHODS

Water samples were taken from the public water supplies of the three largest by the number of population cities of all of the 19 Hungarian counties. Radon was separated on site by the Pylon Water Degassing Unit WG 1001 and measured by Pylon AB-5 radiation monitor 3.5 hours after radon separation.

Table 1. Natural radioactivity of drinking water of cities in 19 Hungarian counties

County	**City**	**^{222}Rn (Bq l^{-1})**	**^{226}Ra (mBq l^{-1})**	**U (mBq l^{-1})**
Bács-Kiskun	Solt	2,43	51	6
	Kecskemét	4,52	27	<LLD
	Kiskunfélegyháza	3,09	38	7
	Kalocsa	2,61	32	8
	Baja	4,14	41	490
Baranya	Pécsvárad	28,13	154	90
	Pécs	4,95	12	58
	Pellérd	9,21	27	152
Békés	Szarvas	7,63	18	<LLD
	Békéscsaba	2,4	49	3
	Orosháza	4,81	34	11
Borsod-Abaúj-Zemplén	Miskolc	1,36	<LLD	16
	Kazincbarcika	5,83	73	77
	Tiszaújváros	1,35	13	50
Csongrád	Szeged	1,16	9	4
	Hódmezővásárhely	1,4	13	4
	Szentes	2,5	18	<LLD
Fejér	Bicske	1,69	238	92
	Székesfehérvár	3,28	78	113
	Dunaújváros	4,9	34	108
Győr-Moson-Sopron	Sopron	5,63	45	403
	Csorna	6,31	21	29
	Győr	3,55	7	4
Hajdú-Bihar	Hajdúszoboszló	1,0	15	5
	Hajdúböszörmény	1,64	22	13
	Debrecen	1,37	16	<LLD
Heves	Hatvan	2,67	17	35
	Gyöngyös	2,15	58	7
	Eger	8,05	57	102
Jász-Nagykun-Szolnok	Szolnok	0,31	31	934

Table 1. (cont.)

	Törökszentmiklós	1,46	37	16
Komárom-Esztergom	Komárom	2,46	70	112
	Tata	1,12	67	109
	Esztergom	1,02	21	109
Nógrád	Balassagyarmat	1,05	48	44
	Szécsény	6,67	45	600
	Salgótarján	0,31	32	11
Pest	Budapest	8,99	15	44
	Vác	4,78	43	82
	Szentendre	1,32	8	126
	Százhalombatta	5,06	22	36
	Dömsöd	29,90	116	41
	Cegléd	6,14	17	66
Somogy	Nagykanizsa	5,24	22	50
	Kaposvár	1,3	33	183
	Balatonboglár	0,97	16	80
	Siófok	0,42	70	213
Szabolcs-Szatmár-Bereg	Nyíregyháza	0,26	17	22
	Kisvárda	2,15	27	15
	Mátészalka	3,73	81	17
Tolna	Szekszárd	1,9	15	2
	Bonyhád	11,19	53	172
	Dunaföldvár	3,81	26	40
Vas	Sárvár	4,75	38	15
	Szombathely	4,2	44	112
	Körmend	16,87	88	24
Veszprém	Ajka	0,54	63	192
	Veszprém	9,33	21	95
	Tapolca	2,35	80	148
Zala	Zalaegerszeg	1,97	60	6
	Keszthely	3,04	56	137
	Lenti	8,83	34	14

Table 2. Mean radon, radium and uranium concentration in drinking water

County	**^{222}Rn mean±S.D. (Bq l^{-1})**	**^{226}Ra mean±S.D. (mBq l^{-1})**	**U mean±S.D. (mBq l^{-1})**
Bács-Kiskun	3,36±0,93	38±9	103±217
Baranya	14,10±12,34	64±78	100±48
Békés	4,95±2,63	34±15	5±5
Borsod-Abaúj--Zemplén	2,85±2,58	30±38	48±31
Csongrád	1,69±0,71	13±5	3±1
Fejér	3,29±1,61	117±107	104±11
Győr-Moson--Sopron	5,16±1,44	24±19	145±223
Hajdú-Bihar	1,34±0,32	18±4	7±6
Heves	4,29±3,27	44±23	48±49
Jász-Nagykun--Szolnok	0,89±0,81	34±4	475±649
Komárom--Esztergom	1,53±0,8	53±27	110±2
Nógrád	2,68±3,48	42±9	118±331
Pest	9,37±10,36	37±41	66±34
Somogy	1,98±2,2	35±24	132±79
Szabolcs-Szatmár	2,05±1,74	42±34	18±4
Tolna	5,63±4,91	31±20	71±89
Vas	8,61±7,16	57±27	50±54
veszprém	4,07±4,64	55±30	145±49
Zala	4,61±3,69	50±14	52±73
Mean	**4,34± 3,29**	**43± 22**	**100±107**

2.

The LLD for radon measurements was 2 mBq l^{-1}. For radium and uranium measurements water samples were pre-concentrated by distillation. Radium was chemically separated and measured by activity of daughter radon after reaching equilibrium by Lucas scintillation technique by NP-420 P radon meter. The LLD of the radium determination was about 8 mBq l^{-1}. Uranium was chemically separated by direct extraction from water into the organic phase of the liquid scintillation solution and measured by LSC spectrometer. The LLD for uranium measurements was around 1 mBq l^{-1}.

Table 3. ^{222}Rn and ^{226}Ra in waters by literature data and previous measurements

County	**Eff. dose from ^{222}Rn-ingestion ±S.D.**	**Eff. dose from ^{226}Ra-ingestion ±S.D.**	**Eff. dose from U-ingestion ±S.D.**
Bács-Kiskun	9,8±2,7	7,7±1,09	7,5±15,8
Baranya	41,2±36,0	13,1±15,9	7,3±3,5
Békés	14,4±7,6	6,9±3,2	0,4±0,4
Borsod-Abaúj--Zemplén	8,3±7,54	6,1±7,7	3,5±2,2
Csongrád	4,9±2,1	2,7±0,9	0,2±0,1
Fejér	9,6±4,7	23,8±21,9	7,6±0,8
Győr-Moson--Sopron	15,1±4,2	5,0±3,9	10,6±16,3
Hajdú-Bihar	3,9±0,9	3,6±0,8	0,5±0,4
Heves	12,5±9,5	9,0±4,8	3,5±3,6
Jász-Nagykun--Szolnok	2,6±2,4	6,9±0,9	34,7±47,4
Komárom--Esztergom	4,5±2,3	10,8±5,6	8,0±0,1
Nógrád	7,8±10,2	8,5±1,7	15,9±24,2
Pest	27,3±30,2	7,5±8,3	4,8±2,5
Somogy	5,8±6,4	7,2±4,9	9,6±5,7
Szabolcs-Szatmár	6,0±5,1	8,5±7,0	1,3±0,3
Tolna	16,5±14,3	6,4±4,0	5,2±6,5
Vas	25,0±20,9	11,6±5,6	3,7±3,9
Veszprém	11,9±13,6	11,2±6,2	10,6±3,5
Zala	13,5±10,9	10,2±2,9	3,8±5,4
Mean	**12,7± 9,6**	**8,8± 4,5**	**7,3± 7,8**

3. 3. RESULTS AND DISCUSSION

Results of the measurements are given in the Table 1 and Table 2. The radon levels are two orders of magnitude higher than activity concentrations of radium. This is in good accordance with the available literature data for drinking, mineral, thermal and other underground waters (see Table 3.). The uranium concentration of the investigated samples varied widely between LLD and 934 mBq l^{-1}. It is somewhat higher that the uranium content of Hungarian surface waters (80–120 mBq l^{-1}). The reason of that phenomenon could be the dissolution of the uranium from minerals during water migration or can be explained by deposition of uranium salts in the water tubing with subsequent dissolution caused by changes of water chemistry.

In Hungary there is still no legislated ALI value for ^{222}Rn ingestion by the public. The ALI values for ^{226}Ra and U are 7 × 10^3 Bq and 5 × 10^4 Bq respectively [20]. The annual intakes of these radionuclides calculated by mean 43 mBq l^{-1} ^{226}Ra and 100 Bq l^{-1} U concentration and by 2 l d^{-1} water consumption are 0.4% and 0.01% of the corresponding ALI values.

According to the WHO guidelines [21] for drinking water quality the water is suitable for human consumption if reference concentrations corresponding to the reference levels of committed effective dose 0.1 mSv y^{-1} are lower than 1 Bq l^{-1} for ^{226}Ra and 4 Bq l^{-1} for U. The calculated mean radionuclide concentrations in the investigated samples are much lower than reference concentrations (1–10%), consequently the waters meet the WHO water quality guideline requirements.

There are no reliable available literature data that could prove the harmful health effects of the ingested radon. In spite of this in the accordance with the conservative Linear No Threshold theory of the stochastic effect of the low doses, there are some publications, where dose-conversion factors were calculated for ingested radon. According these data the dose-conversion for radon varies between 0.4–4 nSv Bq^{-1} for the whole body [22, 23, 24, 25, 26, 27]. Effective dose values for the public from radionuclide intake were calculated using the highest 4 nSv Bq^{-1} conversion factor for ^{222}Rn, the results are given in the Table 3. Effective doses were calculated for radium and uranium ingestion using $2,8 \times 10^{-7}$ Sv Bq^{-1}, and $^{234}U + ^{238}U$: $4.5 \times 10^{-8} + 4.9 \times 10^{-8} \approx 1 \times 10^{-7}$ Sv Bq^{-1} dose conversion factors [28], the results are shown in the Table 3. It was found that radiation doses to the Hungarian public from water consumption are 12,7±9,6 μSv y^{-1} from radon, 8,8±4,5 μSv y^{-1} due to radium, and 7,3±7,8 μSv y^{-1} from uranium in the drinking water. Comparing to the 2.18 mSv y^{-1} effective dose of the Hungarian public from radon inhalation in dwellings [29], and to the 2.4 mSv y^{-1} value of the worldwide average of the public dose from natural sources of radiation [30], these doses are negligibly small.

4. 4. CONCLUSIONS

Radioactivity of the drinking water in Hungary is in the order of magnitude of the worldwide average.

The measured radioactivity levels never exceeded the limits of the valid Hungarian standards for annual intake limits and were adequate to WHO guidelines.

Public doses from radon, radium, and uranium ingestion by drinking water are negligably small comparing to the public dose from other natural sources of radiation

ACKNOWLEDGEMENT

Work was supported by the National Environmental Health Program (NEKAP).

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Adopted levels and derived limits for Ra-226 and the decision making processes concerning TENORM releases

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Abstract

A fraction of a primary dose limit can be, in general, agreed upon as a dose related level to be adopted in decision-making processes. In the case of TENORM releases, fractions of primary dose levels for ^{226}Ra, ^{228}Ra, and ^{210}Po may be of particular importance to establish adopted levels and derived limits to guide decision-making processes. Thus, for example, a registration level for ^{226}Ra could be adopted at the highest portion of the natural background variation. Above such level, intervention and remedial action levels could also be adopted. All those levels would be fractions of the primary level, but translated in terms of derived limits expressed in practical units. Derived limits would then be calculated by using environmental models. In such approach "critical groups" would have to be carefully defined and identified. In addition, the size of a critical group would be chosen to be used in environmental modeling. Site specific environmental models and parameters are desirable, though unavailable, or very difficult to obtain, in most cases. Thus, mathematical models and parameters of more generic nature are often used. A sensitive parametric analysis can make a ranking of the parameters used in a model, allowing one to choose how important each parameter will be for the model output. The paper will point out that when using the adopted levels and derived limits, as suggested above, the uncertainties and importance of the parameters entering an environmental model can make the difference for decision makers to take the right or wrong decision, as far as radiological protection is concerned.

1. INTRODUCTION

The International Commission on Radiological Protection (ICRP) was created in 1928 by independent scientists to gather the most updated scientific information at any given time in order to publish sets of recommendations concerning radiation protection. Such sets of recommendations end up being followed, to a large extent, by national and international bodies whose objectives and responsibilities were to protect workers and the general public from potential deleterious effects of ionizing radiation. As time passed, the ICRP underwent several transformations in both, structure and composition. After the World War II, the ICRP received worldwide recognition as an important international independent organization, much needed as the world was entering into the nuclear age. As a consequence, the ICRP published a large number of technical documents that became respected guidelines for radiation protection throughout the world. In the United States of America, the field of radiation protection developed somewhat differently because of the experience accumulated in the Manhattan Project [1-2]. However, many American investigators in radiation protection have been giving their contribution to ICRP development since its inception.

The National Committee on Radiological Protection (NCRP) was formed in the United States with the objective of developing recommendations on radiation protection. The NCRP succeeded in 1946 the National Committee on Radiation Protection and Measurements, which had been created in 1929 as the Advisory Committee on X-ray and Radium Protection. The NCRP is na advisory independent organization without authority to establish or enforce any requirements for radiation protection. However, the NCRP recommendations are highly influential in the development and guidances for radiation protection in the United States, and even in other countries. As far as NORM and TENORM are concerned, the NCRP has published a number of reports [3-9].

Recently the National Academy of Sciences – National Research Council (NAS-NRC) of the United States published an authoritative report which examined the guidelines for exposures to TENORM [10]. The relationships among risk, dose, exposure, and concentration of radionuclides in environmental media were discussed in this NAS-NRC report. Figure 1 illustrates such relationships [10]. A concept underline in Figure 1 is taht a measure of risk due to exposure to radiation may be cancer mortality, or in some cases cancer incidence (morbidity), however, in many environmental-radiation assessments the end point of the calculations is dose rather than cancer risk. When such is the case an assessment of risk corresponding to given concentrations of radionuclides in the environment can be used, or vice versa.

This paper deals with adopted levels and derived limits, expressed in practical units, as surrogates for risks and doses used in the standards used for radiation protection.

2. RISK ASSESSMENT

The subject of *risk assessment* has been part of an intense debate following the publication, in 1977, of the recommendations made by the International Commission on Radiological Protection (ICRP) in its Publication 26 [11].

Here it is worth mentioning that many investigators in the field of radiation protection, as well as a large number of officials from national authorities throughout the world failed to perceive promptly that the intense debate on *risk assessment* that followed the set of recommendations published by the ICRP in 1977 was in reality a consequence of an evolution of concepts. At that time the ICRP recognized that, for purposes of regulation and monitoring, the quantity called radiation dose was difficult to determine directly; accordingly, it suggested simplified models establishing interrelationships for radiation doses, environmental quantities and parameters, and planned releases of radionuclides into the environment [12]. The ICRP recommended also derived and secondary limits, explained in detail in ICRP Publication 30 Part 1 [13]. The metabolic data and models used in the ICRP Publication 30 were essentially those of an adult person with anatomical and physiological characteristics of the Reference Man [14].

The system of *risk assessment* and dose limitation devised by the ICRP Publication 26 is to be used within the framework of *risks* versus benefit and cost-effectiveness. This is essentially a system of dose reductions. The key phrase was already written in paragraph 52 of ICRP Publication 9 [15]: "*As any exposure may involve some degree of risk, the Commission recommends that any unnecessary exposure be avoided, and that all dose be kept as low as is readily achievable, economic and social considerations being taken into account.*"

Not withstanding, the concepts associated with *risk* had already been used for many years in the previous ICRP recommendations. As early as 1959, the ICRP Publication 2 introduced a dose limitation system based on a fraction of the maximum permissible concentration (MPC); this system contrasted the concept of acceptable *risk* to the individual and society with the benefits which might be derived from activities involving exposure to radiation [16]. ICRP Publication 9 explicated that any exposure to radiation[1] might carry *risks* of somatic and genetic effects [15]. Paragraph 34 of ICRP Publication 9 explains that the permissible radiation dose must limit *risk* to an acceptable level, and suggests that such a dose might also be called an acceptable dose [15]. In addition, Paragraph 74 of Publication 9 states that at very low levels of *risk*, such as those associated with the dose limits for members of the public, only minor consequences to the health of those exposed (or their progeny) may occur if the dose limits are exceeded [15]. The concept of maximum permissible dose (MPD) was introduced to quantify a degree of risk associated with a limit of radiation dose at which the assumed risk could be considered acceptable to the individual and to society in relation to the benefit derived from activities involving exposure to radiation. These earlier concepts associated with *risk* were somewhat related with the United Nations Scientific Committee on the Effects of the Atomic Radiation (UNSCEAR) Reports [17-18].

The Publication 8 of the ICRP had already moved closer to UNSCEAR position by considering useful to estimate *risks* for radiation protection purposes [19]. Three types of *risks* were considered in the ICRP Publication 8 [19]: somatic *risks* to the exposed generation, genetic *risks* to the first generation offspring of exposed persons, and genetic *risks* to later generations. Absolute *risks* were expressed as [19]: "*the number of disabilities expected per unit dose of radiation in the lifetime of a million members of a population or as the number of disabilities per year in such population.*" Orders of risk were also used in such a way that a *risk* of death or injury would be defined as a *fifth order risk* if in a total population of 10^6 persons, 10 to 100 deaths (or injuries) would be expected. Relative *risks* were considered when the *risk* associated with an effect supposedly caused by 1 rad could be compared with the *risk* of a similar effect caused by natural causes [19]. Tentative estimates of genetic *risks* proved to contain too high uncertainties to be taken quantitatively into account. The genetic *risks* which might be associated with low level ^{226}Ra releases from the front end of the nuclear fuel cycle, for example, could not be estimated with any degree of certainty based on the concepts of *risk* used in the ICRP Publication 8.

The ICRP Publication 9 established that the MPD for occupational exposure should be regarded as upper limits and the annual dose limits for members of the public should be one-tenth of the corresponding MPD for workers. The MPD concept gave rise to the maximum permissible concentrations in air $(MPC)_a$ and in water $(MPC)_w$. The dose limitation system introduced by the ICRP in 1959 was based on a 5 rem (50 mSv) 30 years genetic dose limit, which through models and calculations led to MPCs in air and water [16]. Both, the $(MPC)_a$ and $(MPC)_w$ can be derived from a power function or an exponention model. The $(MPC)_w$ values for ^{226}Ra, for example, were derived based on the assumption that the maximum permissible burden to bone (the critical organ for ^{226}Ra) was 0.1 μCi (3.7×10^3 Bq), which could be obtained by consuming 1.1 L of water in working day periods of 8 hours, corresponding to one half of the water consumed in 24 hours. Such maximum permissible body burden to bone supposedly would carry "*no effect*" as far as bone tumors were concerned. It was observed that there was a built in risk factor in recommendations made on the basis of comparisons with ^{226}Ra body burdens, because $(MPC)_w$ values for ^{226}Ra concealed a degree of *risk* assumed to be acceptable [20].

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[1] The word **radiation** as used in the ICRP Publication 9 and in the context of this work refers only to **ionizing radiation**, and is used interchangeably.

3. RADIATION PROTECTION GUIDE (RPG) AND NORM/TENORM

The cumulative wastes from surface uranium mining in the United States from 1950 to 1977 amounted to about 1.7 x 10^3 Gt [21]. This fact was one of the main reasons why the Public Law 95-604 was enacted. As a practical consequence to this law the U. S. Department of Energy (USDOE) established the uranium mill tailings remedial actions [22]. Later on, in 1983, the United States Environmental Protection Agency (USEPA) issued a report to the United States Congress that presented a generic assessment of the general impacts of the uranium industry in the United States [23]. However, at that time *risk* assessments for the ^{226}Ra releases were not available. The USEPA position became clearer with the final decisions on the "National Emission Standards for Hazards Air Pollutants (NESHAPs) under section 112 of the Clean Air Act (CAA) for emissions of radionuclides from the following sources category: DOE facilities, Licensees of the Nuclear Regulatory Commission and Non-DOE Federal Facilities, Uranium Fuel Cycle Facilities, Elemental Phosphorous Plant, Coal Fired Boilers, High-level Nuclear Waste Disposal Facilities, Phosphogypsum Stacks, Underground and Surface Uranium Mines, and the operation and disposal of Uranium Mill Tailings Piles" [24]. In this USEPA document, the *safe or acceptable level of risk* is tentatively explained taking into account the Natural Resources Defense Council, Inc.(NRDC)v.EPA decision 824 F.2d at 1146 (1987) - better known as the *Vinyl Chloride Decision* - at the District of Columbia Circuit [24]. In a later publication the USEPA specifies that the non-threshold model (for the dose-response curve) is used to assume "*an estimated risk to an average member of the U.S. population of* $5x10^{-2}$ *fatal cancers per sievert (*$5x10^{-4}$ *fatal cancers per rem) delivered at low dose rates*" [25]. The same document also says that the *risk per sievert* of severe mental retardation from doses to a fetus is estimated to be at least one order of magnitude greater than that of fatal cancer to the general population. The risk of inducing severe hereditary effects is of the order of 10^{-2} *per sievert* (10^{-4} *per rem*) [24]. USEPA tried, to the extent possible, to harmonize its guidance with the knowledge of the effects of ionizing radiation on humans, taking into proper account the scientific data gathered throughout many years by the BEIR Committee of the National Academy of Science-National Research Council on health risks of low levels of ionizing radiation [26-28]. In addition, the USEPA document considered the UNSCEAR reports published from 1977 to 1988 [29-31]. This USEPA's radiation protection guidance constituted a review of the of earlier guidances to Federal agencies on the protection of workers and the general public from radiation (25 FR 4402 and 25 FR 9057). The ICRP recommendations of 1977, in Publication 26 [11], and 1990, in Publication 60 [32], as well as NCRP Report No. 116 [9] were also considered relevant to the USEPA guidance. The USEPA guideline proposed to change the "*Radiation Protection Guide (RPG) limiting the average genetic dose to members of the U.S. population to 5 rems (50 mSv) in 30 years and the annual whole body dose to 500 mrem (5 mSv) dose equivalent be replaced by a single RPG of 1 mSv (100 mrem) effective dose equivalent received by or committed in a single year to any individual from all sources combined; doses from individual sources normally be limited to a fraction of the RPG; and increased emphasis be given to the principle that all exposure should be maintained as low as reasonably achievable, within the RPG*" [24]. USEPA's 1994 recommendations are summarized in Table I.

The application of the USEPA's RPGs to NORM/TENORM, however, pose a number of problems. The natural radiation background presents significant spatial and temporal variations. There is not a well defined baseline of exposures from natural sources of radiation against which exposure due to TENORM can be compared. The latter has been addressed recently by UNSCEAR [33].

Table I. Recommendations proposed in the USEPA radiation protection guidance. Adapted from ref. [25].

NUMBER	PROPOSED RECOMMENDATION
1	There should be no exposure of the general public to ionizing radiation unless it is justified by the expectation of an overall benefit from the activity causing the exposure.
2	A sustainable effort should be made to ensure that doses to individuals and to populations are maintained as low as reasonably achievable. This includes consideration of economic and societal factors, and apply to radiation exposure that may occur now or in the foreseeable future.
3	The combined radiation doses incurred in any single year from all sources of exposure should not normally exceed 1mSv (100mrem) effective dose equivalent to an individual.
4	Authorized limits for sources should be established to ensure that individual and collective doses in current and future populations satisfy the objectives of the Radiation Protection Guide.
5	Risks associated with exposure of the general public to radiation that may occur due to Federal agency decisions and the policies upon which these actions are based should be made public as part of the decision process.
6	Assessments and records appropriate to the origin and magnitude of expected doses and the exposed population be performed and maintained to demonstrate conformance with requirements which implement these recommendations.
7	Exceptions to Recommendation 3 for planned exposure to radiation should be made only for highly unusual circumstances, and only when requirements which implement these recommendations.

4. UNSCEAR, IAEA AND THE NORM ISSUE

Although there is a concealed degree of *risk* assumed to be acceptable in the $(MPC)_w$ values for ^{226}Ra, the last UNSCEAR Report does not address the risk issue. However, the 1997 UNSCEAR Report calculated the effective doses resulting from intake of natural radionuclides in air, food and water from measured concentrations in the body or estimated from concentrations in intake materials. The worldwide average committed dose from annual intakes was estimated to be 0.23 mSv, being 0.17 mSv due to ^{40}K and 0.06 mSv from radionuclides of the ^{238}U and ^{232}Th series, excluding radon and its decay products. The

Table II. UNSCEAR estimations on the average annual effective dose to adults from natural sources of ionizing radiation. Taken from ref. [33].

Component of exposure	Annual effective dose (mSv)	
	Normal	Elevated
Cosmic rays	0.38	2.0
Cosmogenic radionuclides	0.01	0.01
Terrestrial radiation: external	0.46	4.3
Terrestrial radiation: internal*	0.23	0.6
Terrestrial radiation: internal**		
Inhalation of Rn-222	1.2	10
Inhalation of Rn-220	0.07	0.1
Ingestion of Rn-222	0.005	0.1
Total	2.4	----

* Exposure excluding radon

** Exposure from radon and its decay products

Table III. Annual effective doses from ingestion of uranium and thorium-series radionuclides. Taken from ref. [33].

Radionuclide	Annual effective dose (μSv)			
	Infants	Children	Adults	Age-weighted
^{238}U	0.23	0.26	0.25	0.25
^{234}U	0.25	0.28	0.28	0.28
^{230}Th	0.42	0.50	0.64	0.59
^{226}Ra	7.6	12	6.3	8.0
^{210}Pb	54	49	25	34
^{210}Po	227	114	75	95
^{232}Th	0.26	0.32	0.38	0.36
^{228}Ra	33	42	10	21
^{228}Th	0.38	0.28	0.22	0.24
^{235}U	0.011	0.012	0.012	0.011
TOTAL	320	220	120	160

UNSCEAR estimations of the average annual effective dose to adults from natural sources are reproduced in Table II.

It is interesting to notice that, taking into account the data presented in Table II, the average annual effective dose from external exposure to terrestrial radionuclides is double than that due to internal exposure. These two modes of exposure represent about 29% of the total exposure, radon inhalation is responsible for 50%, cosmic radiation accounts for 16%, while all other modes of exposure contribute with less than 5% of the total annual effective dose. When one does not consider high exposure to cosmic rays, in areas of high natural background the main doses are due to inhalation of radon, and external and internal exposures to terrestrial radiation. These latter modes of exposures are the most likely way that NORM/TENORM will incur doses to humans.

The UNSCEAR evaluated the internal doses from ingestion of uranium and thorium-series radionuclides, taking into account a fractional population distribution of 0.05, 0.3 and 0.65, respectively for infants, children and adults. The UNSCEAR annual effective doses form ingestion of uranium and thorium-series radionuclides are summarized in Table III.

The age-weighted total value of 160 μSv reported in Table III is more than three times higher than the 52 μSv derived in the earlier UNSCEAR Report [34]. The total annual effective dose from inhalation (≈ 10 μSv) and ingestion of terrestrial radionuclides is about 340 μSv, of which 170 μSv is from ^{40}K [33]. It is not clear, however, whether those effective doses from natural radionuclides can be used as representatives or not. Further data are necessary to establish a dose baseline due to the intake of natural radionuclides. Such baseline becomes more important as TENORM may reach the foodchains.

The ICRP Publication 26 reviewed critically the former concept of genetic dose limit of 5 rem (50 mSv) in 30 years from all sources of radiation additional to the dose from natural radiation background and from medical procedures [11]. The revision made in the ICRP Publication 26 was made under the following assuption [11]: "*continuance of the former genetic dose limit could be regarded as suggesting that acceptability of a higher population exposure than is either necessary or probable, and a higher risk than is justified by any present or easily envisaged future development.*"

The International Atomic Energy Agency (IAEA) adopted principles based on the system of dose limitations recommended by the ICRP Publication 26, stressing that cost-benefit analysis, quantitative assessment, and value judgements should support decision making processes [35-37]. However, the IAEA recommendations did not address the issue of naturally occurring radioactive materials (NORM).

5. CURRENT BASIC SAFETY STANDARDS (BSS) AND NORM

A number of well respected international organizations — the Food and Agriculture Organization (FAO), the International Atomic Energy Agency (IAEA), the International Labour Organization (ILO), the Nuclear Energy Agency of the Organization for Economic Co-operation and Development (OECD/NEA), the Pan American Health Organization (PAHO) and the World Health Organization (WHO) — recently sponsored the International Basic Safety Standards for Protection against Ionizing Radiation and for the Safety of Radiation Sources (BSS) [38]. The BSS was approved by the IAEA's Board of Governors in September 1994. The NORM issue was not specifically contemplated in the BSS, however, exempt activity concentrations and exempt activities of radionuclides were established based on the following general principles [38-39]:

Table IV. Exempt activity concentrations for the most relevant radionuclides (plus their progeny) in the case of NORM releases, as established in the Basic Safety Standards and activity concentrations found in selected extractive industries.

RADIONUCLIDE	ACTIVITY CONCENTRATION (kBq/kg)	
	Exempt [39]*	Extractive industries
Rn-222	10	
Ra-224	10	
Ra-226	10	2.7 [40] - 658 [41]
Ra-228	10	368 [42]
Th-228	1	1.1 [40] - 200 [41]
Th-natural	1	0.7 [43-45] - 111 [40]
U-230	10	
U-natural	1	3 [43-45] - 30 [40]

* The reference numbers are indicated between brackets.

"(a) the *radiation risks* to individuals caused by the *exempted practice* or *source* be sufficiently low as to be of no regulatory concern;

(b) the collective radiological impact of the *exempted practice* or *source* be sufficiently low as not to warrant regulatory control under the prevailing circumstances; and

(c) the *exempted practices* and *sources* be inherently safe, with no appreciable likelihood of scenarios that could lead to a failure to meet the criteria in (a) and (b)."

Table IV lists the exempt activitiy concentrations established in the BSS for ^{222}Rn (plus ^{218}Po, ^{214}Pb, ^{214}Bi, ^{214}Po), ^{224}Ra (plus ^{220}Rn, ^{216}Po, ^{212}Pb, ^{208}Tl -36%-, ^{212}Po -64%), ^{226}Ra (plus ^{222}Rn, ^{218}Po, ^{214}Pb, ^{214}Bi, ^{214}Po, ^{210}Pb, ^{210}Po, ^{210}Pb), ^{228}Ra (plus ^{228}Ac), ^{228}Th (plus ^{224}Ra, ^{220}Rn, ^{216}Po, ^{212}Pb, ^{208}Tl -36%-, ^{212}Po -64%), Th-nat (including ^{232}Th and progeny), ^{230}U (plus ^{226}Ra, ^{222}Rn, ^{218}Po, ^{214}Po), and U-nat (including the ^{238}U progeny), which are the most relevant radionuclides in the case of NORM releases, and activity concentrations found in some selected extractive industries [38].

It would be helpful to be able to establish easy to measure limits, so industries that deal with NORM or have TENORM as byproducts could benefit from these practical limits. Derived limits for ^{226}Ra releases will be presented here for illustration purposes only.

6. SECONDARY AND DERIVED LIMITS FOR RA-226 RELEASES

One must bear in mind that a primary dose limit is established based on an amount of effective dose which is not supposed to be exceeded. The ICRP defined, for practical purposes, secondary, derived and authorized limits which were since then adopted by the IAEA and EU [37;46-48].

Metabolic and environmental modeling are necessary to make possible intercomparison involving measurable quantities instead of effective dose. Thus, for example, the use of metabolic and environmental models in association with a derived limit (DL) for ^{226}Ra releases allows a direct comparison with measurable and/or estimated ^{226}Ra concentrations in environmental and biological media due to actual or potential releases of this radionuclide into the environment.

Derived limits for ^{226}Ra, as well as for any other radionuclide, should be based on the annual limit of intake (ALI). The ALI for ^{226}Ra is 7 x 10^4 Bq/yr (1.9 μCi/yr). This ALI shall not be exceeded ever, and is to be used for the control of occupational exposure. However, for adult members of the public a ^{226}Ra ALI of 7 x 10^3 Bq/yr (0.19 μCi/yr) has been suggested as appropriate, and was actually adopted by the EU to be used by the Member States in theirs radiation protection programs [47]. It is interesting to notice here that this EU ALI is about twice the maximum permissible body burden adopted by the ICRP much earlier [16].

A ^{226}Ra DL has been suggested for a manioc growing Brazilian region where thorium and uranium rich pyrochlore and apatite [49]. However, practical applications of DLs for ^{226}Ra releases in more general terms can also be used, as well as for other radionuclides.

DLs for ^{226}Ra releases can be linked to primary or secondary limits, like an ALI, with an accuracy which will depend on the realism and adequacy of the environmental model used in the derivation. Thus, environmental modeling is essential for calculating DLs for ^{226}Ra releases.

Generic models and parameters can be used in the preliminary assessment of environmental transfer of radionuclides from routine releases. Thus, a generic derived limit (GDL) either for ^{226}Ra releases from a specific source or for ^{226}Ra concentrations in environmental or biological media can be easily calculated based on generic models and parameters for this radionuclide.

Potential *critical groups* must be defined or identified for the application of a GDL for ^{226}Ra or any other radionuclide. The concept of *critical group* was introduced to circumvent the lack of precision in the definition of the expression "*members of the public*," frequently used in the ICRP publications. On the one hand, "*members of the public*" imply large differences in age, size, metabolism, customs, and environmental variations in the places of working and living. On the other hand, *critical groups* must be small enough to be relatively homogeneous with respect to those characteristics that can affect the doses received; like age, diet, and behavior [11;35;37]. An homogeneity requirement establishes that, in general, the maximum to minimum ratio within a critical group do not exceed an order of magnitude. *Critical groups* may be either identified among existing members of the general population, or defined as a group of persons; in either case a critical group is expected to be exposed to a higher dose level than that received by the general population. A typical size of a *critical group* is up to a few tens of persons, mostly to restrict habit surveys. However, when large populations are uniformly exposed, the size of the *critical group* can be considerably larger. The size, as well as the identification or definition of *critical groups* are relevant aspects to be considered in environmental modeling concerning ^{226}Ra or any other radionuclide releases into the environment.

In addition to *critical groups*, environmental modeling requires the use of *critical pathways* for a critical radionuclide. In the case of ^{226}Ra releases into the environment, the relative importance of ^{226}Ra vis-a-vis ^{210}Po as the critical radionuclide should be considered in some pathways, because the latter may be also an important contributor to internal dose levels under certain circumstances [50].

Critical pathways to be considered for ^{226}Ra releases will be essentially terrestrial or aquatic, because air is usually an unimportant pathway for ^{226}Ra intake. Simplified pathways

Table V. Selected derived limits (DLs) for ^{226}Ra.

DERIVED LIMIT FOR	PRACTICAL UNITS*
Water	Bq/L
Pasture or soils	Bq/kg
Rate of discharge	Bq/year
Air	Bq/m^3

* Not necessarily SI units.

for ^{226}Ra released into ground and surface waters, and in soils are presented in Figure 2. One must observe, however, that the direct radiation exposure pathway is only important when the *critical group* is located near the site of ^{226}Ra releases or is living near surface soils or sediments that accumulated high ^{226}Ra concentrations. Direct radiation might be considered a *critical pathway* when, for example, TENORM bearing tailings are inadvertently used as construction material or are not isolated from a *critical group*. In such cases, however, radon rather than ^{226}Ra should be considered the critical radionuclide.

The basic conditions for an useful DL are the following:

1. be comparable with measurable quantities. Thus, for ^{226}Ra one can expect, for example, to determine DLs with units in accordance with Table V.
2. be related with the ALI for ^{226}Ra. That means 7 x 10^3 Bq/yr (0.19 μCi/yr) for adult members of the public;
3. be chosen in such a way that once not exceeded, the dose limit will not be exceeded also.

It is well recognized that the physical descriptions of the critical pathways followed by ^{226}Ra from the source of release until will reach humans, and the appropriate values for parameters used in generic environmental models may differ considerably of site specific environmental models and parameters.

Site specific models and parameters are desirable in most cases, but by and large, they are unavailable and are very difficult to obtain. As a consequence, mathematical models and parameters of more generic nature are often used.

Concerning the uncertainties of radio-ecological assessment models it has been observed the following [51]:

"*(i)* *there is a need to distinguish between research and assessment models, mainly regarding the objectives for developing and applying such models;*

(ii) *limits specifying the applicability of the results of modeling should be clearly indicated when using deterministic models for decision-making; and*

(iii) *the introduction of further complexities in a model does not necessarily assure any improvement in the predictions.*"

When the calculated doses approach dose limits, that means, whenever doses predicted by models are less than about one order of magnitude below the relevant dose limit, the model structure, its parameters and all associated values should be re-evaluated. The criterion to decide to re-evaluate a model is a matter to debate.

Figure 3 suggests a sequence of dose related levels that can be useful in decision-making processes. Once a primary dose limit is established, fractions of this primary limit can be agreed upon. Thus, for example, a registration level would be established at the highest portion of the background variation. Above this registration level investigation, intervention and remedial action levels would also be established. All those levels could be established in terms of fractions of the primary dose, but translated in terms of derived limits expressed in practical units, as in Table V. The derived limits would be calculated by using environmental models. A sensitive parametric analysis can make a ranking of the parameters used in the model, allowing one to choose how important each parameter can be in the model output.

A detailed discussion on the uncertainties involved in radiological models, as well as an application of ranking parameters, based on sensitive analysis of an environmental model can be found in the literature [51-52]. When using adopted levels and derived limits as those suggested in Figure 3, the uncertainties and importance of the parameters entering an environmental model can make the difference for decision-makers to adopt a right or wrong decision concerning radiological protection.

7. CONCLUDING REMARKS

1. A brief review of the concept of *risk* as used in radiation protection was presented, taking into consideration its evolution since the earlier uses.
2. The adoption of secondary levels of dose and derived limits for ^{226}Ra releases have been proposed and illustrated.
3. Attention has been called in regarding the need of parametric analysis to rank parameters entering the models used to obtain the derived limits.

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Methods for storage and disposal of residues from wastewater treatment of former uranium mining and milling facilities in Germany

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Abstract. In connection with the flooding of uranium mines in Saxony and Thuringia, there are contaminated pit waters that must be purified before discharge into surface waters. The expected duration of the water purification process until concentrations of natural radionuclides, various heavy metals and arsenic are low enough to allow direct discharge into surface waters amounts to decades . To prevent or minimize the leaching of the contaminants from the sludge of the water treatment in the long term, the contaminants are either transformed into chemical compounds of low solubility or affixed within ion exchange resins. Due to the accumulation of those contaminants during the water processing procedure, the residua must be disposed of for reasons of radiation protection and waste management. A final storage of the residua in accord with nuclear regulatory stipulations is unnecessary because of the contamination levels and also because of the mining origin. The method of residua-storage chosen to be best suited to a particular site has to be based on costs-to-benefit analyses, giving due consideration to the different aspects e.g. radiation and environmental protection, long term safety, form of immobilization, site specific conditions. These methods will be described and illustrated using specific examples of applications.

1. INTRODUCTION

In southern East Germany, extensive uranium ore mining and milling was put into operation by the Soviet-German WISMUT company. With a total yield of about 216,000 t uranium the former GDR was the world's biggest uranium producer. After the decommissioning of uranium ore mining, restoration and re-utilization of the mines and residua from the mining and milling began.

The flooding waters of the mines and the seepage waters of the tailing ponds contain various heavy metals and arsenic besides the natural radionuclides of the uraniumradium decay chain in a concentration that makes the direct discharge into surface waters impossible.

The calculations predicting the pollutant trend in the flooding water demonstrated that the duration of the water purification process necessarily comprises several decades. Therefore, it is necessary to provide temporary repositories and capacity for final storage beyond the duration required for water purification.

2. WASTE WATER TREATMENT AND IMMOBILISATION METHODS

2.1. Water treatment methods

An overview of the currently applied and anticipated water treatment methods at the rehabilitation sites of WISMUT is given in Table 1.

Table 1: Water treatment at the WISMUT rehabilitation sites

Site	Poehla	Schlema	Ronneburg	Koenigstein	Crossen	Seelingstaedt
State of MWTF	In operation	Trial runs	Anticipated	Anticipated	In operation	In operation
capacity	80 m^3/h	$\leq$ 700 m^3/h	$\leq$1,000 m^3/h	$\leq$ 1,500 m^3/h	250 m^3/h	500 m^3/h
Waters to be treated	Mine water	Mine water	Mine water	Mine water	Waters from tailing pond	Waters from tailing pond
Chemistry of waters to be treated (in mg/l; Ra 226 in Bq/l)	Aug. 1998	Febr. 1999	prediction	prediction	Aug. 1998	Aug. 1998
	U: 0.2 (0.2)	7.5 (0.5)	< 1.5 (0.5)	60 (0.8)	8.0 (0.5)	5.0 (0.5)
	Ra: 4.8 (0.3)	4.0 (0.4)	< 0.2 (0.4)	0.2 (3.0)	0.4 (0.2)	0.2 (0.4)
	As: 2.5 (0.1)	1.5 (0.3)	-	-	55 (0.3)	-
	Fe: 13 (2.0)	6.0 (2.0)	< 150 (3.0)	1,100 (10.0)	-	-
	Mn: 1.5 (2.0)	5.0 (2.0)	< 15 (1.0)	-	-	-
	SO_4:6.2 (400)	1,900 (2,000)	<5,000	6,000 (2,000)	4,300 (7,500)	8,000
	Cl: 5.8 (250)	100 (1,000)	< 200 (250)	750 (2,000)	1,300 (5,500)	500
	pH*: 7.2	7.1	4.5 – 6	2 – 3	9.8	7.5

In brackets (...): authorised discharge concentration (ADC); for Ronneburg and Koenigstein, in discussion
* permitted pH range for all sites: 6.0 – 8.5

The mine-water treatment facility (MWTF) at the Poehla site has been in operation since September 1995; at the Schlema site trials continue. The technology applied at both sites represents a multi-step technique with selective extraction of the different pollutants. The Ra-extraction results from the co-precipitation with barium to sulphateby supplement of barium chloride. Uranium is Precipitated through selective flocculation by the polymer GoPur 3000. The arsenic extraction occurs by absorption of ferric oxide hydrate formed by the supplement of ferric-111-chloride. Iron and manganese are oxidized to ferric oxide hydrate or, respectively, to manganite.

After the selective purification steps the precipitated residues are concentrated, and finally by means of chamber filter presses partly de-watered up to a dry matter content of 35–40%. Then the sludge is put into plastic drums of 220 1 volume at the Poehla site. According to [1] the total amount of sludge predicted for the operating time of about 20 years will be ca. 700 t (about 3,700 drums). For the Schlema site the covering of the sludge with concrete (40,000 rectangular blocks of I M3 each) was chosen. Table 2 roughly provides a glimpse of typical sludge composition from the MWTF sites at Poehla [1] and Schlema [2].

Table 2: Typical composition of the sludges (dry matter) from the Poehla and Schlema MWTFs

Element	Unit	Poehla site			Schlema site
		9/95 – 3/96	4/96 – 12/96	1/97 – 6/97	
U	g/kg	4.0	4.4	1.9	30.0
Ra 226	Bq/kg	4,200	10,800	20,200	35,000
As	g/kg	1.1	1.0	1.0	40.0
Fe	g/kg	153	120	110	140
Mn	g/kg	0.34	0.20	0.15	100

2.2. Immobilization methods

Because of the experimentally verified low dilution capability of the pollutants and the negligible hydrolysis of GoPur 3000 at normal temperatures, and the foreseen underground storage in cement filled galleries as well, there was no need to take account of further immobilization measures after the water treatment at the Poehla site.

For the Schlema MWTF, conventional Portland cement/fly ash solidification was initially chosen. However, because of the planned above ground storage at a waste rock heap and the need to guarantee safe handling during operation, and to minimize the risk of uncontrolled spread of contaminated matter over the next several hundred years, it cannot meet requirements satisfactorily. A technology was therefore sought which satisfies the above mentioned standards. Furthermore, an overrun of the cost figures projected for sludge conditioning and disposal should not be unacceptably high.

According to [3] Geopolymerg (high-alkali (K-Ca)-Poly(sialate-siloxo) binders) was shown to offer a solution satisfying these requirements. Laboratory tests and a largescale experiment for solidifying the sludge from one of the WISMUT mine-water treatment plants have demonstrated that the stability requirements are met even under extreme conditions. Nevertheless, at present the sludge is still solidified by using Portland cement.

3. FINAL STORAGE OF MWTF SLUDGE

3.1. Site selection methods

The location of the disposal site is a central issue in the application and licensing procedure. Apart from the general requirements such as geo-technical stability and radiation protection during handling, interim storage and disposal, an extensive array of criteria is applied to identify the preferred option. This includes the available means of transportation, the number of people affected, anticipated regulation and public acceptance, environmental impact, long term stability, and conflicts with other remediation activities of WISMUT.Site options are evaluated with respect to these criteria using models and methods developed for radioactive waste repositories. Practically speaking only very few criteria actually influence the final decision.

The following options were considered for the storage of the MWTF Poehla residua:

(A) Disposal in a specially prepared cell on a waste rock pile (Luchsbach pile) close to the mine-water treatment facility (MWTF).
(B) On-site underground storage above the final flooding water level in the decommissioned Poehla mine.

(C) As in (A), but at the Schlema site (waste rock pile H 371/1).

Multi-Attribute Utility Analysis (MAUA) demonstrated that option B is a clearly favoured option. Option A was ruled out owing in particular to the more than 10 times larger long term pollutant release, even upon confinement of the sludge within the cement and due to the relatively low pollutant inventory of the Luchsbach waste rock pile compared to that of the sludge. Decisive for the ruling against option C was the existing lack of public acceptance for the transport of radioactive substances via public roads (about 30 km) through 5 communities.

In order to specify the remaining storage option B, a risk analysis of the multi-barrier system of the foreseen pit area was conducted [4]. Owing to the lack of legal regulations in regard to the storage of these residua, a period of 1,000 years was cited and agreed upon by the licensing authority. Referring to the de-minimis-concept, an individual equivalent dose limit of 10 ~tSv/yr corresponding to an maximum Uranium concentration in the seepage water of 6 pg/L must be respected during this time. Hereto the values of the radionuclide concentration were defined for the waters discharging from the storage site, and compliance with the limits was checked for various release scenarios some of which are illustrated in Table 3.

Table 3: Computed results from various release scenarios for the Poehla pit storage site

Kf [m/s]	Gradient I	Area [m^2]	Q [l/d]	Eluat C(U_{nat}) [mg/l]	mobilized Uranium [g/d]	Release time [a]	Concentration increase, U_{nat} [mg/l]
$1*10^{-7}$	0.1	2733	2361.3	0.350	0.826	1,143	$1.14*10^{-3}$
$1*10^{-7}$	0.01	2733	236.13	0.350	0.08	11,436	$1.14*10^{-4}$
$1*10^{-7}$	0.001	2733	23.61	0.350	0.008	114,368	$1.14*10^{-5}$
recently Q			3.0	0.350	0.001	900,195	$1.46*10^{-6}$

Overall flow through the storage galleries was calculated using different gradients from 0.1 to 0.001 referring to [1, 5]. The result of analysis demonstrates that even the most conservative case does not compromise the agreed upon limit of 6 pg/1 Un,t. Also upon assuming the currently measured amount of water, the presupposed higher leaching values remain in part significantly below the allowed limits. By assuming the most improbable scenario with complete severing of the pit galleries, given the maximum possible gradients and leaching values, there would be no violation of the recommended value for U_{nat}

For the disposal of the sludge from the Schlema-Alberoda MWTF, options (B) and (C) mentioned for the Poehla site had to be compared in the final stage of the licensing procedure. An underground storage option at the Schlema-Alberoda site was rejected early on because of costs and owing to the insufficient geornechanical stability of potentially suitable pits.

It has been clearly shown by means of Multi-Attribute Utility Analysis (MAUA) that the Poehla mine option would be dominated by the pile H 371/1 option [2]. Extensive sensitivity analyses supported this view. However, since MAUA lumps together a wide range of quantitative and qualitative criteria into one utility measure, it may evoke objections over whether the essential aspects would have received due consideration, especially the long term aspect of the release of contaminants from the disposal cell on the waste rock pile compared to the release from the underground repository. Therefore, a probabilistic estimate of the long term release of contaminants from both sites has been carried out.

This result applies at first only to the underground option at the Poehla site. In contrast to the ruled out option of storing Poehla mine sludge on the Luchsbach pile, the H 371/1 pile exhibits 10 times the activity inventory (U, Ra 226) thus making the supplementary contribution by the residua of the water treatment seemingly small. Nevertheless, the 10 ~tSv criterion agreed upon for the storage in the Poehla pit would not be violated in this case since the dose rate limit for waste rock pile rehabilitation has been specified at < I mSv/a. Taking the limiting conditions into consideration the following statements can be made to substantiate the favoured pile option:

- The release of uranium from the disposal cell on the H 371/1 site leads to negligible doses and health risks compared to the release from the pile itself

- The release from the disposal cell would in no way lead to a measurable increase in the concentration in the waste rock seepage water

- There are no long term health risks associated with the H 3 7 1 /1 disposal option.

Nonetheless, this conflicts strongly with other WISMUT remediation measures, which might lead to severe delays and additional costs, because of the required upkeep of the disposal site during the entire period of the water treatment.

3.2. Storage Technology

In the Poehla pit, storage of sludge from the water treatment facility as an analogue to a technology of radioactive waste storage is carried out as follows:

- Storage of the sludge — containing drums in a gallery segment 10 m long

- Closure of the I " segment by a brick wall (with a gap at the ridge of the gallery)

- Filling with concrete shielding and closure of the ridge area

These steps are repeated throughout the entire storage gallery. A 5-m thick dam of concrete is lastly set at the end of the gallery. Ultimately, this technology provides the geo-mechanical long term stability of the pit construction for compliance with legal mining provisions.

In order to store the residua from water treatment at the Schlema-Alberoda site, an area with the ground sealed was prepared at the 371/1 waste rock pile, corresponding approximately to the requirements posed by the German Technical Guidance for above round repositories for chemically toxic wastes. Nevertheless, the long term stability requirements for the period of 1,000 years considered can not be met by using this method but are met by underground storage with concrete shielding. On the basis of computer simulations pollutant-leaching is related to the malfunction (occurring early on compared to the period under consideration) of the sealed ground at the repository. There is need to further pursue cost-benefit-analysis to check whether a kind of simple seal, the efficiency of which is limited to the storage period, would fit the purpose.

4. CONCLUSIONS

The mine-water treatment facilities (MWTF) designed and constructed to rule out the discharge of radioactive and toxic substances as demonstrated and described by the example of the WISMUT rehabilitation sites Schlema-Alberoda and Poehla are operating under the principle of selective chemical extraction of pollutants.

In order to ensure the long term stability of residues resulting from the water treatment, technologies are applied that provide a high degree of immobilization. By means of subsequent solidification (concrete, Geopolymers) long term stability can be assured.

To select appropriate sites for the final storage of MWTF sludge, methods and models are applied analogous to those for the final storage of radwaste. As the preferred options for the Poehla and Scblema-Alberoda sites have demonstrated, the implementation of an individual option depends on various aspects. Addressing only the long term leaching aspect of contaminants from the repository, preference should be given to the option of underground storage of the sludge over the surface-related storage options. In view of quantitative risk analysis and other aspects, for example the lower hazard potential as the nuclear material storage, the surface storage options cannot be ruled out as the example of the Schlema site demonstrates.

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Radiological impact from atmospheric releases of ^{238}U and ^{226}Ra from phosphate rock processing plants

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Abstract. Phosphate rocks are used extensively, mainly as a source of phosphorus for fertilizers and secondly for phosphoric acid and gypsum (phosphogypsum). Phosphates are, therefore one of the sources of technologically enhanced exposure to man from natural radionuclides (TENR). Emissions from phosphate rocks processing plants in gaseous and particulate form contain radioisotopes, such as ^{238}U and ^{226}Ra, which are discharged into the environment causing radiation exposures to the population. About 10 MBq of ^{238}U and ^{226}Ra, respectively, are discharged to the environment each year from a phosphate rocks processing plant in Thessaloniki area, Northern Greece. The collective dose commitment to lung tissue resulting from atmospheric release was estimated to be ~2 × 1O^{-9} man Gy t^{-1} for ^{238}U and ~O.1 × 1O^{-9} Plan Gy t^{-1} for ^{226}Ra, i.e. about 2 times higher than that reported in UNSCEAR 1992 Report.

1. INTRODUCTION

Phosphate rocks are used extensively, mainly as a source of phosphorus for fertilizers and secondly for phosphoric acid and gypsum (phosphogypsum). Sedimentary phosphate ores tend to have high concentrations of uranium, whereas magmatic ores, such as apatite do not. Typical activity concentrations of ^{238}U are 1500 Bq kg^{-1} in sedimentary phosphate deposits and 70 Bq kg^{-1} in apatite. Uranium-238 is generally found in radioactive equilibrium with its decay products, such as Radium-226. The activity concentrations of ^{232}Th and ^{40}K in sedimentary phosphate rocks are much lower than those of ^{238}U, and comparable to those observed normally in soil [11].

Mining and processing phosphate ores redistribute ^{238}U and its decay products among the various products, by-products and wastes of the phosphate industry. Effluent discharges into the environment as well as the use of phosphate fertilizers in agriculture and of by-products, such as gypsum (phosphogypsum) in the building industry are possible sources of radiation exposure to the public [2].

Phosphoric acid is produced by two methods, the wet process and the thermal process. (a). In the wet process method, usually employed for the production of fertilizers, sulfuric acid is mixed with ground phosphate rock. The subsequent reaction results in the production of phosphoric acid and gypsum as follows: $Ca_{10}\ F_2(PO_4)_6 + 10\ H_2S0_4 + 20\ H_20-10\ CaS0_4.2\ H_20 +6\ H_3PO_4 + 2\ HF$.

In the above reaction, Radium-226 is coprecipitated with the gypsum, while Uranium-238 and Fhorium-232 follow the Phosphorus into the phosphoric acid, which is then used to manufacture various fertilizer products [3]. Apart from gaseous fluorides, which are not radioactive, the airborne effluents of wet phosphoric acid consists of dust resulting from the transferring of phosphate rock within the plant.

(b) In the thermal process normally used for high-grade acid and phosphates, coke and silica are added to phosphate rock in an electric furnace (oven). The chemical reaction at high temperature produces elemental Phosphorus, which is relatively free of radioactivity and several by-products among which calcium silicate slag, which carries the bulk of the activity initially contained in the phosphate rock, and ferrophosphorus are the most important [4–6]. The smelting of the ore results in ^{210}Po and other volatile radioactive material releases [4].

This paper deals with the phosphate rock processing plant of SICNG (Société Industries Chimiclues du Nord de la Grèce) at Thessaloniki, Northern Greece, and the doses arising from effluent discharges.

2. MATERIALS AND METHODS

A sufficient number of phosphate rocks (raw material), phosphate fertilizers, phosphoric acid and gypsum (phosphogypsum) were obtained from SICNG, a phosphate rock processing plant at Thessaloniki, in five different periods, December 1981, March 1983, June 1987, January 1991 and July 1993. All samples were homogenized, packaged to preclude radon emanation, and then counted for natural gamma radiation on a low-background Ge detector linked to an appropriate data-acquisition system. A plot of gamma spectrum of phosphate rock (sample C9, Table 1) is shown in fig.1, up to the peak of 609 keV gamma rays for determination of ^{238}U and ^{226}Ra. Part of the spectrum was included for the 1460 keV gamma rays of ^{40}K and 2614 keV gamma rays of ^{208}Tl (^{232}Th series). It is evident from the spectrum that ^{238}U and ^{226}Ra were in high concentrations, while ^{232}Th and ^{40}K were not. The experimental method has been described elsewhere [7–8]. Instrumental nuclear activation analysis (INAA) was also applied in order to confirm the ^{238}U and ^{232}Th data.

3. RESULTS AND DISCUSSION

Table 1 presents the concentrations in Bq kg^{-1} of ^{238}U, ^{226}Ra, ^{232}Th and ^{40}K of (a) phosphate rocks, (b) phosphate fertilizers, (c) phosphoric acid, and (d) gypsum. In phosphate rocks, ^{238}U concentrations ranged from 182 to 1800 Bq kg^{-1} (avge. 984.4 Bq kg^{-1}), while ^{226}Ra concentrations ranged from 112.4 to 1801 Bq kg^{-1} (avge. 1053.3 Bq ka^{-1}). In phosphate fertilizers, ^{238}U concentrations ranged from 312 to 936 Bq kg^{-1} (avge. 638 Bq kg^{-1}), while ^{226}Ra concentrations ranged from 18.7 to 1128.5 Bq kg^{-1} (avge. 417.6 Bq kg^{-1}). In phosphoric acid, as H_3PO_4, ^{238}U concentrations ranged from 662.3 to 2260 Bq kg^{-1} (avge. 1314.1 Bq kg^{-1}), while ^{226}Ra concentrations ranged from 162 to 1294 Bq kg^{-1} (avge. 677.4 Bq kg^{-1}). In phosphogypsum, as $CaSO_4$. 2 H_20 ^{238}U concentrations ranged from 150.2 to 211.3 Bq kg^{-1} (avge. 180.75 Bq kg^{-1}), while ^{226}Ra concentrations ranged from 260.9 to 472.5 Bq kg^{-1} (avge. 379.8 Bq kg^{-1}). Thorium-232 was not found in significant specific activities in all the samples examined. Potassium-40 concentrations in phosphoric acid was found ranging from 9.5 to 151.7 Bq kg^{-1} (avge. 41.7 Bq kg^{-1}) and in phosphogypsum between 25.9 and 92.1 Bq kg^{-1} (avge.59 Bq kg^{-1}).

Reported results for the activity concentrations of natural radionuclides in phosphate rocks are presented in Table 2 for various countries of origin mentioned in Table 1. The results of Table 1 and Table 2 are comparative. In Table 2a, average activity concentrations of ^{238} U and ^{226} Ra in phosphate rocks, phosphate fertilizers and phosphogypsum as taken by UNSCEAR 1982 Report, for comparison with the data of Table 1.

TABLE 1. ACTIVITY CONCENTRATIONS IN PHOSPHATE ROCKS, PHOSPHATE FERTILIZERS; PHOSPHORIC ACID AND GYPSUM (PHOSPHOGYPSTI) (Bq kg^{-1})

~a) *Phosphate ores as Ca3~P04)2*

Period			Code No.	Origin	238 U	^{226}Ra 232 Th	40 K
December 1981				P5 Gafsa 65–68%	825.8 + 128.3	543.2 + 60.03885.0 + 66.0	
11			P6	Taiba 80–81'1o 1697.2		+	153.7
1175.1 +	65.0						
March 1983			C9			1720.5 + 154.61529.2 +	74.5
	198.3 + 5.1						
June 1987				Taiba		473.6 + 92.4307.1 + 17.5	
		Togo "A I in e"				1591.0 + 477.3	
		Togo		691.2 + 190.1		1010.1 +	38.4
		Morocco calcined			1021.3 + 20.4	1505.9 +	45.2
		Jordan		447.7 + 188.0		958.3 +	42.1
January 1991			PH2	Israel Zin1300.0 + 102.6		1801.0 +	3.6
6.8 + 1.0	12.0						
11			PH3	Palfos 88182.0 + 4.4		112.4 +	1.0
374.7 + 1.1	56.1 +7.5						

(b) *Phosphate fertilizers as NH 4 H 2PO41 (NH4)2 HP041 (NH4)2SO4*

Period				Origin	238 U	^{226}Ra 232 Th	40 K
December 1981				P1		830.3 + 118.8 257.2 +	37.2
	52.9 + 1.2						
March 1933				C11		868.8 + 111.7 549.5 +	57.6
	75.1 + 1.3						
June 1987				11–15–15 (Taiba)		629.0 + 164.8 1128.5 +	33.9
	a-						
July 1993				PH6 0–20– 0	936.0 + 20.0	820.0 +	2.0
	12.0 + 0.5 163.0 + 7.9						
ii						PH 70-	0-50
1b700. 0							
	PH8			11-15-15 434.0 + 37.0		55.0 + 1.0	3.0 +
	0.6 3904.0 + 25.0						
	PH9			8-16-16 456.0 + 33.0		94.0 +	1.0
		81.0 + 28.0	4060.0 + 23.0				
	PH10			8-16-24 312.0 + 33.0		18.7 +	0.7
		7.0 + 0.6	6370.0 + 29.0				

* compounds: nitrogenous-phosp~,oric-pntassium

TABIE 1. (CONTINUED)

	(c) Phosphoric acid, H3PO4					
March 19817		CIO		1567.7 + 118.2617.2 + 58.6	151.7 + 3.5	
June 1987.			Taiba	662.3 + 107.3403.3 + 13.7	14.9 + 3.7	
11			Toqo	662.3 + 88.1421.8 + 16.9	28.4 + 4.8	
11			Morocco	1783.4 + 146.21166.0 + 23.3	38.1 + 0.8	
January 1991		PH4	Jordan	949.0 + 21.8162.0 + 22.5	<2.6	7.7 + 2.5
It		PH5	Israel	^{226}0.0 + 35.31294.0 +187.6	3.3 + 0.3	9.5 + 2.9
	(d) Gypsum as CaSO 4 * 2H20					
December 1981		P3		150.2 + 68.0472.5 + 45.9	25.9 + 0.6	
March 1983 + 2.3				C12211.3 + 77.4	357.1 + 55.0	92.1
June 1987				Taiba ~& 429.2 + 20.6	A~	
11		Togo	a	260.9 + 12.5	-	-

TABLE 2. ACTIVITY CONCENTRATIONS OF NATURAL RADIONUCLIDES (Bq kg^{-1}) IN PHOSPHATE ROCKS FROM LITERATURE (UNSCEAR 1982 REPORT)

Origin	^{238}U	^{226}Ra	^{232}Th	^{40}K
Israel	1500–1700			
Jordan	1300–1850			
Morocco (1)	1700	1700	30	
(2)	1500	1500	30	200
(3)	1700	1570	20	10
Togo	1300	1200	110	–100

TABLE 2a. AVERAGE ACTIVITY CONCENTRATIONS OF ^{238}U AND ^{226}Ra IN PHOSPHATE, ROCKS, PHOSPHATE FERTILIZERS AND PHOSPHOGYPSUM (Bq kg (UNSCEAR 1982 REPORT)

Material	^{238}U	^{226} Ra
Phosphate rocks	1500	1500
Phosphate fertilizers	600	400
Phosphogypsum	-	900

The ratio of ^{226}Ra/^{238}U in phosphate ores ranged from 0.6 to 2.0 and the average approached 1. This means that radioactive equilibrium did not exist in the phosphate rock (raw material) as well as in the products of phosphate rock processing (Table 1).

Table 3 presents the releases of ^{238}U and ^{226}Ra for the phosphate rock processing plant of SICNG at Thessaloniki, Northern Greece, including the annual consuming rates of the raw material and the production rates of the products. About 10 MBq of ^{238}U and ^{226}Ra, respectively, are released into the environment by the effluent discharges, each year.

4. DOSES ARISING FROM EFFLUENT DISCHARGES

The major airborne emissions occur in the form of fine rock dust from drying and grinding operations of phosphate rock. The atmospheric discharges of ^{238}U and ^{226}Ra correspond to approximately 59 Bq and 63 Bq, respectively, per tonne of processed phosphate rock with a specific activity of each one of ^{238}U and ^{226}Ra 984.4 Bq kg^{-1} and 1053.3 Bq kg^{-1}, respectively, in phosphate ore, which are the average activities derived from Table 1. The estimated factor of ^{238}U ^{226}Ra releases 6 × 10^{-5} for each one was derived from the data of Partridge et al [9].

Collective dose commitments resulting from atmospheric releases of ^{238}U and ^{226}Ra from phosphate rock processing plants were estimated for the case of inhalation during the passage of radioactive cloud. The collective dose Commitment $M^c{}_q$ in organ or tissue q from with radionuclide (^{238}U or ^{226}Ra) due to inhalation during the cloud passage is given by

$$M^c{}_q = \frac{A_o}{v_d} \delta_N \; B \; \frac{D_q}{I_{ih}}$$

TABLE 3. RELEASES OF ^{238}U AND^{226}Ra FROM PHOSPHATE ROCK PROCESSING PLANT AT THESSALONIKI AREA (SICNG)

Material	Production rate	Activity concentrations		Production		Releases	
		^{238}U	^{226}Ra	^{238}U	^{226}Ra	^{238}U	^{226}Ra
	x10^8 kg y^{-1}	(Bq kg^{-1})	(Bq kg^{-1})	(TBq y^{-1})	(TBq y^{-1})	(MBq y^{-1})	(MBq y^{-1})
Phosphate rock	1.7	984.4	1053.3	0.167	0.179	10	10.7
Phosphate fertilizers	3.0	638.0	417.6	0.190	0.124		
Phosphoric 3cid	0.6	1314.1	677.4	0.078	0.040		
Gypsum	3.75	180.8	379.8	0.068	0.142		

TABLE 4. ESTIMATES OF COLLECTIVE DOSE COMMITMENTS (man Gy t^{-1}) FROM ATMOSPHERIC RELEASES OF ^{238}U AND ^{226}Ra FROM PHOSPHATE ROCK PROCESSING PLANTAT THESSALONIKI AREA (SICNG) DUE TO INHALATION DURING THE PASSAGE OF THE CLOUD

Organ or tissue	^{238}U x10^{-9}	^{226}Ra x10^{-9}
Lungs	1.957	0.152
Bone surfaces	0.0214	0.065
Red bone marrow	0.0014	0.0057
Liver	0.0000356	0.00076
Kidneys	0.0089	0.00076
Spleen	0,0000356	0.00076
G.I. track	0.000249	0.00114
Other soft tissues	0.0000356	0.00076

where A_0 is the annual release of the radionuclide (Bq), which will eventually be deposited onto the ground, $v_d = 10^{-2}$ m s^{-1} the deposition velocity which takes into account both dry and wet deposition [10], δ_N is the human population density for which it was assuming to be uniform and equal to 2.63×10^{-4} m^{-2} or 263 km^{-2} around the plant. The population lived in the Thessaloniki area of 3683 km^2, latitudes 40^0 21'N — 41^0 01'N, longitudes 22^0 28'E — 23^0 46'E, was 969486 in accord with the last. national census of 1991 [11], B is the individual breathing rate, taken to be 2.3 × ,10^{-4} m^3 s^{-1} or 20 m^3 d^{-1} for an adult [12] D_q/I_{ih} is the committed absorbed dose in organ or tissue q per unit intake (Gy Bq^{-1}) as determined by Jacobi [13].

Estimates of collective dose commitments from atmospheric releases of ^{238}U and ^{226} Ra due to inhalation during the cloud passage for various organs or tissues are presented in Table 4. Lung tissue is more suffered from ^{238}U and ^{226}Ra inhaled during the cloud passage as compared with the other organs or tissues. The estimated collective dose commitment was found to be 1.96×10^{-9} man Gy t^{-1} due to ^{238}U and 0.15×10^{-9} man Gy t^1 due to ^{226} Ra for lungs from phosphate rock processing. In UNSCFAR 1982 Report, collective dose commitments to lungs from ^{238}U 1.14×10^{-9} man Gy t^{-1} and from ^{226} Ra 0.08×10^{-9} man Gy t^{-1} from phosphate rock processing were reported. That means, the collective dose commitment for the case of the population living at the Thessaloniki (Greece) area due to the phosphate rock processing plant (SICNG) is 2 times higher than that in the UNSCEAR 1982 Report. .

5. CONCLUSIONS

Phosphate rock processing is one of the sources of technologically enhanced exposure to man from natural radionuclides (TENR), such as ^{238}U and ^{226}Ra by the gaseous effluents emitted from plants (non-nuclear industries). Inhalation during the passage of the cloud is the main pathway of radiation exposure to the population living around the plants. About 10 MBq of ^{238}U and ^{226}Ra, respectively, are released into the environment every year from the phosphate rock processing plant at Thessaloniki (Greece) area (SICNG). That releases result in collective dose commitments to the population due to inhalation, from ^{238}U ~ 2×10^{-9} man Gy t^{-1}, and from ^{226} Ra~$0.1 \times 1O^{-9}$ man Gy t^{-1}, that is 2 times higher than that reported in UNSCEAR 1982 Report.

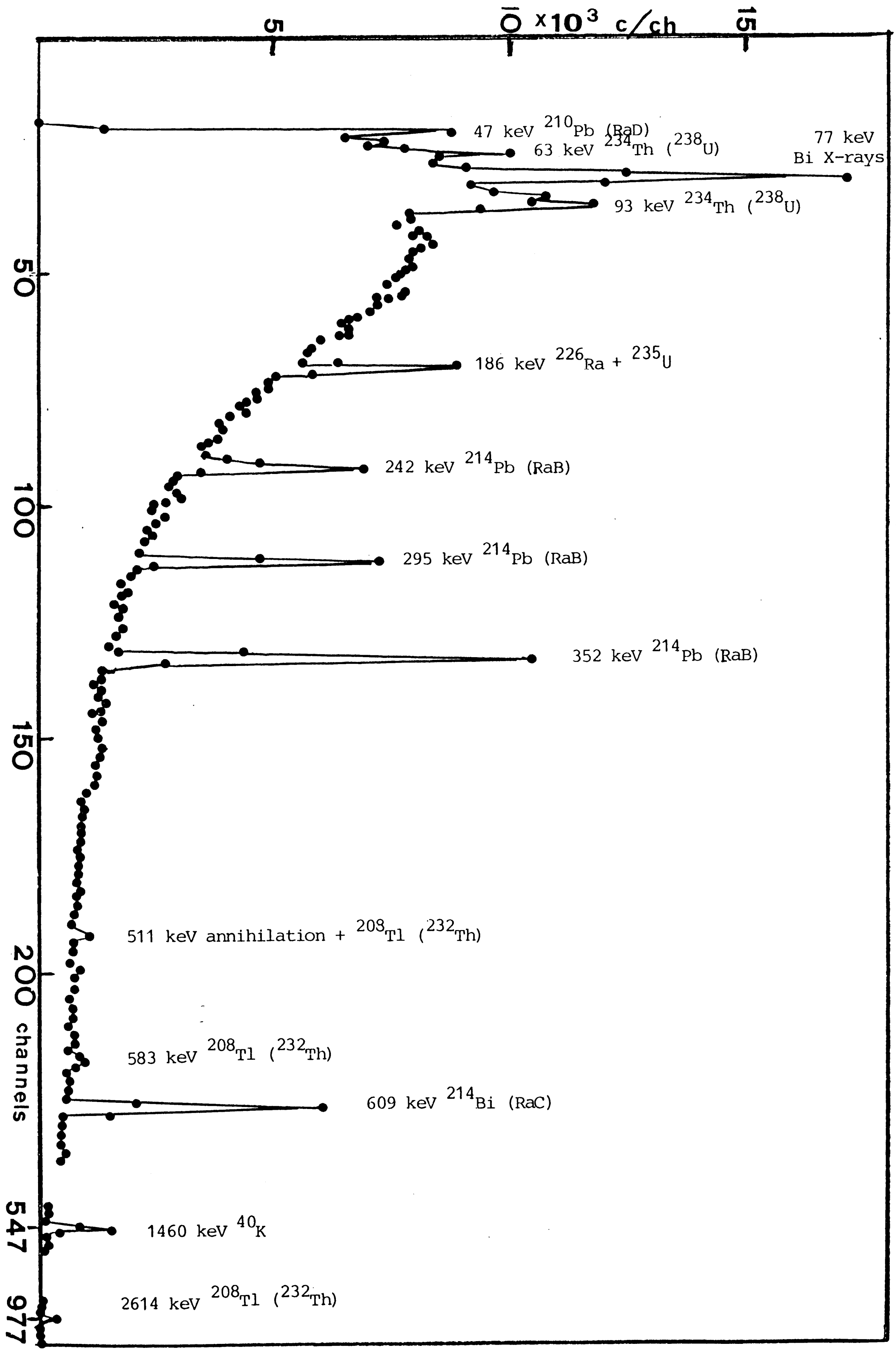

Fig. 1. Plot of gamma ray spectrum of phosphate rock (sample C^9, Table I) Sample mass 40 g. Accumulation time 5 × 10^4 s.

ACKNOWLEDGEMENTS

The author expresses many thanks to the staffs of SICNG (Société Industries Chimiques du Nord de la Grèce) for providing the materials, particularly the chemists S. Stavroulias and V.Plastiras. Also many thanks to my colleagues M.Manolopouolou, S.Stoulos and A.Ioannidou for the activity determinations of the collected samples.

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Parametric study of a thorium model

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Abstract. Models for radionuclides distribution in the human body and dosimetry involve assumptions on the biokinetic behavior of the material among compartments representing organs and tissues in the body. One of the most important problem in biokinetic modeling is the assignment of transfer coefficients and biological half-lives to body compartments. In Brazil there are many areas of high natural radioactivity, where the population is chronically exposed to radionuclides of the thorium series. The uncertainties of the thorium biokinetic model are a major cause of uncertainty in the estimates of the committed dose equivalent of the population living in high background areas. The purpose of this study is to discuss the variability in the thorium activities accumulated in the body compartments in relation to the variations in the transfer coefficients and compartments biological half-lives of a thorium-recycling model for continuous exposure. Multiple regression analysis methods were applied to analyze the results.

1. Introduction

Biokinetic models are used to estimate organ doses resulting from internal deposition of radionuclides and consequently they are used in the evaluation of radiation exposure. The biokinetic models most commonly applied in radiation protection are those recommended by the International Commission on Radiological Protection (ICRP), in publications 30 [1], which addresses intakes of radionuclides by workers and contains the currently used gastrointestinal tract model; 53 [2] and its addendum 80 [3], which addresses doses to patients from radiopharmaceuticals; 66 [4], describing the respiratory tract model; and publications 56 [5], 67 [6], 69 [7], dealing with age-specific doses coefficients to the public from intake of radionuclides and updates the systemic models for workers.

Most of the information available on the kinetics of radionuclides relies on experimental data obtained with laboratory animals, measurements of stable elements in autopsy tissues of environmentally exposed human and data on human subjects exposed to radionuclides in experimental, medical, occupational settings and accidents.

Despite the evolution in the formulation of the ICRP's biokinetic models over the years [8], and the effort to achieve biological realism, uncertainties about the metabolic behavior of the radionuclides still persist and consequently about the calculation of the committed dose equivalent.

In Brazil there are many areas of high natural radiation background where people are exposed to thorium ingestion [9,10]. The uncertainties of the thorium biokinetic model are a major cause of uncertainty in the dose estimating of the population. The influence of f_1 on the calculated dose is known, the dose is directly dependent on the f_1 value. In fact, the systemic activity and variations on mass and size of source and target organs have a significant influence on the dose.

It is necessary to perform a quantitative evaluation of the reliability of the biokinetic models, which can be done through the uncertainty analysis of the model's parameters. The gastrointestinal uptake factor (f_1) of thorium is a source of uncertainty in dose calculations, due the large range of values cited in the literature [11, 12].

The purpose of this study is to quantify the reliability of the prediction of a specific systemic thorium model in relation to cumulative activities in the body compartments. A parametric uncertainty analysis was used to identify how much of the compartment activity variations may be attributable to variations in the transfer coefficients and half-lives, since the correct assignment of those parameters is an important problem to be solved in biokinetic modeling.

2. Procedure

Lipsztein et al. [13] performed a study in which different sets of transfer coefficients and half-lives were assigned to a thorium model to verify which values best fitted experimental data obtained in studies with human subjects. One of these sets of values is shown in Figure 1, which illustrates the model under study. The intervals of variation for the parameters that were chosen to perform the parametric analysis are based on this publication. The intervals of variation of half-lives adopted are: 400 to 2000 days for bone compartment, 20 to 600 days for liver and other compartments and 20 to 150 days for kidney compartment. The transfer coefficient from plasma to bone compartment varies in the range of 0.40–0.95 and consequently, the other three compartments add to a maximum of 0.60. It was assumed that the transfer of radionuclides to and from compartments follow first order kinetics and a 5% transfer from liver to feces. A continuous intake of 1 Bq d^{-1} via plasma was considered. The compartment denominated "others" represents other organs and tissues.

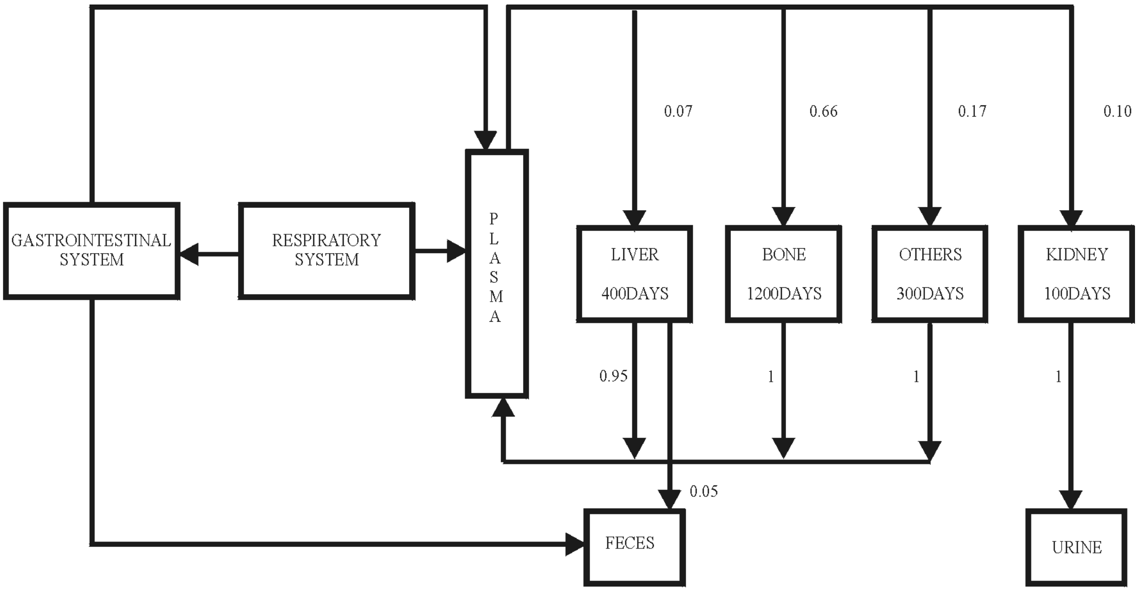

Fig. 1. A specific thorium model.

A computer code [14] specially developed to calculate activities present in human body compartments after intakes of radionuclides, for different exposure times was used. A program that randomly selects values for the parameters, from a specified interval was added to this code, as well as a program, which actualizes the information on the kinetics of the element and permits the performance of a great number of simulations. Files with approximately 1000 (one thousand) values for each parameter were generated [15, 16].

The estimation of the relative contribution of each parameter to the compartment activity variations was based on the statistical technique of multiple linear regression analysis through the study of the coefficient of multiple determination (R^2) [17] that estimates the proportion of the variation of the dependent variable (compartment activity) that is explained by the independent variables (transfer coefficients and biological half-lives). One way to assess this proportion is to consider the increase in R^2 when a variable is entered into the regression model previously fitted to the other independent variables. This increase is represented by $R_{change}^2 = R^2 - R_{(i)}^2$, where $R_{(i)}^2$ and R^2 are, respectively, the multiple determination coefficient when all the independent variables except the i^th are in the model and when all the independent variables, including the i^th, are in the model. The multiple regression analysis was performed using the statistical computer program "SPSS for Windows", release 6.0.

3. Results and discussion

Increases in the multiple determination coefficient (R_{change}^2) are shown in Tables I, II and III for liver, bone and kidney compartments of the specific thorium model. The transfer coefficients from blood to liver, bone and kidney compartments are represented by a_l, a_b and a_k, respectively, while the biological half-lives are represented by $t_{1/2(l)}$, $t_{1/2(b)}$ and $t_{1/2(k)}$, respectively.

Table I. The increment in the coefficient of multiple determination and the coefficient of variation to *liver* compartment

Time(years)	R_{change}^2(%)				R_{total}^2(%)[a]	CV(%)[b]
	a_l	$t_{1/2(l)}$	a_k	$t_{1/2(b)}$		
0.5	92	3	-	-	95	85
5	64	18	-	1	85	103
20	51	20	3	3	78	113
50	41	20	8	-	72	119
70	36	20	10	-	70	122

[a] Coefficient of multiple determination considering all variables selected to regression model

[b] Coefficients of variation of mean activities in compartments

Table II. The increment in the coefficient of multiple determination and the coefficient of variation to *bone* compartment

Time(years)	R_{change}^2(%)			R_{total}^2(%)[a]	CV(%)[b]
	a_b	$t_{1/2(b)}$	a_k		
0.5	95	-	-	97	24
5	81	4	9	95	24
20	68	9	18	95	35
50	61	10	18	90	51
70	59	10	18	87	59

[a] Coefficient of multiple determination considering all variables selected to regression model

[b] Coefficients of variation of mean activities in compartments

Table III. The increment in the coefficient of multiple determination and the coefficient of variation to *kidney* compartment

Time(years)	R_{change}^2(%)			R_{total}^2(%)[a]	CV(%)[b]
	a_k	$t_{1/2(k)}$	$t_{1/2(b)}$		
0.5	83	10	-	93	88
5	61	21	2	86	91
20	47	31	4	83	78
50	31	44	3	80	66
70	25	50	2	78	62

[a] Coefficient of multiple determination considering all variables selected to regression model

[b] Coefficients of variation of mean activities in compartments

The liver compartment and the compartment that represents other organs and tissues are similar, except for a small quantity of the activity presents in liver compartment, which is eliminated through feces. Since this elimination is constant and the focus of this study is on the total variation of the activity the results obtained for both compartments were similar.

For each compartment, a significant proportion of the total variation in its activity may be explained by the variations in the value of the transfer coefficient from blood to the compartment. This influence decreases with time as the half-life and the transfer coefficient from blood to kidney compartment is selected into the regression model. The influence of the value of the transfer coefficient from blood to kidney compartment in the amount of activity accumulated in the compartment is justified since the kidney compartment does not participate in the recirculation process, and thus its activity is eliminated through urine with no feedback to the system.

It can be observed, in Tables I and III, a small contribution of the bone compartment's half-life ($t_{1/2(b)}$), reflecting the contribution of the compartment that receives the higher fraction of the activity present in blood (bone).

The relative dispersion on the activities of each compartment of the model, due to the variation of the parameters was determined by the coefficient of variation (CV) of the mean activity in the compartment. This is the standard deviation expressed as a percentage of the mean [18]. The values of the coefficients of variation obtained over 70 years of exposure to liver, bone and kidney compartments are shown in Tables I, II and III, respectively. It can be observed that over the exposure time the relative dispersion of the mean activity in liver, bone and kidney compartments varies on the intervals of 85%–120%, 25–60% and 60%–90%, respectively. The relative dispersion of the mean activity is significantly reduced in the compartment that presents a higher half-life and receives a higher fraction of activity present in blood. Particularly, despite the others sources of uncertainties related with parameters involved on the dose calculation, the maximum error of the dose associated to bone compartment is approximately 60%.

4. Conclusions

For the compartments which participate in the recirculation process (liver, bone, other) the transfer coefficient from blood to the compartment under the study is the most important variable in terms of influence on the variation of the activity in the compartment. In the first year of exposure more than 85% of the variation in the compartment's activity is explained by the variation of this variable. The biological half-life and the transfer coefficient from blood to the kidney compartment have some influence on the variation of the activity of the compartments under study. The maximum value of the coefficients of variation for the mean activities of the compartments is 120%. Particularly, for the compartment that receives the higher fraction of the activity present in blood (bone), the maximum value of the coefficient of variation for the mean compartment activity is 60%.

For the compartment that does not participate in the recirculation process (kidneys), the transfer coefficient from blood to the compartment and the biological half-life are the only variables that explain the total variation in the activity of the compartment. In the first year of exposure the transfer coefficient is the most important parameter. As the exposure time increases the biological half-life becomes the most important variable. The coefficient of variation for the mean compartment activity shows a maximum value of 90%. Particularly, for the bone compartment the values of the coefficient of variation indicate that the influence on dose calculation, related to variations on the systemic activity due to variations in the transfer coefficients and half-lives, is not higher than 60%.

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“In vitro” solubility of ^{232}Th and ^{238}U present in Pandaíta

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Abstract

Thorium and uranium occur associated to the crystal lattice of several minerals. Pandaita is a thorium and uranium bearing niobium mineral. The airborne particles generated during the mining and milling processes to obtain Nb concentrate could be inhaled by the workers causing potential risk of internal exposure. In order to estimate the risk of the workers due to inhalation of mineral dust particles it is necessary to estimate the thorium and uranium solubility in the lung fluid.

The aim of this work was to develop a methodology to evaluate *in vitro* dissolution rate of thorium and uranium compounds present in the pandaita. The dissolution rate of thorium and uranium in the simulated lung fluid (SLF) were determined.

The pandaita samples were collected during the mineral crushing process. The mineral samples were mixed with SLF. The ^{232}Th and ^{238}U concentration in each sample were determined by alpha spectrometry.

The results suggest that the thorium and uranium present in the pandaita from a Nb mine should be classified as Type S according to ICRP 66 (1993) classification for solubility in lungs.

I. INTRODUCTION

The mining and milling processes of minerals are the principal source of workers exposure to mineral dust particles. Inhalation of these particles cause serious disease to the workers. The risk associated to inhalation of dust particles depends on the chemical and physical characteristics of the inhaled particle and on the physiological parameters.

Thorium and uranium occur associated to many minerals, one of the most important is pandaita. The workers involved in the mining and milling process of pandaita to obtain Fe-Nb alloy are exposed to thorium and uranium bearing particles. In order to estimate the dose due inhalation of these particles it is necessary to determine the particle size, the activity concentration in the respirable fraction of aerosol and the dissolution rate of the thorium and uranium in the lung fluid [1].

The dissolution rate of chemical compound present in the aerosol is an important parameter to estimate the elemental transfer rate from the lung to other organs and to calculate the internal dose [2].

Absorption into blood is material-specific and is assumed to occurs at the same rate from all region. Absorption into blood is a two stage process: the first one is the dissociation of particles into material that can be absorbed into blood (dissolution). The second one is the uptake of material dissolved from the particles or the material deposited in a soluble form into blood of soluble material and of material dissociated from particles ("uptake"). Each stage can be time-dependent. It is assumed that time-dependent dissolution can be approximated by dividing the material into two fractions, with different dissolution rates. Uptake into blood is treated as instantaneous for the fraction of material absorbed immediately after dissolution. Another fraction of dissolved material may be absorbed slowly as a result of binding to respiratory tract components [1].

The absorption parameters for thorium and uranium in lung fluid were estimated based on experimental data using pure compounds of thorium and uranium [3].

The aim of this work was to develop a methodology in order to evaluate *in vitro* dissolution rate of thorium and uranium compounds present in the pandaita. The dissolution rate fast of thorium and uranium in the simulated lung fluid (SLF) were determined.

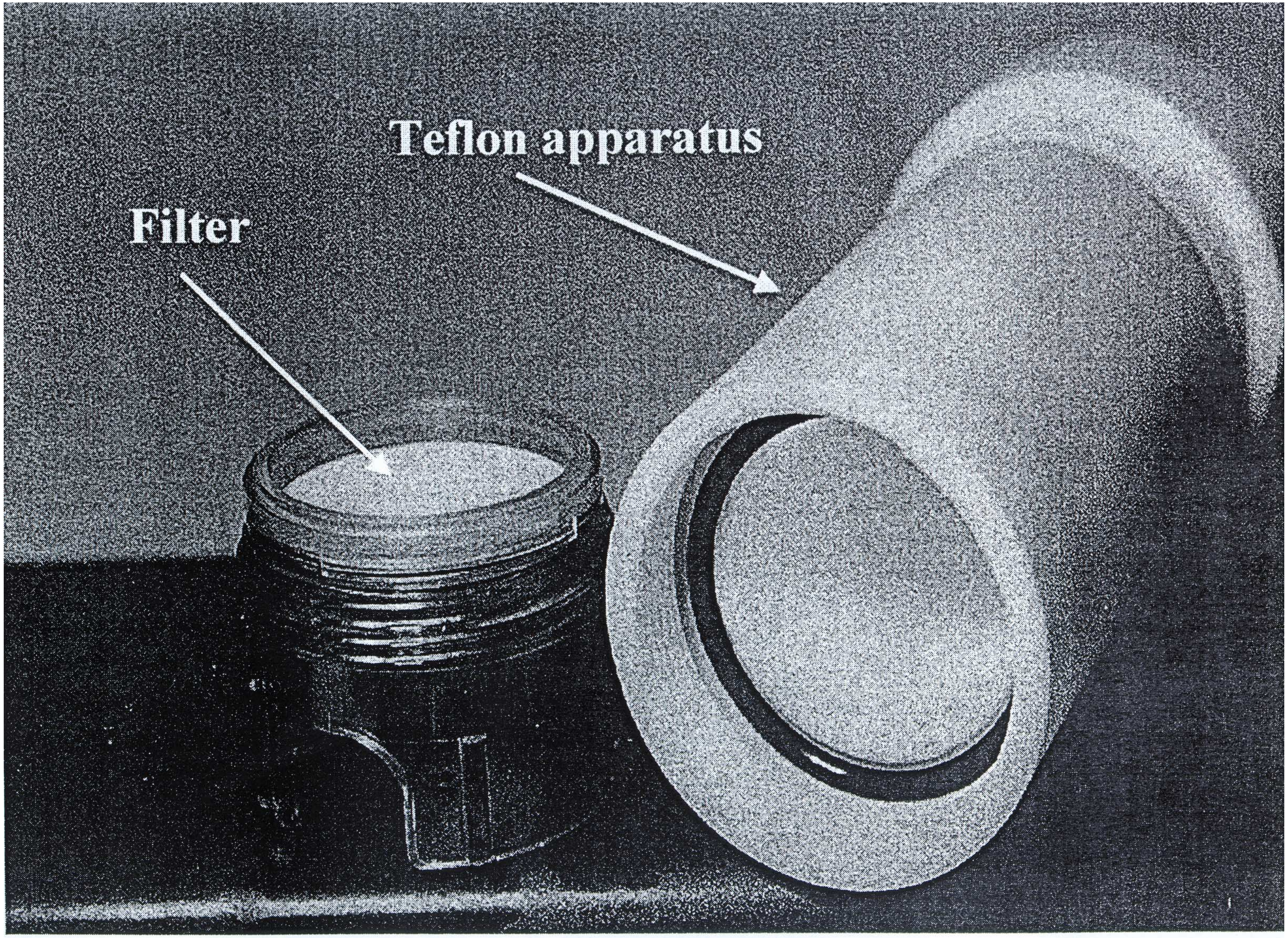

Figure 1 Experiment arrangement.

II - MATERIAL AND METHODS

The solubility of ^{232}Th and ^{238}U in the lung fluid was estimated using simulated lung fluid (SLF), based on a composition given by Moss for blood plasma [4]. After the preparation of SLF, the pH was adjusted for 7.4 with hydrochloric acid 1 M and was kept under refrigeration.

The pandaita samples were collected in a Brazilian niobium mine after the mineral crushing and gravimetric concentration processes. The samples were pulverized and dry-sieved to obtain particles with diameter <38 μm (400mesh). The samples were dried in greenhouse during 24 h and stored in a desiccate.

The experimental arrangement shown in Figure 1 was based on the "bach/filter" method. A Teflon cylinder was adapted to the filter holder. One gram of homogenized pandaita sample was mixed with 100 ml of SLF. This solution was stirred and then it was filtrated using a filter of nitrate of cellulose (pore size equal to 0.1μm).

The dissolution rate of uranium was determined using two different experiment proceedings: the first one the SLF was replacing at periods: 1, 2, 3, 6, 24, 48 and 72 h and the second one the SLF was replacing at 0:30, 1:00, 1:30, 2:00, 2:30, 3:00 and 3:30 h. For determination of thorium dissolution rate the SLF was replaced at 2, 4 and 20 h and the experiment was repeated replacing the SLF at 1:30, 2:30, 3:30 and 21:30 h. The periods for samples collection were determined considering the start of experiment.

The ^{232}Th and ^{238}U concentrations in the pandaita and in the SLF were determined by alpha spectrometry [5, 6].

The dissolution rates of thorium and uranium were estimated considering the activity concentration of these radionuclides in the solution (SLF) at each time interval.

III. RESULTS AND DISCUSSION

The average ^{232}Th and ^{238}U activity concentration in the pandaita sample after granulometric separation were, 1,407± 86 and 4,145 ± 416 mBq/g, respectively.

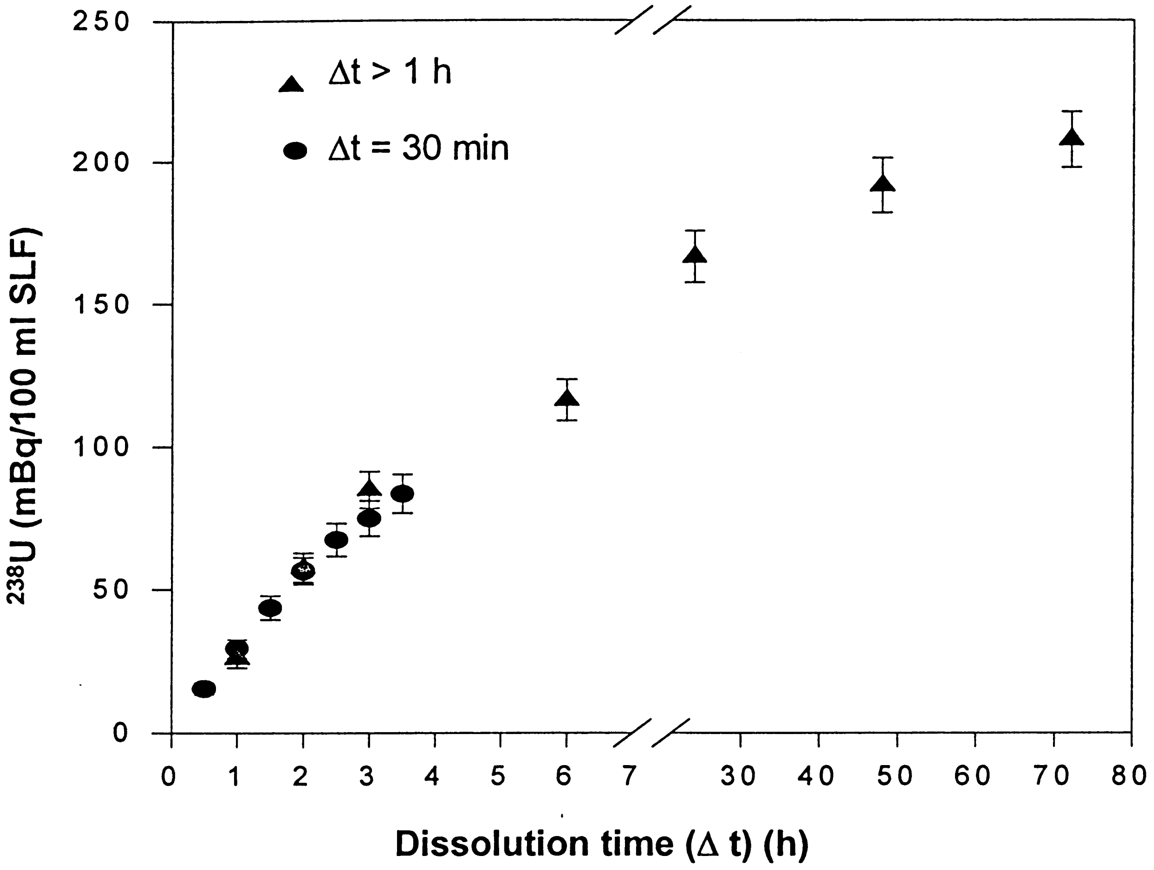

Figure 2 Cumulative activity of ^{238}U dissolved in SLF.

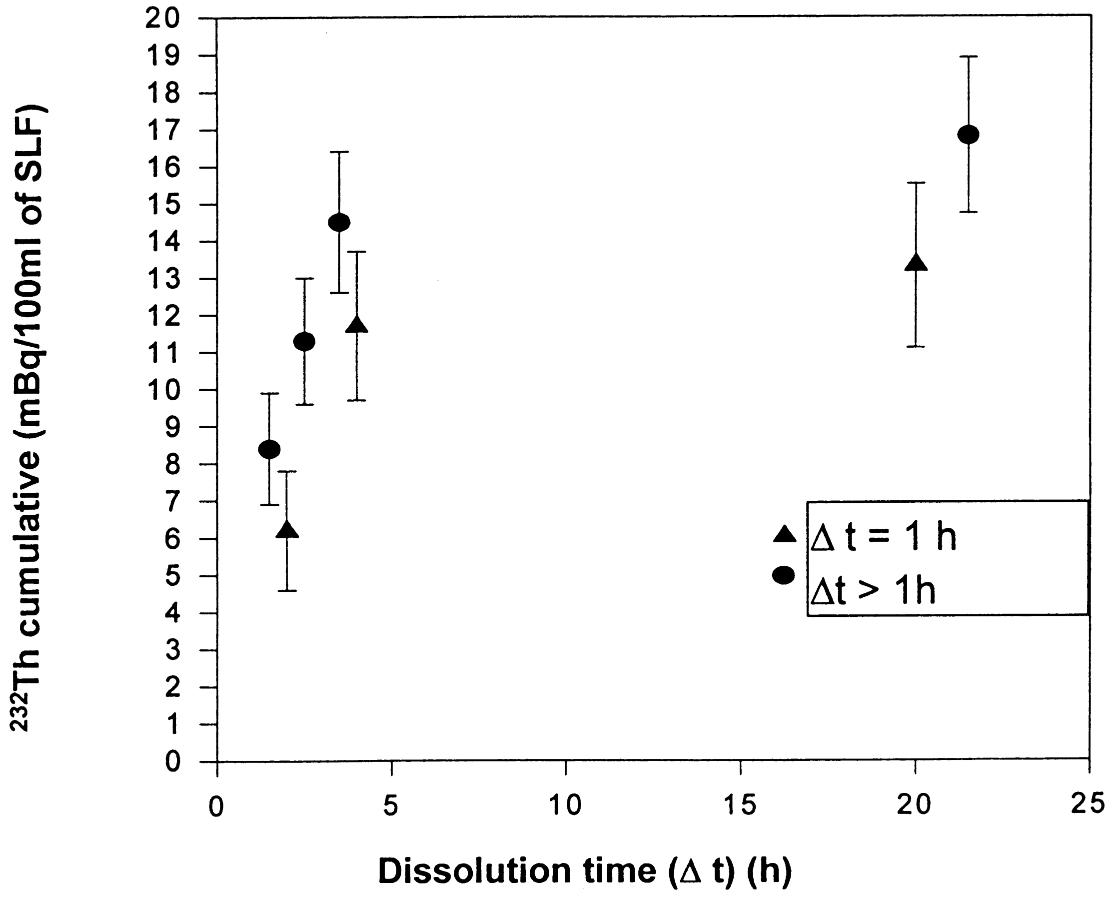

Figure 3 Cumulative activity of ^{232}Th dissolved in SLF.

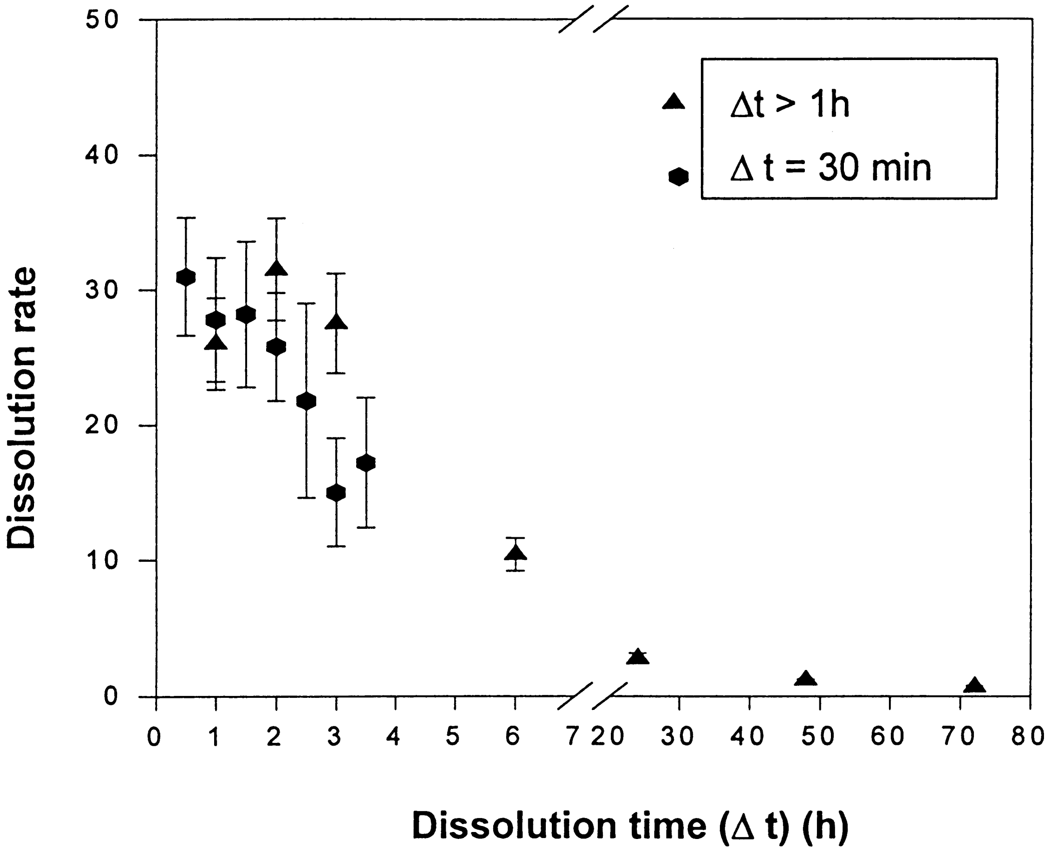

Figure 4 Dissolution rate of ^{238}U.

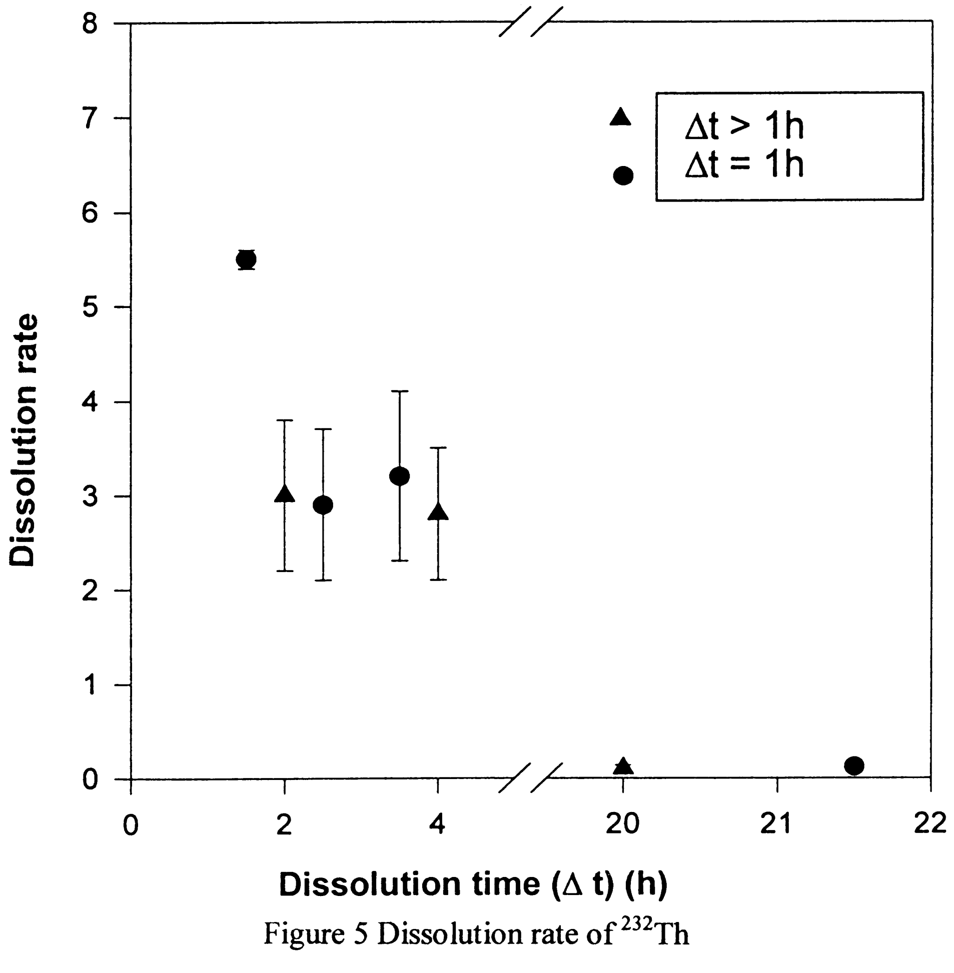

Figure 5 Dissolution rate of ^{232}Th

The cumulative activity of ^{238}U and ^{232}Th dissolved in SLF are shown in Figures 2 and 3, respectively. The results of samples collected with periods larger than 1 h and those collected with periods equal 30 min showed the same behavior (Figure 2). This result indicates that during the first 3 h the cumulative activity of ^{238}U in SLF is time depend. However it is not depend of the number of SLF replacement. The results obtained in the experiment to determine the ^{232}Th cumulative activity dissolved in SLF (Figure 3) indicate that the ^{232}Th present in pandaita had the same behavior of ^{238}U.

The dissolution rate of ^{238}U and ^{232}Th are shown in Figure 4 and 5, respectively. The results show that dissolution rate of ^{232}Th present in pandaita is lower than the dissolution rate of ^{238}U.

The type of absorption behavior of ^{238}U and ^{232}Th compounds could be estimated based on the relationship between the dissolution rate and the biokinetic behavior of these radionuclides, after inhalation of ^{238}U and ^{232}Th bearing particles.

The type of absorption behavior of ^{238}U and ^{232}Th compounds present in the pandaita was determined following criterion [7]:

a) Tipo F: the solubility rate in 10 minutes is 100%.

b) Tipo M: the solubility rate in 10 minutes is 10%.

c) Tipo S: the solubility rate in 10 minutes is 0,1%.

The solubility rate of uranium and thorium in 10 min was estimated based on the accumulated activity. For uranium it was estimated a rate of 0,1% and for thorium 0,06%. These results suggest that uranium and thorium compounds present in pandaita could be considered as Type S (slow dissolution rate).

IV. CONCLUSION

The solubility rate of ^{238}U and ^{232}Th present in the pandaita were 0.1 % and 0.06%, respectively. These results indicate that the uranium and thorium present in pandaita should be classified as Type S (slow dissolution rate).

The knowledge of solubility of thorium and uranium in minerals give us important information for dose estimation for workers exposed to inhalation of thorium and uranium bearing particles.

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Characterization of naturally occurring radioactive materials and Cobalt-60 contaminated ferrous scraps from steel industries

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Abstract

Since the occurrence of radioactively contaminated rebar incident in 1992, steel industries in Taiwan were encouraged by Atomic Energy Council (AEC) to install portal monitor to detect the abnormal radiation in shipments of metal scrap feed. From 1994 through 1999, there were 53 discoveries of radioactivity in ferrous scraps by steel companies. These include 15 orphan radioactive sources, 16 cobalt-60 contaminated rebars, 20 Naturally Occurring Radioactive Material (NORM) contaminated scraps, and two unknowns. Most NORM-contaminated scraps were from abroad.

The NORM and cobalt-60 contaminated scraps were taken from the steel mills and analyzed in laboratory. The analytical results of scales and sludge sampled from NORM-contaminated scraps combining with the circumstantial evidences indicate that five possible industrial processes may be involved. They are oil production and treatment, heavy mineral sand benefication and rare earth processing, copper mining and processing, recovery of ammonium chloride by lime adsorption in Ammonium-soda process, and tailing of uranium enrichment process.

The cobalt-60 activity and trace elements concentrations of contaminated rebars confirm that all of them were produced domestically in the period from Oct. 1982 to Jan. 1983, when the cobalt-60 sources were lost and entered the electric arc furnace to produce the contaminated rebars.

1. INTRODUCTION

Since the occurrence of radioactively contaminated rebar incident in 1992, steel industries in Taiwan were encouraged by AEC to install portal monitor to detect the abnormal radiation in shipments of metal scrap feed [1]. From 1994, the radiation source devices, Co-60 contaminated rebars, and NORM-contaminated metals have been discovered in shipments of metal scrap, and the number of discoveries was generally increasing every year. Most NORM-contaminated scraps were from abroad, especially from U.S., South Africa, and Australia where plants of the process industry were dismantled [2].

The discovery of radioactive scrap presents a vexing problem to steel industry. The current industry practice is to store the contaminated scraps temporarily or to return scraps to the supplier. It is quite costly and manpower consumptive. Furthermore, melting radioactive scraps could threaten worker safety and health and is potentially harmful to consumers and environment [3-6]

Department of Radiation Protection, AEC initiated a project [2] to characterize the NORM and cobalt-60 contaminated scraps by radiochemical methods and to study the origin of its industrial process. The aim is to provide proper information and observation to competent authority to stop the import of contaminated scraps and protect general public from accidental radiation exposure.

2. EXPERIMENTS

For the study of industrial origin of NORM-contaminated scrap, about 50 grams of scale, sludge, and process material absorbed on the scraps (pipe, valve and tank wall) from steel mills were sampled and analyzed in laboratory. The activity concentrations of ^{226}Ra (or ^{238}U) and ^{228}Ra (or ^{232}Th) were measured from their progeny of ^{214}Bi (609.3 keV) and ^{228}Ac (911.1 keV) respectively by gamma spectrometer equipped with HPGe detector and multichannel analyzer under secular equilibrium condition. The morphology of sampled materials was characterized by scanning electron microscopy equipped with energy dispersion spectrometry (SEM-EDS) and X-ray diffraction (XRD) technique. In addition, ^{235}U/^{238}U ratio of depleted uranium was measured by inductively-coupled plasma mass spectrometry (ICP-MS).

To make a comparison among the ^{60}Co-contaminated rebars, about 0.5 gram of metallic scrap were sampled and dissolved in 1:1 nitric acid solution. The activity of ^{60}Co was measured at 1173 keV and 1332 keV by the above-mentioned gamma-ray spectrometer and corrected to the first sampling date (March 31, 1994) for the sake of comparison. The concentrations of trace elements (Cr, Cu, Mn, Ni and Si) in rebar were determined by inductively-coupled plasma atomic emission spectroscopy (ICP-AES).

3. RESULTS AND DISCUSSION

3.1. Radioactivity discovered from steel mills in Taiwan

Table I summarized the discoveries of radioactively contaminated scraps from steel mills in Taiwan since 1994 [2]. The radioactively contaminated scraps can be categorized as radiation sources, ^{60}Co-contaminated rebars, and NORM-contaminated scraps. It can be seen from Table I that a total of 53 discoveries were observed and number of discoveries was increasing every year. Except that the ^{60}Co-contaminated rebars were produced domestically, most radiation sources and NORM-contaminated scraps were from abroad, especially the NORM-contaminated scraps were from U.S., South Africa, and Australia where plants of the process industry were dismantled.

3.2. Industrial origin of NORM-contaminated scraps

Table II summarized the analytical results of NORM-contaminated scraps from steel mills only if the industrial origin could be identified. It can be seen that both scale and sludge with composition of divalent metallic sulfate have higher activity concentration of ^{226}Ra or ^{228}Ra. This reflects that Group IIA elements will coprecipitate easily to form complex inorganic sulfates.

Scale sample 951206 taken from 4" steel pipe was imported from Amsterdam, The Netherlands. It has an average 1.25 mm of thickness and contains 212.6 Bq/g and 100.4 Bq/g of ^{226}Ra and ^{228}Ra respectively with composition of $Ba_xSr_{1-x}SO_4$ (x=0.75). The SEM study shows that the scale consists of large and well-defined tabular mixed crystals (Fig. 1). Scale formation and growth on the pipe is quite analogous to the pipe scale in oil production facility [7, 8]. Meanwhile, a ^{226}Ra source was discovered in the same shipment, we therefore could reasonably speculate that this shipment of scraps was dismantled from oil production industry [9].

Samples 971212-1,2 taken from steel pipe and cover were imported from Australia. Scale 971212-1 consists of $Ba_xSr_{1-x}SO_4$ (x=~0.75) and contains 230.9 and 758.5 Bq/g of ^{226}Ra and ^{228}Ra respectively. Sludge 971212-2 consists of Ce(Th)PO_4, $FeTiO_3$ and $ZrSiO_4$ and contains 13.5 and 94. 4 Bq/g of ^{238}U and ^{232}Th respectively. SEM-EDS also shows that a single grain of sludge represent a type of mineral and the amounts of grains are in the order of zircon, ilmenite and monazite (Fig. 2). It is obvious that this shipment of scraps could be originated from a heavy mineral sand benefication and rare earth processing plant [10].

TABLE I. SUMMARY OF RADIOACTIVELY CONTAMINATED SCRAPS DISCOVERED BY STEEL MILLS (from June, 1994 to June, 1999) [2]

Category	Year						Total
	1994	1995	1996	1997	1998	1999	
Orphan radiation source	0	3	1	3	6	2	15
^{60}Co contaminated rebar	0	5	2	4	1	4	16
NORM contaminated scrap	1	1	1	3	11	3	20
Unknown	-	-	1	-	1	0	2
Total	1	9	5	10	19	9	53

TABLE II. ANALYTICAL RESULTS OF SAMPLES TAKEN FROM NORM-CONTAMINATED SCRAPS

Sample Number[1]	Country of Origin	Characterization	Chemical Composition	^{226}Ra(^{238}U), Bq/g	^{228}Ra(^{232}Th), Bq/g
951206	The Netherlands	Pipe scale, 0.5~3.7 μSv/h	$Ba_{0.75}Sr_{0.25}SO_4$	212.6±0.4	100.4±0.8
971212-1	Australia	Pipe scale, 64~75 μSv/h	$Ba_{0.75}Sr_{0.25}SO_4$	230.9±2.6	758.5±10.2
971212-2	Australia	Sludge, 1.2~2.4 μSv/h	$Ce(Th)PO_4$, $FeTiO_3$, $ZrSiO_4$	(13.5±0.4)	(94.4±1.4)
980105	South Africa	Pipe scale, 92 μSv/h	$PbSO_4$, $CuSO_4$	12,800±66.4	<LLD
981012-1	Yi-Lan, Taiwan	Pipe scale, 10 μSv/h	$(Mg,Ca,Sr,Ba)SO_4$	393±2.83	9.67±1.65
981012-2	Yi-Lan, Taiwan	Process material, b.g.	$Ca(OH)_2$, $CaCO_3$	<LLD	<LLD
990111-1	Yi-Lan, Taiwan	Tank scale, ~2 μSv/h	$(Mg,Ca,Sr,Ba)SO_4$	379±1.1	4.53±0.62
990111-2	Yi-Lan,, Taiwan	Process material, b.g.	$Ca(OH)_2$, $CaCO_3$	<LLD	<LLD
990202-1	Scrap yard, Yi-Lan	Sludge, ~2 μSv/h	-	21.7±0.11	<LLD
990202-2	Soda Mfg. Co. Ltd., Yi-Lan, Taiwan	Lime slurry, b.g.	$Ca(OH)_2$, $CaCO_3$	<LLD	<LLD
990517	Hong Kong	Metal block, ~45 μSv/h (25 cm L×10 cm W×8 cm H, 14.56 kg)	U(99.9%), $^{235}U/^{238}U$ (0.212%)	-	-

[1] According to the date of discovery.

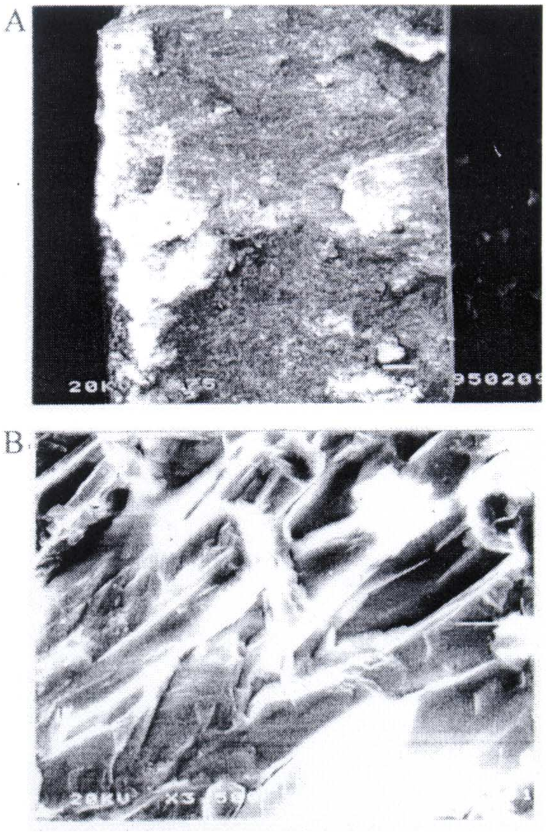

FIG.1. SEM photographs. A – Cross section of scale (75X), B – Close-up of internal scale (3500X).

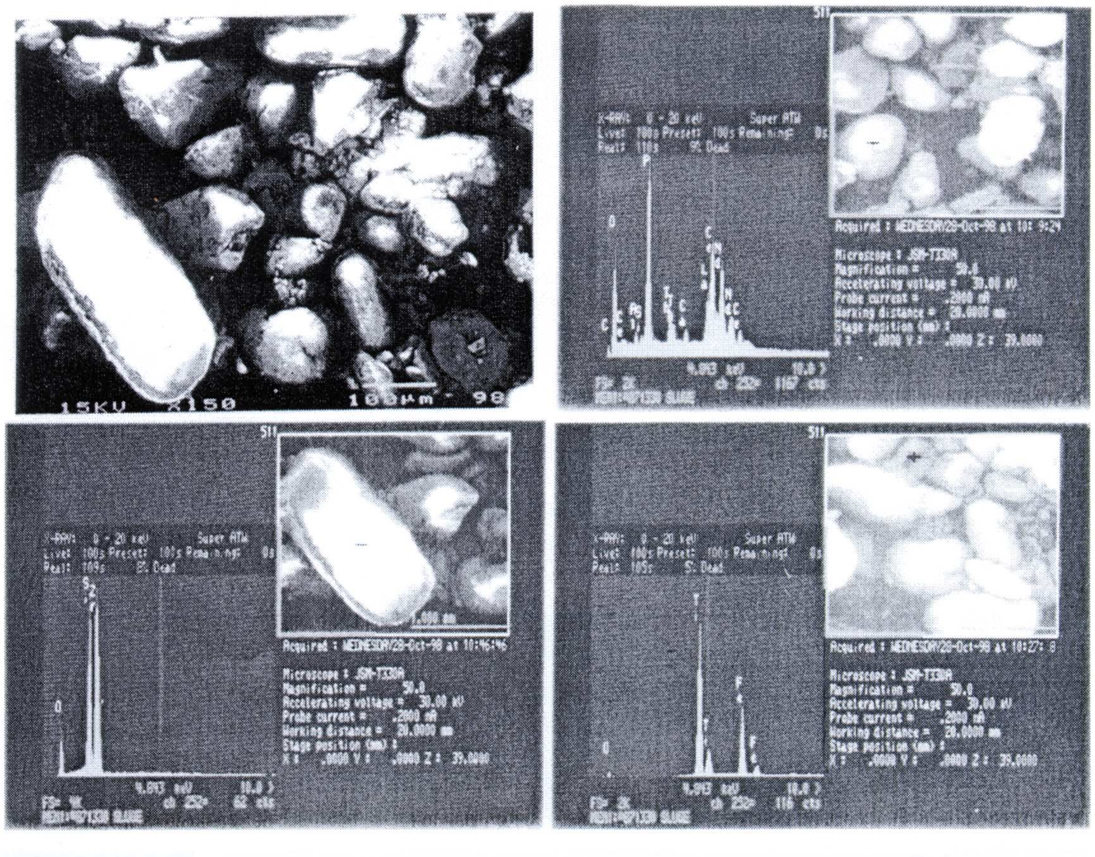

FIG. 2. Single grain analysis by SEM-EDS.

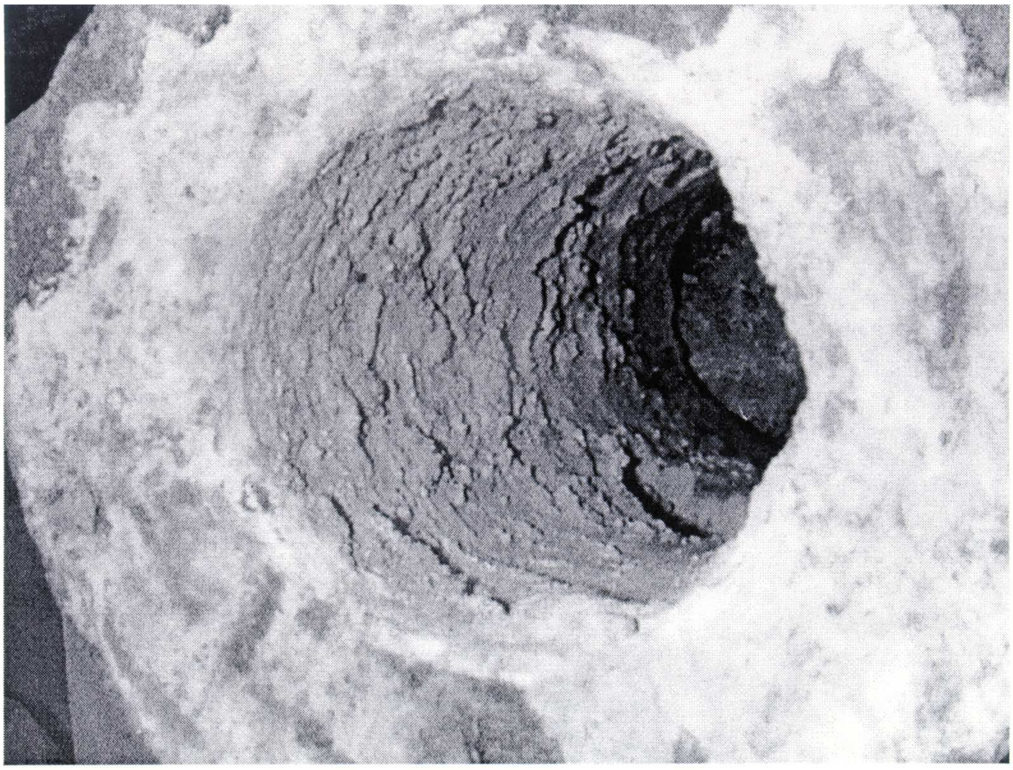

FIG. 3. Pipe scale and process materials.

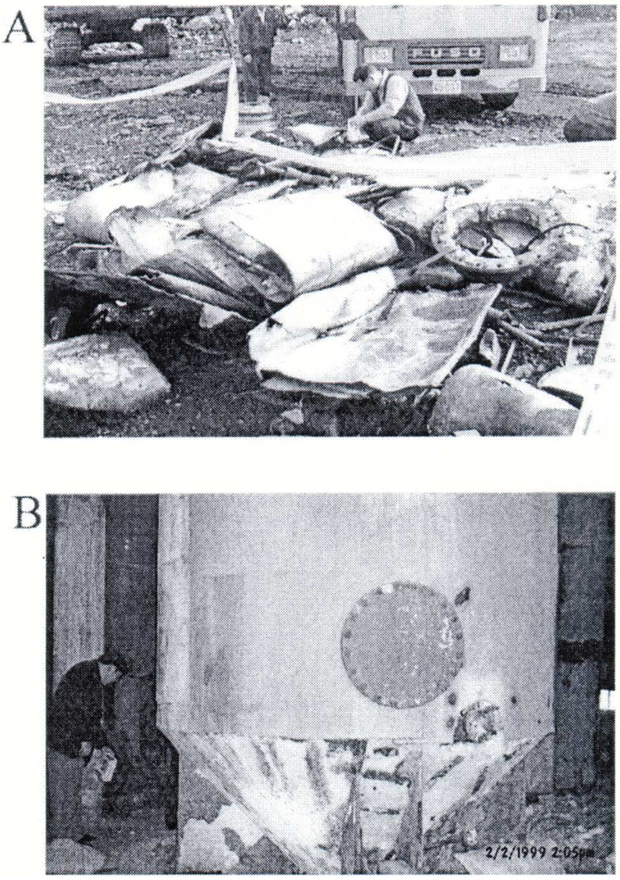

FIG. 4. NORM contaminated scraps. A – discovered by steel mills, B – Ammonium chloride adsorption tank left in Soda ash manufacturing company.

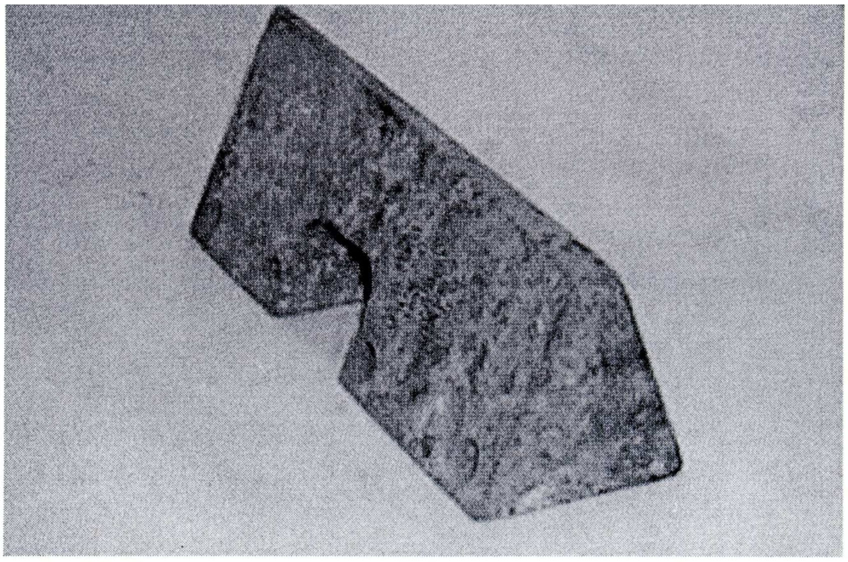

FIG. 5. Photograph of depleted uranium counterbalance weight (~45 μSv/h, 25 cm L×10 cm W×8 cm H, 14.56 kg).

Sample 980105 taken from steel pipe was imported from South Africa. It consists of $PbSO_4$ and $CuSO_4$ and contains 12,800 Bq/g of ^{226}Ra only. According to literature [11], the main ore mineral in Palabora, South Africa is chalcopyrite ($CuFeS_2$) and the uranium occurs in uranothorianite. In addition, pyrite, magnetite, quartz, calcite, sphalerite (ZnS), and galena (PbS) exit together. The copper is produced from an open pit mine and uranium is recovered as a by-product from mining at Palabora. The analytical results combining with the circumstantial evidences indicate that this shipment of scraps could be originated from copper mining and processing industry.

Three steel mills in northern Taiwan discovered abnormal radiation in their shipments of scrap provided from the same supplier in the period of October 1998 to January 1999. Sample 981012-1, 2 and 990111-1, 2 were the scales and process materials taken from the scraps of two steel mills, respectively (Fig. 3 and 4A). The analytical results show that both scales consist of (Mg, Ca, Sr, Ba)SO_4 and process materials consist of $Ca(OH)_2$ and $CaCO_3$, and only scales contain average of 386 Bq/g and 13.7 Bq/g of ^{226}Ra and ^{228}Ra respectively. The process materials indicated that the scraps could be dismantled from soda ash related industry. A soda ash manufacturing company near scrap yard at Yi-Lan, Taiwan was identified from sales record and confirmed by radiation survey. This company was established 40 years ago and produced $NaHCO_3$ and Na_2CO_3 by Ammonia-soda process. The reaction product, ammonium chloride, is then recovered by lime slurry adsorption. Although the detailed mechanism of radioactive scale formation is unknown, the old process was dismantled several months ago. One of the adsorption tank left there to store ammonium chloride and the other one still on production showed an abnormal radiation (~2 μSv/h). In addition, these adsorption tanks have a similar appearance with the radioactive scrap discovered by steel mills (Fig. 4A and 4B). Therefore, a new NORM contaminated industry is confirmed by this study in Taiwan, which has never been reported by the literatures.

Sample 990517 was taken from a radioactive metal imported from Hong Kong with a surface dose rate of ~45 μSv/h. Preliminary examination from the density (d~19.0) and appearance showed that this metal may be a counterbalance weight. Subsequent analysis also proved this metal block was made of depleted uranium with purity of 99.9% and $^{235}U/^{238}U$ ratio of 0.211 wt%. This value was well below the natural concentration level of 0.71 wt%, and indicated that this depleted uranium metal block was produced from the tailing of uranium enrichment process [12].

3.3. Origin of ^{60}Co contamination rebars

There are 16 discoveries of ^{60}Co contaminated rebars by steel mills since 1995. The ^{60}Co activity and trace elements concentration of contaminated rebars were summarized in Table III. The analytical results show that these rebars contain four different kinds of concentrations with regard to ^{60}Co and trace elements. It reflects that these rebars were made from four different batches of steel products. Comparison of the results in Table III with the previous study [1] also confirms that these rebars were

TABLE III. ANALYTICAL RESULTS OF ^{60}Co CONTAMINATED REBAR

Sample number[1]	^{60}Co activity Bq/g[2]	Trace element concentration, wt%				
		Cu	Ni	Mn	Cr	Si
950519	558.7	0.25	0.14	0.50	0.15	0.27
950610	5994	0.30	0.10	0.46	0.11	0.22
950619	6142	0.30	0.10	0.46	0.11	0.22
950620	6142	0.32	0.11	0.48	0.12	0.19
951223	5920	0.32	0.11	0.49	0.12	0.19
960911	5883	0.32	0.11	0.48	0.12	0.22
960923	5920	0.33	0.11	0.49	0.12	0.20
970224	5883	0.31	0.10	0.46	0.11	0.23
970310	5920	0.32	0.11	0.48	0.12	0.26
970610	5957	0.32	0.11	0.47	0.12	0.20
970925	6068	0.32	0.11	0.48	0.12	0.26
980623	5846	0.32	0.11	0.48	0.12	0.22
990210	5883	0.33	0.11	0.48	0.12	0.25
990312	6105	0.32	0.12	0.48	0.13	0.27
990512-1	37.7	0.25	0.08	0.62	0.12	0.35
990512-2	3.9	0.29	0.11	0.61	0.10	0.25

[1] According to the date of discovery.

[2] Corrected to the first sampling date (March 31, 1994) [1].

contaminated in the periods of October 1982 to January 1983, when the cobalt-60 sources were lost and entered the electric arc furnace. If it is true, the magnitude of cobalt-60 source was estimated to be at least 740 GBq (20 Ci) at that time by assuming 25 tons of steel produced for each batch.

4. CONCLUSIONS

Industrial origin of NORM contaminated scraps and ^{60}Co-contaminated rebars discovered in steel mills were identified by analytical results of samples combining with circumstantial evidences. Five possible industrial processes, namely oil production and treatment, heavy mineral sand benefication and rare earth processing, copper mining and processing, recovery of ammonium chloride by lime adsorption in Ammonium-soda process, and tailing of uranium enrichment process, may be involved in the production of NORM-contamination scraps. Among these, Ammonium-soda process is a new NORM contaminated industry confirmed by this study in Taiwan.

Since 1995 sixteen ^{60}Co contaminated rebars from steel mills were discovered domestically. All of them were dismantled from old buildings and were produced in the periods of October 1982 to January 1983, when the cobalt-60 sources were lost and entered the electric arc furnace. Since then, there is no other case of ^{60}Co contamination incident.

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Occupational exposure to radon progeny: Importance, experience with control, regulatory approaches

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Abstract. An overview of possible occupational exposures to enhanced natural radiation in Germany is given, based on an analysis of the German Radiological Protection Commission. So far, the most significant exposure source is radon at underground and above ground workplaces. As a result of relevant regulations, in East Germany since the 70´s a systematic monitoring of exposures to radon progeny has been introduced step by step in the uranium industry, in conventional ore mining, in show caves and mines, in enterprises for securing mining areas against subsidence, in radon spas and in water works in radon affected areas. Individual exposures have been assessed. The monitoring results for the period 1975–1998 are presented. Successful protection measures leading to a significant reduction of the exposures are discussed. using workplace monitoring results and registered occupancy times. In West Germany no regulations in this area were in force. Nevertheless, voluntary measuring programmes at similar workplaces were carried out. In case of unacceptable exposures successful protection measures were implemented. At present a systematic approach to control occupational exposures to radon is laid down in the European Directive 96/29/Euratom which has to be taken over in the national legislation to come. The expected number of workplaces to be included in the radiation protection system in Germany, the recommendable way of including different workplace types taking into account appropriate reference levels, and possible approaches to a graded system of workplace and individual monitoring are discussed in detail.

1. INTRODUCTION

In the European Council Directive on basic safety standards for radiation protection [1] requirements for enhanced natural radiation exposure are laid down. It is a great challenge to implement them in the future national regulations. Generally we are faced with multiple problems if we deal with natural radiation: occupational exposure of air crews to cosmic radiation, public exposure to radon in dwellings, exposures in industries where occupational exposure to radon and occupational and public exposure to natural radionuclides other than radon ("NORM") should be distinguished, and remediation of mining and industrial relics. Even though it is very difficult to solve all these problems in a consistent manner one should strive for solutions that are not contradictory to each other [2]. At the beginning a pragmatic rather than a comprehensive regulatory approach seems to be prudent. Any step in the direction of controlling enhanced natural radiation exposures is a progress if one begins with monitoring and reducing the highest individual exposures.

This paper is focused on the occupational exposure to radon and radon progeny incidental to work. The exposure of uranium miners is outside the scope of this paper although the predominant pathway is their radon exposure [3]. Uranium mining and milling have been traditionally controlled as parts of the nuclear fuel cycle like other practices. There are other workplaces where natural radionuclides are not or have not been processed in view of their radioactive, fissile or fertile properties and within which the presence of natural radiation sources leads to a significant increase in the exposure of workers or of members of the public which cannot be disregarded from a radiation protection point of view. They may be regarded as practices or as intervention situations since most of these workplaces with enhanced exposure to natural radiation already exist. That is why for them in the European Directive [1] the term ”work activities” was introduced.

2. THE SIGNIFICANCE OF ENHANCED OCCUPATIONAL EXPOSURE TO RADON PROGENY

The European Directive requires that each member state of the EU shall ensure the identification, by means of surveys or by any other appropriate means, of work activities which may be of concern. The German Commission on Radiological Protection (SSK) has analysed relevant workplace types and assessed the expected number of workers in the dose ranges of 1–6 mSv per year and above 6 mSv per year [4]. Relevant workplace types are, among others, production and use of thoriated welding electrodes, production, transportation, storage and use of thorium gas mantles, use of phosphate fertilizers, processing of zircon sands and pyritic ore as well as scrap recycling and copper slag processing. However, the largest number of workers and the highest exposures are expected at workplaces with exposures to radon and its progeny. Table I gives an overview.

Table I: Assessment of numbers of workers with enhanced exposure to radon

	1000–3000 $Bq \cdot m^{-3}$	> 3000 $Bq \cdot m^{-3}$
Underground mining (except uranium and coal mining)	1000	300
Coal mining	some 100	-
Water works and water supply facilities	2000	300
Spas, sewage systems	Single cases	-
Normal buildings	50,000	10,000

Obviously radon is the most significant "technologically enhanced natural radiation exposure" (TENR), at least under the conditions prevailing in Germany. Since this fact has been suspected for decades, efforts to monitor and control enhanced natural radiation exposures at workplaces have concentrated on radon exposures.

3. EXPERIENCES WITH THE CONTROL OF HIGH EXPOSURES TO RADON PROGENY

In Germany, there are different legal regulations with regard to exposures to radon and radon progeny in the old and in the new Federal States (Länder).

A legal basis [5] for the radiological protection monitoring of work places with exposures to radon and short lived radon progeny outside of the uranium industry has only existed in the new Federal States in the eastern part of Germany. A systematic monitoring has been introduced step by step since the 70´s, and includes mainly underground work places of particular groups of workers with significant exposures to radon progeny, i. e. uranium mining and milling and the closeout of the uranium industry (since 1991), conventional ore and mineral underground (non-uranium) mining, shaft construction and securing abandoned mines against mechanical damage (subsidence). Other workplaces, such as show caves and tourist mines, radon spas and certain water works have also been included.

Maximally 28,000 employees have been involved in this monitoring. The present figure is approximately 3,000 persons (Figure 1).

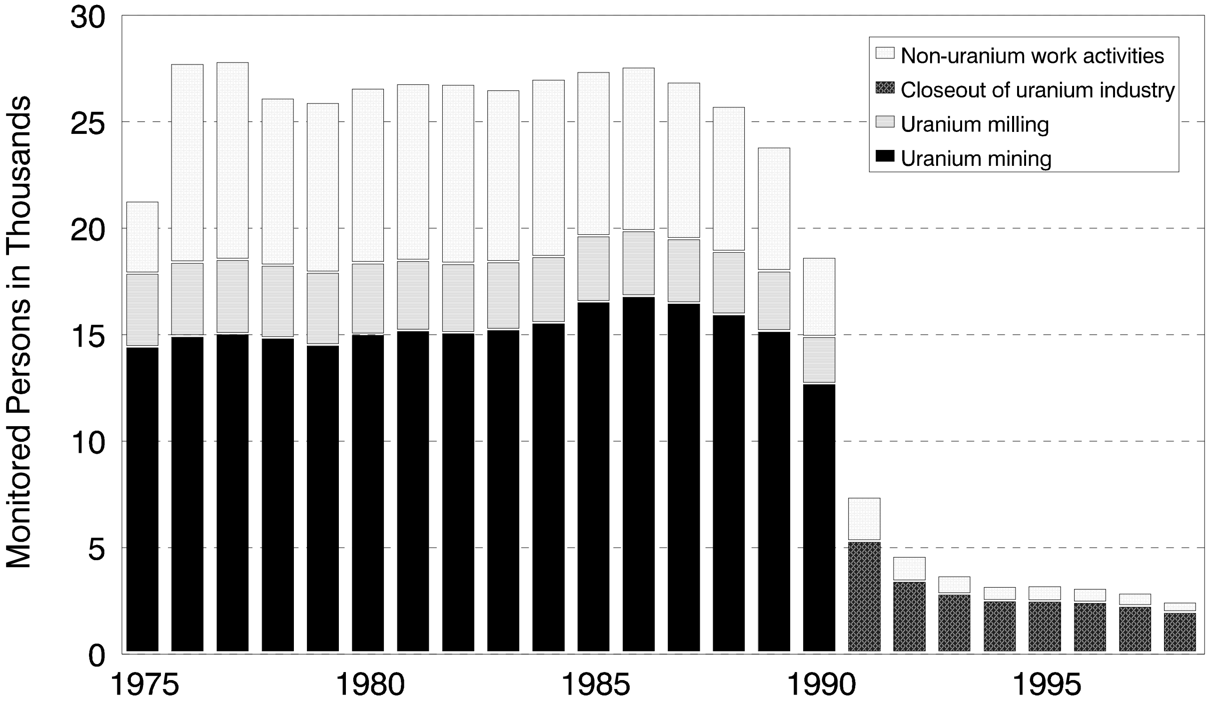

Figure 1. Number of monitored persons with exposures to short lived radon progeny.

The primary objective of the monitoring in the first decade was not the assessment of the exposure as such but to provide necessary information for the further optimisation of protection at the workplace.

The VOAS Regulations [5] of the former German Democratic Republic, which remain in force until the federal German radiation protection law will be amended with regard to this type of exposure, include limits for occupational exposures to radon and radon progeny. These limits have been expressed in terms of the potential alpha energy of the short lived radon progeny corresponding to the exposure.

$ALE_{pot} = 8 \cdot 10^{10}$ MeV·h·m^{-3} (12.8 mJ·h·m^{-3})

Consequently the quantities used for practical radiation protection in the case of exposures to radon progeny are the *integral exposure* E_{pot} and the *workplace concentration* C_{pot} with their respective derived annual limits.

$DAC_{pot} = 4 \cdot 10^{7}$ MeV·m^{-3} (6.4 µJ·m^{-3})

Individual exposures have been assessed using workplace monitoring results of the potential alpha energy concentration and registered occupancy times. Where necessary, protection measures were required [6].

This method for the estimation of occupational radiation exposure on the basis of short term operational measurements has been widely applied — as in other countries with uranium industries as well. So-called mine radiometers have been used which have been adapted to the special conditions underground.

The effective dose equivalent values shown in figures 2 through 4 have been determined on the basis of the ICRP 32 dose conversion factors [7]. The contribution of external radiation and of long lived alpha emitters was determined as a constant fraction of the whole exposure. From 1991 on, during the closeout of the uranium industry with heavily changing exposure condition, these contributions have been measured and assessed separately by means of individual devices [8].

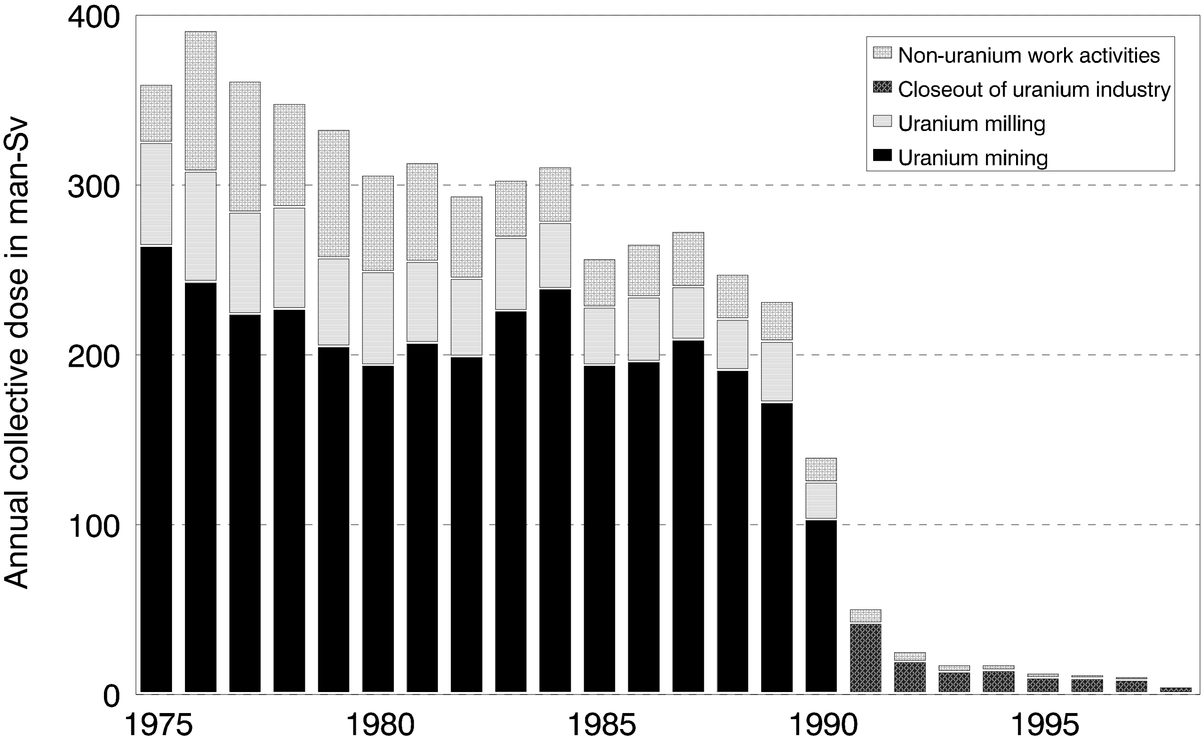

Figure 2. Annual collective dose in different types of occupation (dose calculation according to ICRP 32).

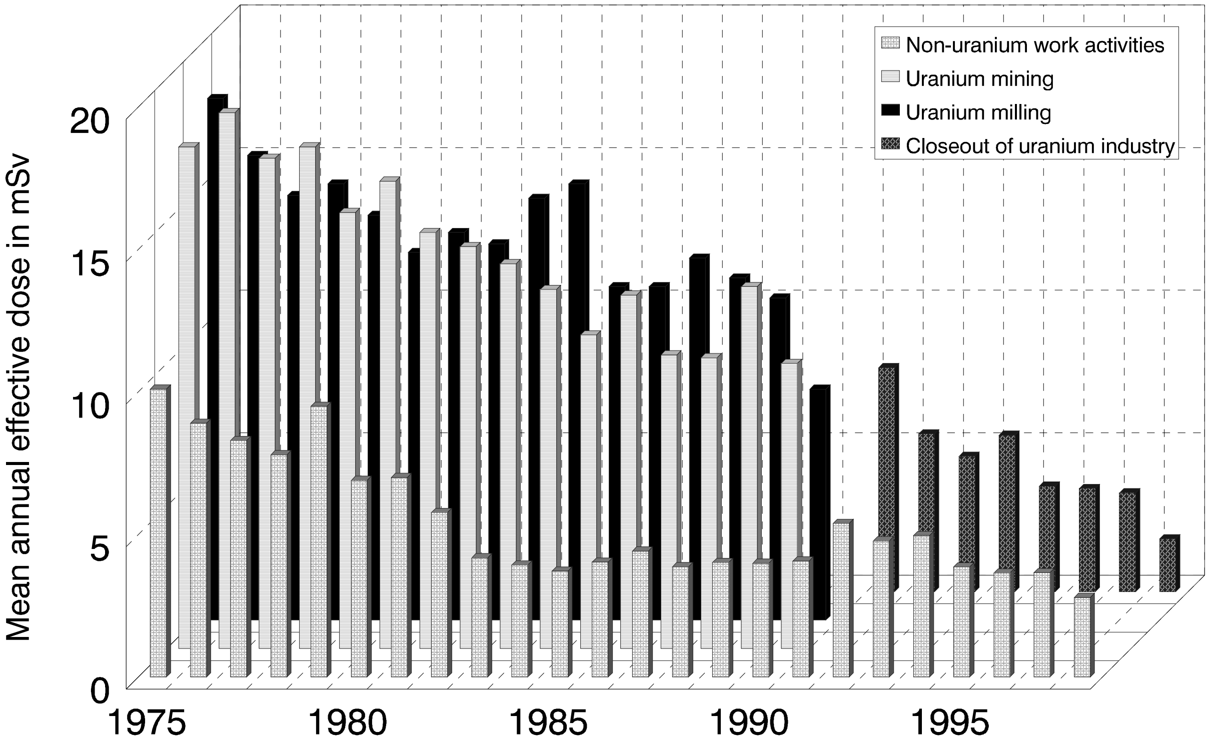

Figure 3. Mean effective dose in different types of occupation (dose calculation according to ICRP 32).

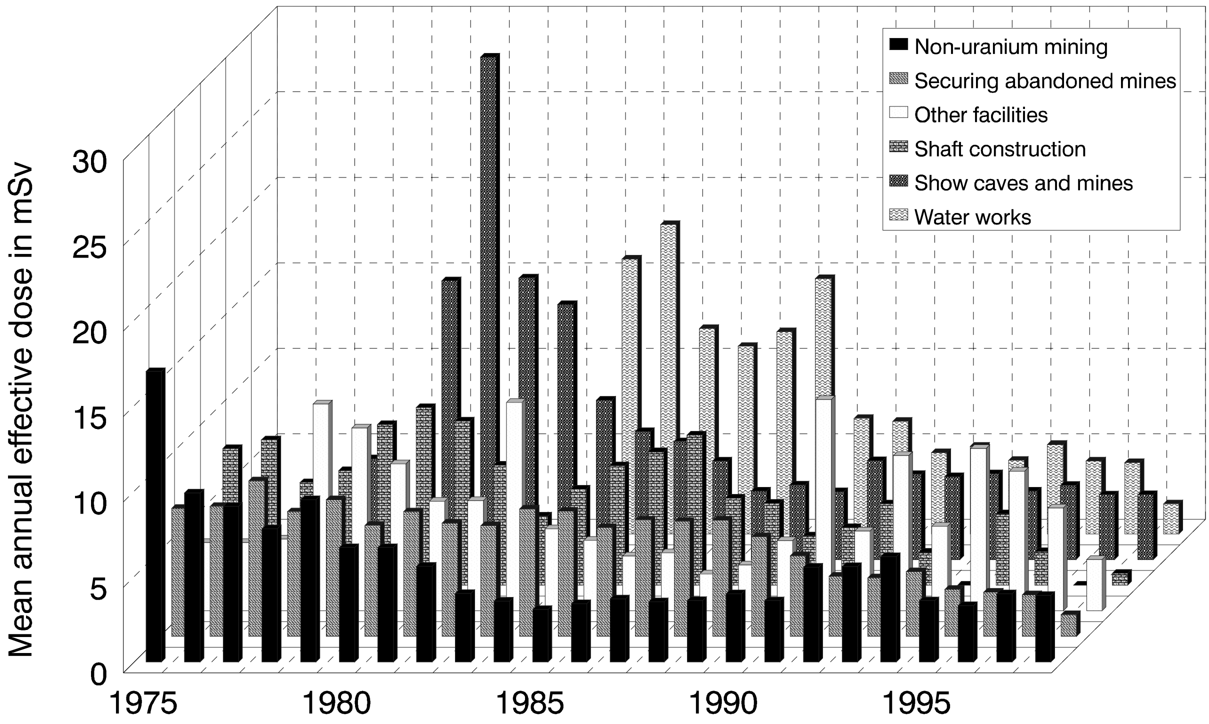

Figure 4. Mean effective dose in different types of occupation excluding the uranium industry (dose calculation according to ICRP 32).

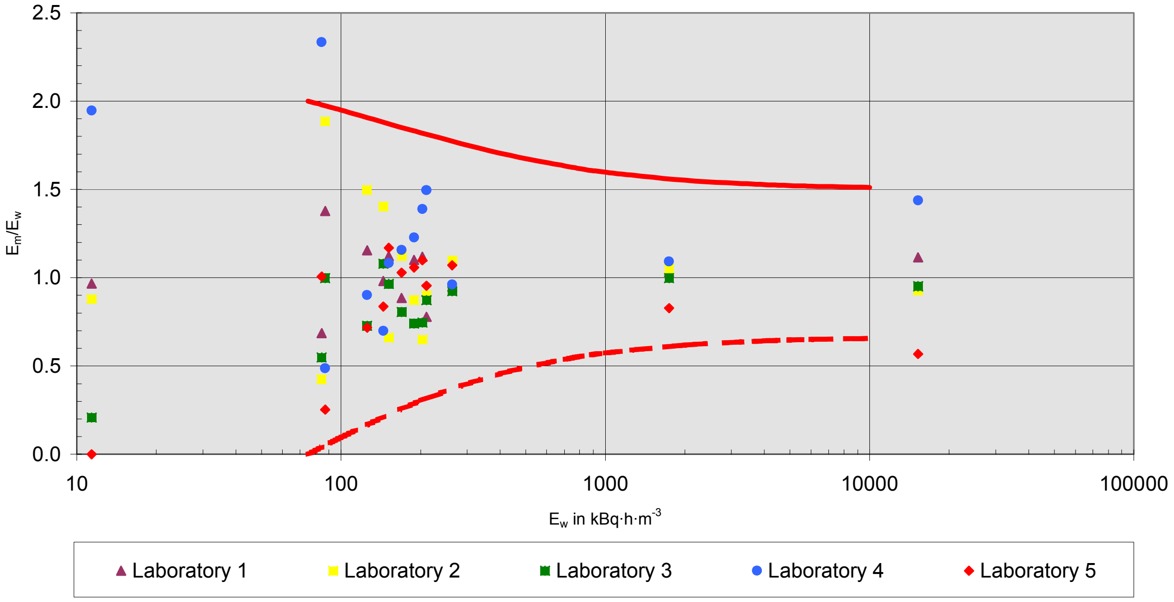

Figure 5. Quotient of measuring value E_m to true value E_w of the exposure in dependence on the true value E_w.

When applying the ICRP 65 dose convention [9] for the calculation of doses, the values given above decrease by approximately one half; the exact reduction depends on the contribution of exposures caused by long lived alpha emitters and external radiation.

More than twenty years experience in this field have shown that individual and collective occupational exposures to radon progeny are in many cases significantly higher than occupational exposures to artificial radiation sources.

The slight reduction in the number of workplaces as a result of efficiency measures in the second half of the eighties and the drastic reduction in the number of workplaces as a result of the decommissioning of many enterprises from 1990 on, have affected only the collective dose (Figure 2).

The decreases with time of the mean annual individual effective dose, which are given in Figures 3 through 4, result from the extensive radiation protection and organisational measures which have been implemented in workplaces. It is particularly important that above all the highest individual exposures could be reduced.From 1984, some workplaces in water work institutions in the southern area of the former German Democratic Republic were also included in the radiation protection monitoring program. The work regime for the persons employed there is characterized by the fact that single employees must carry out a variety of tasks with very different and frequently very high radon and radon progeny concentrations, but mostly enter these places only for short periods of time. The necessary remedial measures may be constrained by existing requirements of hygiene or may not completely be effective for organisational reasons. Necessary investigations of the exposure conditions require often monitoring of individual exposures.

Improvements in ventilation have proved to be the most effective radiation protection measure for reducing exposures in all fields of work. Three components are particularly important:

(a) air volume of the ventilated area,
(b) air throughput,
(c) direction of ventilation (change from underpressure to overpressure).

In addition in mines a more or less efficient decrease of concentrations was achieved by covering the mine drainage system or hermetic sealing of abandoned tunnels and galleries ore in rare cases means of filtration of air of an auxiliary ventilation at the workplace. The reduction of occupancy time was possible in some cases.

In the western part of Germany no regulations were in force in this area. Nevertheless, voluntary measuring programmes and protection measures were carried out with reference to general labour safety regulations and the legislation of mines at similar workplaces. For these measurements devices for long term determination of both radon and radon progeny exposure and concentration were preferentially used [10]. In case of high exposures protective measures were implemented. Altogether it can be said that, as exercised in both parts of Germany, a regulatory and a pragmatic approach resulted in a similar improvement of the exposure conditions.

4. REGULATORY APPROACHES

4.1. Basis

The discussion on the future German radiation protection legislation is not yet finished. That is why the information on it, given in the following paragraphs, is not finally confirmed.

Basic recommendations on the control of exposures to radon and its progeny are laid down in ICRP publication 65 [9]. Further guidance on occupational exposure is given in ICRP publication 75 [11].

The stipulations in the European Directive [1] and in the International Basic Safety Standards [12] are based on the ICRP recommendations.

4.2. Identification of workplace types

There is a general consensus that the first step should be the identification of types of work activities that may be of concern as required in the European Directive. In ICRP publication 75 [11] it is said that a precondition for the introduction of controls is "a sound overview of the patterns and levels of exposure as a basis for discussion of the types of workplaces which should be subject to a system of radiological protection." Although identified workplaces of concern comprise also exposures to natural radionuclides other than radon, in this paper only occupational exposures to radon and its progeny are discussed.

Underground work activities with enhanced occupational exposure to radon progeny may be non-uranium mines, shaft construction, subsidence prevention, tunnels, galleries in radon spas, show caves, tourist mines, water treatment works and stores, subways, sewage systems, military facilities etc. They can exist within and outside radon-prone areas. Work activities above ground may be radon spas, waterworks, factories and workshops, schools, hospitals and other public buildings, and last but not least normal offices and shops where the exposure conditions are the same as in dwellings. Relevant above ground work activities are usually located in radon-prone areas.

Based on the workplace analysis of the SSK the following work activities with exposure to radon are specified to be included in the German radiation protection system: underground mining including show caves and tourist mines, radon spas and water works in radon-prone areas. According to the SSK analysis the highest number of workers is expected in normal offices and shops. However it is the prevailing conviction that these workplaces should not be controlled as long as a national policy regarding radon in dwellings has not been established.

4.3. Requirements

Employers are required to assess the potential radon exposure at relevant workplaces. In the recommendations of an Article 31 Group on the implementation of Title VII of the European Directive [13] it is recommended that the action level for workplaces above which the exposures are subject to regulatory control should be set in the range of 500–1000 $Bq \cdot m^{-3}$ time averaged radon gas concentration (ICRP: 500–1500 $Bq \cdot m^{-3}$ [9], IAEA: 1000 $Bq \cdot m^{-3}$ [12]). In order to clarify that the averaging refers to the worker, in the German legislation the action level is given as an annual individual radon exposure of $2 \cdot 10^6$ $Bq \cdot h \cdot m^{-3}$ corresponding to an average radon concentration of 1000 $Bq \cdot m^{-3}$ when the working time is 2000 h per year. If the equilibrium factor between radon and radon progeny significantly deviates from 0.4 the authority may establish different action levels for the individual radon exposure.

If the action level is exceeded, at first remedial measures like in an intervention should be implemented to reduce the exposure to values below the action level. If this is not possible or if the remedial measures were not successful the exposure of the workers has to be controlled like in a practice. Of course, the actual control and protection measures have to be adapted to the particular problem. The annual limit of the individual radon exposure is set at $6 \cdot 10^6$ $Bq \cdot h \cdot m^{-3}$. This corresponds to a potential alpha energy exposure of 14 $mJ \cdot h \cdot m^{-3}$ assuming an equilibrium factor of 0.4. In the case of significantly from 0.4 deviating equilibrium factors a different value for the annual limit of the radon exposure may be established.

If the action level was not exceeded as a result of the exposure assessment, a re-testing of the exposure conditions after a certain time interval may be advisable. If compliance with the action level was achieved only after a remedial action the re-testing may be necessary after a shorter time interval. Details have not been established yet. The same is true for the monitoring methods to be used. The costs of monitoring have to be taken into consideration. In many cases operational workplace monitoring and individual assessment of occupancy times may be sufficient as it was shown in section 3. In other cases individual monitoring may be necessary, preferably of the radon exposure. In rare cases operational individual monitoring of the potential alpha energy exposure by means of cheap ("passive") electronic devices may be appropriate. Details are left to a future guideline.

Any monitoring system requires a quality assurance. As a first step in Germany an intercomparison of radon monitoring services was carried out. The results are shown in Figure 5. Nearly all values are located within two lines characterizing accuracy requirement to individual dosimeters for external radiation in Germany [14]. That means that reliable measurements of the individual radon exposure are possible.

5. SUMMARY AND CONCLUSION

On the basis of experiences with monitoring of occupational exposures to radon progeny and related protective measures for more than 20 years and of international recommendations and standards a pragmatic regulatory approach was presented. It is not part of a comprehensive, complete and consistently risk-based solution of all problems of radiation protection against technologically enhanced natural radiation exposures, but it is focused on the decrease of the highest occupational exposures to radon progeny and tries to avoid an unjustifiable imbalance between protection efforts in the fields of occupational and public radon exposures. This approach should be considered only as a milestone on the way to an ultimate solution of all problems faced today. Certainly after having successfully solved the envisaged problems the system should be further improved using the experiences meanwhile gathered.

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PDMS method used to identify the thorium compounds in dust particles

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Abstract. The aim of this study was to apply ^{252}Cf-PDMS (Plasma desorption Mass Spectrometry using a ^{252}Cf source) technique for identification of chemical composition of thorium in the respirable fraction of aerosols. The dust particles were generated during the separation process of mineral sands to obtain concentrates of rutile, ilmenite, zircon and monazite concentrates. The aerosol samples were collected during the reprocessing of ilemenite. A cascade impactor with six stages was used to collect mineral dust particles with aerodynamic diameter in the range of 0.64 to 19.4 mm. The particles impacted on each stage of the cascade impactor were analyzed by PIXE (Particle Induced X ray Emission) which permits the determination of elemental mass concentration and the MMAD (Mass Median Aerodynamic Diameter). By employing the ^{252}Cf-PDMS technique the chemical compound present in a mineral dust particles sample, in a cerium oxide sample and in a concentrate of monazite sample were identified. Clusters of cerium oxide were identified in the cerium oxide sample, cerium phosphate were identified in the concentrate monazite sample. Molecules of thorium oxide were identified in both samples. The mass spectra (^{252}Cf-PDMS technique) of dust samples showed the presence of the thorium silicate, thorite and zircon in the fine fraction of aerosol.

1. INTRODUCTION

The mineral mining and milling processes are the main source of workers exposure to mineral dust particles. The inhalation of these particles can cause serious diseases to the human being. In order to evaluate the risk of the workers due to mineral dust particles inhalation, it is necessary to determine the deposition rate, the concentration and the kinetics of the particles when they go into the respiratory tract. Furthermore, the chemical composition, particle size and the elemental mass concentration in the respirable fraction of aerosol are necessary for evaluation of the worker's risk [1, 2, 3, 4].

The main source of workers exposure to thorium bearing particles are the separation processes of the mineral sands. In Brazil, the most important deposit of mineral sands occurs in the north of the state of Rio de Janeiro. In the plant which processes these mineral sands, the silica is separated by a hydrogravimetric process. The concentrate of mineral sands is then processed by eletrostatic and magnetic separation process to obtain rutile (TiO_2), ilmenite ($TiFeO_3$), zircon ($ZrSiO_4$ and monazite ($RE_3(PO_4)$)) concentrates. During these separation processes the workers are exposed to thorium bearing dust particles.

In this work PIXE (Particle Induced X ray Emission) and PDMS (Plasma Desorption Mass Spectrometry) methods were used to characterize mineral dust particles generated at this plant.

The airborne dust particle were collected during the mineral-sands separation processes using a six stage cascade impactor. The MMAD (Mass Median Aerodynamic Diameter) and the elemental mass concentration of the airborne particles were determined by PIXE method. The chemical composition of the elements in the samples was identified by employing the PDMS technique.

A sample of monazite concentrated and cerium oxide were analyzed using both techniques to compare the mass spectra. The cerium oxide used in this analysis was obtained by reprocessing the chloride of rare earth which was extracted by chemical processing from the concentrate of monazite.

2. EXPERIMENTAL METHOD

The aerosols samples were collected during the reprocessing of ilmenite to obtain concentrates of ilmenite following the steps of the mineral sands separation process. The flowchart of the mineral sands separation process is shown in Figure 1. A six-stage cascade impactor with an operational flow-rate of 12 l/min was used to collect airborne dust particles. The cut-off diameter of the each stage of the cascade impactor are 19.4, 9.9, 4.7, 2.4 and 0.64 mm [5].

Airborne particles, concentrate of monazite and cerium oxide were analyzed by PIXE using a 4 MV Van de Graaff accelerator at PUC-RIO and a 2 MeV proton beam with a current of 30 nA [6].

The aerosol collected at 6th stage of the cascade impactor, the concentrate of monazite and the cerium oxide were also analyzed by PDMS. The experimental arrangement used in the PIXE and PDMS analyses is shown in Figure 2.

The PDMS technique which is based on the electronic sputtering mechanism (sputtering induced by MeV ions) and on the time-of-flight mass spectrometry (TOF-MS) [7, 8, 9, 10, 11, 12], using a ^{252}Cf radioactive source to provide two fission fragments which are emitted in opposite directions at the same time. One of the fission fragments collide with the target inducing desorption of molecules and/or cluster of ions. The other fission fragment is detected by a surface-barrier detector producing the start signal to trigger the Time-to-Digital Converter (TDC). The secondary ions emitted from the sample are accelerated towards a field-free time-of-flight tube by an electric field of ~1 kV/mm, applied between the biased target and the grounded grid. Secondary ions with different mass/charge ratio reaching the micro-channel plate assembly (MCP) at the end of the time-of-flight tube produce the stop signals for the time-of-flight measurement. The masses of the secondary ions are related to the time-of-flight [13, 14].

3. RESULTS AND DISCUSSION

The cerium oxide sample and the sample of concentrate of monazite were analyzed by PIXE method in order to identify the main elements presents in the samples. The X ray spectra of both samples show that cerium was the main element. The samples were also analyzed by the PDMS method.

The mass spectrum of positive ions of cerium oxide sample is shown in Figure 3. This spectrum shows that the cerium is associated to oxygen (CeO_n). Compounds of thorium (ThO_2) and ($ThSiO_4$), Sr, Ca, Zr were also observed in this spectrum.

The positive ions mass spectrum of the concentrate of monazite is shown in Figure 4. The analysis of this spectrum shows that Th was associated to oxygen (ThO_n) and Ce was associated to (PO_n). Compounds of other rare earth as La, Nd and Y were also identified. Ions of $ZrSiO_3$, TiO_2 and $TiFeO_3$ present in this spectrum indicate that this sample contains zircon, rutile and ilmenite. The compounds of Cl, Ca, Mn, V, Cu, Zn and Pb identified in the mass spectrum indicate that this samples contains other compounds besides mineral sands. The cerium present in the monazite is associated to (PO_n) and the thorium to ThO_n while in the cerium oxide sample cerium is associated only to oxygen. Based on these results it is possible to identify the monazite dust particle by employing PDMS technique.

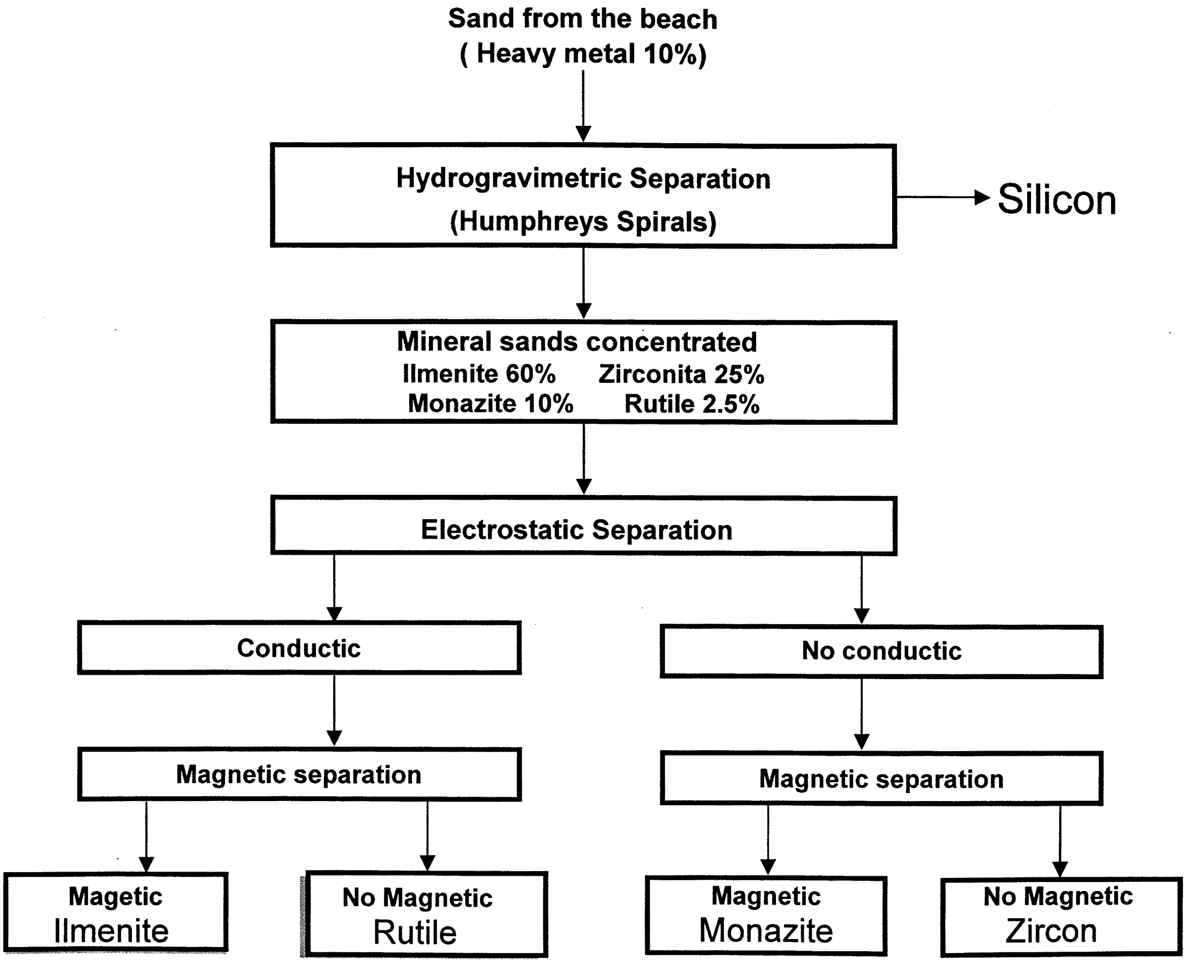

Figure 1. Flowchart of the mineral sands separation process plant.

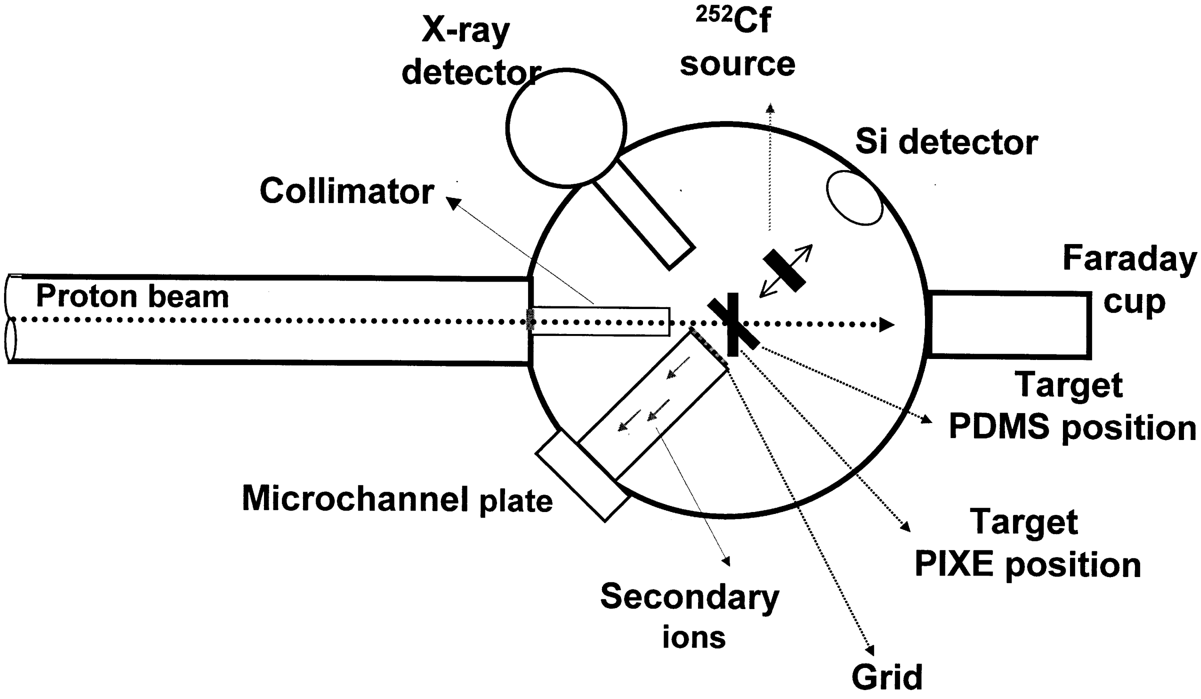

Figure .2 The experimental arrangement used in the PIXE and PDMS analyses.

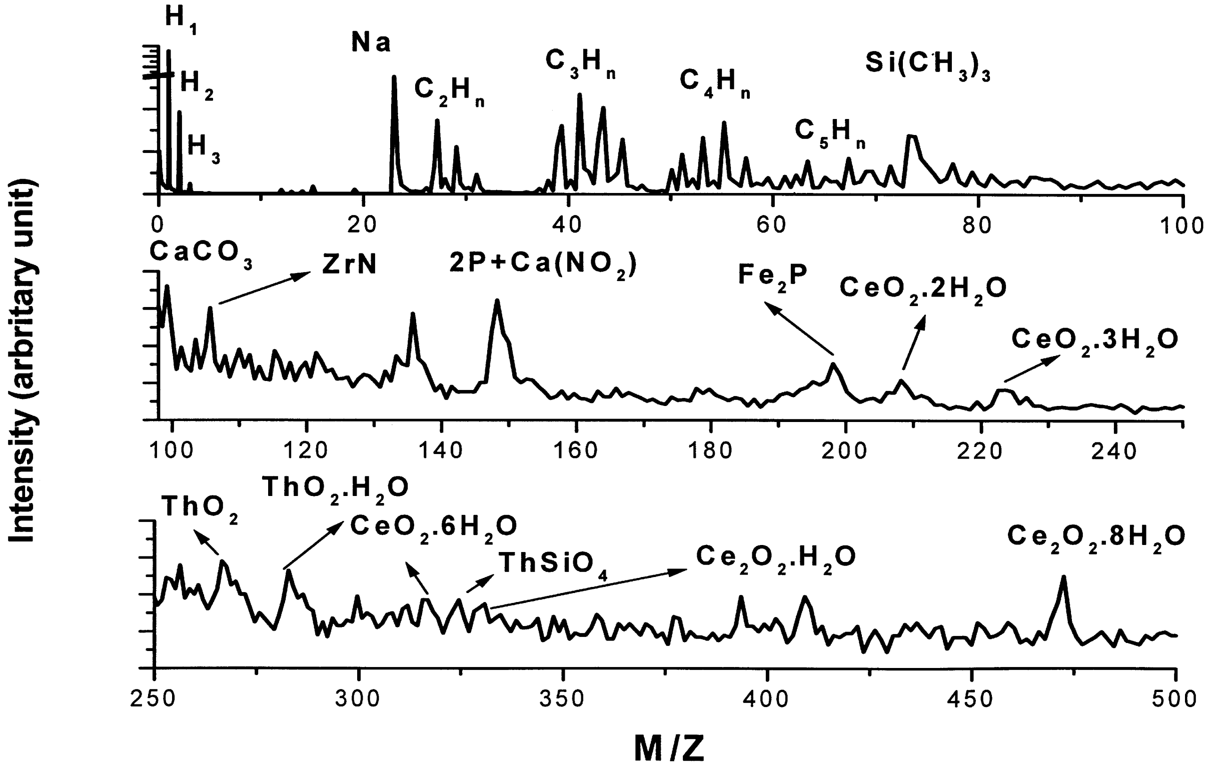

Figure 3. Mass spectrum of positive ions of cerium oxide.

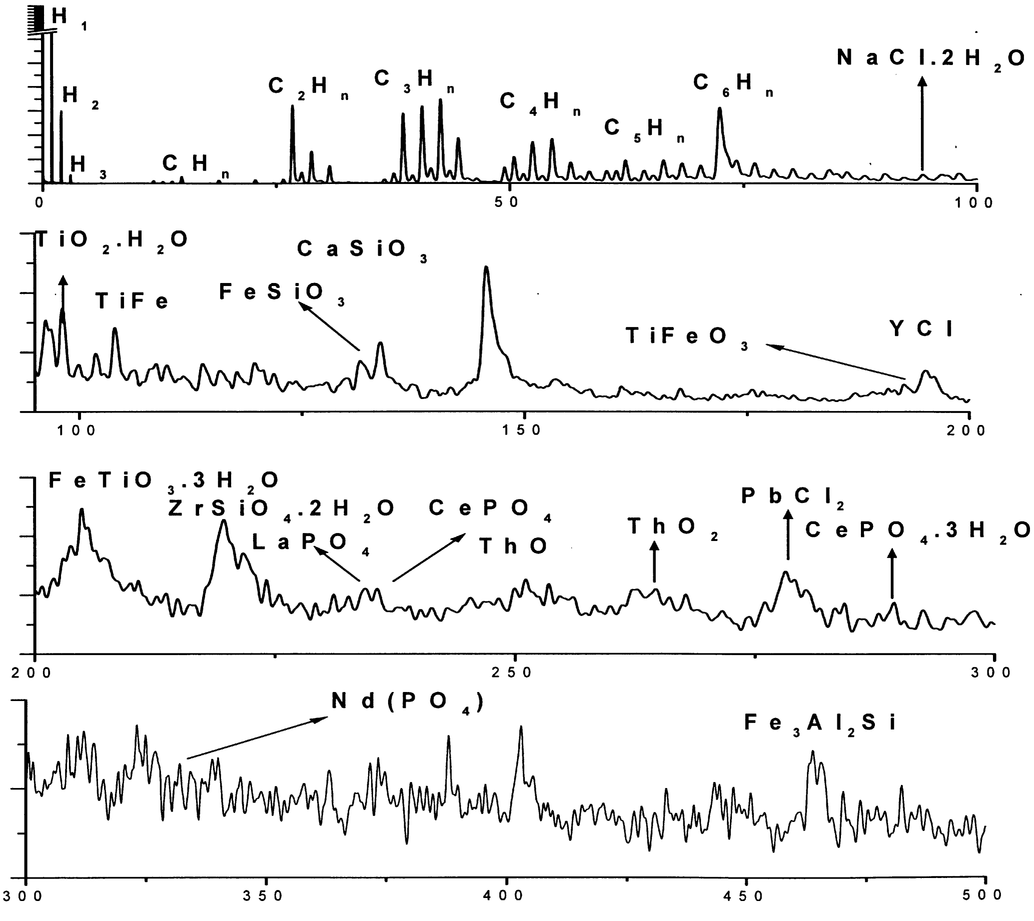

Figure 4. Mass spectrum of positive ions of concentrate of monazite.

The elemental mass air concentration in the respirable fraction[1] and MMAD were determined based on the X ray spectra analysis of airborne dust particles. The elemental mass concentrations and MMADs of the airborne dust particles are shown in Tables 1 and 2, respectively. As can be observed in the Table 1 the highest thorium concentration occurs during the electromagnetic separation process however the cerium concentration was below the detection limit of PIXE method (4.3 ng). These results suggest that monazite dust particles were not present in the respirable fraction of aerosol and that the thorium bearing particles were due to other aerosol source. The presence of Ti and Fe in the dust particle X ray spectra suggest that of rutile and ilmenite were the source of Fe and Ti bearing particles.

The mineral dust particles impacted on the 6th stage of the cascade impactor during the electromagnetic separation process were analyzed by PDMS and the mass spectrum of positive ions is shown in Figure 5. This mass spectra showed that Th was associated to oxygen (ThO_n) and silicon ($ThSiO_4$), indicating that thorite, not monazite, was the source of airborne particles containing thorium. The presence of cerium compounds was not observed in this mass spectrum, showing that there were not monazite dust particle in the respirable fraction of aerosol.

The ions of Ti and Fe observed in the mass spectra (PDMS method) (Figure 5) showed that ilmenite ($TiFeO_2$) was the source of Ti and Fe bearing dust particles. The presence of zircon airborne dust particles ($ZrSiO.H_2O$) was also observed in the mass spectra.

The elements Ca, Cr, Mn, Ni, Cu, Zn and Pb observed in the X ray and in the mass spectra indicate the existence of other sources of aerosol besides the mineral sands. Since of these sources could be the mechanical wearing of equipment, particles of oil used to lubricate or the burning fossil oil. Besides these sources, there were particles from soil (Al, Ni, Si, Zn, Fe and Ca) and marine aerosol (Cl, Ca, Na, K, Zn and Fe) which were transported into the plant by the wind.

The phenyl (C_6H_7), $Si(CH_3)_3$, Si(OH) molecules and carbon cluster ions are observed in the mass spectra. These ions are from the Mylar film used as impactor surface and from the residual gas present in the scattering chamber.

4. CONCLUSIONS

These results shown that, although PIXE spectroscopy be an accurate and multi-elementary analytical technique it does not provide information about the chemical composition of the elements present in the sample. Being the PDMS a mass spectrometry technique, it allows to identify the composition of the molecules present. Since the cross sections for the molecules and ion desorption are not completely determined, it is not possible to determine the concentration of molecules. However the analysis of mass spectrum allow to identify the principal chemical compounds present in the samples.

By using both technique, thorium oxide and cluster of $Ce(PO_n)$ were identified in the sample of concentrate of monazite and cluster of cerium oxide were identified in the cerium oxide as sample. Thorium oxide was identified in both samples.

The analysis of mineral dust particles by PIXE and PDMS techniques allowed to characterize mineral dust particles determining the elemental mass concentration, mass median aerodynamic diameter and their chemical compounds. These informations are very important for identification of aerosol sources and for estimation of the risk of the workers to due to the inhalation of dust particles.

Table I. Elemental mass concentration in the respirable fraction of aerosol

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[1] Respirable particles are able to enter the deep lung during nose breathing [15].

Table I. Elemental mass concentration in the respirable fraction of aerosol

STEP	ELEMENTAL MASS CONCENTRATION IN THE RESPIRABLE FRACTION OF AEROSOL (μg/m^3)										
	ELEMENT										
	Ca	Ti	Cr	Mn	Fe	Ni	Cu	Zn	Zr	Pb	Th
Drying	0.89	0.52	0.25	0.10	0.53	0.45	<DL	0.01	0.04	0.01	0.02
Electromagnetic Separation	3.58	3.03	2.42	0.11	3.81	0.03	2.36	0.46	8.23	0.09	0.14
Gravimetric Separation	3.75	5.77	1.59	0.14	5.25	0.03	<DL	0.03	0.36	0.05	<DL
	3.41	2.33	2.63	2.67	3.18	0.03	0.02	0.02	<DL	<DL	<DL
Average	2.91 ±1.35	2.92 ±2.18	1.72 ±1.08	0.76 ±1.28	3.19 ±1.98	0.14 ±0.21	1.19 ±1.66	0.13 ±0.22	2.84 ±4.67	0.05 ±0.04	0.08 ±0.09

Table II. Mass Median Aerodynamic Diameter of the airborne particles

STEP	MASS MEDIAN AERODYNAMIC DIAMETER - MMAD (μm)																					
	ELEMENT																					
	Ca		Ti		Cr		Mn		Fe		Ni		Cu		Zn		Zr		Pb		Th	
	ϕ	σ_g	ϕ	σ_g	ϕ	σ_g	ϕ	σ_g	ϕ	σ_g	ϕ	σ_g	ϕ	σ_g	ϕ	σ_g	ϕ	σ_g	ϕ	σ_g	ϕ	σ_g
Drying	1.7	2.1	1.7	1.9	1.5	2.3	1.4	2.1	1.6	1.9	1.6	2.0	-	-	2.1	1.9	2.2	1.9	1.6	2.0	1.7	1.9
Electro-magnetic	1.5	2.2	1.4	2.1	1.3	2.3	1.0	2.5	1.3	2.0	1.5	2.2	1.5	2.1	1.7	2.1	1.4	2.2	1.4	2.1	1.4	2.1
Gravimetric	1.7	2.1	2.0	1.8	1.5	2.3	1.6	2.0	1.5	1.9	1.7	2.0	-	-	1.9	2.0	2.4	1.7	2.4	1.8	-	-
	1.6	2.2	1.5	2.0	1.0	2.5	1.1	2.4	1.4	2.0	1.3	2.3	2.4	1.5	1.6	2.2	-	-	-	-	-	-

The MMAD values and elemental mass concentration showed that the workers could inhale mineral dust particles. The PDMS results showed that although the plant processes mineral sands, the source of thorium bearing particles was thorite sand present in the soil of the region from which monazite is extracted. The ilemenite, zircon and thorite particles were identified in the fine fraction of aerosol. Based on the PIXE and PDMS analysis it was possible to conclude that there were others sources of aerosol which produce airborne dust particle containing Th in the respirable fraction.

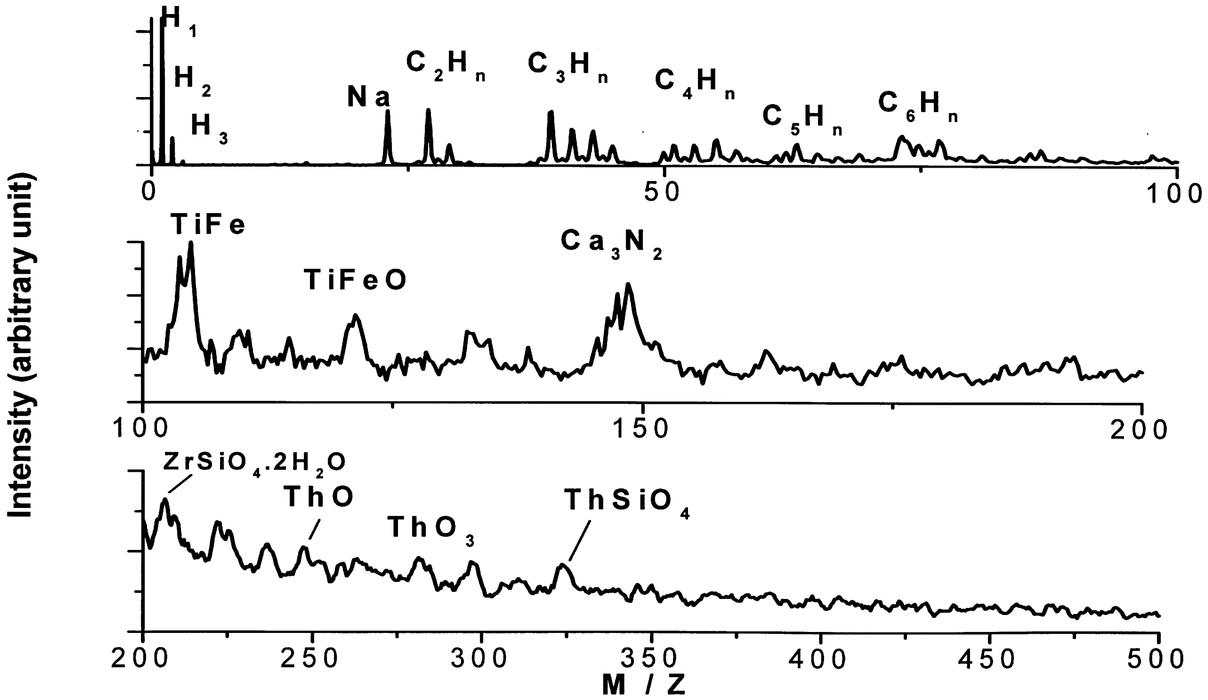

Figure 5 Mass spectrum of positive ions of mineral dust particles impacted on the 6th stage of the cascade impactor.

In summary, PIXE analysis allowed to identify and quantify trace of elements present in the sample and by using PDMS method it is possible to identify the chemical composition of these elements. PIXE and PDMS can be used as complementary techniques for the aerosol analysis and using both method it is possible to determine the physical and chemical characteristics of airborne particles. These techniques, when used together, provide important information about the aerosol characterization.

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Combined effect of environmental radiation and other agents: Is there a synergism trap?

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Abstract. Most assessments of possible deleterious outcomes from environmental and occupational exposures concentrate on single agents and neglect the potential for combined effects, i.e. synergisms or antagonisms. Biomechanistic considerations based on multistep processes such as carcinogenesis indicate the potential for highly detrimental interactions, if two or more consecutive rate limiting steps are specifically effected by different agents. However, low specificity towards molecular structure or DNA-sequence - and therefore exchangeability — of many genotoxic agents indicate little functional specificity and therefore little vulnerability towards synergism at most occupational and environmental exposure situations. The low potential for significant combined effects for those common low exposure situations where non-genotoxic agents with highly non-linear dose effect relationships and apparent thresholds are involved, is also evident. Nevertheless, a quantitative assessment of the contribution of synergistic interactions to the total detriment from natural and man-made toxicants based on experimental data is far away. The existing database on combined effects is rudimentary, mainly descriptive and rarely covers exposure ranges large enough to make direct inferences to present day low dose exposure situations. In view of the multitude of possible interactions between the large number of potentially harmful agents in the human environment, descriptive approaches will have to be supplemented by the use of mechanistic models for critical health endpoints such as cancer. Finally an important question considering the shape of dose effect relationships for ionizing radiation arises from the unresolved question whether real or apparent thresholds may be used for any genotoxic agent separately or only one time for an exposed genome.

1. INTRODUCTION

Even for the most protected human populations, disease and mortality rates still average more than 10^{-2} per year. Critical health outcomes from environmental exposures such as cancer are the result of multistep processes, driven in most cases by a multitude of endogenous and exogenous factors but not by one single agent.

Even the lifetime risk of active smoking in the range of 10^{-1} cannot be explained by the action of a single agent. Tobacco smoke itself represents a multi-agent exposure of many genotoxic and toxic substances. There are only a few historic examples from earlier occupational exposures in which one critical agent such as radon, asbestos or vinyl chloride is the main cause for lung or liver cancers, respectively [1, 2].

Therefore, a single agent such as ionizing radiation may be considered one of many interchangeable detrimental forces acting on human organisms and translating into a combined lifetime cancer mortality risk of 20–30 % from all endogenous and exogenous causes.

If a multitude of agents are contributing to human cancer, a change of paradigm in risk analysis is needed. The study of single agent dose effect relationships has to be extended through consideration of combined interaction and effects.

2. DEFINING COMBINED EXPOSURES AND INTERACTIONS

Since 1928, models to describe the combined effect of exposures to different agents have been developed [9]. Most important is that the conceptualisation of combined effects from two or more agents has to be built on a clear understanding of the terms used [3, 4].
The terms additivity, synergism, and antagonism should only be used to describe an interaction between two or more different agents when information about the dose-effect relationship of the single agents and the combination is available.

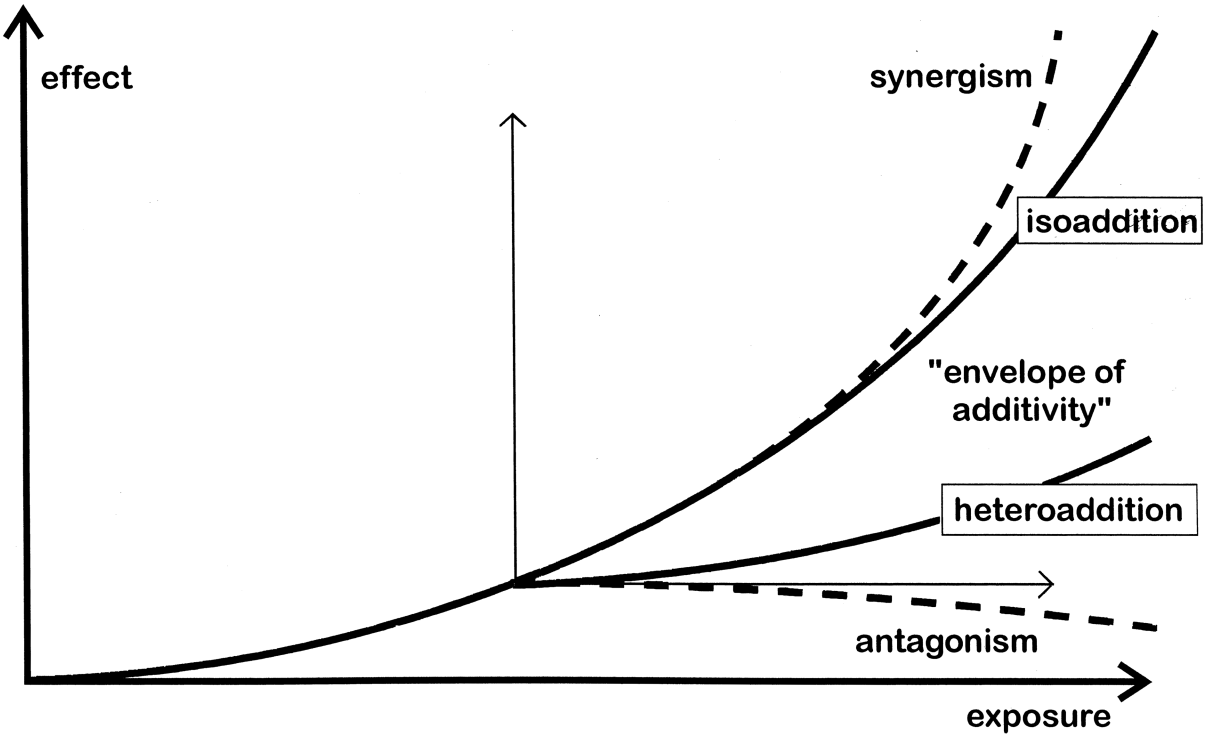

Fig. 1. Interaction of two agents having non-linear dose-effect relationships. Isoaddition results from mechanistically similar agents, heteroaddition for independently acting agents.

To define the range of deviations from additivity that may be caused by non-linear dose-effect relationships, the concept of heteroaddition and isoaddition has been developed:

- Heteroadditivity or effect additivity (Fig. 1, lower solid line) is present when two agents act on different molecules or pathways, i.e., truly independent in a molecular or mechanistic sense, and the single effects can be added independent of the form of the dose effect curves [5]. The resulting curve for heteroaddition forms one part of the envelope of additivity.
- Isoadditivity or concentration additivity (Fig.1, upper solid line), in contrast, is present when two agents act by the same or similar mechanism within the same pathway or on the same molecular target.

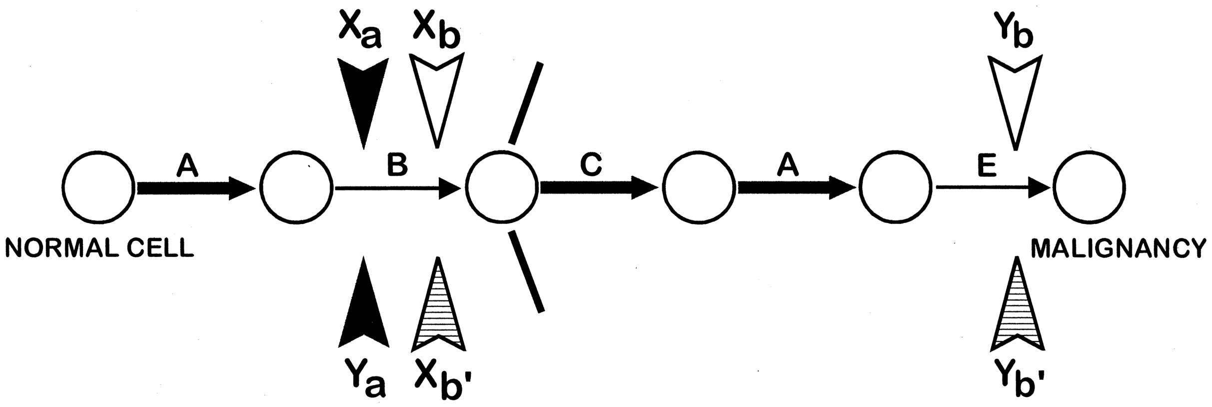

Fig. 2. Multi-stage model for carcinogenesis showing two critical (rate-limiting) steps (B, E) and three examples of interactions between two specifically acting agents X and Y:

	Action	***Effect***
(X_a, Y_a)	*Promotion of the same step*	*Iso- or heteroaddition*
(X_b, Y_b)	*Promotion of different rate-limiting steps*	*Synergism*
$(X_{b'}, Y_{b'})$	*Promotion of different steps, exposure by Y preceding exposure by X*	*Heteroaddition*

The term synergism should be defined and used in a restricted manner to describe the combined effects of two and more different agents which interact and result in a more than additive effect (Fig. 1, upper dotted line). This should be based on a mechanistic understanding of the interactions. The action of different agents should result (i) on different rate-limiting steps within a multistep process, (ii) at different sites of a molecule or (iii) by different molecular mechanisms. If the mechanism of action is unknown, any deviation from additivity of single agent effects should be classified sub- or supraadditive.

The consequences of these definitions in the multi-stage model of carcinogenesis are shown in figure 2. For example, highly synergistic effects from combined exposures could result only if exposure to X preceeds exposure to Y.

There are many examples of interactions between radiation and other toxic agents. Responses range from additivity to strong synergism. Some examples of synergistic effects in humans are listed in table I. But the available database is not comprehensive and is generally more observational/descriptive rather than mechanistic in orientation.

3. DOSE RESPONSE RELATION AT LOW DOSES

The lower end of dose-effect relationships for cancer from genotoxic agents are usually unknown. Sensitive experimental systems and mechanistic considerations are commonly referred to to correlate risk coefficients from higher exposures with measurable risks to the area of low dose exposure.

Since the elucidation of DNA structure and cellular DNA repair functions, it has generally been accepted that many classes of primary damage and also of fixed molecular damage from genotoxic agents in this important structure show no threshold. For ionizing radiation, where a single hit, i.e. a single traversal of an electron through a cell nucleus, already infers a considerable minimal dose in a very short time, linearity for primary events

Table I

Selected examples of synergistic interactions between ionizing radiation and other agents in humans

RADIATION QUALITY	EXPOSURE SITUATION	SYNERGISM WITH	RISK/EFFECT	REF
α Radiation	Radon daughters in miners	Tobacco smoke arsenic	lung cancer	1
X rays	Breast cancer therapy	Tobacco smoke	lung cancer [a]	7
γ Radiation	Lung cancer therapy	Cisplatin	tumor control	8
γ Radiation	Head and neck cancer therapy	Radiosensitizers: nimorazole	tumor control	9

[a] Statistical significance questionable

and their longer lasting imprints on DNA can be assumed for a considerable dose range from zero to several times the annual natural exposure in the range of 2 mSv effective dose. Interactions between different tracks only become important at high dose rates. Similar conditions are found at low concentrations of genotoxic chemicals as long as enzyme functions for substrate activation/inactivation or DNA repair show neither saturation nor induction phenomena.

An argument against linearity is the impressive wealth of data on adaptive responses in cells and organisms [6], which might support a threshold hypothesis.

At higher dose rates, non-linearity becomes the rule. In the case of ionizing radiation, multiple hits in one single cell might increase the complexity of DNA damage and modulate repair proficiency. Non-linearity at low doses and thresholds are generally found for non-genotoxic mitogens and cytotoxicants which need minimal concentrations to elicit a direct or indirect (e. g. through cell killing) growth stimulus.

Epidemiology is not sensitive enough to enlighten such risks at low doses or the effect of occupational exposure in a lifetime. Highly standardized test systems were developed in experimental research to control any possible variable and unknown confounder. These systems are successful in the prediction of effects from high single agent exposure but differs from the real life situation of complex and changing human environments.

4. CONCLUSIONS AND OUTLOOK

Health effects from exposures to ionizing radiation are in general the result of complex multi-step reaction chains involving changes and responses on the level of molecules, cells, tissues and organisms. Many of these steps are embedded in a web of interactions with other exogenous and endogenous factors. Therefore, any risk assessment will have to consider the question whether combined effects, i e. interactions between two or more agents will influence the health outcome from specific exposure situations. The potential of combined effects increases the uncertainties in estimates of risk for populations from low exposures to single agents.

The most important parameters for the assessment of risks from combined exposures include an in-depth knowledge of the primary actions involved like quality of interaction, dose, dose rates and time sequences of combined exposures. Important host characteristics are cell types and tissue sites affected, age, sex, genetic traits and predisposition, lifestyle, hormonal conditions and immune status. The time relations between exposures to different agents are also critical parameters.

The risk assessment of combined effects must be based on mechanistic knowledge of single agents. This requires further improvement in the understanding of single agent effects on molecules, cells, organisms and especially on dose response.

Mechanistically based classifications of interactions into groups may be helpful to predict health effects from complex exposure situations and is to be promoted. The development of such comprehensive approaches for the study and quantitative assessment of combined effects will also help to fill the gap between differing conceptual approaches in chemical toxicology and radioprotection and to force multi-disciplinary research on this field.

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Radium contamination of the Laak river banks as a consequence of phosphate industry in Belgium

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Abstract. For over half a century, phosphate ores of marine origin, containing ^{226}Ra have been processed in Belgium, to produce calcium phosphate for use in cattle food. As a result, the wastewaters contained ^{226}Ra, which was discharged into two little rivers, one of which is the Laak. The purpose of this study was to chart the radium contamination of the river banks, and of some areas that are regularly flooded by the river. It was seen that enhanced concentrations of ^{226}Ra do occur along the river banks, but that the contaminated area is mostly confined to a 10 m strip on both sides of the river, even in the flooding zones. At present, no dwellings are present on top of the contamination, and no crops for direct human consumption are grown there, so there is no immediate threat to the population.

1. INTRODUCTION

The phosphate industry uses the wet acid process [1] as the main production method for phosphoric acid. There are two main variants: the most widely used is based on acidulation with sulphuric acid, the other one makes use of hydrochloric acid. In the first case, $CaSO_4xH_2O$ is produced as a by-product, which can be transformed into gypsum if so desired. In the plant under consideration however, for over half a century, HCl is used, to process ore of Moroccan origin, containing about 1500 Bq/kg of ^{226}Ra. Here the reaction products are quite different. The main by-products are CaF_2 and $CaCl_2$. The first is insoluble in water and precipitates in the sludge, the second remains in solution in the effluents. This means that $^{226}RaF_2$ precipitates in the sludge whereas $^{226}RaCl_2$ remains in solution and is discharged into the surface waters, unless special decontamination measures are taken at the end of the process.

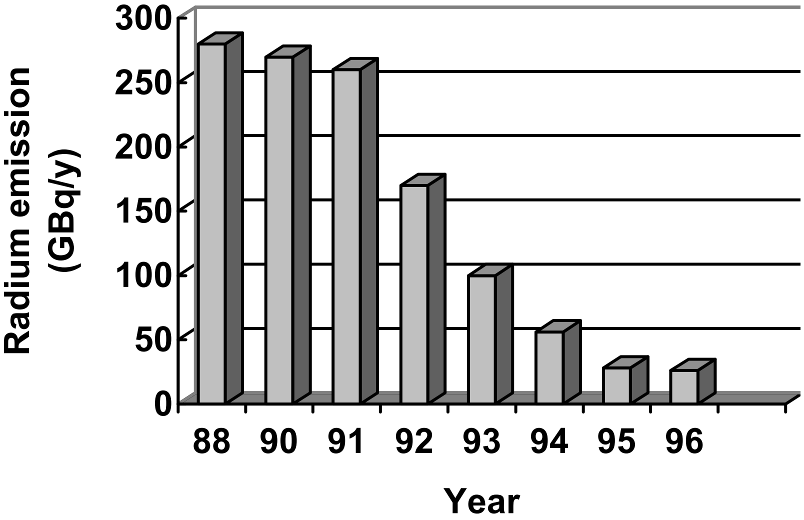

Fig.1. The yearly emissions of ^{226}Ra from 1988 until 1996. In 1991 the decontamination stage was put in operation.

Only since 1991, a decontamination stage, based on dissolved barium salts, was put in operation, decreasing the ^{226}Ra contents of the effluents from a previous 20 Bq/l down to about 3 Bq/l. In Fig.1, the yearly ^{226}Ra emission is shown for the period 1988–1996. This radium is diluted in the surface waters and can be transported over large distances. Besides radium, the effluents also contain other heavy metals, originating from the raw ore, and high concentrations of salts. There are two plant discharges of waste waters, into the Laak, separated about 3 km between them, with the most upstream one about 20 km from the river mouth.

2. GEOGRAPHIC CONSIDERATIONS

The Laak (more precisely Grote Laak) is a small river, situated in the Belgian plane, in an area characterised by a sandy soil. The fall between the sources of the pollution and the river mouth is only about 15 m for a total length of 20 km. Hence, the water flows very slowly, and follows a very meandering path, where it is left to its natural trajectory. However, for a large part of its course, it has been artificially straightened. The average flow rate is 1.2 m^3s^{-1} with seasonal variations between 0.8 and 2.3 m^3s^{-1}. Between 1989 and 1998, the average total waste flow rate diminished gradually from 0.28 to 0.14 m^3s^{-1}. At about ten year intervals, the river was dredged, and the sludge was simply deposited on the river banks. Along the banks of the river, in the vicinity of the river mouth, a few flooding zones occur, typically stretching out between a few tens up to several hundreds of meters perpendicular to the river, covering a total area of about 1.4 km². These zones are flooded in case of persistent heavy rainfall, which on average can happen a few times a year. Although Belgium is one of Europe's most densely populated countries, and the Laak flows through a densely populated area, hardly any dwellings occur within a distance of about 50 m of the river. Fig.2 shows an image of the Laak and the flooding zones, on a section of a map of the Belgian national geographic institute.

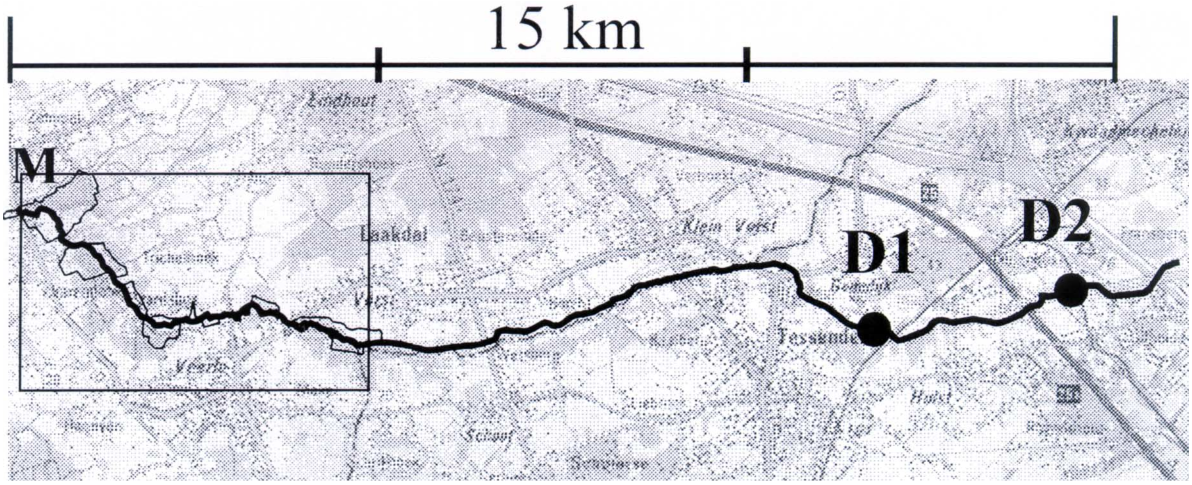

Fig.2. The fat black line represents the Laak. D1 and D2 are the two plant discharges, M is the river mouth, all flooding zones are situated within the rectangle and are indicated in thinner black lines.

3. SCOPE AND METHODS

The main idea was to chart the ^{226}Ra contamination of the river banks as a result of plant discharges and dredging works. Therefore measurements were done from about one km upstream of the highest discharge, down to the river mouth. Every 50 m, on both river banks, sections perpendicular to the river were measured, taking one value at a distance of 1 m of the water, and subsequently a series of values every to 2 m moving away from the river until background levels were reached or until obstacles prohibited further progression. The flooding zones were measured, moving away from the river, until only background was measured, taking as much values as needed to effectively chart the contamination of the whole zone. Measurements were done at about 10 to 20 cm above the ground, close to the vegetation. The measured quantities were surface dose rates, taken with portable plastic scintillators, type Automess 6150 AD6, with a measuring range between 50 and 99000 $nSv.h^{-1}$. It was also the intention to test for correlation between contamination with ^{226}Ra and with other heavy metals. Therefore 150 soil samples were taken unevenly distributed over both river banks, where emphasis was put on finding samples that were as radioactive as possible, but collecting at least 2 samples on each river bank per km. The samples were taken at the surface. Half of these samples were analysed for ^{226}Ra contents through gamma spectroscopy, all of them will be chemically analysed for other contaminants, to see if useful correlations can be found, linking the now available ^{226}Ra data to other contaminants. Due to the nature of the terrain, and the sometimes very dense vegetation, the measuring campaign was carried out on foot, and it took 10 workdays with teams of three persons on each side of the river.

4. RESULTS

Fig 3. shows 2.5 km of the Laak, from the river mouth upwards. It can be taken as representative for the whole river. We can see that the contamination is largely confined to a narrow zone of about 10 m on both sides of the river indicating that it is primarily due to dredging of the river, and deposition of the sludge on the river banks. Generally speaking, the right river banks are more contaminated than the left river banks. The contaminated area is larger and higher dose rates are found. This is due to the nature of the terrain, making deposition of sludge much easier on the right bank. Between 0.5 km and 1.0 km very little contamination on the right bank occurs, and this coincides with slightly higher contamination levels on the left bank, reconfirming the dredging as main cause of contamination. Fig. 4. shows a typical example of a flooding zone, consisting of pastures that quite regularly are flooded to the extent indicated by thin curved line. Here also it can be seen that contamination stays confined to a narrow zone of about 25 m perpendicular to the Laak. Overall, the maximum dose rates are of the order of 20 to 40 times the background level. Fig 5. shows the maximum dose rates, found for both left and right banks of the Laak, along all of its length. The most contaminated zones can be found at distances between 12 and 17 km downstream from the plant discharges. This might be due to the fact that the river here follows a very meandering path, whereas more upstream it is more artificially straightened. The analysis of the soil samples yielded average values of 2800 Bq/kg and 3800 Bq/kg ^{226}Ra activity with a standard deviation of 1800 Bq/kg for both values. This is several orders of magnitude more than the 13 Bq/kg we would normally expect in this region [2]. Of course, they are not the average ^{226}Ra activities for the Laak river banks, since the samples were all taken in local maxima. For each soil sample, the dose rates at the sampling spot increased after retrieving the sample. This is not surprising since the contamination has been building up for over half a century, and the top layer is not necessarily the most contaminated one. Taking depth profiles might be useful to get a better estimate of the total amount of contaminated soil present.

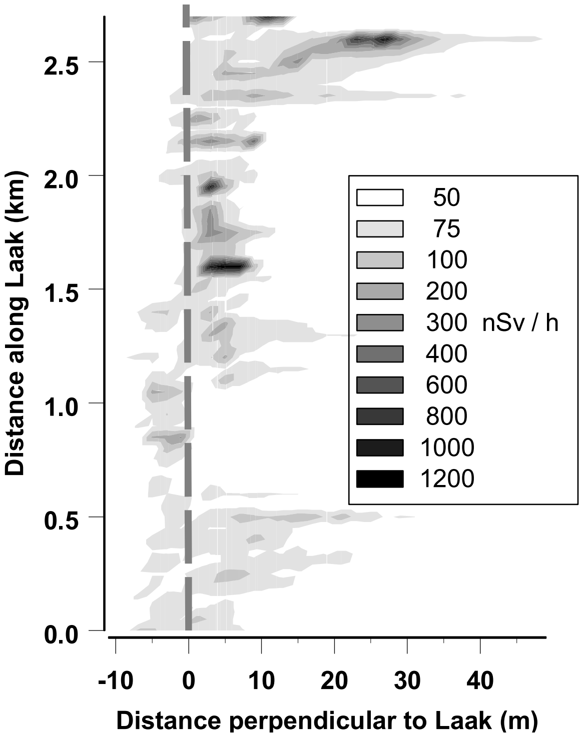

Fig.3. Representation of a 2.5 km long section of the Laak, with the dose rates due to ^{226}*Ra contamination. The Laak is represented as a straight dashed vertical line, for clarity. Background levels in this region, are typically between 50 and 100 nSv* h^{-1}*.*

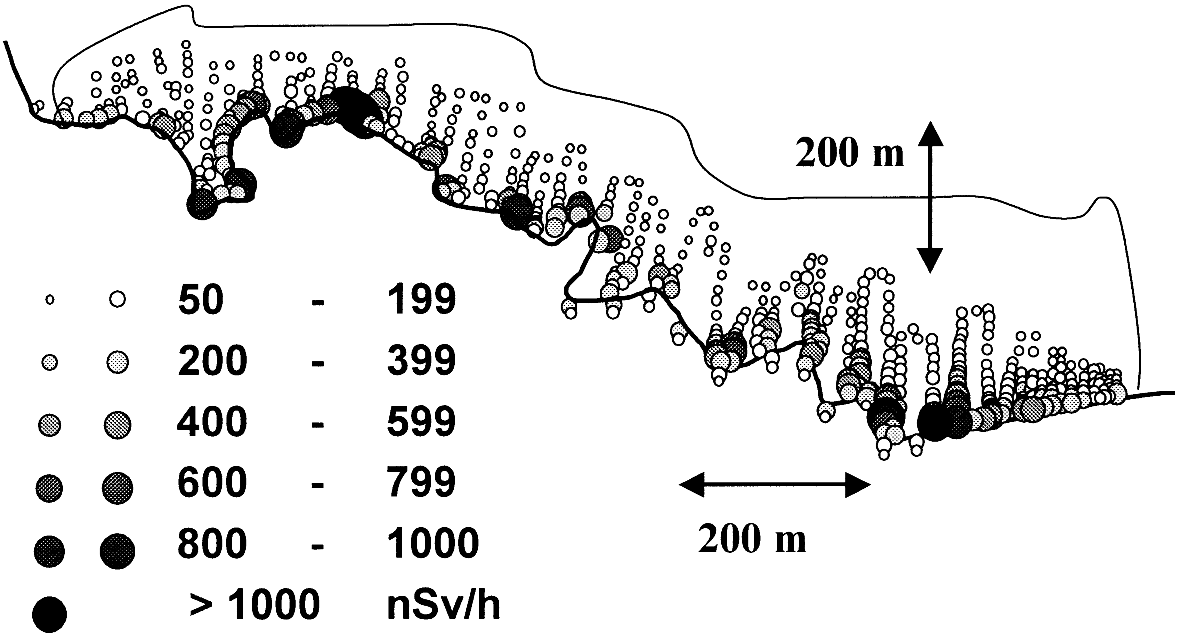

Fig.4. Bubble plot of the contamination of a typical flooding zone, which consists of pastures, regularly flooded up to the marked boundary. The contamination stays confined within about 25 m of the river banks. Further only near background levels are found.

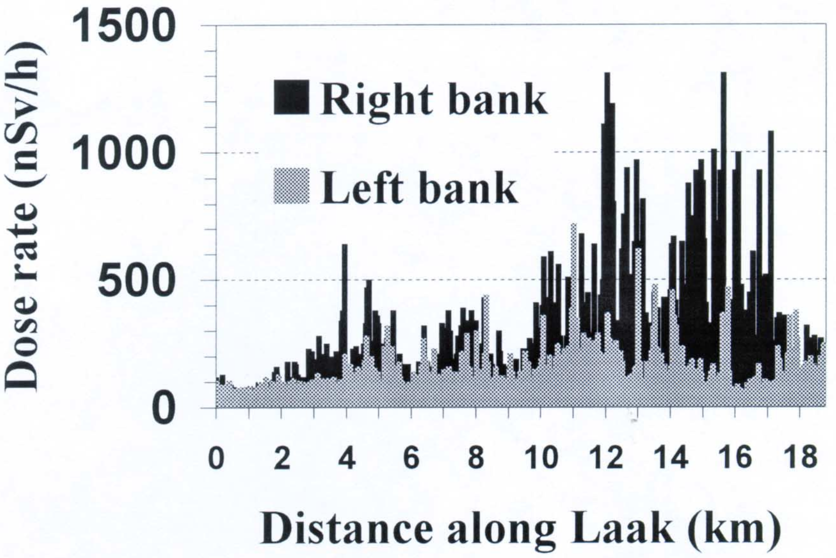

Fig. 5. Maximum dose rates measured along the Laak, on both banks, from the contamination source to the river mouth. The background in this area varies between 50 and 100 nSv h^{-1}.

5. DISCUSSION

About 12 hectares ($12x10^4$ m²) of terrain is contaminated with ^{226}Ra yielding dose rates above 150 nSv/h, 3 hectares on the left and 9 hectares on the right river bank. These areas are all freely accessible to the public. However, there are no dwellings built directly on these terrains, so nobody actually lives on top of the contaminated land. No long residence times of persons occur in these areas, so that only insignificant doses through external gamma radiation are to be expected. Enhanced ^{226}Ra concentrations can lead to an increase in radon concentrations. But, in open air, and with a geometry of a long small stroke of land, the radon enhancement will be negligible. No food crops for direct human consumption are grown on the contaminated land. Where the land is used, we find mostly pastures or corn for animal consumption. This extra step in the food chain greatly reduces the possible human intake of the radionuclides. All these factors, make that in the current situation all realistic scenarios lead to doses of only fractions of 1 mSv/y. However caution must be taken in the future. The area must not be used for construction, since a radon buildup inside a dwelling of several hundred Bq/m³ is easily attainable with the present ^{226}Ra concentrations. This combined with external gamma radiation, could easily lead to doses of 5 to 10 mSv/y or more. Also cultivation of crops for direct human consumption should be avoided.

6. CONCLUSION

The contamination with ^{226}Ra is confined to a narrow stroke along the river, even where regular flooding occurs. The main cause of the contamination is periodic dredging and deposition of the sludge on the river banks. In the current situation there is no immediate risk for the health of the population. Conversion of the contaminated zone into a residential area however should be avoided, since this would drastically change this picture.

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Occupational exposure to thorium and niobium bearing particles

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Abstract. The aim of this study is to evaluate the worker's exposure to thorium and niobium bearing particles in a Brazilian plant that processes pandaite. A cascade impactor with six stages was used to collect dust particles with aerodynamic diameter in the range of 0.64 to 19.4 μm. The particles impacted on each stage of the cascade impactor were analyzed by PIXE (Particle Induced X ray Emission) technique, which permits the determination of elemental mass concentration and the MMAD (Mass Median Aerodynamic Diameter). Personal air samplers were used by the workers to collect dust particles in the range of 0.5 to 2.5 μm. The ^{232}Th and ^{228}Th air concentration in these samples were determined by alpha spectrometry technique. Feces and urine samples of the workers were analyzed for determination of thorium and niobium concentrations. The air monitoring indicates that the workers were exposed to airborne particles in the inhalable and respirable fractions of aerosol. The thorium and niobium concentration in feces samples suggests that the main pathway of incorporation of thorium and niobium in this plant is ingestion. The niobium concentration in urine samples from workers indicates that there was a systemic incorporation of niobium.

1. Introduction

There are about 15.000 workers, in Brazil, involved in the mining and milling processes of minerals containing thorium. In order to evaluate the exposure of these workers to niobium (Nb) and thorium (Th) bearing particles it is necessary to characterize the particle in the respirable (particles that are able to enter the deep lung during nose breathing) and inhalable (particles that are able to enter the head) fractions of the aerosol [1].

In the State of Goiás, Brazil, there is a plant where pandaite mineral is processed to obtain a Nb-Fe alloy. The mineral (pandaite) is extracted from two open pit mines by using mechanical process. The flowchart of the process is shown in Figure 1. The concentrate of pandaita is obtained by physical separation process, the concentrate of niobium by chemical leaching and the Fe-Nb alloy is produced by aluminothermic process. The Fe-Nb alloy is then crushed for packing.

2. Experimental procedures

Three visits in different years during the dry season were done in order to evaluate the exposure of the workers to dust particles.

The particle size distributions were determined using a six stage cascade impactor with an operational flow rate of 12 l/min, and cut off diameters of 0.64, 1.0, 2.4, 4.7, 9.9 and 19.4 μm [2]. The cascade impactor was located near the workers at the point of highest total dust concentration and at 1.5 m from the soil. The sampling time at each point was chosen in order to avoid saturation in the stages of the cascade impactor.

The elemental composition of the mass impacted at each stage of the cascade impactor was measured by PIXE (Particle Induced X ray Emission) using a 4.0 MV Van de Graaff accelerator. Further details of the experimental arrangement and the calibration procedures are described in the literature [3,4].

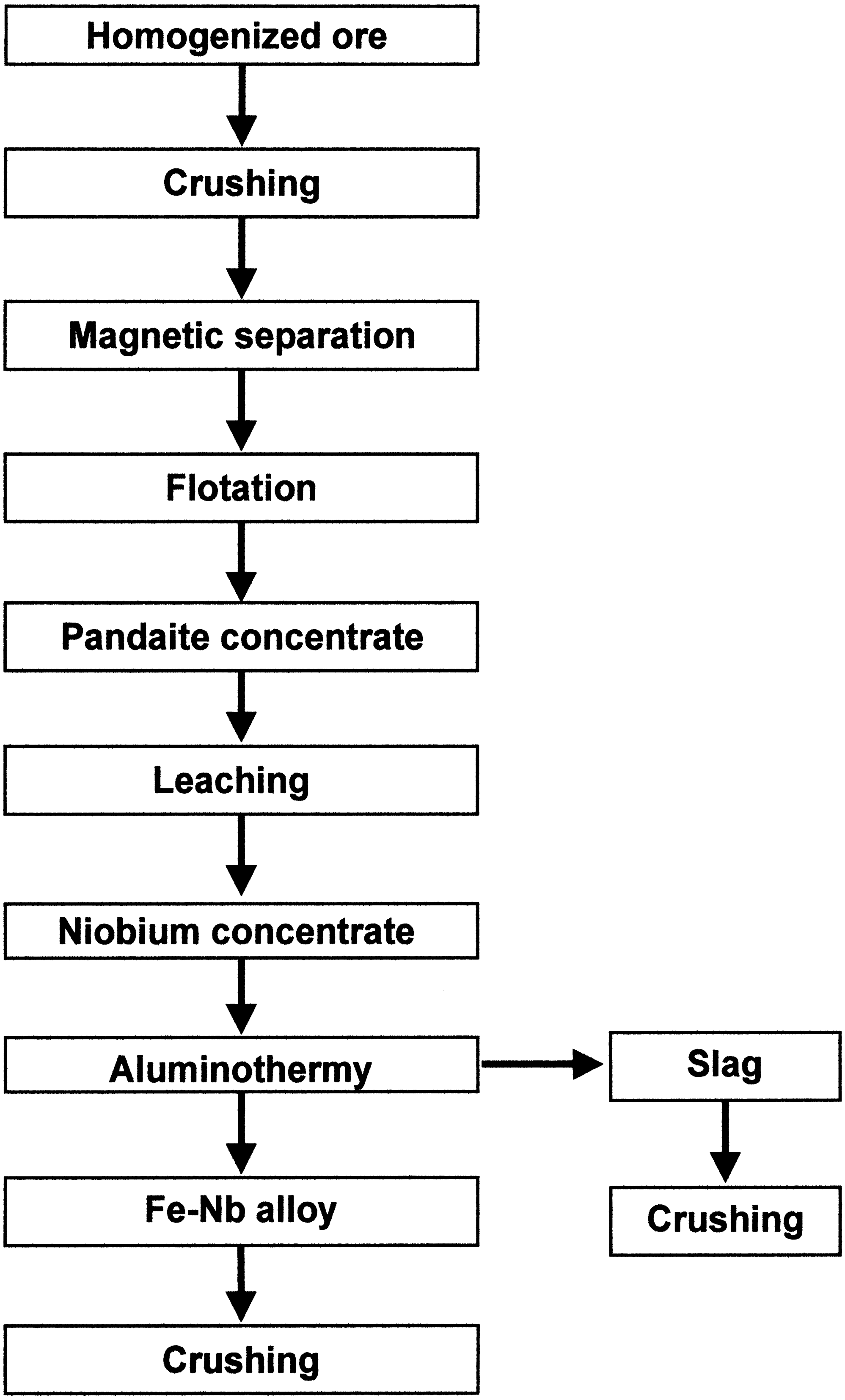

Figure 1. Flowchart of the process to obtain Fe-Nb alloy.

A group of workers were asked to use personal air samplers with a cyclone. These samplers collect particles with aerodynamic diameter smaller than 2.5 μm (respirable fraction of the aerosol). The workers used the air samplers during 8 h (one working day) and were also asked to collect feces and urine samples. During the second and third visits a group of workers` wives were asked to collect feces samples.The ^{232}Th and ^{228}Th activities in these samples were determined, using alpha spectrometry technique [5]. The niobium concentration in feces and urine samples from workers were determined by ICP-MS [6].

3. Results

For the air samples that were collected using the cascade impactor, the elemental mass concentration in the respirable fraction of aerosol and the particle size (Mass Median Aerodynamic Diameter — MMAD) are shown in Table 1 and 2, respectively. The highest niobium and thorium concentrations occurred during the first sampling at the metallurgic processing area (Fe-Nb alloy crushing).

Table 1. Elemental mass concentration in the respirable fraction of the aerosol

Steps	Visit	Mass concentration in the respirable fraction of aerosol ($\mu g.m^{-3}$)	
		Element	
		Th	Nb
Mineral crushing	1	0.56	3.05
	1	0.29	1.66
	1	0.26	1.70
	1	0.18	7.45
	2	1.45	2.79
	2	0.48	1.08
	3	0.01	0.10
Leaching	1	0.50	22.94
	1	0.23	26.00
Aluminothermy	1	3.09	108.44
	1	1.91	112.89
	2	0.57	22.40
	2	0.68	20.83
	3	0.01	24.30
Fe-Nb alloy crushing	1	4.24	445.30
	1	3.04	506.25
	2	0.47	23.57
	3	0.51	44.89
Waste crushing	2	1.49	9.03
	2	1.78	8.56

Table 2. Mass Median Aerodynamic Diameter (MMAD) of thorium and niobium bearing particle and geometric standard deviation (σ_g)
σ_g = Standard geometric deviation

Steps	Visit	Th MMAD (μm)	Th σ_g	Nb MMAD (μm)	Nb σ_g
Mineral crushing	1	1.9	1.9	2.2	1.7
	1	1.9	2.1	2.0	2.1
	1	1.5	2.3	2.5	1.9
	1	1.4	2.2	2.3	1.9
	2	1.6	2.0	1.6	2.1
	2	1.1	2.1	1.3	2.5
	3	1.4	1.4	1.0	1.4
Leaching	1	2.1	2.0	3.3	1.6
	1	1.8	2.1	2.6	1.9
Aluminothermy	1	2.1	2.0	3.4	1.7
	1	2.1	1.9	3.3	1.6
	2	2.3	1.9	3.1	1.6
	2	2.1	2.0	2.9	1.7
	3	1.0	1.4	1.0	1.4
Fe-Nb alloy crushing	1	3.4	1.8	3.5	1.7
	1	2.7	1.9	3.4	1.7
	2	1.8	2.3	1.4	1.7
	3	1.0	1.2	0.8	1.1
Waste crushing	2	2.3	2.0	2.2	2.1
	2	2.4	2.1	2.3	2.0

The MMAD values of particles generated during the mineral crushing show that the particles are in the respirable fraction of aerosol. During the leaching process the thorium bearing particles are generated with MMAD values of about 2.0 μm, but niobium bearing particles are larger than 2.5 μm as shown in Table 2. It is also observed in this table that during the aluminothermic process the particle size increase. The particles containing thorium are in the respirable fraction of aerosol, however the niobium bearing particles are in the inhalable fraction. This is due to the agglomeration of the particles caused by the high temperature, humidity of the air and the high concentration of particles during the aluminothermic process. The Fe-Nb alloy is crushed in different sizes. The variation observed in the particle sizes during the Fe-Nb alloy crushing is probably due to the differences in the crushing process. The particles were in the inhalable and in the respirable fractions of aerosol during the first and second visits, respectively. The σ_g value larger than 1.2 suggests that the particle size distribution is polimodal and it is not possible to identify each one of the modes. However during the third visit, at the aluminothermic process the particle size showed a bimodal distribution and only one mode was considered for MMAD determination.

Table 3. ^{232}Th and ^{228}Th concentrations in respirable fraction, average inhalation rate and concentrations in feces samples from workers

Steps	Worker	Air samples: Concentration in the respirable fraction (mBq.m^{-3})		Air samples: Rate ^{228}Th/^{232}Th	Average activity inhalation rate (mBq.d^{-1})		Feces samples: Concentration (mBq.d^{-1})		Feces samples: Rate ^{228}Th/^{232}Th
		^{232}Th	^{228}Th		^{232}Th	^{228}Th	^{232}Th	^{228}Th	
Open pit mine	W01	<DL*	<DL*	-	<DL*	<DL*	4.7	11.3	2.4
	W02	2.5	3.3	1.3	24.0	31.7	44.9	114.0	2.5
	W03	<DL*	<DL*	-	<DL*	<DL*	27.4	103.1	3.8
	W04	<DL*	<DL*	-	<DL*	<DL*	48.2	244.4	5.1
Mineral crushing	W05	7.0	7.9	1.1	67.2	75.8	13.1	85.7	6.5
Leaching	W06	<DL*	<DL*	-	<DL*	<DL*	38.4	299.9	7.8
Aluminothermy	W09	<DL*	<DL*	-	<DL*	<DL*	20.6	86.6	4.2
Fe-Nb alloy crushing	W07	<DL*	<DL*	-	<DL*	<DL*	6.2	186.9	30.1
	W10	3.0	3.1	1.0	28.8	29.8	25.8	176.7	6.9

Table 4. ^{232}Th and ^{228}Th concentrations in feces samples from workers and their wives

Concentration (mBq/d^{-1}): Workers				Wives			
Sample	^{232}Th	^{228}Th	Rate ^{228}Th/^{232}Th	Sample	^{232}Th	^{228}Th	Rate ^{228}Th/^{232}Th
W04	48.2	244.4	5.1	S01	5.2	67.1	12.8
W06	38.4	299.9	7.8	S02	6.9	112.9	16.4
W07	6.2	186.9	30.1	S03	2.4	117.5	49.2
W09	20.6	86.6	4.2	S04	9.5	200.9	21.3

The variations in the thorium and niobium mass concentrations and in the values of MMAD for the same sampling location are probably due to differences in the composition of the minerals that were processed when the sampling was done.

The ^{232}Th and ^{228}Th concentrations in the respirable fraction (samples collected by personal air samplers), the calculated amount of ^{232}Th and ^{228}Th inhaled by a worker during one day of work and the ^{232}Th and ^{228}Th concentrations in the feces samples of the workers are shown in Table 3. The inhalation of ^{232}Th and ^{228}Th during a working day (8 h) was determined considering the ventilation rate of the reference man adopted by ICRP in the publication number 66 (20 L.min^{-1}) [7]. The worker involved in the mineral crushing process had the highest calculated uptake of ^{232}Th and ^{228}Th. However the measured ^{232}Th and ^{228}Th concentrations in feces of this worker were not the highest. The ^{232}Th and ^{228}Th concentration in feces of these workers (Table 3) show that there is no correlation between the variables thorium air concentration and the thorium concentration in feces ($p>0.05$).

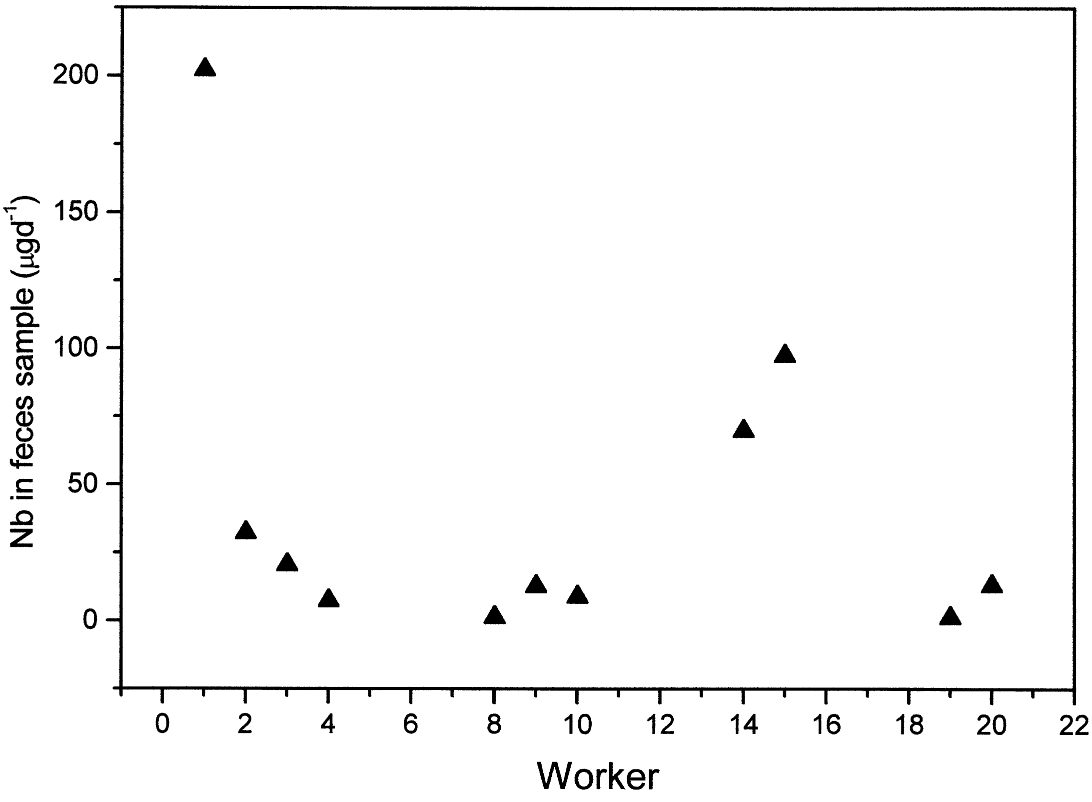

Figure 2. Niobium concentration in feces samples from workers.

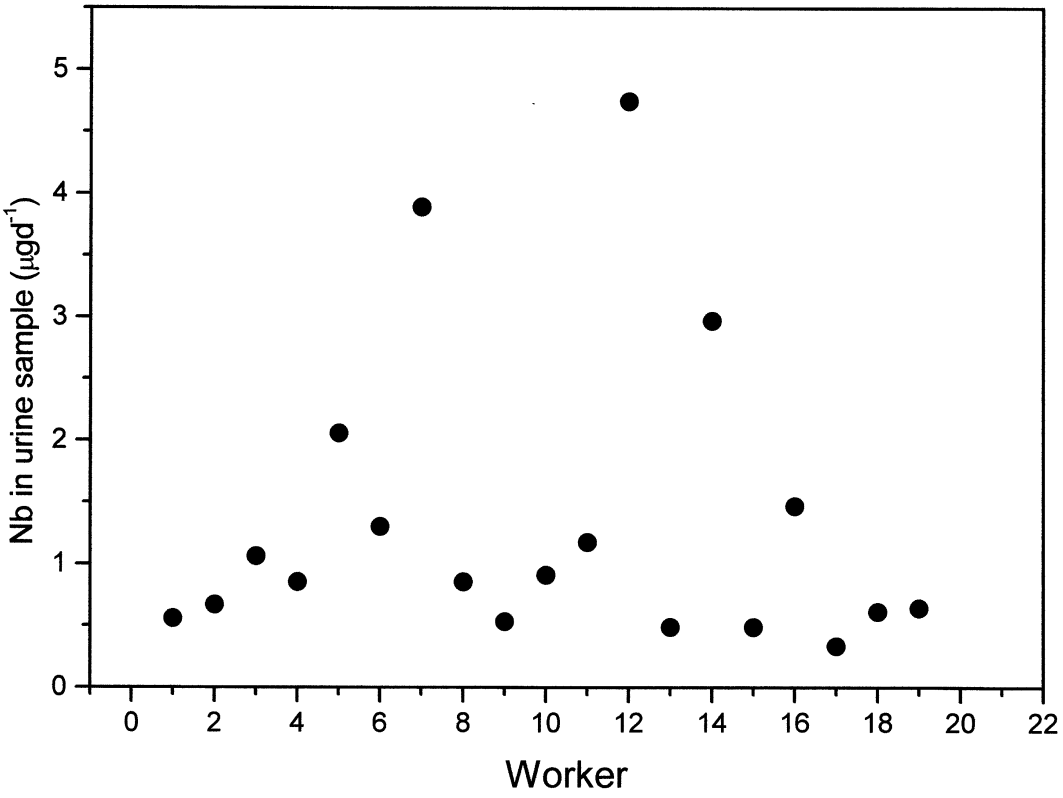

Figure 3. Niobium concentration in urine samples from workers.

In Table 4 the ^{232}Th and ^{228}Th concentrations in feces samples of a group of workers and their wives are shown. The ^{232}Th and ^{228}Th concentrations in feces samples of the workers` wives are lower than the ^{232}Th and ^{228}Th concentrations in feces samples from workers. In a previous study at this plant [8] the ^{232}Th and ^{228}Th concentrations in feces of these workers were measured in samples collected before and after 30 days vacation, prior to their return to work. After vacation, the ^{232}Th concentrations in the feces of the workers varied from the detection limit up to 11,7 mBq.d^{-1} and the ^{228}Th concentrations were in the range of 1.8 to 63.4 mBq.d^{-1}. The ^{232}Th concentrations in feces samples from wives (Table 4) are in the same range of the ^{232}Th concentration in feces from the workers in samples collected after vacation.

The rate between ^{228}Th and ^{232}Th concentrations in air samples (Table 3) are about 1 indicating radiological equilibrium between these radionuclides. However in the feces samples of the workers and of their wives the rate between ^{228}Th and ^{232}Th are larger than 1 indicating a lack of radiological equilibrium. These results indicate that ingestion of food might be another pathway of thorium ingestion, since the lack of radiological equilibrium was also observed in food [9].

The niobium concentration in feces and urine samples from workers are shown in Figures 2 and 3, respectively. For workers the mean Nb concentration in feces was 42.36 ± 39.6 μgd^{-1} and in urine it was 1.34 ± 0.45 μgd^{-1}. The workers of a nickel mine were not exposed to Nb bearing particles and was considered as control group. The mean niobium concentration in feces and urine samples from control group were 3.36 ± 3.2 μgd^{-1} and 0.60 ± 0.45 μgd^{-1}, respectively. By using a parametric test (Stundent type *t*) the mean niobium concentration in feces and urine samples from both groups (workers and control group) were compared [10, 11]. The results showed that the niobium concentration in feces and urine samples from workers are different from the niobium concentration in samples from the control group ($p>0.05$). The niobium concentration in feces samples from workers suggests that the worker inhale coarse particles and he ingests mineral dust particles probably as he touches his mouth with dirty hands. The niobium concentration urine samples indicates that there was a systemic incorporation.

The results of air samples and of feces and urine samples from workers show that inhalation of Th and Nb bearing particles in the respirable fraction of aerosol, inhalation and ingestion of coarse particles containing Th and Nb should be considered as a source of worker exposure.

4. Conclusions

The results of the monitoring programs for evaluating exposure of the workers to dust particles generated during the process to obtain Fe-Nb alloy have shown the availability of thorium and niobium bearing particles in the respirable fraction of aerosol. These results indicate that aerosol characteristics did not change during the period of monitoring program.

Although the workers were exposed to dust particles in the respirable fraction of aerosol, the bioassay results have shown that there is no correlation between ^{228}Th and ^{232}Th concentrations in the respirable fraction and the concentration of these radionuclides in feces, when feces samples were taken during the working week. The bioassay results have also shown significantly higher thorium concentrations in the fecal excreta of the workers compared to the concentration in the respirable fraction of aerosol. The worker is probably ingesting Th, as he touch his mouth with dirty hands or utensils.

This study indicates that the aerosol characteristics did not change during the period of monitoring. The workers are exposed to thorium and niobium bearing particles in the respirable fraction of aerosol, however inhalation and ingestion of coarse particles containing Th and Nb should be considered as a source of worker exposure. The main pathway of incorporation of thorium and niobium in this mine is probably ingestion, although the effective dose is probably due to inhalation. The niobium concentration in urine samples showed that there is a systemic incorporation. This study suggest that a monitoring program for evaluating workers exposure to thorium and niobium airborne particles is necessary and it has to be carefully designed.

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Nuclide migration and the environmental radiochemistry of Florida phosphogypsum

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Abstract. Phosphogypsum, a waste by-product derived from the wet process production of phosphoric acid, represents one of the most serious problems facing the phosphate industry today. This by-product gypsum precipitates during the reaction of sulfuric acid with phosphate rock and is stored at a rate of about 40 million tons per year on several stacks in central and northern Florida. The main problem associated with this material concerns the relatively high levels of natural uranium-series radionuclides and other impurities which could impact the environment and which makes its commercial use impossible. We have studied the potential release of radionuclides from phosphogypsum by: (i) analysis of stack fluids, groundwaters, and soils associated with gypsum stacks; and (ii) geochemical modeling via MINTEQA2. Stack fluids were observed to be very high in dissolved uranium and ^{210}Pb with only moderate concentrations of ^{226}Ra. Underlying soils tend to be enriched in U and ^{210}Pb indicating precipitation when acidic stack fluids enter a buffered environment. Modeling results showed significant increases in radionuclide complexes with sulfate and phosphate, resulting in relatively mobile uncharged or negatively charged solution species within the stacks. On the other hand, precipitation of multicomponent solids would be expected with increasing pH below the stack. Our evidence thus suggests that while phosphogypsum stacks do contain significant quantities of dissolved radionuclides, removal mechanisms appear to prevent large scale migration of radionuclides to the underlying aquifer.

1. INTRODUCTION

Phosphogypsum, a waste by-product derived from the wet process production of phosphoric acid, represents one of the most serious problems facing the phosphate industry today. This by-product gypsum precipitates during the reaction of sulfuric acid with phosphate rock and is stored at a rate of about 40 million tons per year on several stacks in central and northern Florida. The main problem associated with this material concerns the relatively high levels of natural uranium-series radionuclides and other impurities which could impact the environment and which currently makes its commercial use impossible.

One of the prime concerns often expressed about phosphogypsum storage is the potential for contamination of fresh water aquifers underlying the stacks [1–4]. Data from previous studies have shown that there is often influence from the gypsum stacks for some chemical parameters. The data for radionuclides is less clear. Past studies have usually relied on monitor wells which are historically situated more on a regulatory rather than a scientific basis, i.e., wells are often placed on the property lines rather than where they would provide the best information. In addition, since most gypsum stacks are located on mineralized land, there are likely going to be elevated levels of some radionuclides (as ^{226}Ra) associated with the natural uranium-enriched phosphate rock. Thus, the finding of elevated levels of radionuclides in a monitor well near a gypsum stack does not necessarily imply contamination.

Because of these problems in interpretation, we specifically designed this study to address the question of whether or not a gypsum stack contributes significant amounts of radionuclides to the underlying aquifer. We focused on one inactive stack at Piney Point Phosphates, Inc. in Florida and established monitor wells both around and directly into the stack. Cores of phosphogypsum were also obtained through the entire stack. We thus had the opportunity to investigate migration of radionuclides by looking at both fluid and solid phase components.

2. STUDY SITE, MATERIALS, AND METHODS

The research reported here expands the work of Miller and Sutcliffe [5] at the same site — the Piney Point Phosphates facility (formerly AMAX) near Palmetto, Florida (south of Tampa). The pre-existing monitor wells at Piney Point, drilled mainly in 1979 and 1980 for the studies of Miller and Sutcliffe, have 5.0 foot long screens. Seventeen new monitor wells were drilled into the surficial aquifer around the gypsum stack and eleven wells were drilled directly into the older phosphogypsum stack at Piney Point (**Fig. 1**). All new monitor wells were constructed with filter screens (0.010 inch slotted liner) in the deepest 10.0 feet of the total depth of the well. Screens were packed in 20–30 mesh sand with an approximately 1.5 ft bentonite hole plug overlying the sand pack. The 4-inch diameter risers were grouted to the surface with a bentonite-cement mixed grout compound.

Two continuous cores of phosphogypsum were recovered at sites PP1-1 (March 1995) and PP2-0 (March 1996). The PP2-0 well in the stack had a 5.0 foot screen set at a well depth of 66.8–71.8 feet (top of the screen is 3.3 feet beneath the base of the stack) and is completely within the surficial aquifer with no direct connection to the stack. That well has a 6–7 foot thick bentonite plug over the sand pack.

2.1. Sample collection

All monitor wells were pumped using a submersible pump system for a period adequate to replace at least three well volumes and reach stable in situ measurements of pH, electrical conductivity, and temperature prior to collecting samples. Samples for radiochemical analyses were collected first followed by the chemical compositional samples. Liquid samples (3 liters for analysis of dissolved ^{238}U, ^{226}Ra, ^{210}Pb, and ^{210}Po) were filtered using a 0.45 μm filter, acidified with ultrapure HNO_3 to a pH <1, and appropriate isotopic spikes and carrier solutions added in the field immediately after collection. Separate samples for ^{222}Rn were collected in triplicate by drawing 10-mL aliquots with a syringe and placing each directly into 20-mL glass liquid scintillation vials with premeasured cocktail. Filtered and unfiltered non-acidified aliquots of well solutions were also collected for analyses of anions and cations, laboratory pH, and other parameters.

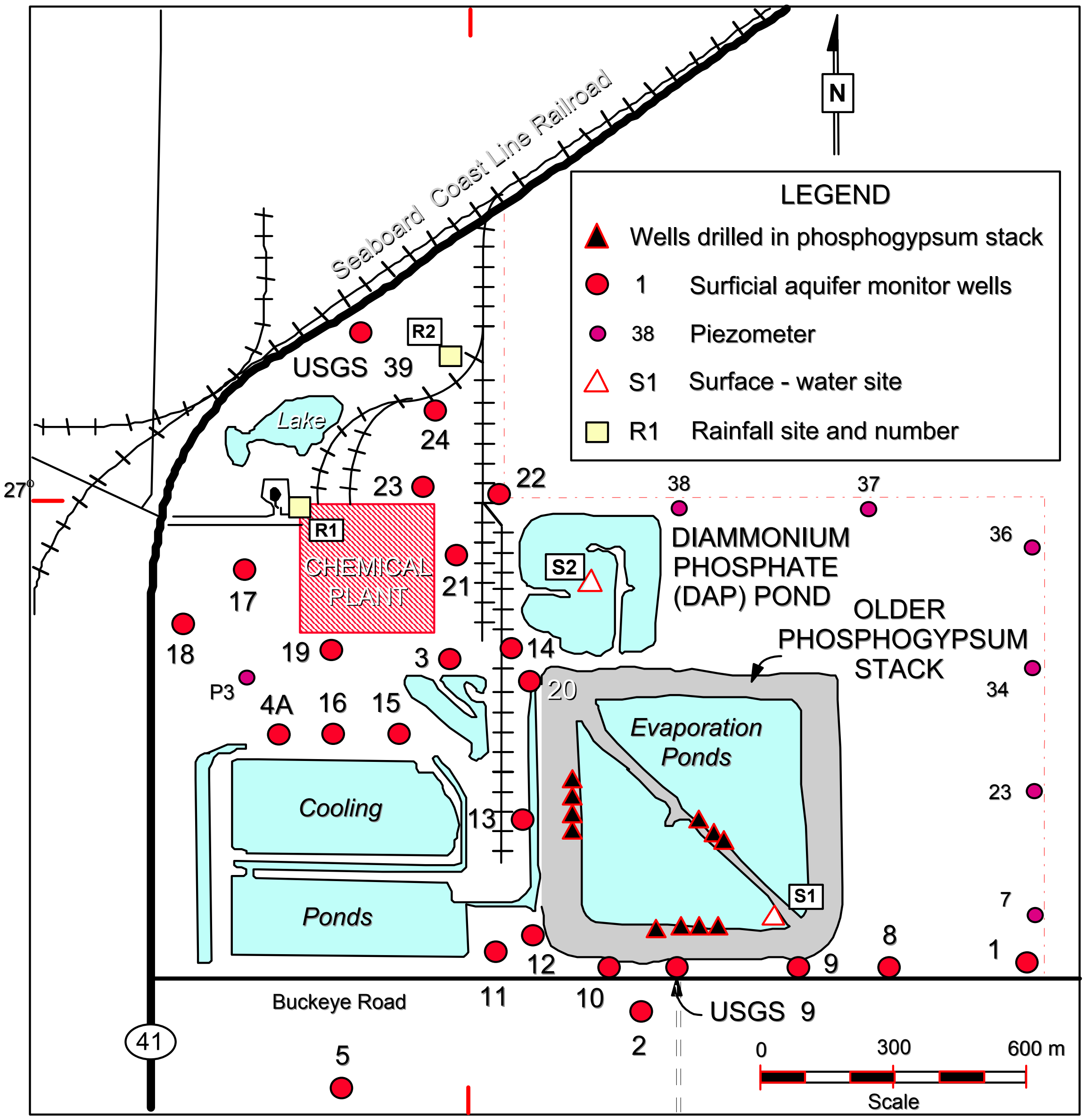

Figure 1. Map of the Piney Point Phosphates site showing the locations of surficial aquifer monitor wells, piezometers, wells drilled into the older phosphogypsum stack, and surface sampling locations.

2.2. Radioanalytical techniques

Fluid samples. With a few exceptions, stack and monitor well samples were analyzed for radionuclides by methods described in Burnett et al. [6]. U isotopes were analyzed by a combination of alpha spectrometry and PERALS spectrometry. Ra-226 was determined by radon emanation following the procedures adapted from Key et al. [7] and Mathieu et al. [8]. Po-210 activities were determined by spontaneous deposition onto pure Ag plates following by low level alpha-particle spectrometry. A calibrated ^{209}Po solution was used as an isotopic tracer for the ^{210}Po measurements [9]. Polonium in Florida groundwater and its possible relationship to the sulfur cycle and bacteria. Geochim. Cosmochim. Acta 53: 143–150.. Pb-210 was scavenged using a known amount of a stable Pb carrier, precipitated as a sulfate, filtered, weighed, and counted on a low level gas flow proportional counter. Rn-222 was assayed by standard liquid scintillation counting techniques. The short lived radionuclides (^{222}Rn and ^{210}Po) have been corrected for ingrowth and/or decay to the time of sampling.

Chemical analyses. Analyses of selected cations, anions, complex anions, laboratory pH, and F^- were performed using inductively coupled plasma spectrometry, turbidimetric, ion-specific electrode, atomic absorption spectrometry, colorimetric, and temperature-correcting pH probe techniques. All of these analyses were performed by Western Analysis, Inc. (Salt Lake City, Utah).

Phosphogypsum analyses. Since water exists in the crystalline lattice of both dihydrate (DH) and hemihydrate (HH) forms of phosphogypsum and there exists a potential difference of about 15.7% between the formula weights of the two crystal forms, it is important not to use high temperatures when drying these types of samples. All phosphogypsum samples for this study were thus prepared by drying the sample under atmospheric conditions until moisture was sufficiently reduced to allow a preliminary grinding of 400–600 grams of sample to a grain size of less than 500 μm (30 mesh). After drying to constant mass in a vacuum desiccator at room temperature, samples were ground to a grain size of less than 250 μm (60 mesh), split with a powder sample splitter, and stored in sealed containers.

We used a closed-end coaxial intrinsic germanium (IG) detector to determine activities of ^{238}U, ^{226}Ra, and ^{210}Pb in phosphogypsum samples. Samples and standards for measurement on the coaxial IG detector were thoroughly homogenized prior to packing the sample powders in 100 cm^3 aluminum cans that were then sealed with an aluminum lid lined with a gas impermeable compound. The detector was calibrated using natural matrix soil, sediment, and rock standards having radionuclide activities certified by the National Institute of Standards and Technology (NIST) and the International Atomic Energy Agency (IAEA).

The ^{226}Ra activities were determined by taking the mean activity of three separate photopeaks of the daughter nuclides ^{214}Pb at 295.2 keV and 351.9 keV, and ^{214}Bi at 609.3 keV. Because phosphogypsum does not retain ^{222}Rn well, it was necessary to wait for about three weeks after sealing the aluminum sample cans to ensure that ^{222}Rn had reached equilibrium with ^{226}Ra before counting [6]. Self-absorption corrections for the low-energy ^{210}Pb and ^{234}Th photopeaks were calculated using an approach modified from that suggested by Cutshall et al. [10]. A mixed, sealed transmission source was produced so photon transmission measurements for ^{210}Pb and ^{234}Th could be quickly and simultaneously measured through individual samples and directly related to a relative absorption factor over a broad range of density [11].

2.3. Modeling techniques

Geochemical equilibrium speciation and precipitation modeling. All geochemical modeling was accomplished with MINTEQA2, Version 3.11 (December 1991), available from the US Environmental Protection Agency, Office of Research and Development, College Station Road, Athens, GA 30613-0801 (phone: 706-546-3549). The program runs on PC computers in the DOS mode (any processor or speed).

This popular equilibrium speciation model has a thermodynamic database that is easily modified. In fact, the thermodynamic database used in this investigation has been updated over several years to include more species of radionuclides (a copy of this database is available from A. Elzerman by request). However, these modifications would have affected only a few of the results reported here.

In all cases the pH was set as a fixed parameter. Although the program is capable of estimating resultant pH, known field data were available and were used for the solutions.

Temperature was fixed at 25° C. Although temperature is a factor in equilibrium speciation, the deviations present from 25° C would not make a significant difference. The model was allowed to calculate ionic strength. Cation/anion ratios were usually within the range 0.9 to 1.1, except in those cases where a component was deliberately removed, consistent with (while not proving) accurate data for the major anions and cations. Since all solutions came from systems considered to be oxidizing, pe was not allowed to be a variable in the model calculations. All oversaturated solids were allowed to precipitate, but adsorption was not allowed. The carbonate concentration was input as total carbonate, not as alkalinity. A closed system was assumed for the groundwaters, and carbon dioxide excluded. This approach was considered most appropriate for the groundwater samples since they are isolated from the atmosphere and analytical values for HCO_3^- were reported. The number of allowed iterations was set at 200, since in some cases 40 was not sufficient.

Selection of model solutions for calculations. Evaluation of the data quickly indicated the samples had fairly uniform characteristics within two distinct groups, those which had been significantly influenced by input of stack solutions versus those which had not. Also, there was no significant variation, for purposes of geochemical modeling, in results from one sampling day to the next. Consequently, rather than produce numerous outputs for each sample varying only a little from each other, it was decided it would be more instructive to define an "uncontaminated" and a "contaminated" model solution to use in the geochemical modeling. Some MINTEQA2 runs were also made for solutions containing only the major components and for solutions with the dissolved silica removed to test the sensitivity of the outputs to these factors.

3. RESULTS AND DISCUSSION

3.1. Chemical characteristics of fluids

A summary of the major cation and anion results, presented as a mean and standard deviation of the stack fluids and the shallow aquifer waters, is given in **Table 1**. In general, the stack solutions are high in Na, K, Ca, Mg, Al, Si, Sr, Mn, NH_4, Cl, F, SO_4, and PO_4 in comparison to the monitor well samples. Both the stack and the monitor wells have comparable amounts of Fe and very low Ba in all wells. Only the monitor wells, with pH values above 6.0, have detectable HCO_3^-.

It is clear from these data that one cannot produce the composition of these fluids by simple mechanical mixing between the stack fluids and the shallow aquifer. Note that while the TDS and several major components (e.g., Na^+, Ca^{2+}, NH^{4+}, and SO_4^{2-}) range between 3–6 times more concentrated in the stack solutions, other components (e.g., SiO_2, PO_4^{3-}, and F^-) are many more times enriched in the stack solutions. Fluoride, for example, is almost 1900 times more enriched in the average stack solution than in the aquifer. The extreme range in the stack/aquifer ratios indicates that a considerable amount of non-conservative behavior (precipitation, adsorption, etc.) must be occurring in the stack in addition to mixing of the stack solutions with underlying groundwaters.

An interesting aspect of the chemical results concerns the apparently strong interdependence of phosphate, fluoride, and silica in the stack solutions (**Fig. 2**). We did not observe any obvious trends in these parameters in the monitor well samples. At least some of the control on PO_4^{3-} and F^- is probably associated with the main mineral phase of the phosphate ore, carbonate fluorapatite [$Ca_5(PO_4,CO_3)_3(F,OH)_2$], which may reprecipitate under these conditions. We suspect that the relationship of F^- to SiO_2 is related to control by the solid phase known in the phosphate industry as "alkali fluorsilicates." This material, often seen growing as large crystals in seeps of discharge fluids on the stacks and known to clog filter screens in the chemical plants, is actually an alkali silica hexafluoride, $(Na,K)_2SiF_6$, since it has no structural oxygen. Note that the mole ratio of F:Si from our regression is about 5.1:1, close to the theoretical ratio of 6.0. It is also possible that some F- may be associated with pachnolite ($NaCaAlF_6 \cdot H_2O$) which Upchurch [12] documented as occurring in Tampa Bay, apparently as a result of precipitation from fluoride-rich effluent from a phosphate chemical plant.

Table 1 Average and standard deviation of major cations and anions, total dissolved solids, and pH of stack solutions and shallow aquifer surrounding the Piney Point stack.

Parameter	Stack ppm	Aquifer ppm
Na^+	1,540±220	500±580
Ca^{2+}	660±60	290±230
SiO_2	740±200	57±65
NH_4^+	1,060±250	300±350
PO_4^{3-}	8,900±1300	420±1000
SO_4^{2-}	5,190±340	1,300±1500
F^-	1,120±380	0.6±0.5
TDS	18,700±2300	3,300±3200
pH	2.43±0.10	6.33±0.65

A very graphic way to illustrate the difference and relationship between the stack fluids and the shallow groundwater is on a SO_4^{2-} versus pH plot (**Fig. 3**). Such a plot resembles a classic acid-base titration curve as performed in freshman chemistry laboratories. In fact, this is a very good analogy to what is actually happening in this situation. High sulfate, low pH fluids in the stack are titrating the relatively low sulfate groundwaters with near neutral pH. Note from the figure that the sulfate occurs over the entire concentration range while pH changes very abruptly as the acidity from the stack solutions is buffered by the shallow groundwater, i.e., there is an equilivalent to the titration "end point."

The near-conservative behavior of sulfate may also be seen when one plots Na, normally considered a very conservative element, against SO_4^{2-} (**Fig. 4**). In this case, we see an almost continuous transition between the high concentrations in the stack fluids and the low concentrations typical of the shallow groundwaters distant from the stack. The only exceptions are for the high-sodium, low sulfate samples collected from MW-23, directly next to the chemical plant. We also show the case for Ca plotted against SO_4^{2-} in an accompanying diagram in the same figure. Here there is evidence for non-conservative behavior at intermediate concentrations of SO_4^{2-}, perhaps due to precipitation of a calcium sulfate phase at the higher pH characteristic of the aquifer waters.

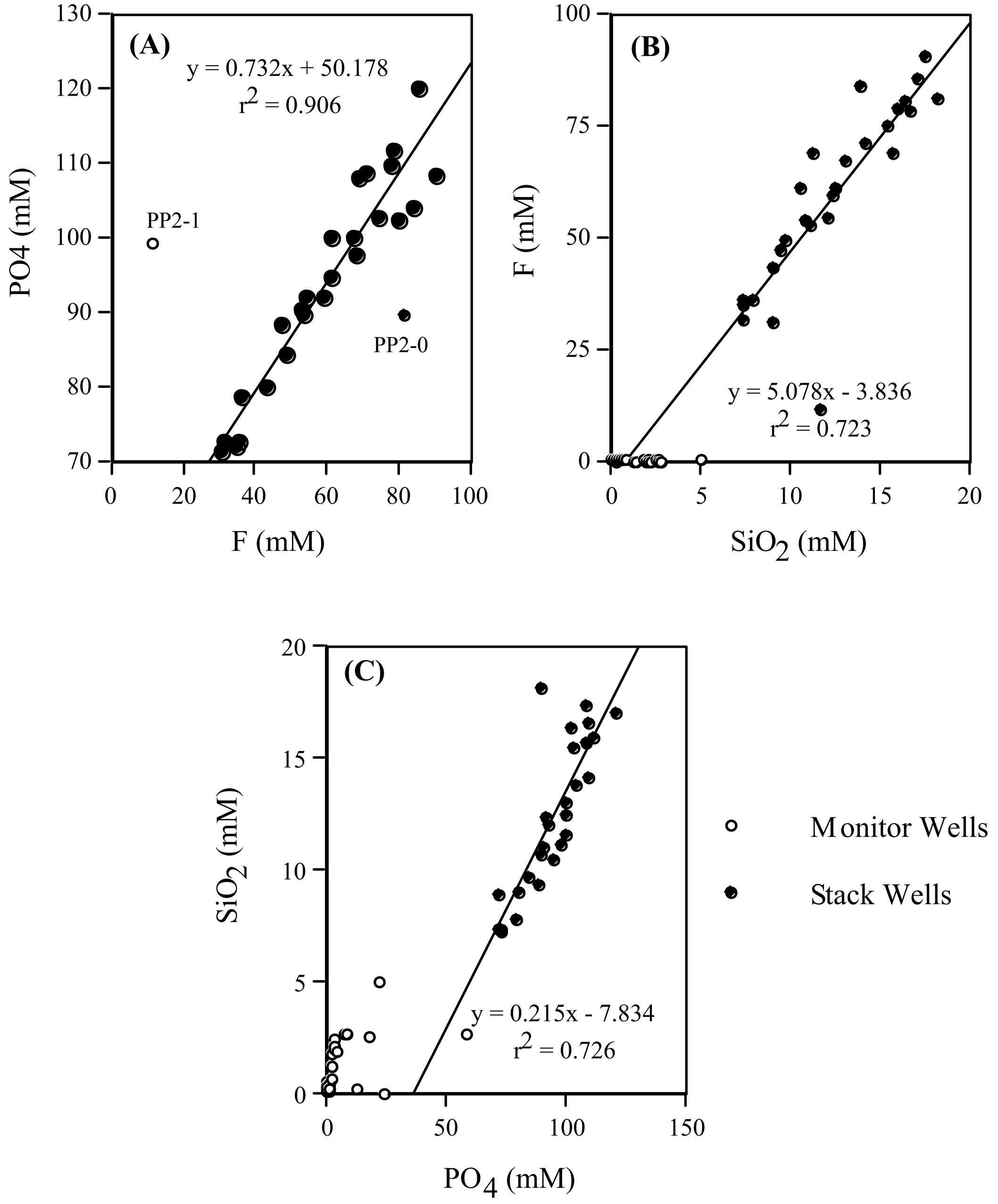

Figure 2. Plots showing relationships in the PO_4-SiO_2-F system in the monitor and stack wells. Regressions have been drawn just through samples from the stack wells.

3.2. Radiochemical characteristics of fluids

Radiochemical results show that the stack wells are very high in activities of uranium (generally 600–1000 dpm/L ^{238}U) and ^{222}Rn (range from about 20,000–70,000 dpm/L) and fairly high in ^{210}Pb (generally 400–4000 dpm/L). Somewhat surprisingly, the activities of ^{226}Ra are only slightly elevated (range about 5–10 dpm/L) above groundwater values for mineralized areas and are, in fact, less concentrated than most of the monitor well concentrations measured around the Piney Point stack. The ^{210}Po concentrations in most stack fluids are high (most values between 3–50 dpm/L) yet significantly less than the corresponding ^{210}Pb activities.

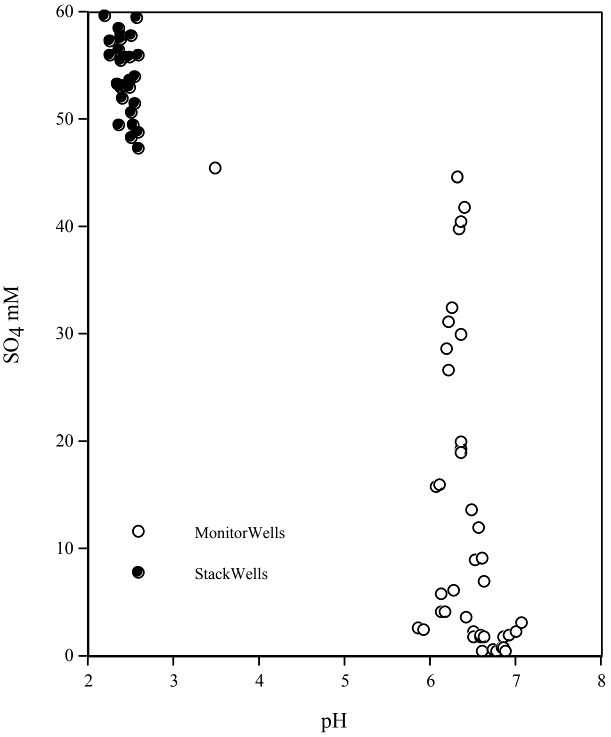

Figure 3. Concentrations of dissolved SO_4^{2-} *versus field pH for both stack and monitor wells. The shape of this curve mimics a classic acid-base titration curve.*

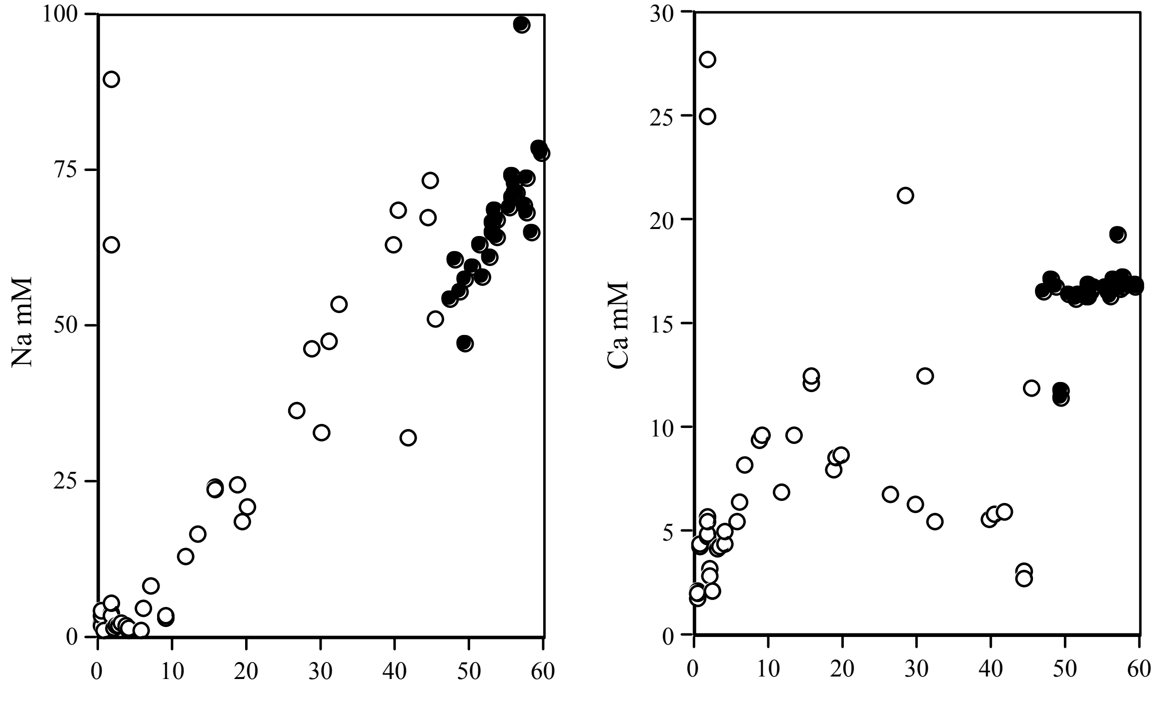

Figure 4. Plots of sodium versus sulfate and calcium versus sulfate for both monitor wells (open circles) and stack wells (closed circles). The sodium plot displays near conservative behavior while Ca shows evidence of non-conservative behavior at higher sulfate concentrations.

Table 2 Geometric mean concentrations and average deviations of radionuclides in the stack solutions and shallow aquifer surrounding the Piney Point stack.

Parameter	Stack dpm/L	Aquifer dpm/L
^{238}U	970±350	0.3±1.6
^{226}Ra	7±3	6.0±16
^{222}Rn	20,200±19,200	4,600±4,400
^{210}Pb	1100±900	1.0±0.9
^{210}Po	21±69	0.9±2.0

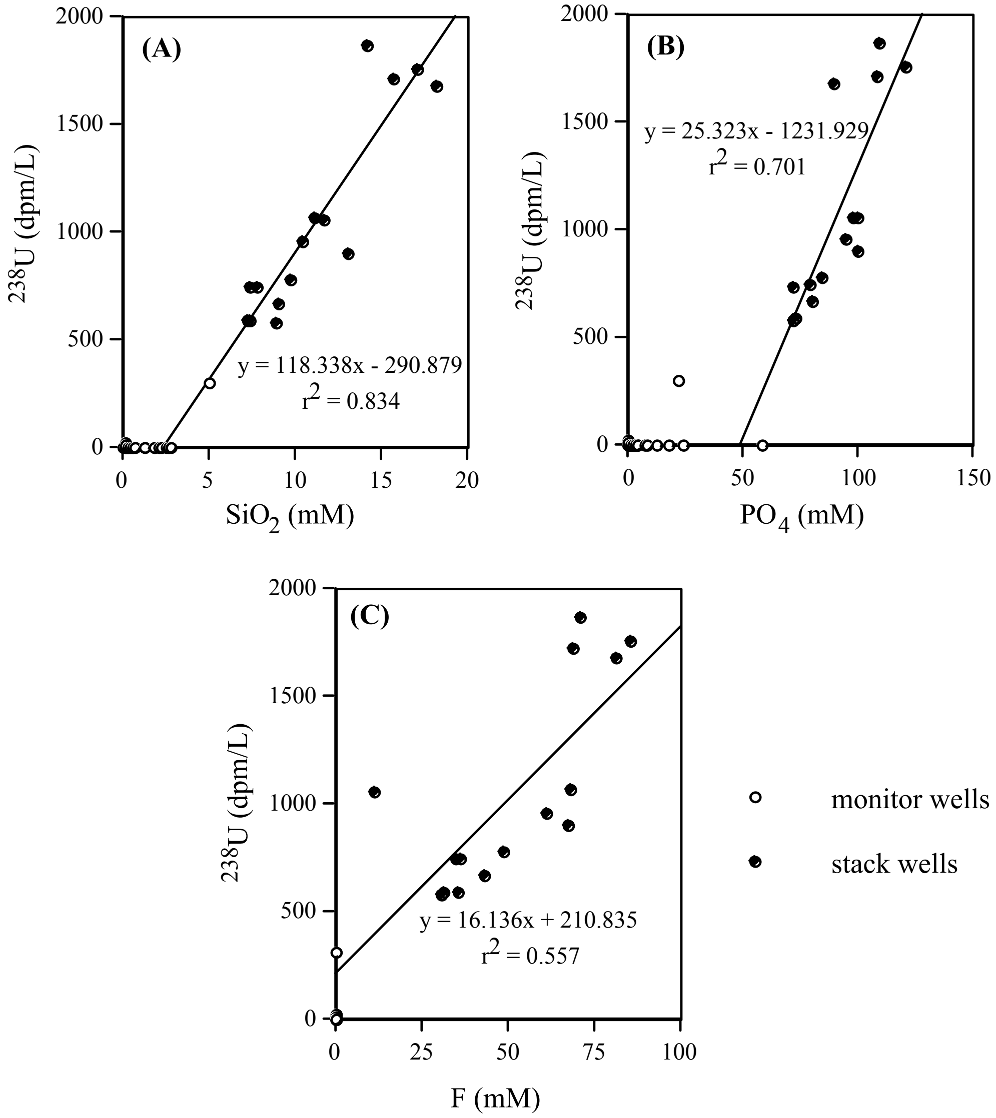

Figure 5. Plots of ^{238}U activity versus SiO_2 (A); PO_4 (B), and F (C) for both monitor wells (open circles) and stack wells (closed circles). The regression lines are drawn through the stack well samples.

The monitor well samples are much lower in U isotopes than the stack solutions. The concentration of ^{238}U is generally less than 1 dpm/L with the notable exception of MW 12 (265 and 304 dpm/L for two samplings) and MW 22 (18 and 15 dpm/L for two samplings). Although high, these two monitor wells still display U concentrations much lower than the stack solutions. The low pH in MW12 (pH=3.48 and 3.19 on the two occasions it was sampled) indicates that there is some effect from the stack solutions in this well (located very close to the stack on the southwest side). MW 22, on the other hand, shows pH values (6.60 and 6.51) comparable to the normal groundwater in the area. The pH of the stack fluids is generally very low (generally pH ranges from 2.2–2.6). A summary which compares the radiochemical character of both the stack fluids and the monitor wells is given in **Table 2**.

We report the geometric mean values for the radiochemical results because they tend to have a log-normal distribution. We did not include the ^{238}U and ^{210}Pb values for MW-12 because that well is obviously impacted by stack fluids as discussed above. No matter how one presents these results, however, the general character of these analyses is reflected in the table, i.e., there are extreme radiochemical differences between the stack and monitor wells with ^{210}Pb and U isotopes showing the greatest enrichment in the stack solutions. Although ^{222}Rn has the highest absolute activity in the stack fluids, its ratio to the aquifer waters is not nearly as high as that for ^{210}Pb and ^{238}U. Significantly, the stack fluids actually contain less ^{226}Ra than the surrounding monitor well waters.

When we examined inter-element relationships of uranium to stable elements in the stack and monitor wells, we found the strongest correlations to SiO_2, PO_4^{3-}, and F^- (**Fig. 5**). It was shown earlier (see Fig. 2) that there are strong relationships between all three of these chemical components themselves, so a link between U isotopes and one of these parameters would give the appearance of a link to all three. Thus, it is not possible to predict which of these parameters may control the speciation of U isotopes in the stack fluids based on these observations alone. Uranium may be complexed by both PO_4^{3-} and F^- so either of these is likely to play an important role in migration of U within the stack. This question will be addressed further in the geochemical modeling section of this paper.

The most striking feature concerning the radiochemistry of the stack fluids, besides the extremely elevated ^{238}U and ^{210}Pb values, are the consistently low specific activities of ^{226}Ra. The low ^{226}Ra is reflected in $^{210}Pb/^{226}Ra$ activity ratios that range from about 20 to 600. We predicted low specific activities of ^{226}Ra in gypsum stack solutions in our laboratory experiments involving selective extractions of phosphogypsum [6]. Those experiments demonstrated that Ra is not significantly mobile when gypsum is present. The relationships of ^{226}Ra to Ca and SO_4^{2-} in both stack and monitor well waters (**Fig. 6**) show that, while the stack fluids may supply dissolved Ca and SO_4^{2-} to the surrounding aquifer, there is no way that the stack can be a source of Ra. Some of the monitor wells are somewhat enriched in ^{226}Ra compared to typical groundwater values with activities of 10–50 dpm/L and, in the case of MW-23, extremely high values of 150–170 dpm/L. That particular monitor well is located several hundred meters to the northwest of the stack, immediately adjacent to the old chemical plant. Phosphogypsum was apparently used for the base of a parking lot built next to the plant although it seems doubtful this has any bearing on the enriched ^{226}Ra. MW-23 water is not enriched in any other of the measured radionuclides but is also very high in Na, Ca, and Cl — higher, in fact, than most of the stack solutions. The origin of the contamination in MW-23 is unclear, but it is certainly not derived from the gypsum stack. We have checked the elemental ratios to see if seawater intrusion could be responsible for the elevated salt levels. Both the Na/Cl and Cl/SO_4 ratios in MW-23 water suggest that these waters are enriched in Cl relative to normal seawater.

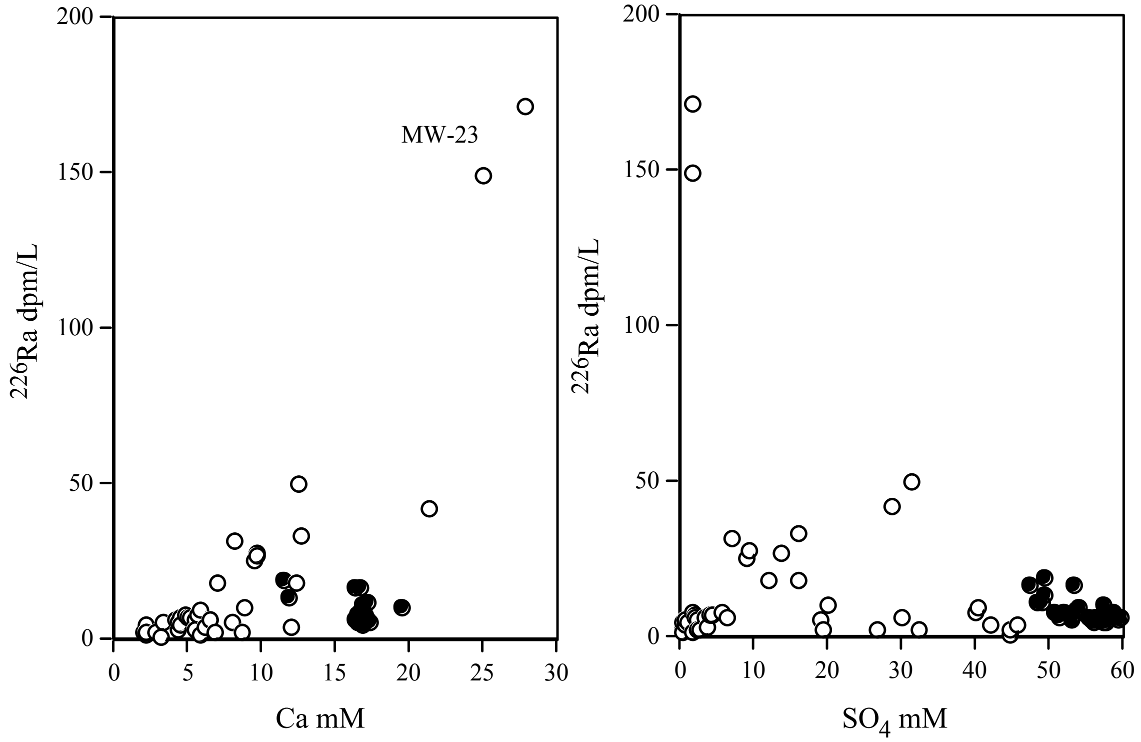

Figure 6. Plots of ^{226}Ra activity versus Ca (A) and SO_4 (B) for both monitor wells (open circles) and stack wells (closed circles). The MW-23 samples (collected next to the old chemical plant) are high in ^{226}Ra and Ca^{2+}, yet low in SO_4^{2-}.

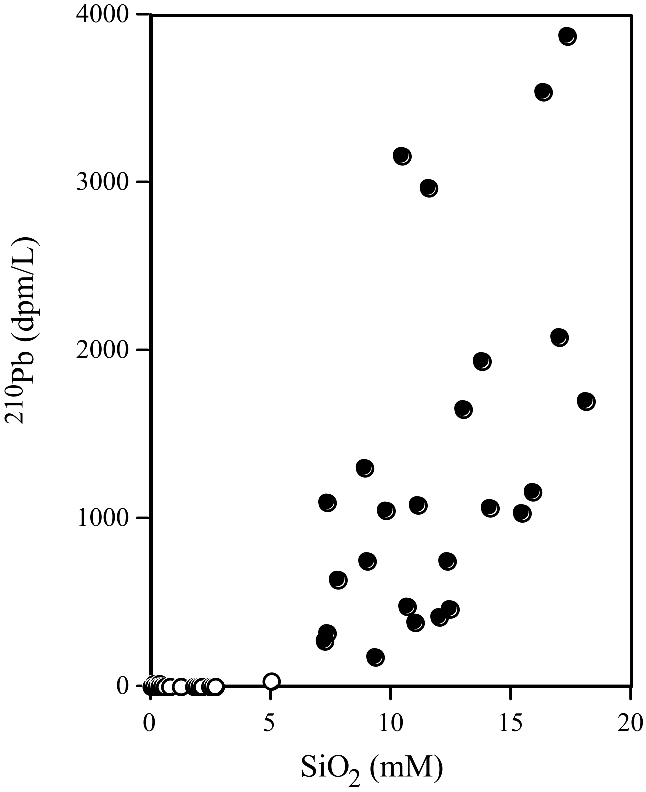

Figure 7. Plot of ^{210}Pb activity versus SiO_2 for both monitor wells (open circles) and stack wells (closed circles).

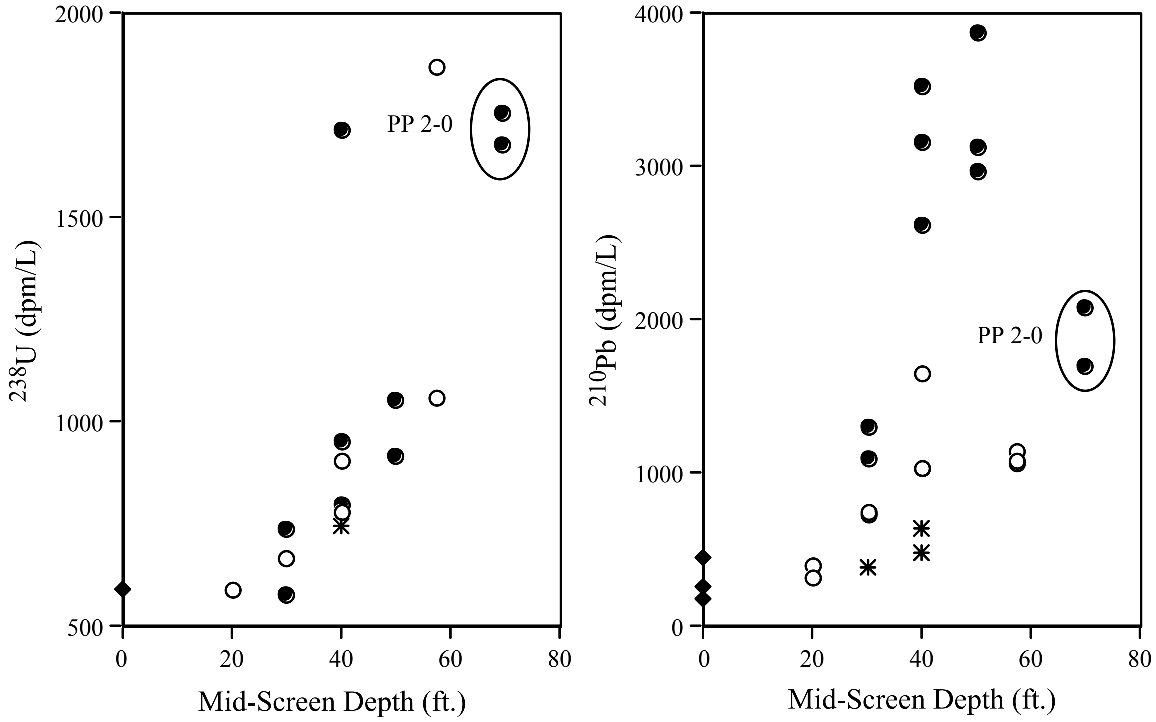

Figure 8. Plot of ^{238}U and ^{210}Pb activities (dpm/L) versus mid-screen well depth for all stack wells. Points at zero depth represent samples from the pond surface. The other symbols refer to the three well clusters: PP 1 (open circles); PP 2 (closed circles); and PP 3 (stars). The results from well PP 2-0, screened below the stack in the surficial aquifer, are circled. Note that the ^{210}Pb displays a significant drop in concentration in this well compared to overlying collection points in the stack.

The fact that the stack fluids are relatively low in ^{226}Ra is an important finding. Radium is one of the most important environmental radionuclides from a biokinetic point of view. Its presence in monitor wells near gypsum stacks is often cited as evidence of contamination from the stack. Yet the data presented here indicate that the stack cannot possibly be a source of ^{226}Ra to the shallow aquifer around the Piney Point stack. Although gypsum contains substantial amounts of ^{226}Ra and the ^{226}Ra can be mobilized when the $CaSO_4$ phase is totally dissolved, radium from recirculating fluids is apparently strongly sorbed by phosphogypsum surfaces. The gypsum stack thus apparently acts as a sink, rather than a source, for dissolved radium.

What then, is the source for the somewhat elevated ^{226}Ra activities in some of the monitoring wells surrounding the gypsum stack? With the exception of MW-23, the only reasonable answer appears to be from the phosphate ore itself. The Piney Point Complex is built on mineralized land [5] which has not, as yet, been mined. Release of ^{226}Ra into surface and groundwaters from phosphate rock has been observed before [13, 14] and is the most logical explanation in this case.

The activities of ^{210}Pb in the stack solutions are extremely high with a range from 320 to 3900 dpm/L, somewhat higher than the activities of ^{238}U found in the same solutions. The monitor well water activities are much lower, most often less than 1.0 dpm/L, with the exception of the contaminated MW-12 which has activities near 30 dpm/L. The waters of MW-12 contain high concentrations of all the components characteristic of the stack fluids

(Ca, SO_4, PO_4, etc.) and is the only monitor well studied with a significantly reduced pH. The only qualitative trend we noticed when plotting the ^{210}Pb activities against other parameters was a rough trend with SiO_2, i.e., the ^{210}Pb concentrations tend to be higher in the stack solutions with the greatest SiO_2 concentrations (**Fig. 7**). At the low pH characteristic of the stack solutions, more than one half the Pb may be in the form on an uncharged (aqueous) sulfate complex (see modeling results below). When the fluids flow into the shallow aquifer and the pH is buffered, the Pb probably hydrolyzes very quickly and precipitates out of solution. Further observational evidence of this process will be shown in a later section when we discuss the radiochemistries of the core materials.

We also examined the radiochemical data for the stack solutions to evaluate whether there was any relationship between concentrations and depth in the stack, i.e., depths to the screened intervals of the monitor wells. The activities of ^{226}Ra and ^{210}Po do not show any trend but stay at comparable levels throughout the stack. The concentrations of ^{238}U and ^{210}Pb, however, do increase more-or-less systematically with depth in the stack (**Fig. 8**). This is what one would expect if these components were acting as soluble species being added to the fluids as they pass through the stack. Note that the PP 2 cluster of wells shows an increased concentration of ^{210}Pb with depth until the very deepest section is encountered (PP 2-0) where the ^{210}Pb concentration drops nearly in half. This is the well that is screened below the bottom of the stack.

3.3. Modeling results

General comments. Several caveats need to be remembered when considering this type of information. The results are *estimations* (subject to the components and data entered and all of the assumptions and limitations of the MINTEQA2 model and the thermodynamic database utilized), and the predictions are for *equilibrium.* While the results obtained are still very useful for identifying the probable speciation, there is no guarantee all of the species are included or the quantitative results are exact. We present below a summary of some of the most important observations.

Calcium. Calcium is an important component since it is a major cation in the solutions, participates in many complexation and precipitation reactions, and may offer clues to the speciation of other important components, such as radium. Calcium speciation results (**Table 3**) are consistent with the known characteristics of calcium. The pH of the uncontaminated solution is low enough (6.73) to keep most of the calcium as free ion, rather than hydroxide complexes, and as bicarbonate rather than carbonate complexes. Complexes formed are with the major anions, bicarbonate and sulfate. In the contaminated solution ligand concentrations are much higher, especially for sulfate and phosphate, so their complexes become more significant. Since all the interactions in Table 3 involve major components, removing the minor components from the solution did not affect the speciation (values in parentheses) for the uncontaminated solutions. Magnesium results, as expected, were similar to the calcium results above. The sulfate complex, being uncharged could contribute significantly to the mobility of the calcium, and other metals that experience similar complexation, such as barium and radium.

Sulfate and phosphate. Since sulfate turned out to be one of the most important ligands in the system, it is useful to look in detail at the sulfate speciation, as shown in **Table 4**. Phosphate showed similar distributions, approximately 50% complexing with calcium and magnesium in the contaminated solution.

Table 3 Calcium distribution in solutions expressed as (%) major and minor components included in the solutions.

SPECIES	UNCONTAMINATED		CONTAMINATED	
Ca^{2+}	93.2	(93.2)	48.1	(60.3)
$CaSO_4$ AQ	3.3	(3.3)	28.5	(39.7)
$CaHCO_3^+$	3.5	(3.5)	<1	(<1)
$CaH_2PO_4^+$	<1	(<1)	23.2	(<1)

Notes:

1. *Values in parentheses represent solutions containing only major components.*
2. *Removing silica as a component made insignificant changes in the above results (< 0.5 %).*

Table 4 Sulfate distribution in solution expressed as (%) major and minor components included in the solutions.

SPECIES	UNCONTAMINATED		CONTAMINATED	
SO_4^{2-}	79.2	(79.2)	65.0	(65.8)
$NaSO_4^-$	1.2	(<1)	6.2	(7.1)
$CaSO_4$ AQ	11.5	(11.5)	<1	(6.4)
HSO_4^-	<1	(<1)	10.5	(11.8)
$MgSO_4$ AQ	8.2	(8.2)	4.3	(7.9)
$NH_4SO_4^-$	<1	(<1)	13.0	(<1)

Notes:

1. *Values in parentheses represent solutions containing only major components.*
2. *Removing silica as a component made insignificant changes in the above results (< 0.5 %).*

Table 5 Pb distribution in solution expressed as (%) major and minor components included in the solutions.

SPECIES	UNCONTAMINATED	CONTAMINATED
Pb^{2+}	5.6	33.2
$PbCl^-$	<1	1.9
$PbSO_4$ AQ	<1	54.3
$Pb(SO_4)_2^{2-}$	<1	10.5
$PbCO_3$ AQ	77.7	<1
$PbHCO_3^+$	14.9	<1

Note:Removing silica as a component made insignificant changes in the above results (< 0.5 %).

Sulfate remains primarily as the free sulfate ion. However, significant fractions complex with calcium and magnesium, and in the contaminated sample also with sodium and ammonia. In addition, in the contaminated sample the pH is sufficiently low (2.44) to keep bisulfate a major component (pK_2 for sulfuric acid is 2.0), which is significant in calculations of total negative charge when doing a charge balance for these solutions. When only major components are considered, the ammonium ion complex drops out since ammonium ion would not be included as a cation.

Table 6 U distribution in solution (%) (added as UO_2^{+2}) major and minor components included in solution.

SPECIES	UNCONTAMINATED	CONTAMINATED
UO_2^{2+}	<1	<1 (<1)
UO_2CO_3 AQ	4.7	<1 (<1)
$UO_2(CO_3)_2^{2-}$	78.4	<1 (<1)
$UO_2(CO_3)_3^{4-}$	16.5	<1 (<1)
UO_2F_2 AQ	<1	<1 (4.1)
$UO_2F_3^-$	<1	<1 (3.1)
$UO_2H_2PO_4^+$	<1	2.4 (2.2)
$UO_2H_2(PO_4)_2^{2-}$	<1	93.0 (85.9)
$UO_2H_2PH_3P^+$	<1	3.6 (<1)

Note: Removing silica as a component DID make significant changes in the above results for the contaminated sample only, as shown by the values in parentheses.

Table 7 U distribution in solution expressed as (%) (added as U^{+4}) major and minor components included in the solutions.

SPECIES	UNCONTAMINATED	CONTAMINATED
UF_3^+	NOT	26.7 (4.8)
UF_4 AQ	APPLICABLE	71.5 (76.7)
UF_5^-		1.6 (10.1)
UF_6^{2-}		<1 (8.5)

Note: Removing silica as a component did make significant changes in the above results, as shown by the results in parentheses.

Silica. Dissolved silica is a major component of the TDS of these samples (53 mg/L in the uncontaminated and 1187 in the contaminated sample, as H_4SiO_4), even though its presence as the uncharged species means it does not contribute to the ionic strength. However, there is an interesting aspect to the silicon speciation. It remains essentially all H_4SiO_4 except in the contaminated sample with the minor components included, when 97.6% is predicted to be SiF_6, and only 2.4% H_4SiO_4 . Obviously, one factor to consider in relation to the effect of the stack solutions is solubilization of silicon containing minerals by fluoride ion (the low pH is also important here). When these silicon fluoride complexes are transported to groundwater and the concentrations diluted, silicon would probably be supersaturated relative to one or a number of solid phases and precipitation reactions could ensue. Indeed, observations of precipitates formed in and below the stacks are probably related to this mechanism.

Lead. Lead results are presented below (**Table 5**) as an example of the expected equilibrium speciation of a transition metal. Lead results are of particular interest because of the observed mobility of the radionuclide ^{210}Pb.

Table 5 confirms what would be expected, speciation of transition metals in aqueous solutions is often more complicated than for alkaline or alkaline earth metals. First, a greater diversity of complexes formed for lead. Second, the complex formation is very pH dependent. Neither solution had a sufficiently high pH to produce the significant amounts of hydroxide complexes that occur in alkaline solutions. Also note that, despite the much higher ligand concentrations in the contaminated solution, there is a greater fraction of free lead ion than in the uncontaminated solution, a result of the much lower pH (2.44 vs. 6.73). The strength of the carbonate complex of lead is evident in these results. Even though bicarbonate would dominate over carbonate at pH 6.73 in the uncontaminated solution, there is a larger fraction as the carbonate complex. Chloride is a strong ligand with lead, so a chloride complex shows up in the major species in the contaminated solution. However, due to the relatively high sulfate concentrations, two sulfate complexes dominate the predicted complexation. Note that fully half of the lead is predicted to be in the uncharged sulfate complex, which could contribute significantly to its mobility (since it would be less prone to adsorb to charged aquifer solids). Other transition metals (radioactive and non-radioactive) would be expected to exhibit similar characteristics.

Uranium. Results for uranium added as uranyl ion (UO_2^{+2}, the expected stable form in oxygenated solutions) are presented in **Table 6**.

In the acidic environment of the contaminated solution (pH 2.44), U^{4+} may be stable, so MINTEQA2 runs were also made using U^{4+} as the input component (**Table 7**). Since redox reactions were not allowed, conversion between these different redox states of uranium was not allowed (the thermodynamic database is not yet reliable for such calculations).

Obviously, uranium exhibits a complicated speciation behavior (made even more complicated when redox state transitions are considered). UO_2^{2+} speciation is dominated by a doubly charged phosphate anion. Such an anion would not be expected to adsorb to the normally negatively charged soil particles. However, specific (chemical) adsorption might still occur, and it is probable that positively charged soil particles would exist that could attract the complex at the pH of the PG stack solutions (approximately 2.5). The U^{4+} speciation, on the other hand, is dominated by the fluoride complexes. In particular, the uncharged complex dominates, which could result in significant uranium mobility. Furthermore, for both forms of added uranium, including or not including dissolved silica did significantly affect the resultant speciation. In combination with information on predicted oversaturated solid phases (see below), a complicated set of interactions between Si, F and U emerges. Consequently, fundamental understanding of the speciation and fate of uranium in the PG stack system is multifaceted.

Radium. The MINTEQA2 outputs for radium indicated 100% would remain as the free ion, Ra^{2+}. One factor that tends to keep the radium in the free ion form is its low concentration compared to the major cations, which effectively out compete the radium for ligands. However, it should be noted the available thermodynamic database for radium complexes is not extensive. If any complexes were significant, it would probably be the sulfate complexes in the contaminated sample solution (although the monosulfate radium complex was included in the database, it did not account for >1% of the radium). As discussed for calcium, above, the sulfate complexes could increase the mobility of the radium in the aquifer when present in the PG stack plume.

Other factors concerning speciation. Other factors must also be considered in relation to geochemical modeling of the dissolved components of the groundwater and the stack solutions. First, the contaminated field samples showed increased concentrations of organic carbon compared to the background samples, increasing to approximately 80 ppm TOC from approximately 9 ppm TOC. Should the organic matter be a strong ligand for any of the metals of interest, or should it coat and thereby modify the surfaces of the aquifer solids, it may be a factor in metal and radionuclide mobility. Other processes that must be considered relative to mobility are adsorption, especially for transition metals, and coprecipitation, for example Ra may possibly coprecipitate with gypsum or barite.

Table 8 Predicted equilibrium solids precipitation including both major and minor components.

UNCONTAMINATED GROUNDWATER MODEL

HEMATITE (Fe_20_3) (only when Si was not added)
UP_2O_7:20H_20 (when UO_2^{2+} was added)
DIASPORE ($AlHO_2$)
FCO_3APATITE ($[Ca]_{9.5}[Na]_{36}[Mg]_{14}[PO_4]_{4.8}[CO_3]_{1.2}[F]_{2.5}$)
QUARTZ (SiO_2)
LEONHARDITE (Ca,Si,Al,H &O) or KAOLINITE (mostly Si,O and Al)

Percentages of Components in Precipitates:

U	85
Ca	0.4
F	6.1
Al	100
P	99
Si	82

CONTAMINATED GROUNDWATER MODEL

FLUORITE (CaF_2)
UP_2O_7:20H_20 (when UO_2^{2+} was added)
$MnHPO_4$
BARITE ($BaSO_4$)
QUARTZ (SiO_2)
STRENGITE ($FePO_4.2H_2O$)

Percentages of Components in Precipitates:

U	100
Ca	98
F	55
P	99
Si	70
Fe	88
Mn	99
Ba	77

Prediction of precipitation of solids from groundwater solutions. MINTEQA2 was utilized to predict oversaturated solids that would be predicted to precipitate. In fact, the gypsum stack solutions do appear to be oversaturated relative to a number of components, so observations of precipitates forming in the stacks, below the stacks, and in process solutions are no surprise. Even considering just the major components, the uncontaminated sample was predicted to be oversaturated with respect to quartz, and the contaminated sample oversaturated with respect to quartz and gypsum (precipitating up 57% of the calcium, 99.2% of the silicon, and 18% of the sulfate). Adding the minor components results in a variety of predicted oversaturated solids. **Table 8** presents data on the solids predicted to precipitate in the uncontaminated and contaminated solutions.

Obviously, the oversaturated state of the uncontaminated solution and, especially, the contaminated solution, leads to a potentially complicated system relative to precipitation. The situation is further complicated by the fact that precipitation kinetics are notoriously slow and difficult to predict. Consequently, the equilibrium predictions of the model are limited not only by the solids contained in the database, but also by the fact that equilibrium relative to all solids is unlikely. Complexation reactions controlling the solution speciation that were discussed above are generally fast compared to the time scales of interest in and around gypsum stacks. However, that may not be true for precipitation reactions. Kinetic hindrances, for example, may lead to the formation of metastable solids, or solids which will later dissolve in favor of more stable ones. Hence the reason for doing runs without Si added. If the Si precipitation is slow compared to another solid (e.g., hematite in Table 8), the faster precipitating solid may form and be metastable over long periods of time.

What can be said is that geochemical modeling indicates solids are likely to form in the gypsum stacks and in the groundwater receiving the stack solutions. It can also be concluded that the presence of the stack solutions will probably influence the actual solids formed (and probably their rate). Oversaturation relative to calcium, iron, manganese, silicon, uranium, sulfate, phosphate and fluoride are particularly noteworthy. Solids containing these materials are to be expected in the stack solutions and groundwater receiving such contamination.

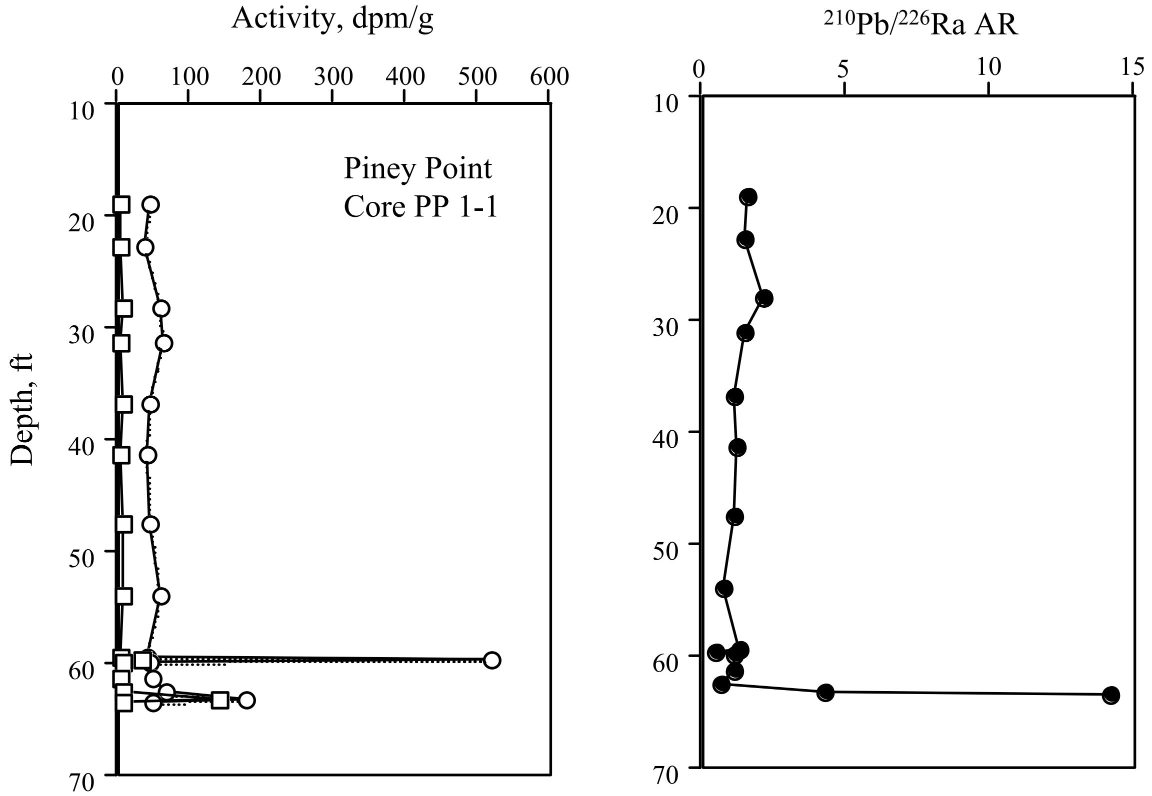

Figure 9. Plot of ^{238}U (open squares) and ^{210}Pb (circles) activities (dpm/g) versus depth in stack core PP 1-1. The right hand drawing shows the activity ratio ^{210}Pb/^{226}Ra versus depth in the same core. The last two data points represent samples of soils underlying the gypsum stack.

3.3. Phosphogypsum analyses

Core PP 1-1, drilled on the west side of the old stack at Piney Point (Fig. 2), was found to contain substantial amounts of phosphatic pellets and cobbles in the soil below the stack, consistent with the observations of Miler and Sutcliffe [5]. Plots of the radiochemical distribution as a function of depth show that ^{238}U and ^{210}Pb (**Fig. 9**) have relatively uniform concentrations down to about -60 feet below the surface where there is a huge ^{210}Pb spike. The concentration of ^{226}Ra (not shown on the diagram for clarity) is even higher at this level (1098 dpm/g). This layer is composed of a dark, laminated material which appears to be organic-rich and thus appears very similar to the high-radium gypsum material from another stack in Florida (CF Bartow) described in Burnett et al. [15]. The ^{238}U is also higher at the -60 foot level but displays a stronger peak further downcore at about -63 feet depth below the surface of the stack. The fact that the uranium spike was a few feet further downcore may imply that uranium is at least somewhat more mobile in the stack solutions than radium. Also note that there is a secondary ^{210}Pb peak just above the bottom of the core. That secondary peak corresponds to an analysis of soil at the base of the gypsum stack, i.e., the topmost soil is significantly enriched in ^{210}Pb. If the enrichment of these radionuclides is secondary, i.e., occurring as the solutions move through the stack, these observations suggest that substantial amounts of radionuclides are redistributed within the stack and sequestered within the soil at the base of the stack *before* entering the underlying aquifer.

The distribution of the ^{210}Pb/^{226}Ra activity ratio with depth in the core shows that the ratio varies within a relatively narrow range of about 0.5–2.0 through much of the core until near the bottom where it rises first to about 4.3 (an organic sand soil horizon at the very base of the stack) and then to 14.1 in the lowest sample (which consists of sediments from the surficial aquifer). Apparently the ^{210}Pb, which migrates preferentially to the ^{226}Ra in the stack solutions, precipitates very rapidly when the underlying soil horizon is encountered. The incorporation of ^{210}Pb from stack solutions into the soil may be by adsorption, coprecipitation with iron hydroxides, or other secondary process. This observation is very significant in terms of potential migration of radionuclides away from the stack into the underlying shallow aquifer.

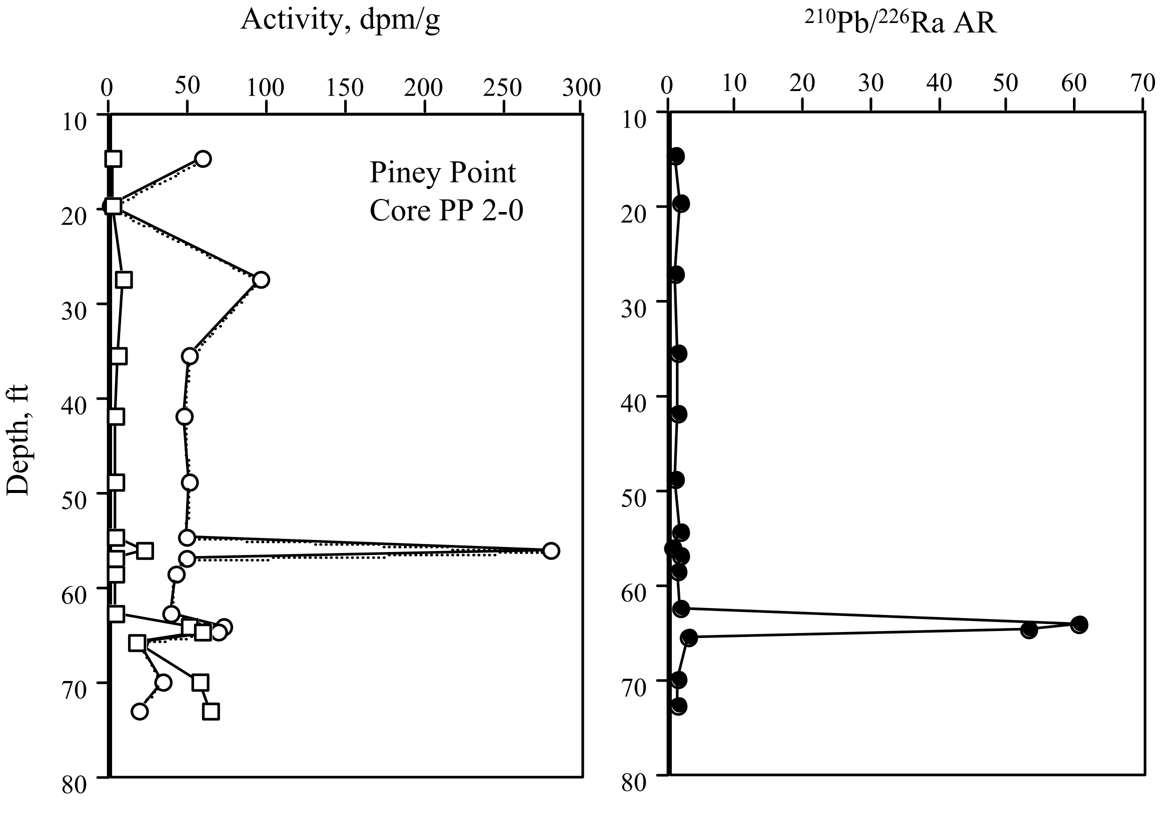

Figure 10. Plot of ^{238}U (open squares) and ^{210}Pb (circles) activities (dpm/g) versus depth in stack core PP 2-0. The right hand drawing shows the activity ratio ^{210}Pb/^{226}Ra versus depth in the same core. This core penetrated the bottom of the stack — the lowest 5 samples are from the soils and sediments directly underlying the gypsum stack.

Core PP 2-0, drilled in the central area of the old stack at Piney Point, has a distribution of radionuclides within the core similar to that described for core PP 1-1. There is a dark colored, organic-rich, laminated layer at 56 feet below the stack surface which is greatly enriched in radionuclides. This layer shows clearly as a spike in a plot of ^{238}U and ^{210}Pb versus depth (**Fig. 10**). Again, both nuclides show a secondary maximum lower in the core, just at the point where the gypsum is in contact with the underlying soils. Since core PP 2-0 was drilled completely through the stack (the well was actually screened in the underlying aquifer), we had the opportunity to collect more samples under the stack and get a more complete picture of the radionuclide distribution with depth. Since ^{210}Pb is apparently behaving much differently than ^{226}Ra in the stack fluids, the ^{210}Pb/^{226}Ra activity ratio shows a dramatic increase right at the base of the stack with a quick return to values near secular equilibrium. This is excellent evidence that ^{210}Pb, although very high in the stack solutions, precipitates quickly upon encountering the higher pH groundwaters and is incorporated into the shallow soils. The observational evidence suggests that there is little radionuclide transfer from the stack solutions to the aquifer.

4. SUMMARY

This study was initiated to investigate the processes responsible for controlling the interaction and release of radionuclides from phosphogypsum from an actual phosphogypsum stack. Our approach used samples from monitor wells placed both around and directly into the Piney Point gypsum stack. Samples of fluids drawn from these wells showed that in general, the stack solutions are acidic with high ionic strength, containing high total dissolved solids (TDS) of 18,700±2300 ppm and a pH of 2.43±0.10. The waters from the monitor wells surrounding the stack have a much lower average TDS of 3,300±3200 ppm and a pH of 6.33±0.65. Qualitative relationships between dissolved PO_4^{3-} and F^- and F^- with SiO_2 are thought to imply solution controls by the solid phases carbonate fluorapatite and alkali fluorsilicates. A plot of pH versus SO_4^{2-} ion concentration was shown to resemble a classic acid-base titration curve.

Radiochemically, the stack wells are exceptionally high in activities of uranium (generally 600–1000 dpm/L ^{238}U) and ^{210}Pb (generally 400–4000 dpm/L). Activities of ^{222}Rn are also elevated (range from about 20,000–70,000 dpm/L) although this is not surprising in view of the radium-rich nature of the surrounding phosphogypsum. One very significant result is that the activities of ^{226}Ra in the stack fluids are only slightly elevated (range about 5–10 dpm/L) above normal groundwater values and are, in fact, less than most of the monitor well concentrations measured around the Piney Point gypsum stack. These consistently low specific activities of ^{226}Ra in the gypsum stack fluids argues against the stack as a source of radium to the aquifer.

Geochemical modeling showed that the increased concentrations of many ligands results in significant changes in predicted equilibrium speciation. Most pronounced are increases in metal and radionuclide complexes with sulfate and phosphate, resulting in uncharged or negatively charged solution species which would likely be more mobile in the aquifer than positively charged metal or radionuclide ions. Fluoride from the stack solutions can significantly affect the speciation of aluminum, silicon, iron and possibly uranium. The second major effect of stack solution inputs is to cause oversaturation of a variety of solids. The low pH of the contaminated solutions would generally indicate few solids would precipitate in most fresh waters. However, the dissolved solids content and some specific ion concentrations are sufficiently high to cause oversaturation. Although the model results should not be considered comprehensive in consideration of various potential solid phases that could form, the general trend of predicted precipitation reactions does indicate precipitation reactions are likely for certain components. Silicon containing solids are particularly likely since it is oversaturated in the uncontaminated solutions and much more so in the contaminated solutions. Precipitation of quartz was predicted in both contaminated and uncontaminated solutions, as well as other solids with silicon in the contaminated solutions. Other predicted solids formed included the components iron, aluminum, phosphate, calcium, manganese, barium, fluorine and uranium. Precipitation of various and probably multicomponent solids should be expected in and directly below the phosphogypsum stacks.

Observations in solid phase materials from the two cores in the Piney Point stack, are consistent with the results from the fluid analyses and modeling. Results suggest that substantial amounts of radionuclides are sequestered within or just below the stack before entering the underlying aquifer. One of the strongest lines of evidence is the ^{210}Pb data in the cores. The ^{210}Pb/^{226}Ra activity ratios are near or below equilibrium throughout the entire stack until the underlying soils are encountered. At this point there is a large excess amount of ^{210}Pb observed (^{210}Pb/^{226}Ra activity ratios as high as 60) in the soils indicating precipitation of ^{210}Pb when the low pH stack solutions are buffered by the underlying soils and sediments. Although many of the sediments under the stack are enriched in U-series radionuclides, concentrations below the upper surficial sands appear to be associated with the natural phosphatic minerals in those strata. The bulk of the observational evidence suggests that there is little radionuclide transfer from the stack solutions to the underlying aquifer.

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Unattached fraction of radon progeny in Polish coal mines

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Abstract. The system of the monitoring of the radiation hazard in Polish coal mines is based on the monitoring of the workplaces. This system works since 1989 in all coal mines. It gives a very good basis for further epidemiological investigation and assessment of the health detriment within the population of the mines as a result of the exposure for natural radiation. It is very important problem, due to the fact of the presence in the mines another factors, which probably have a synergetic effects on the respiratory tracts. As the routine instrument, a device called ALFA-31 sampling probe was developed in our laboratory. This device was accomplished to regular dust sampler and simultaneous measurements of dust content and potential alpha energy concentration of radon progeny are obligatory in all underground mines in Poland. But the microcyclone used a separator of the respirable fraction which causes the cut-off of unattached fraction of radon progeny, On the other hand measurements of the unattached fraction of short lived radon progeny play a very important role in the investigations of the adequate dose from this source of radiation hazard. During field experiments the use of the alpha spectroscopy system is necessary, while measurements are done not in the vacuum chambers but under normal pressure. It leads to situation, when particular peaks in alpha spectrum are very wide and interfere with other peaks of another alpha-emitting radionuclides. Such instrumentation was designed and completed, and a survey in several underground mines was performed. The analysis of the obtained results must be done very carefully; in other case it may cause a very big uncertainty of the result. In this paper a new approach to the analysis of the alpha spectra has been described. This approach can be used also in other applications of alpha spectroscopy, in which the analysis of energy of alpha peaks in spectrum is needed. The method of the analysis is based on a non-linear regression. The results of the approximation were tested by the method of non-linear regression and very good fitting have been found. Results of the survey show, that the average ratio of unattached and attached fractions is in Polish coal mines at level 3-5%. But it may cause the significant increase of the dose equivalent, due to our calculations at least 15-20% in comparison with dose equivalent caused by attached fraction.

Introduction

The occurrence of enhanced natural radioactivity in Polish coal mines was discovered in early 60’s (Sałdan,1965). Investigations, performed during 70’s showed, that underground galleries sources of high gamma radiation were present, as a result of precipitation of deposits of radium and barium sulphates from radium-bearing waters (Tomza and Lebecka, 1981). Further research activities on this field enabled to identify main sources of radiation hazard in underground coal mines (Lebecka et. al., 1985). Results of these investigations showed, that the most important source of ionising radiation in underground galleries are short lived radon progeny. Other sources are radium-bearing waters and radioactive deposits. Enhanced natural radioactivity, especially radon progeny in air (^{218}Po, ^{214}Pb, ^{214}Bi and ^{214}Po), leads to the increase of radiation exposure for the miners.

Since 1989 monitoring of radiation hazard in Polish coal mines is obligatory. Due to the mining regulations in all underground mines following measurements must be done with the certain frequency:

- concentration of radium isotopes in waters;
- concentration of natural radionuclides in deposits;
- gamma dose rates and gamma doses;
- concentration of potential alpha energy of short lived radon progeny.

Results of the systematic monitoring of the radiation hazard revealed, that radon progeny is the most significant source of doses - more than 90% of cumulative dose equivalent for mines is due to the exposure on radon daughters. But dose equivalent depends also on the aerosol's size distribution and a contribution of the unattached fraction. This fraction consists of very small, charged particles and clusters with the size up to 15nm, showing a detached section in the size distribution curve (Reineking and Porstendörfer, 1986). The theory of the interaction of the aerosols with the respiratory tracts indicates, that unattached fraction is much dangerous as typical aerosols with average diameter 200nm (Birchall et. al. 1994). So, the influence of the unattached fraction on the exposure is much higher than its percentage contribution to activity of radon progeny. Therefore reliable results of measurements of unattached fraction concentration are so important for the evaluation of dose in the mining industry.

In this paper results of measurements of unattached fraction in several Polish coal mines are presented. The assessment of dose equivalent and discussion of errors is also done.

Experimental and methods

The percentage contribution of the unattached fraction (f_p) is a radio of the potential alpha energy of the free fraction to total alpha energy concentration:

$$f_p = \frac{\alpha_1 C_{f1} + \alpha_2 C_{f2} + \alpha_3 C_{f3}}{\alpha_1 C_{o1} + \alpha_2 C_{o2} + \alpha_3 C_{o3}} \qquad (1)$$

$$\alpha_1 = 0.1042 \quad \alpha_2 = 0.5144 \quad \alpha_3 = 0.3814$$

where C_{f1}, C_{f2}, C_{f3} are concentrations of unattached fraction of ^{218}Po, ^{214}Pb, ^{214}Bi and C_{o1}, C_{o2}, C_{o3} are total concentrations of above-mentioned isotopes.

Calculations of the concentrations of particular isotopes can be done for instance on the basis of results of measurements done for filters, through which air with aerosol was sucked earlier.

Our counting system consists of two parallel alpha spectrometers for simultaneous measurements and analyses of alpha spectra, emitted by radon progeny, collected on two filters (fig.1. and 2). First filter is the open face one, on which attached and unattached progeny is deposited during sucking of the air. Above second filter a wire screen is placed, therefore only attached fraction could pass the screen and reach the filter. The flow rates through both filters were controlled by two separate flowmeters of the same type.
The pumping time was usually equal 10 minutes, and the flow rate was of about 0.9m^3/h for each filter. At the end of pumping period two semiconductor detectors were placed over filters as soon as possible (fig.2). Later several consecutive measurements of alpha activity collected on the filter were done.
Our considerations were based on the theory of filtration of the air through diffusion screens, described by Cheng and Yeh (1980), Cheng et al. (1980). The screen thickness, screen wire diameter and the solid volume fraction of the screen were chosen for the used air velocity.

Unfortunately, the diffusion screen cuts off also a portion of the attached fraction, what introduces an uncertainty into the equations.

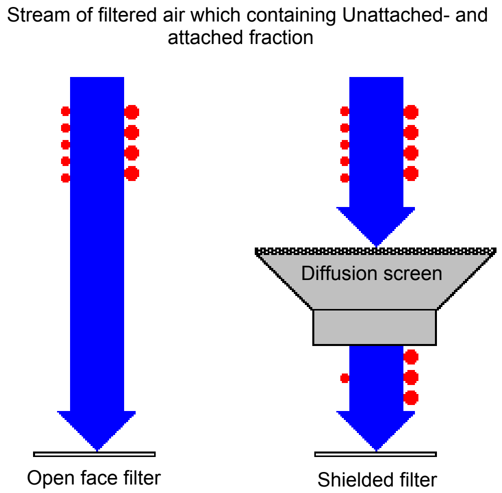

Fig. 1. Pumping of air through the open face - and shielded filter

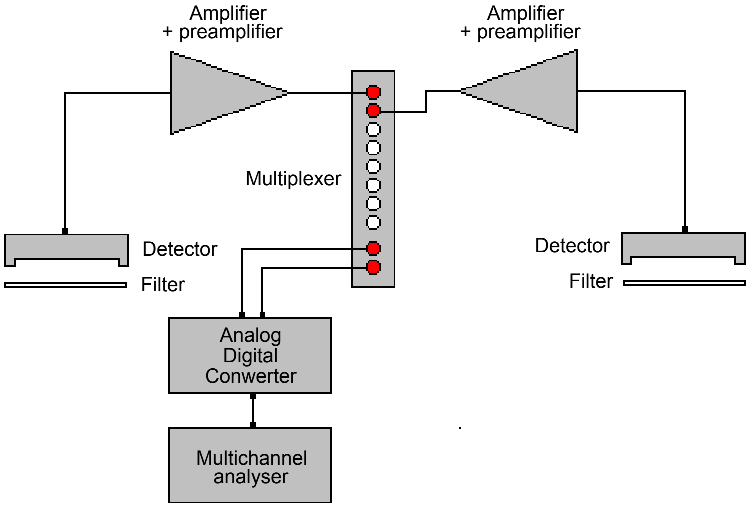

Fig. 2. The schematic picture of the instrumentation for the activity measurements of filters.

Theoretical considerations lead to the solution, connecting results for open face filter (C_{o1}, C_{o2}, C_{o3}) and shielded filter (C_{S1}, C_{S2}, C_{S3}). These results are related due to the following equations:

$$C_{oi} = C_{Si} + \psi C_{fi} + C_{Gi} \quad i = 1,2,3 \text{ for } {}^{218}\text{Po}, \ {}^{214}\text{Pb i } {}^{214}\text{Bi respectively} \qquad (2)$$

where C_{Oi} are concentrations of the certain radionuclide (i) on the open face filter, C_{Si} are concentrations of the *i-th* radionuclide on the shielded filter; ψC_{fi} *and* C_{Gi} are fraction of the *i-th* radionuclide from the unattached- and attached fraction; caught by the diffusion screen.

Without simplifying of these equations, calculations of the activities are impossible. The solution was proposed by Reineking and Porstendörfer (1990). From experiments with unattached fraction authors drew following conclusions:

- the particle size distributions of the aerosol-attached activities for all short-lived radon daughters are identical within a constant multiplier and the unattached activities of ^{214}Bi (^{214}Po) are negligible.

And than:

$$f_p = \frac{\alpha_1 C_{f1} + \alpha_2 C_{f2}}{\alpha_1 C_{o1} + \alpha_2 C_{o2} + \alpha_3 C_{o3}} \tag{3}$$

where:

$$C_{fi} = \frac{C_{oi} C_{S3} - C_{Si} C_{o3}}{C_{S3} - (1-\psi) C_{o3}} \quad \text{lub gdy} \quad \psi \to 1 \quad C_{fi} = C_{oi} - \frac{C_{o3}}{C_{S3}} C_{Si} \quad i = 1,2 \tag{4}$$

Applying these parameters we were able to calculate parameters of the diffusion screen, with the best properties of cutting off the unattached fraction. The parameters of the used diffusion screen are shown in table 1.

Table 1. Parameters of the diffusion screen

Radius of a screen	Screen thickness	Screen wire radius	Specific density of the screen material	Solid volume fraction
4 cm	59.7 μm	14.7 μm	7.8 g/cm^3	0.282

For the filtration of the aerosols from the air, filters of NUCLEOPORE POLYCARBONATE PC (Costar Corporation, USA) were used. Pore size is equal 0.8μm, while the thickness of the filter was 10μm. These filters ensure better energy resolution of the alpha spectra in comparison with membrane filters FM-1, used by us for routine measurements of dust concentration and potential alpha energy concentration in mines (Pore size 1.5μm and thickness 200μm). Both the energy resolution and the detection efficiency was better by tens of percent for aerosols with diameter of 3μm and for tobacco smoke.

Elements of alpha spectrometers were bought in CANBERRA (USA). It consists of supply unit, two alpha semiconductor detectors, two units with preamplifiers and amplifiers, a multiplexer, and finally, on-board multichannel analyser together with analog digital converter, installed in the notebook.

For the detection of alpha particles two semiconductor detectors ULTRACAM-1700-AM with active surface 1700mm^2 were applied. We had to use such detectors, with the aluminium screen (thickness 0.5μm). These detectors are not sensitive for high moisture and light, moreover, it is possible to clean the surface. Additionally, detectors work not only in the vacuum chamber but also under normal atmospheric pressure and the minimum distance between filter and detector is only 1mm. These features are very important, because as it was above mentioned, that measurements were done in coal mines. The main reason of such choice was that the instrumentation had to be used in very aggressive environment in underground galleries.

Error analysis

The uncertainty of the measurements have been solved accordingly with Currie (Currie, 1969). At first the critical level f_C was calculated:

$$f_c = k_\alpha \sigma_o \qquad (5)$$

where σ_o is a standard deviation for $f_p=0$, while k_α is a reduced variable for chosen confidence level α. Due to the previous equations the variance is equal:

$$\sigma_o^2 = \frac{\alpha_1^2\left(C_{S1}^2\sigma^2(C_{o3}) + C_{o1}^2\sigma^2(C_{S3})\right) + \alpha_2^2\left(C_{S2}^2\sigma^2(C_{o3}) + C_{o2}^2\sigma^2(C_{S3})\right)}{\left(\alpha_1 C_{o1} + \alpha_2 C_{o2} + \alpha_3 C_{o3}\right)^2 (C_{S3} - (1-\psi)C_{o3})^2} \qquad (6)$$

Later, comparing the result of measurement and the critical level, we were able to calculate the uncertainty of the result:

$$f_p \le f_c \quad \Rightarrow \quad \textit{unattached fraction} \le f_p + t_{1-\gamma} \bullet \sigma(f_p) \qquad (7)$$

$$f_p > f_c \quad \Rightarrow \quad f_p - t_{1-\gamma/2} \bullet \sigma(f_p) \le \textit{unattached fraction} \le f_p + t_{1-\gamma/2} \bullet \sigma(f_p) \qquad (8)$$

Value $t_{1-\gamma}$ is a reduced variable for the chosen confidence level γ in the one-tiled test, while $t_{1-\gamma/2}$ is a corresponding value for the two-tiled test.

Results

We performed 30 measurements in four underground mines. Three of these coal mines are operating but the fourth one is an abandoned mine, only de-watering system works there. All measurements were done in mines without methane hazard, due to two main reasons. Firstly, in mines with methane hazard the intensity of the ventilation is always higher, therefore radon concentrations are lower than in non-methane mines. On the other hand, in mines with methane hazard, regulations concerning intrinsic safety of applied instrumentation are very rigid, therefore we obtained no permission to do our measurements in such mines.

Sampling sites were chosen thanks to the help of the ventilation services of particular mines. Analysis of the result of obligatory monitoring of potential alpha energy concentration have been done, because we wanted to find places, where enhanced concentration of radon progeny have been measured. Accordingly to the error analysis. Equilibrium-equivalent concentration (EEC) of the total activity of short-lived radon daughters should be higher than 30Bq/m^3. In this case the critical level f_c is better as 2% and we are able to make measurements with the uncertainty of the measured value below few percent.

In several cases, we found the EEC of radon progeny below 30 Bq/m^3, in places, where previous investigations showed much higher values. Such measurements were done mainly in the abandon mine. All such results were not a subject of a further analysis, because the uncertainty exceeded the critical level.

Table 2. Results of measurements of unattached fraction of radon progeny in Polish coal mines.

No.	**Total EEC** C_{oEq} **[Bq/m^3]**	**EEC of unattached fraction** C_{fEq}**[Bq/m^3]**	**Percentage of the unattached fraction** f_p**[%]**	**Critical level** f_c**[%]**	**Environmental parameters** **Humidity/Pressure/Temperature**		
					RH[%]	**P[mbar]**	**t[°C]**
1.	328.5	8.1	**2.5±1.1**	0.7	90	1054	18.8
2.	336.8	10.9	**3.2±1.4**	0.9	77	1046	22.0
3.	526.0	≤6.3	**≤1.2**	0.7	83	1044	21.1
4.	163.0	≤4.2	**≤2.6**	1.8	88	1022	20.5
5.	310.2	≤4.7	**≤1.5**	0.9	96	1031	18.2
6.	330.5	7.6	**2.3±1.2**	0.8	79	1056	22.0
7.	359.9	5.0	**1.4±1.4**	0.9	79	1056	22.0
8.	885.6	≤9.7	**≤1.1**	0.7	87	1071	24.5
9.	290.4	≤5.8	**≤2.0**	1.1	98	1053	21.0
10.	321.6	44.7	**13.9±1.4**	0.8	86	1056	23.0
11.	70.0	9.2	**13.1±1.7**	0.8	89	1049	19.6
12.	1280.1	152.3	**11.9±1.0**	0.6	85	1049	20.8
13.	104.7	≤2.0	**≤1.9**	0.8	91	1022	19.0
14.	440.0	≤8.4	**≤1.9**	1.1	93	1018	20.6
15.	165.1	≤5.1	**≤3.1**	1.5	85	1022	22.7
16.	11.4	≤2.9	**≤25.7**	9.1	51	*awaria*	18.6
17.	15.6	≤0.7	**4.5±5.5**	4.1	51	*awaria*	18.6
18.	91.9	11.1	**12.1±2.1**	1.4	91	1011	18.5
19.	96.5	5.7	**5.9±2.5**	2.0	86	1011	19.2
20.	234.7	20.7	**8.8±1.4**	0.9	86	980	15.0
21.	293.4	5.3	**1.8±1.5**	1.0	89	979	14.3
22.	41.7	9.5	**22.7±2.4**	1.6	90	987	16.6
23.	51.5	6.6	**12.9±2.7**	2.1	92	987	16.6
24.	12.2	≤1.0	**≤8.2**	5.9	83	1022	20.0
25.	9.1	≤2.6	**≤28.1**	21.6	84	1022	17.7
26.	77.4	≤2.2	**≤2.8**	1.8	94	987	16.5
27.	75.9	5.5	**7.3±2.2**	1.7	95	987	16.4
28.	8.5	0.7	**≤8.3**	3.8	46	1006	12.7
29.	10.1	0.9	**8.7±7.8**	5.2	69	1005	13.6
30.	3.8	1.2	**31.2±20.7**	11.2	45	998	13.8

Results of our measurements are shown in table 2. In two out of chosen mines, as sampling site all important places were used, like outflows from longwalls and headings, where enhanced levels of radon progeny have been found earlier. During each measurements, additional parameters were monitored - the barometric pressure, relative humidity and temperature. All these data are also showed in table 2. Analysis of alpha spectra was performed with application of non-linear regression, described in the earlier publication (Skubacz, 1998).

We would like to mention the dependence between the energy resolution of the alpha spectrometry system and a type of aerosols. During calibration of the instrumentation in the radon chamber water aerosols as well as cigarette's smoke aerosols were used. For instance in case of smoke aerosols the *FWHM* was equal 597 keV for alpha peak 6.0 MeV of ^{218}Po and, respectively, 412 keV in case of ^{214}Po and energy 7.7 MeV. When water aerosols were used we measured following values - 396 keV for peak of ^{218}Po and 328 keV for peak of ^{214}Po. Explanation for this phenomenon is that the penetration depth of smaller smoke aerosols is bigger than for big water aerosols. However we took into account the whole energy spectra so there was no difference between efficiency coefficients. This way the analysis of the chosen parts of alpha spectra can introduce some error especially in evaluating of activity concentrations.

Also corrections for the influence of thoron progeny have been done. Into further consideration only the results with critical level better than 2% were taken into account. The confidence level is equal 1σ.

The correlation between concentration of the unattached fraction and concentration of aerosols is known from the literature very well. Unfortunately, we weren't able to measure the concentration of aerosols in underground galleries and the size distribution. Therefore it is very difficult to say, why in certain places the percentage of the unattached fraction was higher as in other sites. We found no correlation of the unattached fraction with dust content nor with moisture. Such measurements we would like to undertake in the future.

Investigations of the unattached fraction, performed by different scientists, were done mainly in uranium mines. Busigin and co-workers (1983) found in two investigated mines, that the maximum contribution of the unattached fraction was 7%, but usually below 2%. Similar results were reported by Porstendörfer (1991) - maximum 7%, an average 3% in a shale mine, while in barite mine contribution of unattached fraction was below 1%. Higher values were found in caves. In Postojna Cave (Slovenia) - maximum contribution of the free fraction was equal 16%, and in average 10%.

In our work, in most sites we measured results below critical level (fig.3). But in 8 cases the contribution of the unattached fraction ranged within 1-10%, in 5 cases within 10-20% and only in one case level 20% was exceeded. The average value was of about 5.2%.

It means, that in the chosen coal mines contribution of the unattached fraction is relatively high. We would like to emphasise, that in two out of 4 mines, concentration of the unattached fraction was measured in all main sites of the ventilation system.

The assessment of the influence of the unattached fraction on the dose equivalents for miners have been done. We applied the method of calculations, described by Zock and co-workers (1996) - we made an assumption that size distribution of the attached fraction is log-normal, with AMD = 200nm and σ = 2.3nm. Such parameters for mines were quoted in publication Birchall et.al. (1994). quoted.

The result of our considerations shows, that the influence of unattached fraction on dose equivalent in Polish coal mines is significant. The average value of the the unattached fraction was calculated as 5.2%, but as an effect of the exposure of the miner, the dose equivalent would increase of about 45% in case of mouth breath with a rate $1.2m^3/h$. As a result of the respiration through nose with lower intensity - 0.75m^3/h – the dose equivalent would be only 12% higher (see fig.4.).

In one site the concentration of the unattached fraction exceeded 20%. Moreover, the measurement showed rather low uncertainty of that result. Taking into account the same assumptions as above, it leads us to the conclusion, that in that site the dose equivalent is two times higher (100%) in comparison with calculations, made on a basis of the concentration of the attached fraction only. During a closer inspection of the site, performed with employees of ventilation service, we found that the air stream came from outlets of two longwalls at the deeper horizon. The dust content was low and probably it was a reason of such high contribution of the unattached fraction.

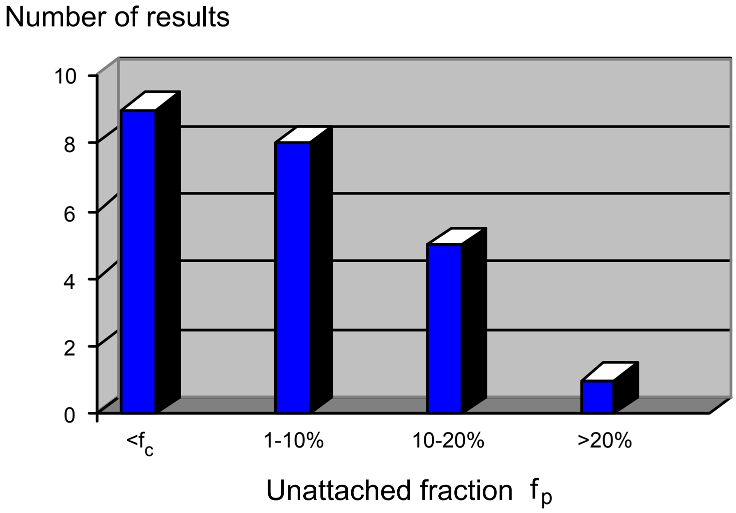

Fig. 3. Distribution of the results of the unattached fraction of radon progeny in coal mines in Poland.

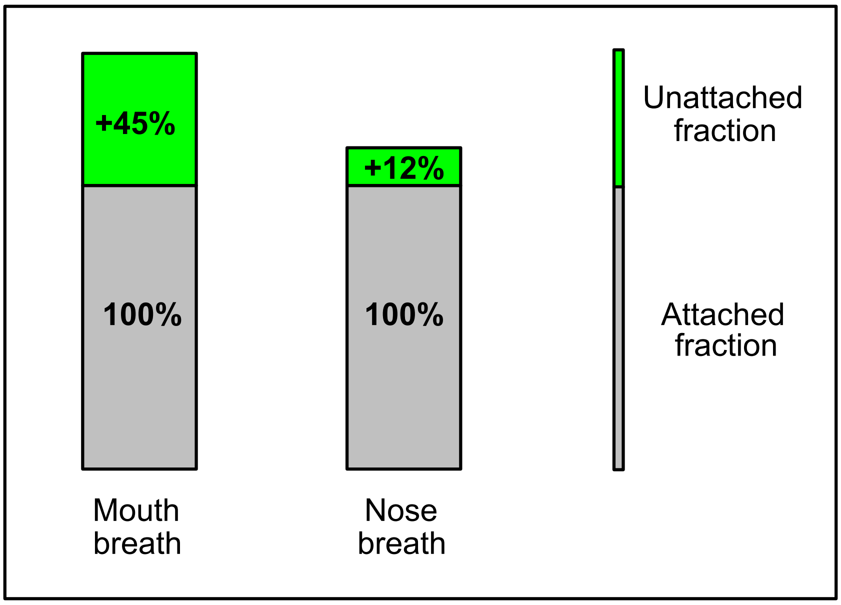

Fig.4. The influence of the unattached fraction (5.2%) on the dose equivalent for the log-normal size distribution of the attached fraction, AMD = 200nm and σ=2.3nm

Finally we would like to point out, that due to our results the concentration of the unattached fraction in chosen coal mines is relatively high. Comparable analysis with measurements in German underground mines (Porstendörfer et. al., 1991) shows, that the average value of the unattached fraction in Polish mines is of about 70% higher. Therefore the dose equivalent for miners seems to be roughly 45% higher as calculated previously, with the assumption that unattached fraction concentration is negligible. Of course, it needs confirmation in the future.

Conclusions

- Investigations of the unattached fraction have been done in four Polish coal mines. In two of these mines measurements were performed at all important workplaces. Collected data show, that the average value of the unattached fraction is of about 5.2%. It would increase the dose equivalent for underground mines – 45% in case of respiration through the mouth but 12% while breathing through the nose. Our campaign was the first one in Poland, therefore we have no possibilities to compare results with other national survey.

- Analysis of uncertainties of measurements of the unattached fraction have been done. Critical level was calculated for the instrumentation, designed and constructed for the survey. Therefore we are able to obtain reliable results for the unattached fraction in cases, when the concentration of the potential alpha energy of the attached fraction is not lower than 30Bq/m^3. But even for much higher PAEC and relatively high contribution of the unattached fraction, critical level is not better than 0.6%. The conclusion can be drawn, that with application of diffusion screen, for all results at level 1-2%, uncertainties are comparable with results.

- The knowledge of the size distribution of the aerosols at the sampling points and in the radon chamber is important. For different AMD the energy resolution in the alpha spectra is different. Typically for smaller particles the penetration depth into the filter media is bigger, therefore the resolution is worse. Our protocol is to analyse whole energy spectrum if we would like to avoid errors due to the different conditions in underground galleries and during calibration.

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Study of thorium uptake by inhabitants of a high background radiation area

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Abstract. Buena, located in the North of Rio de Janeiro, is characterized by its high natural radiation background, due to large deposits of monazite sand. The foodstuffs consumed by the population are basically composed of local products, which contain significant amounts of thorium. The analysis of complete cooked meals have shown an average daily intake of 18 mBq.d^{-1} of ^{232}Th and 189 mBq.d^{-1} of ^{228}Th. The average urine to feces ratio of ^{232}Th from samples of volunteers was found equal to 7.5×10^{-2}. The comparison of the experimental data with the predicted urine to feces ratios derived using the biokinetic model for thorium described by the ICRP publication 69 and simulating inhalation and ingestion separately, lead to the conclusion that the thorium intake is a combination of inhalation and ingestion. The clearance rate of thorium of monazite in lungs has apparently behaved as Type M compound. Inhalation is the biggest contributor for the committed effective dose due to thorium internal exposure.

INTRODUCTION

In Brazil, there are some areas where the concentrations of uranium and thorium in the soil are elevated. The inhabitants of theses areas are chronically exposed to radionuclides from the series of thorium and uranium. Most of the data available in the literature are based on the internal dose estimates through daily diet intake instead of bioassay data. In this study, Buena, a town located in North of Rio de Janeiro State in Brazil, where there is a large deposit of monazite sand, was selected for bioassay data collection and estimation of effective doses due to thorium natural exposure. An important characteristic of the families living in this area is the low mobility. Most of them have been in town for more than 10 years. The food consumed by the population is basically composed of local products. The quantification of the activities present in the diet from the village of Buena and from the city of Rio de Janeiro has been reported by Lauria et al. [1, 2]. The authors have found a significant concentration of thorium, uranium and nuclides from their radioactive series in the cooked meals. The average values of the daily diet intake of some radionuclides found in the cooked meals from Buena and from Rio de Janeiro are shown in Table I. These data characterize a chronic ingestion of foodstuffs with high concentrations of natural radionuclides. As this study is still being conducted, the data related to the control area are not available yet and Rio de Janeiro has been used as a reference of low background radiation area. Radium is the larger contributor to the intake, but this investigation will be focused on thorium.

METHODOLOGY

A total of 17 healthy adult volunteers inhabitants from Buena were selected and monitored by bioassay techniques. The individuals were asked to collect 24 hours fecal and urinary excretion. As thorium in monazite is an insoluble compound, only traces of thorium were expected in urine. The urine samples were analyzed for thorium content by inductively coupled plasma atomic mass spectrometry (ICP-MS), which is suitable for measurement of small amounts of thorium. The thorium in feces samples were high enough to be detected by alpha spectrometry method, which provided the isotopic ratio of these two radionuclides and allowed the comparison of ^{232}Th and ^{228}Th excreted in feces with the daily intake in diet.

The interpretation of the excreta results was done using a computer code, developed in our laboratory, to derive the expected fractions of thorium excreted in urine and in feces due to chronic intakes of the nuclide, through ingestion and inhalation. The thorium biokinetic model described in ICRP publication 69 [3] was used, but the value of the gastrointestinal uptake factor f_1 was changed several times, to test different proposals existing in the literature [4, 5]. The computer code reproduces the thorium predicted values of body contents and daily urinary and faecal excretion as a function of time, published in publication 78 of the ICRP [6], following the intake patterns and the parameters described in the publication. For the dose calculation, the dose coefficients from the ICRP database of dose coefficients for workers and members of the public [7] was utilized.

Table I. Average daily intake of radionuclides in the diet (cooked meals) from Buena and Rio de Janeiro (mBq.d^{-1})

	^{226}Ra	^{228}Ra	^{210}Pb	^{238}U	^{234}U	^{232}Th	^{230}Th	^{228}Th
Buena								
Average	246	722	216	108	111	18	32	189
Rio de Janeiro								
Average	179	456	89	36	35	8	15	146

RESULTS AND DISCUSSION

The ^{232}Th daily urinary and fecal excretion of a group of a group of 20 adults are shown in Table II. The ^{232}Th fecal excretion varied from below to 4 to 82 mBq.d^{-1}, with an average value of 23 mBq.d^{-1}. The average value for ^{228}Th in feces was 160 mBq.d^{-1}. The comparison of the average value of ^{232}Th excreted in feces with the amount of thorium present in the diet shown in Table I, suggests that the fecal excretion reflects the daily intake through diet. The thorium urinary excretion varied from 1.2 to 2.9 mBq.d^{-1}, with an average value of 1.9 mBq.d^{-1}. The variation of ^{232}Th in feces was not correlated to ^{232}Th in daily urinary excretion. Consequently, the urine to feces ratio varied widely from 0.03 to 0.23 and it was influenced by the amount of ^{232}Th in feces, the average ratio was 0.12. While the average values of ^{232}Th found in the daily urinary and fecal excretion from inhabitants of Rio de Janeiro were 0.7 and 9 mBq.d^{-1}, respectively, the urine to feces ratio was 0.072 [8]. The average amount of ^{232}Th in urine samples from inhabitants of Buena was almost three times higher than in urine samples from inhabitants of Rio de Janeiro, characterizing a chronic intake.

In order to investigate the main pathways of thorium intake and interpret the excreta data it was necessary to test some hypotheses and compare with the experimental data. As the amount of ^{232}Th and ^{228}Th in feces samples were similar to quantities present in the daily diet consumed by the population, the first hypotheses assumed that ingestion was the only pathway of thorium intake. The predicted values of daily urinary and fecal excretion were derived using the thorium biokinetic model described in ICRP publication 69 [3], simulating a chronic intake of thorium by ingestion, considering a gastrointestinal uptake f_1 equal to 5×10^{-4}, as suggested by ICRP publication 69 [3] for members of the public. The predicted urine to feces ratio was 1.2×10^{-4}, which is smaller than the experimental one, 1.2×10^{-1}. As a large variety of values of gastrointestinal uptake (f_1) of thorium has been reported in the literature, for insoluble thorium compounds, like thorium compound found in monazite, other values for f_1 were tested. The f_1 value equal to 1×10^{-3} for thorium in food recommended by NEA/OECD [4] by analogy with plutonium ingested in the tetravalent state as recommended in Publication 48 [9] was used. The predicted urine to feces ratio was still low, 2.5×10^{-4}, compared to the experimental one. As Johnson and Lamonte [5] have reported f_1 values in a range of 1×10^{-3} to 1×10^{-2} as suitable values for dietary intake of thorium, the highest f_1 value, 1×10^{-2}, was tested, but the predicted ratio 2.5×10^{-3} was still too small in comparison to the experimental values.

Table II. Thorium in 24 hours excretion of the adult people from Buena

#	Age (y)	^{232}Th urine (mBqd^{-1})	^{232}Th feces (mBqd^{-1})	^{228}Th feces (mBqd^{-1})	^{232}Th U:F ratio
TMOP	19	1.56	7.94	86.75	0.20
ACV	26	1.26	-	-	-
ROGS	32	1.18	37.08	257.50	0.03
FMOP	32	2.99	-	-	-
SVR	33	1.34	6.35	63.48	0.21
ARC	35	2.44	11.72	72.48	0.21
SR	37	2.44	-	-	-
GMS	37	2.73	14.07	338.23	0.19
JLV	40	1.19	47.06	139.44	0.03
GCV	43	1.16	<LMD[a]	-	-
MBS	44	1.73	34.39	209.92	0.05
MMSG	46	1.76	-	-	-
SFR	47	1.57	-	-	-
ADG	47	1.48	<LMD[a]	85.05	-
MD	48	2.69	81.99	214.92	0.03
AR.S	48	2.04	<LMD[a]	44.57	-
ABV	56	2.03	-	-	-
ICS	57	2.78	45.65	157.85	0.06
W AV	59	1.37	17.32	200.47	0.08
ACS	67	2.49	10.75	210.27	0.23

a = 4 mBq.d^{-1}

The comparison above has suggested that the contribution of thorium inhalation may be significant. The expected values of daily urinary and fecal excretion were tested using the thorium biokinetic model described by ICRP publication 69 [3], simulating a chronic intake of ^{232}Th by inhalation. As the thorium in monazite is classified as type S, AMAD = 1 μm, the predicted urine to feces ratio would be 1.4×10^{-3}, which was still low compared to the experimental one. If the compound was classified as Type M, AMAD = 1 μm, the predicted urine to feces ratio was 8.5×10^{-2}, which is close to the average of the experimental one, 1.2×10^{-1}.

In Figure 1 it is shown that there was an inverse correlation between the urine to feces ratio with the amount of thorium in feces. The analysis of this figure has reinforced the suggestion of a combination of intake through inhalation and ingestion. The low urine to feces ratio values were influenced by the high amounts of thorium in feces, indicating a significant contribution of the thorium of diet in feces. The urine to feces ratios higher than 0.08 has indicated that the predominant route of intake was through inhalation. The thorium content in urine may be influenced by the inhalation. These results have indicated that the f_1 value for thorium is really low as suggested by ICRP 69 [3], about 5×10^{-4} or even 1×10^{-3} as suggested by ICRP 48 [9] for plutonium in diet, and the method for thorium determination in urine was not sensitive enough to detect the increment from the contribution of thorium from diet.

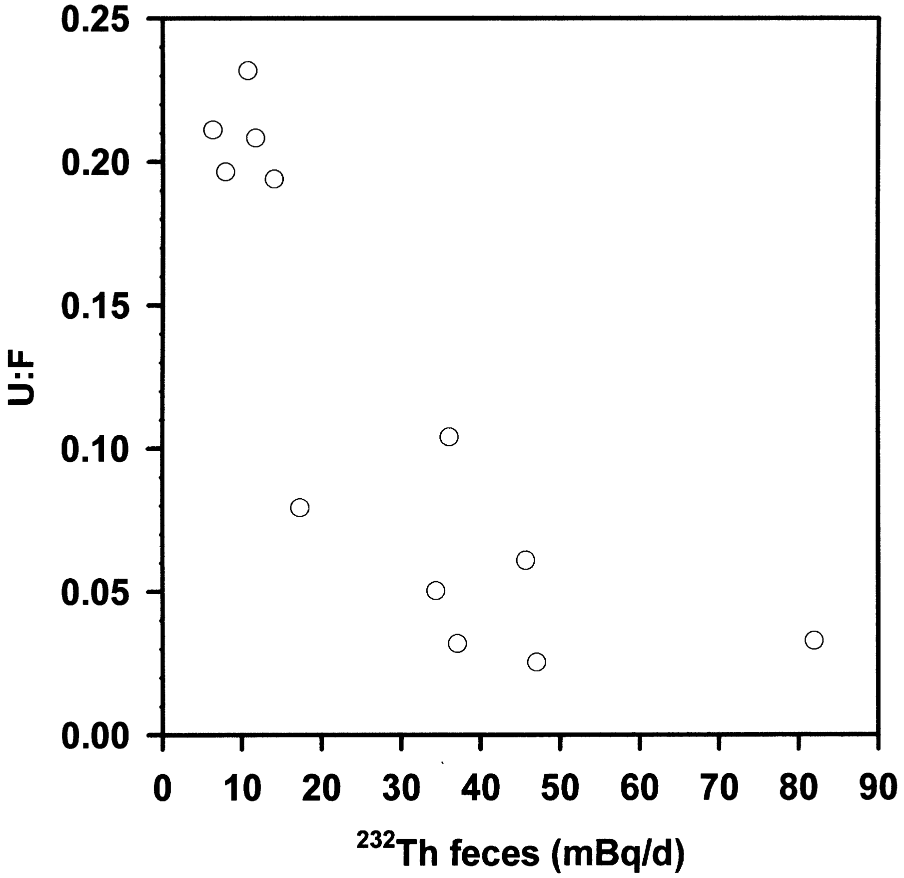

Figure 1. ^{232}*Th urine to feces ratio as a function of the* ^{232}*Th fecal excretion.*

Dose Calculation

For the adults, it was assumed that the thorium chronic intake began after 20y old. The biggest contributor for the dose was the intake through inhalation, since the dose coefficient for inhalation of a ^{232}Th compound Type M (4.5×10^{-5} Sv.Bq^{-1}) is almost two orders of magnitude higher than the dose coefficient for ingestion (2.3×10^{-7} Sv.Bq^{-1}) [7]. The average value for committed effective dose per year of exposure, by inhalation of ^{232}Th, for the chronically exposed adult living in Buena is 1.3 mSv. The committed effective dose from inhalation of $^{228\text{Th}}$ is about 70% of the one due to ^{232}Th. Although the ^{228}Th intake through ingestion was the highest, as seen in Tables I and II, the average value for committed effective dose per year of exposure, by ingestion was of order of 4 μSv.

CONCLUSIONS

- The thorium excretion in urine is related to the amount solubilized from the lungs, the clearance of the thorium from the skeleton and clearance from other organs and soft tissue, with very small contributions from the fraction absorbed from the daily intake through diet. The amount excreted in feces reflects the intake through diet, including the lack of equilibrium between ^{232}Th and ^{228}Th in fecal excretion.
- Although thorium in monazite has been classified as Type S in the literature, the use of Type M compounds was compatible with the experimental data.
- Inhalation was the main contributor for the internal dose due to chronical exposure to ^{232}Th.

- The excretion rate of thorium in urine do not increase as the excretion rate of thorium in feces increases for samples from inhabitants of Buena, reflecting the poor absorption of thorium through the gastrointestinal tract.

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Considerations about TENR due to non-nuclear mining and milling activities

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Abstract. Mining and processing activities dealing with mineral ores containing associated uranium and thorium series elements can make these radionuclides available in their products, byproducts and in the environment, leading to the enhancement of the exposure of the public to natural radiation. Niobium, phosphate, coal and gold plants have been selected as case studies, aiming to identify possible radiological impact sources during and after ceasing the operation on these units. The dose assessment results for present and future exposures scenarios confirm these mining industries as activities potentially enhancing exposure to natural radiation. Thus, the legislation for environmental licensing must be reviewed in order to take into account the potential environmental radiological impact caused by these activities, as well as the establishment of remediation procedures for waste storage areas in the existing sites.

1. INTRODUCTION

Mining and processing activities dealing with mineral ores containing associated uranium and thorium series elements can make these radionuclides available in their products, byproducts and in the environment, leading to the enhancement of the exposure of the public to natural radiation [1–4]. These impacts may be observed during the operational phase of the facilities and, if no proper remediation is carried out, after the ending of the activities.

In Brazil, several non-nuclear mining and milling industries are spread over the entire Brazilian territory. No regulation has been requires to dealing with these industries in respect to radiological protection aspects, although the Brazilian regulatory authority had already recognized that some kind of problems could be associated with non nuclear mining and milling activities and that should be investigated. Therefore, niobium, phosphate, coal and gold mining and milling facilities have been selected as case study, aiming to identify possible sources of radiological impact during and after ceasing the operation on these units. It is important to mention that both niobium and gold mining and milling facilities include chemical processing.

2. MATERIAL AND METHODS

2.1. Methodology

The working methodology consisted of an analysis of the operational process in terms of mass flux and radiological characterization and dose estimation for actual and future scenarios. The steps followed were:

- ✓ analysis of the operational process of the industry and interfaces with the environment;
- ✓ radiological characterization of the processing and environmental samples collected;
- ✓ calculations of the total activity generated by the operational process and identification of the solid waste (waste pond and waste rock);
- ✓ identification of the potential mechanisms involved on the radionuclides mobilization from the solid waste storage areas;
- ✓ estimation of the environmental impacts based on dose assessment in the population that could use the waste area and the around environment; and

- ✓ examination of the need for control actions and remediation or additional studies concerning the area for unrestricted use.

2.2. Sampling, preparation and measurements

The processing samples were separated into liquid and solid phases. The solid part was dissolved in an acid mixture and the liquid one were filtered (< 45 µm). The same procedure was applied to the liquid effluents and surface water samples. The radionuclides determined were: ^{238}U; ^{226}Ra and ^{210}Pb from uranium series and ^{232}Th and ^{228}Ra from thorium series. The analysis procedures are described in the Manual for Analytical Procedures from the Environmental Radiological Protection Department, DEPRA/IRD [5].

2.3. Individual dose assessment

The quantity used to estimate the radiation exposure of the population due to the use of surface water that receives the liquid emissions and of the solid waste storage areas was the effective dose equivalent, H_E.

The estimation of dose due to liquid emissions during the operational phase was performed using the IAEA specific model for exposure to critical groups [6]. The exposure scenarios were defined considering pathways selected according to potential uses of water by population such as drinking water, irrigation, etc. It was used the increment of radionuclide activity concentration in surface water, that was calculated from representative values of the natural background of the region of concern.

The estimation of the environmental commitment regarding the future use of the area where the solid waste is going to be deposited was performed using the RESRAD computational code [7], developed for calculating the resulting dose from exposures to residual material. The exposure scenario was the use of the waste solid as landfill for building construction. It was selected as pathways the external gamma irradiation; inhalation and ingestion of soil; exposure to radon and ingestion of water. As input values were used the radionuclide activity concentration in orders of magnitude.

2.4. Working hypothesis

Since we are interested on the radiological characterization of these facilities regarding the radiation protection regulation, the results of individual dose for each facility and scenario were evaluated according to the following three hypothesis:

- ✓ H1: the industries during the operational phase are exempted of control → $H_E \leq$ 10 µSv/year [8];
- ✓ H2: the industries during the operational phase should be controlled, although observing the dose limits for practices → 10 µSv $< H_E \leq$ 0.3 mSv/year [8 - 9]; and
- ✓ H3: the solid waste storage areas are released for unrestricted use → H_E < 10 mSv/year [10 – 11].

3. RESULTS AND DISCUSSION

3.1. Operational phase – actual scenario

Table I summarizes the dose results due to the liquid emissions during the operational phase of the niobium, phosphate, coal and gold industries.

Table I. Dose results due to the liquid emissions during the operational phase of the industries.

Industry	H_E
Niobium (I and II)	10 μSv $\leq H_E <$ 0.3 mSv/year
Phosphate (I and II)	<< 10 μSv/year
Coal	≅ 10 μSv/year
Gold	10 μSv $< H_E \leq$ 0.3 mSv/year

As we can observe, niobium and gold facilities, where chemical processing is involved, are not exempted of control. Nevertheless, the effluent treatment used by these facilities for chemical pollutants is enough to allow the observation of dose limits for practices, regarding radionuclides. In the other hand, phosphate and coal facilities can be considered exempted of control.

Concerning the coal and gold industries, which have pyrite associated to the ore, it is important to point out that, after ending of the operation, values up to 8 mSv/year were estimated considering the future use of the local water receiving the acid drainage from the waste rock areas.

3.2. Environmental commitment — future scenario

Figure 1 shows the dose estimation as a function of time due to the use of solid waste of the niobium industry I. The high uranium and thorium contents in the ore lead to doses around 50 mSv/year, even for the use of the waste rock. It is important to emphasize that in these type of facilities (non nuclear activities), the uranium and thorium content in the waste rock can be considering as being similar to the ore.

As we can observe, the waste dam material lead to doses similar to the waste rock. This waste comes from physical processing. Therefore, the physical processing in terms of concentration of radioactivity does not alter the pattern observed for the waste rock.

In the order hand, the slag deposit wastes from chemical processing lead to doses of one order of magnitude higher. This is due to the enrichment of radium isotopes and uranium and thorium. The contribution from radium isotopes we observe at the first years and those from thorium and uranium later, after the growth of the radium daughters.

Figure 2 shows the same data for another niobium facility (niobium industry II). It is also observed higher values for dose due to the use of waste rock and the waste from the physical processing. However, at the first years, the contribution of the slag material to the dose is the same. It means there was not an enrichment of radionuclides due to the chemical processing as it was observed in the case of the niobium industry I. This is due to the fact that the chemical processing at these industries are different. The niobium industry II does not have the barium sulfate generation.

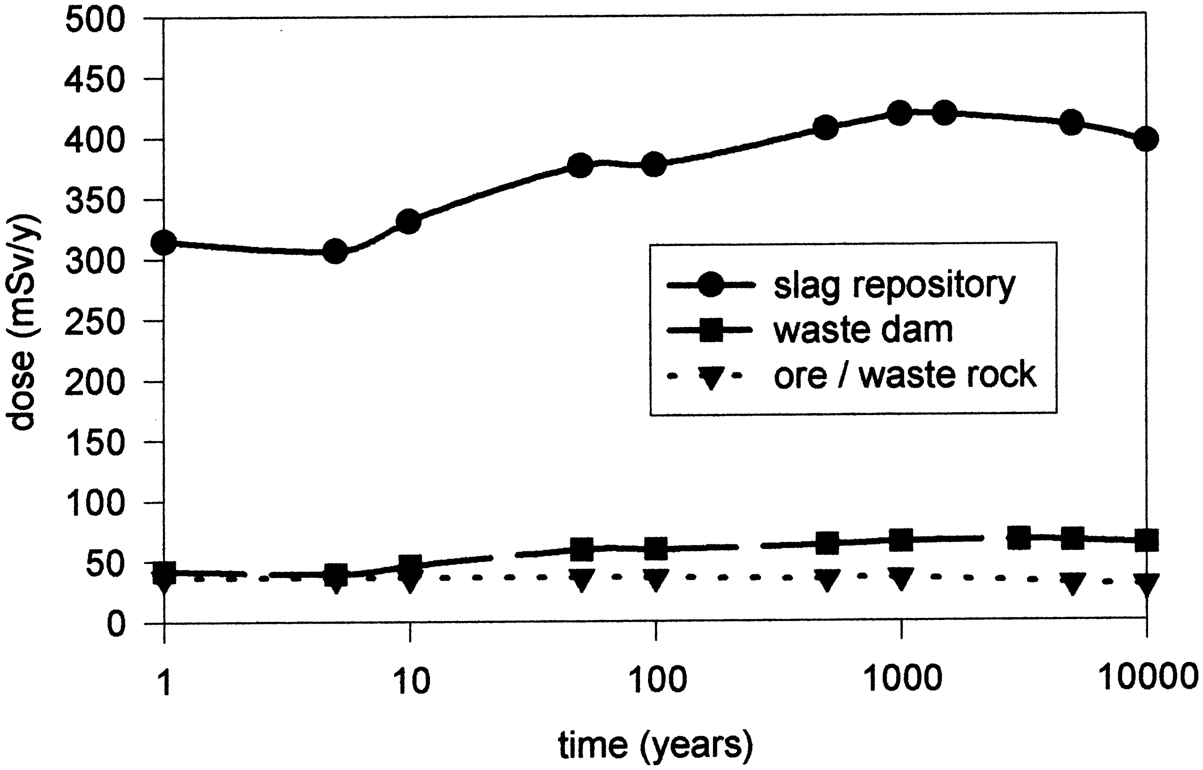

Figure 1. Dose estimation as a function of time due to the use of the solid waste from the niobium industry I.

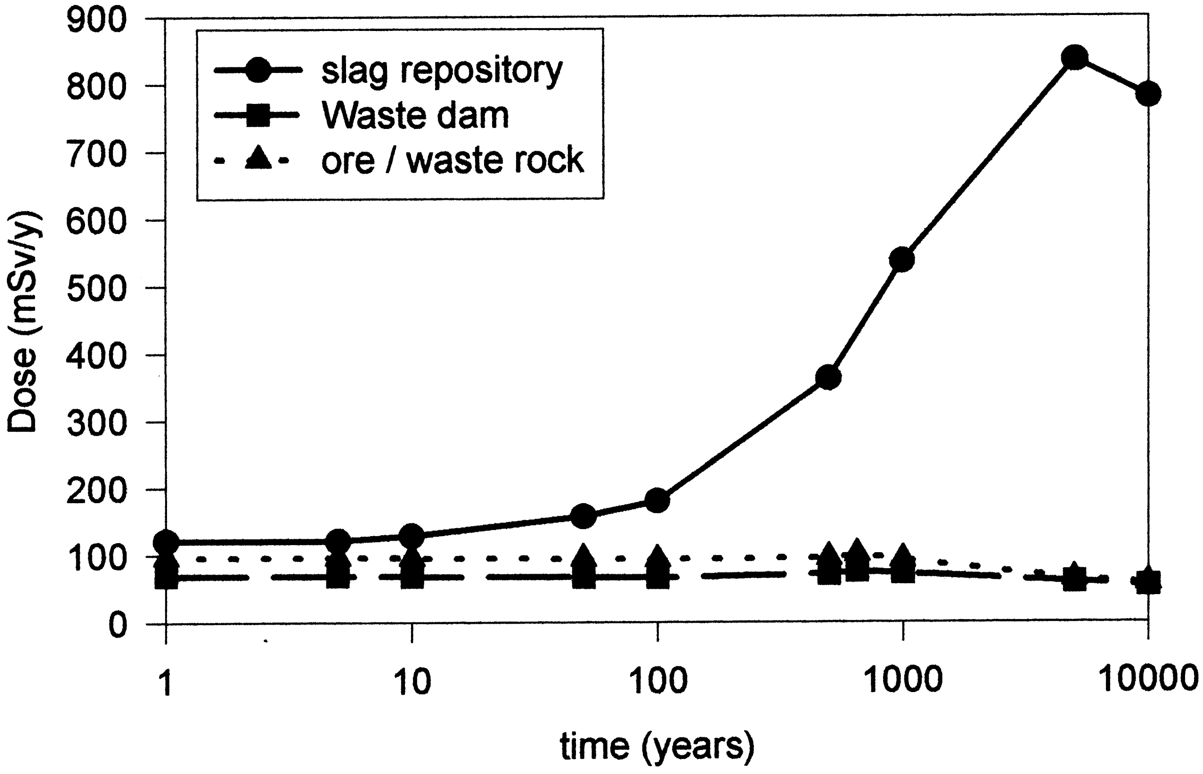

Figure 2. Dose estimation as a function of time due to the use of the solid waste from the niobium industry II.

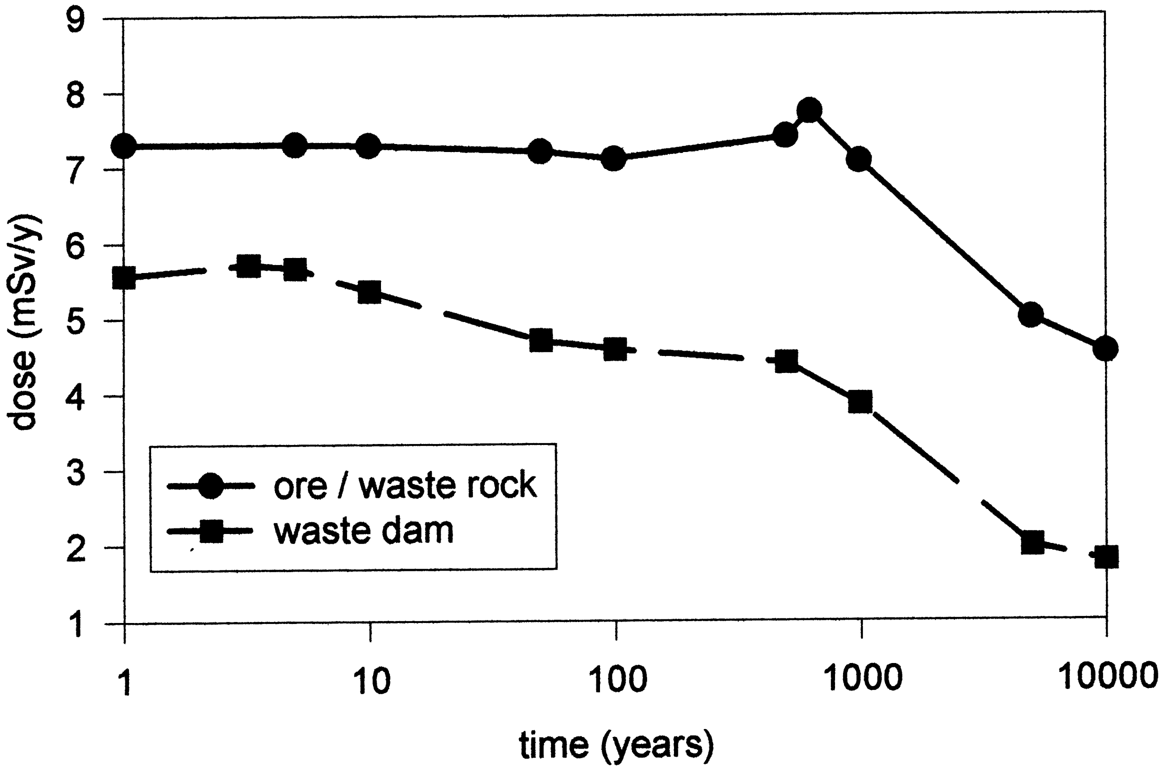

Figure 3. Dose estimation as a function of time due to the use of the solid waste from the phosphate industry I.

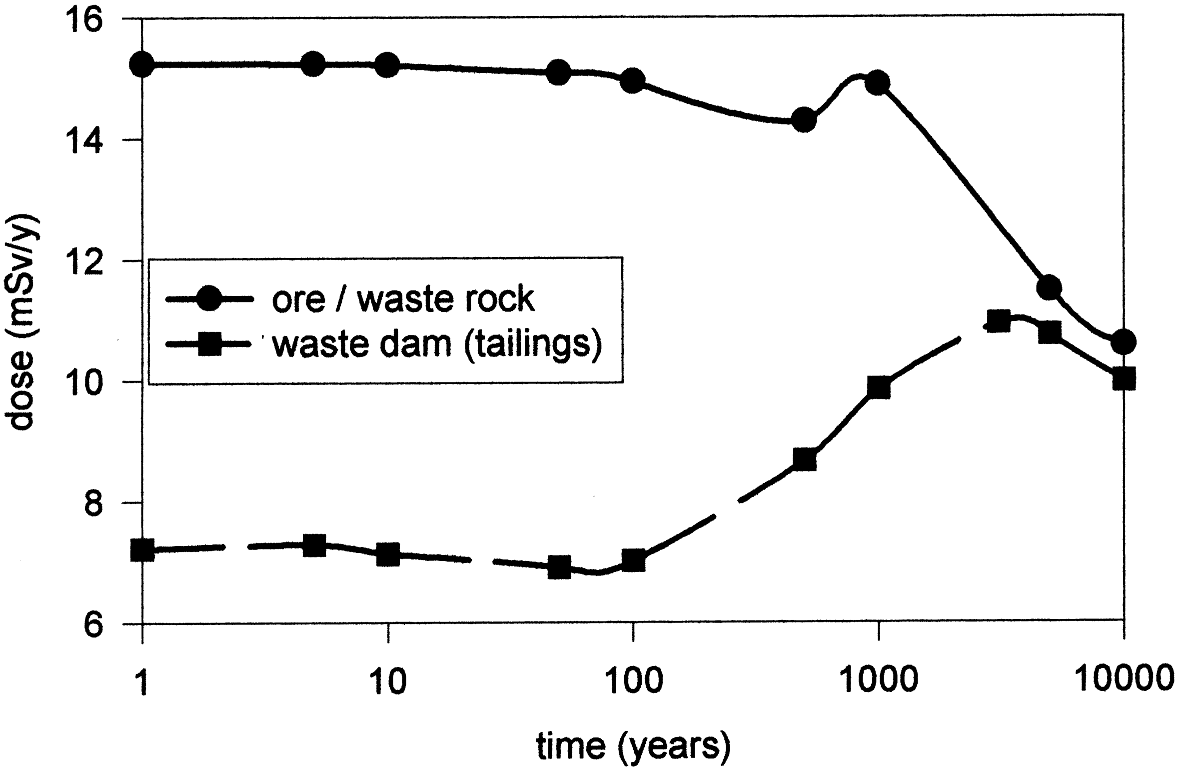

Figure 4. Dose estimation as a function of time due to the use of the solid waste from the phosphate industry II.

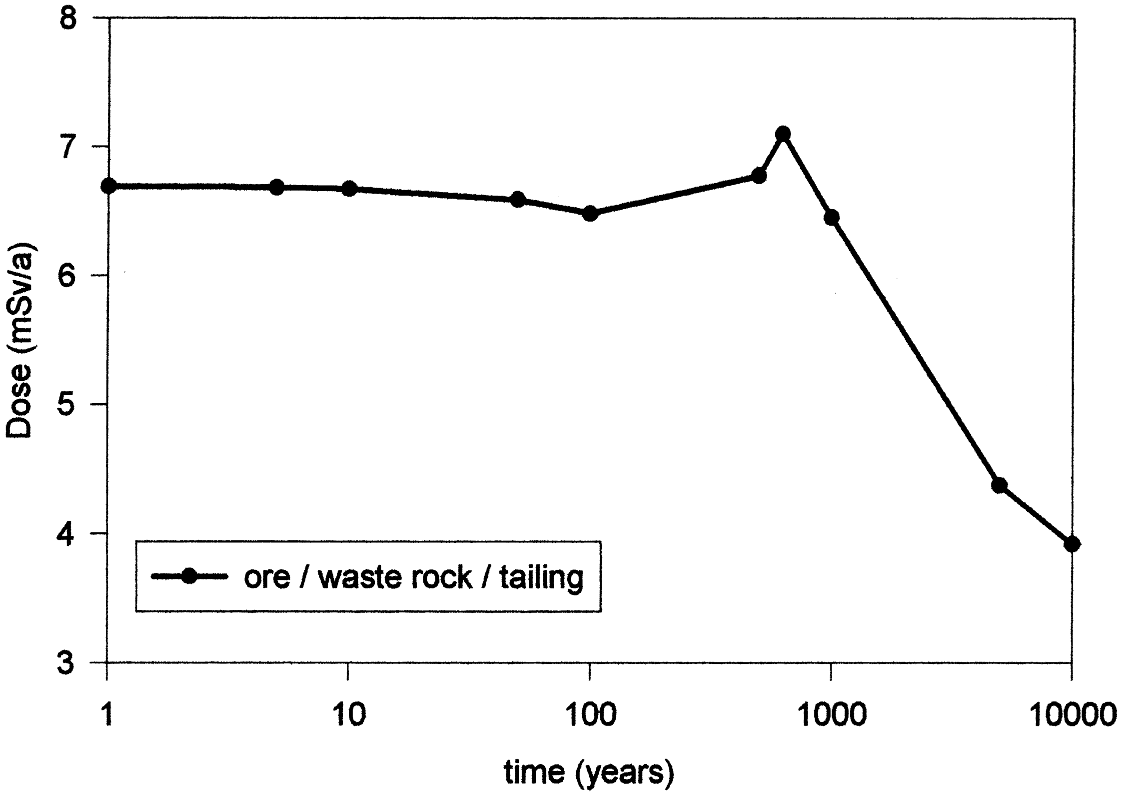

Figure 5. Dose estimation as a function of time due to the use of the solid waste from the coal industry.

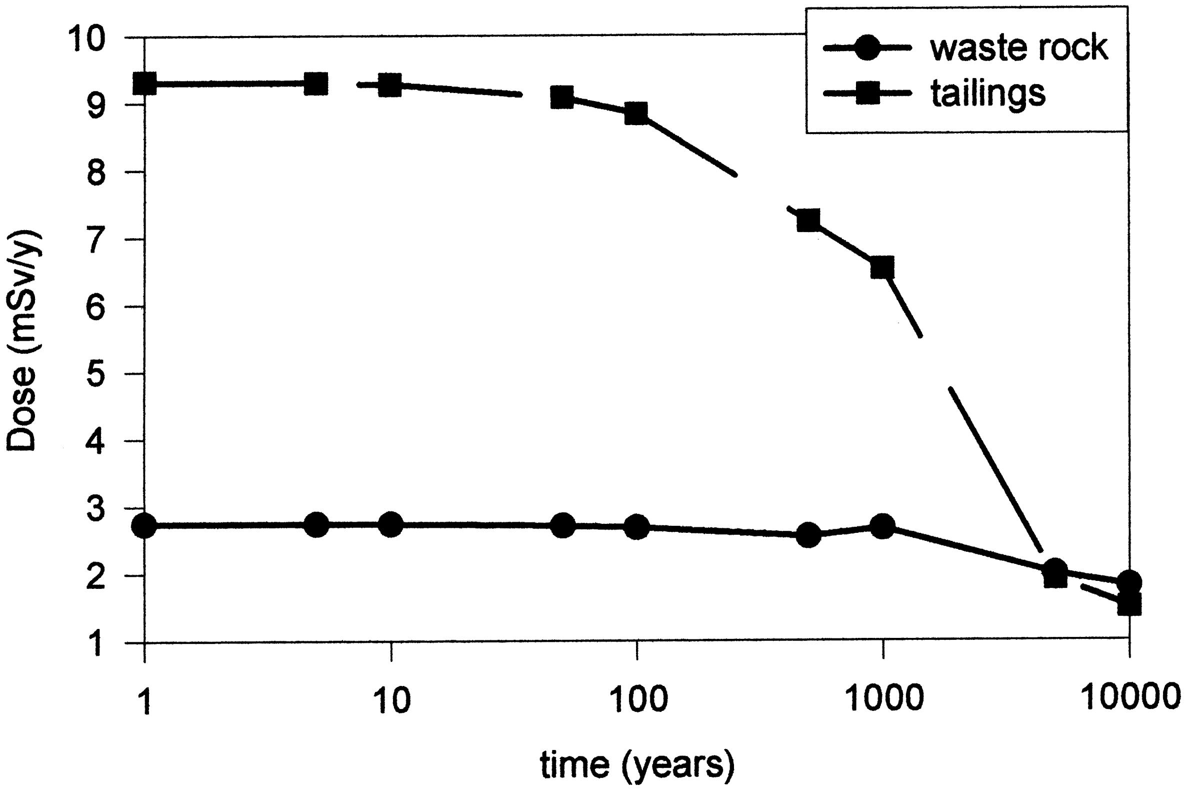

Figure 6. Dose estimation as a function of time due to the use of the solid waste from the gold industry.

It was observed an enrichment of uranium and thorium. Therefore, there is an enrichment of the dose later, after the increase of ^{226}Ra from ^{230}Th. In this case, the radon contribution is up to 85% of the total dose, since in this case the uranium content in the ore is much higher than the thorium one. Therefore, one can see that the chemical processing lead to enrichment of radionuclides and so, to the enhancement of dose. Nevertheless, the ratio of uranium and thorium content in the ore and the chemical processing characteristics are mandatory.

The dose estimation as a function of time due to the use of solid waste of two phosphate facilities are shown in Figures 3 and 4. The dose results for waste rock and waste from the physical processing are lower than 10 mSv/year, since in both cases the uranium and thorium ore content is low. In addition, there is no chemical processing in the operational process of these phosphate facilities.

Therefore, the phosphate facilities can be considered a non radiological problem. However, its important to emphasize that the amount of wastes generated has to be taken into consideration in terms of collective dose.

In the case of the coal industry, lower dose values and no radionuclide enrichment were also observed in Figure 5.

The dose estimation as a function of time due to the use of the solid waste of the gold industry is shown in Figure 6. It can be observed the dose increment due to the chemical processing even though with lower values due to the low uranium and thorium content in the gold ore.

Figure 6 Dose estimation as a function of time due to the use of the solid waste from the gold industry.

4. CONCLUSIONS

- ✓ The mining and milling of ores that contain uranium and thorium associated represent situations of TENR;
- ✓ The potential use of solid waste abandoned at the end of operation represents a long term radiological concern;
- ✓ The acid drainage as well as the chemical processing of mineral ores constitute relevant impact factors for actual and future scenarios;
- ✓ The legislation for environmental licensing must be reviewed in order to take the radiological impact into account.

The results can be used to develop indicators of potential radiological problems at these facilities to be adopted for screening purposes.

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Radionuclide fluxes at a plant manufacturing dicalcium phosphate for domestic animals

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Abstract. The objectives of this study is to map out the fluxes of radionuclides from the ^{238}U decay serie as well as estimate doses to workers at a dicalcium phosphate plant. At the studied plant phosphate rock is used for the production of dicalcium phosphate, which is a source of calcium and phosphorous for domestic animals. *A by-product in the manufacturing process is calcium chloride which is used in the oil industry, food industry and as road salt.* In the phosphate rock, the radionuclides were found in secular radioactive equilibrium with an average activity concentration of 830 Bq·kg^{-1}. Separation and concentration processes was observed. Most of the ^{226}Ra was found in the calcium chloride while the major part of ^{238}U was found in the dicalcium phosphate, about 950 Bq·kg^{-1}. The annual occupational effective dose to workers was found to be below the 1 mSv limit. The studie shows a good example of an important non-nuclear industry with a high input of natural radionuclides and several conceivable pathways to man.

1. Introduction

Phosphate rock of sedimentary origin is a main source of phosphorous for production of fertilizers and feed-supplements for domestic animals [1].

One feature of sedimentary phosphorite is its high abundance in natural radionuclides from the ^{238}U decay serie. Using phospate rock of sedimentary origin as a raw material in an industry process thus will lead to an input of several different radionuclides with different chemical behaviour.

The objective of this study have been examine how radionuclides from the ^{238}U decay serie are distributed in end-products, by-products and waste at the manufacturing process of dicalcium phosphate (DCP).

Effective doses to workers from inhalation of dust and radon have also been estimated.

2. Materials and methods

The DCP product is used as a supplement of phosphorous and calcium for domestic animals DCP can be provided to all kinds of animals but is primarily used as supplement for non-ruminant animals. Of the total food intake for the animals, DCP usually stands for 0.1–1 % of the weight.

The amount of phosphate rock used at the plant is 70300 tons per year.

At the initial step in the process the phosphate rock is partially dissolved in a hydrochloride acid solution. When $CaCO_3$ has been added and the pH adjusted to pH=2, dicalcium phosphate is precipitated from the solution. The sludge (sludge 1) that is formed and separated in this step mainly consists of undissolved phosphate rock, SiO_2 and flourid compounds as CaF_2. The remaining solution is used for production of calcium chloride in an adjacent plant. Before it enters this plant, mainly $Mg(OH)_2$ (sludge 2) is precipitated from the solution by changing the pH to pH=10. Both types of sludges are disposed close to the plant.

A scheme of the manufacturing process can be seen in fig.1.

The calcium chloride has many areas of use, mainly in the oil industry, food industry and as road salt. Several different qualities and concentrations are manufactured, both in soultions and solid forms. To produce calcium chloride of food quality, the solution of calcium chloride is purified by using active carbon.

$CaCl_2·6H_2O$ is obtained from a crystallization process where evaporation to saturation of the calcium chloride in the solution is followed by refrigeration.

Annual production of DCP, calcium chloride and different waste products is listed in table I.

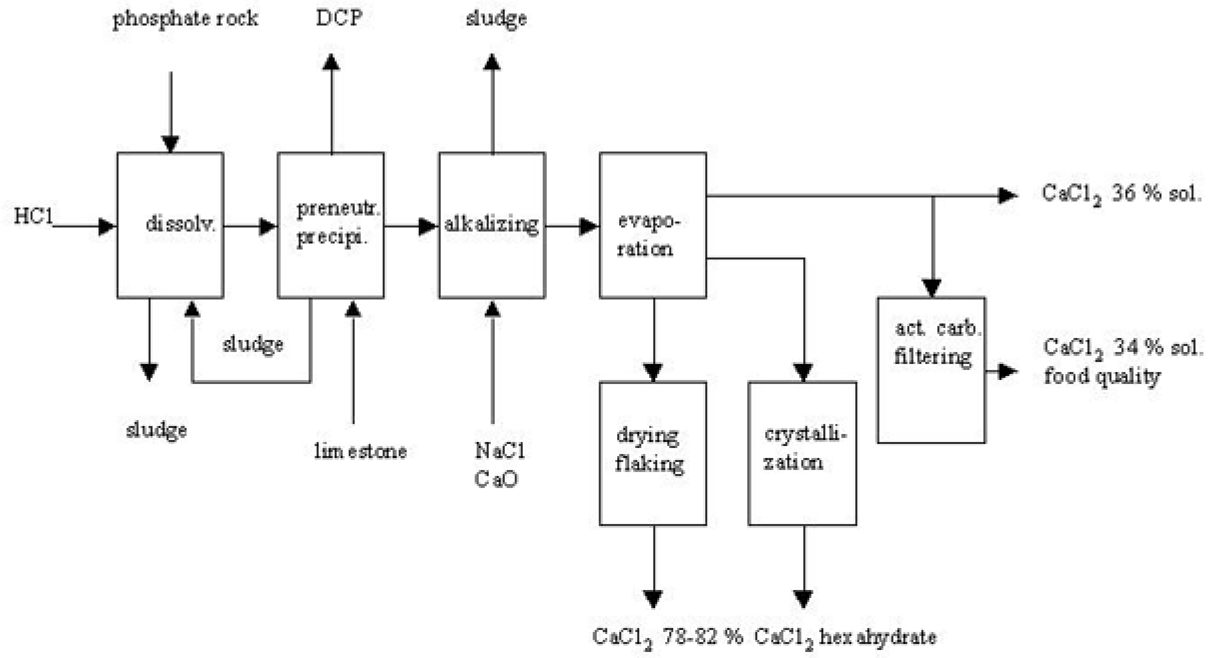

Figure 1. Schematic description of the manufacturing process.

Table I. Annual production of products and wastes

Material	Annual production [tons per year]
DCP	47100
Sludge 1	122000 (14600 dry weight)
Sludge 2	5500 (2000 dry weight)
$CaCl_2$ 36 % solution	42000
$CaCl_2$ 34 % solution (food quality)	6000
$CaCl_2 \cdot 6H_2O$	650
$CaCl_2$ 78–98 % (flakes and powder)	Approximately 70000

2.1. Radiochemical separation procedures and activity measurements

Slightly modified methods described by [2] were used for separation of uranium and thorium. The thorium was further purified from traces of uranium by ion-exchange (DOWEX, AG 1-4X, 100–200 mesh). As yield determinants ^{232}U and ^{229}Th was used.

Finally the uranium and thorium were electrodeposited on stainless steel disc at a current of 1 A for 1 hour from a sodium sulphate electrolyte [3].

For polonium methods described by [4] was used. From diluted hydrochlorid acid the polonium was spontaneously deposited on nickel discs at 65° C for 2 hours.

L-ascorbic acid was added to the sample to avoid deposition of Fe^{3+} on the disc. As yield determinant ^{209}Po was used.

α-spectrometry was carried out with ion-implanted silicon detectors (FWHM 30–40 keV in the region 4.15 – 5.31 MeV).

^{226}Ra was measured by sealing the sample in 200 ml radongas-tight steel containers. After 3 weeks storing when secular equilibrium was reached with its short lived decay products, the activity of ^{226}Ra was determined from the photopeaks of ^{214}Bi (609 keV) and ^{214}Pb (352 keV).

^{210}Pb was measured from its 46.5 keV photopeak. After gamma spectrometric measurement of the sample, it was mixed with reference-ore (Canmet DH-1a) and measured again. From the results of both measurements ^{210}Pb concentration in the sample was calculated.

Gamma spectrometric measurements were carried out with an n-type HPGe-detector with 35 % relative efficiency and 1.8 keV FWHM at 1.33 keV.
Measurement times were sufficiently long to ensure the statistical counting errors to be less than 5 %.

2.2. Dose assessment and measurements

To estimate the annual effective dose from ihalation of dust, dose conversion factors were taken from [5] and [6].
Where information not have been available, as for particle size distribution, conservative assumptions have been made. The breath rate was set to 1.5 $m^3 \cdot h^{-1}$, corresponding to light exercise conditions [7].
According to information from the staff of the plant the average time spent per week in the production area is about 10 h.
The most dominating source for dust in the studied plant was where the DCP is dried after being filtered from the solution. Dust can also be released in connection with different interruptions in the operation of the plant. Most common is dust from the DCP-product. Interruptions producing DCP-dust is estimated to occur approximately 10 times per year while interruptions causing phosphate-dust occur approximately 5 times per year (duration 2 hours).
Concentration of dust in the air have been measured by the company at several occasions giving an average dust concentration of 3.5 $mg \cdot m^{-3}$, of which 3 $mg \cdot m^{-3}$ has been assumed to origin from the DCP and 0.5 $mg \cdot m^{-3}$ from the phosphate rock. Dust concentration in the control room was set to 0.5 $mg \cdot m^{-3}$. Maximum dust concentration measured in the plant is 16 $mg \cdot m^{-3}$.
The external dose measured at the plant was determined by using a doserate instrument (RADOS SRV-2000) calibrated in ambient dose equivalent ($H^*(10)$). The calibration was traceble to the national standard laboratory at STUK (Finland).
The concentration of short lived radon daughters was measured at two occasions. One using the modified Tsivoglous method described by [8]. To calculate the radon gas concentration an equilibrium factor of 0.6 was assumed.
Radon has also been measured by track-etch detectors. Exposure times for the track-etch detectors were 12 days. The time between the two measurements was approximately 3 months.
The dose conversion factor for radon gas exposure ($3.2 \cdot 10^{-6}$ $mSv \cdot h^{-1} \cdot Bq^{-1} \cdot m^3$) was taken from [9].

3. Results

See table II–VI.

Table II. Activity concentration [$Bq \cdot kg^{-1}$ fresh weight]. The standard deviation are based on multiple analyses (n = 2 or 3) for all radionuclides except ^{210}Pb where it is based on results after repeated homogenizations of sample and reference ore. Dry weight to fresh weight ratios were measured to 0.12 for sludge 1, 0.37 for sludge 2 and 0.64 for active carbon

	^{238}U	^{234}U	^{230}Th	^{226}Ra	^{210}Pb	^{210}Po
Phosphate rock	832	830	816	855 ± 7	843 ± 35	820
DCP	954 ± 38	1012 ± 42	10 ± 1	15 ± 1	169 ± 7	350 ± 2
Sludge 1	178 ± 14	170 ± 14	409 ± 8	139	100 ± 5	-
Sludge 2	8 ± 0.5	8 ± 0.2	12 ± 4	78 ± 8	3480 ± 252	-
$CaCl_2$ (82 %)	<0.01	<0.01	<0.01	825 ± 7	70 ± 4	-
$CaCl_2$ (78 %)	<0.01	<0.01	<0.01	493 ± 4	51 ± 3	-
$CaCl_2$ (36 %)	<0.01	<0.01	<0.01	316 ± 14	20 ± 1	-
$CaCl_2$ (stem solution 15 %)	< 0.01	< 0.01	< 0.01	138 ± 4	100 ± 9	-
$CaCl_2 \cdot 6H_2O$ (50 %)	<0.01	<0.01	<0.01	21 ± 1	<5	-
$CaCl_2$ (food quality 34 %)	<0.01	<0.01	<0.01	280 ± 8	10 ± 1	-
Active carbon	10 ± 5	10 ± 5	4	147	114 ± 5	-

Table III. Activity concentrations [Bq·kg^{-1}]. For active carbon the ^{222}Rn concentratiom is expressed as Bq per kg fresh weight. The ratio dry weight to fresh weigt was measured to 0.64

	^{232}Th	^{40}K	^{222}Rn
Phosphate rock	5	4	-
Active carbon (4 h after filtration)	-	-	31000

Table IV. Measured ambient dose equivalent rates [µSv·h^{-1}] at different locations after background subtracktion

Location	Dose rate [µSv·h^{-1}]
DCP-plant (production area)	0.1-0.2
Phosphate mill house (1 m from the mill)	0.1
Outside phosphate storage silo (4500 ton)	0
Surface of active carbon storage container (height 1.5 m, diameter 1m and 0.5 cm steel walls)	1.5-2
Active carbon storage container (1 m distance)	0.1-0.3
Active carbon (surface)	7-8

Table V. ^{222}Rn gas concentration

Location	Track-etch detector results [Bq·m^{-3}]	Modified Tsivoglous method results [Bq·m^{-3}]
DCP-plant (production area)	<70	8
Phosphate mill house	<70	3
$CaCl_2$-plant	<70	1

Table VI. Estimated annual occupational effective doses for a worker at the DCP-plant

Origin	Annual occupational effective dose (mSv)
Dust inhalation (DCP and phosphate rock)	0.06
External exposure	0.1
Radon (70 Bq·m^{-3})	0.1

4. Discussion and conclusions

The average activity concentration for all measured radionuclides in the uranium decay serie is 833 Bq·kg^{-1} while the concentration of ^{232}Th and ^{40}K in the phosphate rock was relatively low.

For uranium, almost 70 % of the total activity ends up in the DCP product. According to [10] uranyl ions can be precipitated as UO_2HPO_4 from acid (pH 1.2–2.3) solutions. The pH of the solution at the time when the dicalcium phosphate precipitates falls within this range and it is thus possible that the uranium coprecipitate as UO_2HPO_4 with the dicalcium phosphate.

Almost all of the remaining uranium can be found in the sludge consisting of undissolved phosphate rock, SiO_2 and fluoride compounds.

Sludge 1 contains allmost all of the ^{230}Th that enters the process. Of the total amount only about 1 % could be found in the DCP product. According to [11] Th has a high ability to adsorb on colloid surfaces which could explain the high concentration of ^{230}Th in the sludge.

The ^{226}Ra present in the process seems to behave similar as its chemical analouge calcium. The major part of the ^{226}Ra, about 75 % of the total output, can be found in the calcium chloride solution where the concentration ^{226}Ra in the different products is more or less proportional to the concentration of calcium chloride. The only exception was the $CaCl_2 \cdot 6H_2O$ where the concentration of ^{226}Ra was considerable lower. Differences in solubility between calcium- and radium chloride or rejection of the radium ions in the formation of the crystalls is probably the explanaition for this.

Almost all of the remaining radium ends up in the sludge consisting of undissolved phosphate rock, SiO_2 and fluoride compounds.

Fresh samples of active carbon, used for the purification of $CaCl_2$, showed high concentration of short lived radon daughters, 31000 $Bq \cdot kg^{-1}$. The activity in the sample decreased with a half-life of about 4 days showing that the parent-nuclide was ^{222}Rn.

As a percentage of the total input, ^{210}Pb is more uniformly distributed between different products and wastes than the other measured nuclides. Noticeable is however the high concentration that was found in the sludge consisting of mostly $Mg(OH)_2$, probably caused by coprecipitation of lead as the slightly soluble $Pb(OH)_2$. This sludge constitute only about 2 % of the output mass from the process but contains approximately 45 % of the total amount of ^{210}Pb.

The concentration of ^{210}Pb in the $CaCl_2$ was not proportional to the concentration of the $CaCl_2$ as for ^{226}Ra. The highest concentration was found in the stem solution having the lowest concentration of $CaCl_2$ (15 % solution). The reason for this is that the concentration of particles and different impurities are high in the stem solution. In the solution holding 36 % $CaCl_2$ the major part of the particles have been removed by sedimentation, and the lower concentration of ^{210}Pb shows that a large part of the ^{210}Pb is associated with these particles.

The concentration of ^{210}Pb in the $CaCl_2$ holding 78 and 82 % are also lower than was measured in the stem solution. Since purification by sedimentation is not carried out for this $CaCl_2$ quality, the reason for this is different storage time for the stem solution, leading to different degree of sedimentation, before it enters the production line of 78 and 82 % $CaCl_2$.

Polonium has only been measured in the phosphate rock and in the DCP product showing that about 25 % of the total input ends up in the DCP.

Calculating a budget for inflowing and outflowing radioactivity for the process gives a inflow/outlow ratio between 0.70 and 1.14 for all nuclides (polonium excluded).

The annual effective dose for a worker at the DCP-plant is below the dose limit of 1 mSv when the plant is runned without too many interruptions that produces dust and force workers to spend time in the production area.

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Overview of the technological enhancement of natural radiation in the Brazilian non-uranium mining industry

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Abstract. The mining and milling of ores with significant amounts of uranium and thorium associated to the main ore has the potential to pose undue health risks to members of the general public and workers. In order to assess the status of this problem in the Brazilian non-uranium mining industries a comprehensive investigation project has been undertaken. The adopted methodology was based on the detailed analysis of each investigated industry operational flowplan, mass balance calculations, risk assessment (operational and post-operational scenarios taken into account) and environmental management principles. This papers addresses the main issues arising from the investigation effort, reports the most relevant conclusions and states the future studies to be implemented. It could be observed that these industries have the potential to cause relevant radiological impacts and must be regulated/controlled as to avoid these problems.

1. INTRODUCTION

The mining and milling of ores with significant amounts of uranium and thorium minerals may lead to the radiological environmental impact of nearby water streams, soils and aquifers. These impacts may be observed during the operational phase of the facilities as well as after the facility close out, if no proper reme diation is carried out.

During the life of the mining operation, and after the plant close out, the tailings and waste dumps that have been formed are constantly subjected to weathering. Upon close out, weathering process, although unchanged externally, may be considerably different within these areas. The rate of leaching of pollutants from the solid material will change with time and be dependent on several factors that will regulate the rate of pollutant release from these sources.

In the assessment of the potential impacts caused by these installations, monitoring programs, envisaged to detect increases in radioisotopes concentrations in environmental samples like superficial water, sediments, soil, vegetables, fish, etc, used to be carried out. This strategy lacks of consistence once it can not cope with impacts in future scenarios. In addition to this, an overall understanding about the amount of radionuclides disposed off with the wastes, radioisotope concentrations in by products that could be used in a wide variety of situations remain unknown.

Another important issue to be emphasised is the fact that these industries, despite the potential radiological impacts that they may cause are not regulated, i.e., they are not licensed as practices, nor controlled by the Regulatory Authority. However, as it will be showed in other paper in this book [1] undesirable exposures of members of the public and workers may result from their operation.

Several are the facilities in Brazil which present potential radiological problems caused by the presence of uranium and thorium associated to the main ore like coal, phosphate, niobium, gold, tin, copper and lead mining and milling facilities. Exposures of members of the general public will also depend, on a very large extent, on the regional characteristics associated to a particular facility location. This is of special concern in a country like Brazil where the development stages of the different regions are not the same, leading to social and economical patterns completely different from region to region.

Presently, a broad research program concerning the assessment of the extent of the technological enhancement of natural radiation caused by non-nuclear mining industries is being developed by the Institute of Radiation Protection and Dosimetry (IRD). The questions to be answered by the investigation program are:

1. Do the non-uranium mining industries have the potential to cause environmental (occupational) radiological impacts?
2. If yes, what are the extent of these impacts?
3. How to deal with the assessment of the problem?

In order to deal with these questions a working strategy was designed. The program relies on a pragmatic approach to identify, characterise and implement remedial actions, whenever necessary, to the sites affected by the operation of these installations.

2. WORKING METHODOLOGY

Once mining operations begin a mineral deposit is disturbed in such ways that many accessory elements and compounds are redistributed in markedly different patterns and concentrations from those that would occur by natural geologic processes. Redistribution of elements can occur during any of the steps involved in the material cycle.

During mining, various elements and minerals are made more accessible to environmental exposure. Waste rock or overburden is generally removed and piled away from the working area; some may be used in road and site construction but most goes into spoil piles.

With most raw materials, the mined ore must be beneficiated to separate the desired minerals from the waste material. This is carried out first by comminution to a size at which the minerals are liberated from each other, followed by concentrating mechanism for the desired ore mineral. Beneficiation technologies utilise physical or surface chemical means for separating minerals, and consequently the minerals are not changed chemically at this processing stage. Generally, chemical processing is required to convert the desired ore minerals into the chemical form suitable for use. Elements in the metallic state, for instance, may accompany the metal whereas elements forming oxides may be separated and discarded as slag. In addition, volatile constituents can separate in gaseous phase and be vented to the atmosphere. In the processing of certain ores or concentrates, leaching with aqueous solutions may be a major separation step. Here, element redistribution follows from the discard leach liquid and any entrained leach residue. During the chemical processing, there may be an opportunity to recover by-products because of the chemical changes induced in the material at this stage. Recovery can often be achieved by modification of specific process in the flowplan,

From the previous discussion it is clear that a precise understanding of the potential impacts caused by a mining industry shall begin by the detailed analysis of the operational flowplan. Concentration of radiosiotopes in the different generated wastes and effluents must be determined, and multiplied by the flux that each waste is produced in the operational process. This will allow (by means of mass balance calculations) the exact knowledge of the amounts of radioactivity involved on each step of the operational process. It will also allow for a better waste management system if it appears that the adopted strategy is likely to cause undue environmental impacts. Moreover, the likelihood for radioisotopes (and any other potential pollutant) mobilisation from the wastes must be addressed. This may be of key relevance in terms of future contamination of aquifers and superficial waters. External exposures as well as radon exhalation shall also be determined in case of unrestricted use of depositional areas are intended in the future. The impacts associated to the use of by-products (e.g., coal ashes and phosphogypsum as building materials and phosphogypsum as fertiliser in the agriculture) shall also be assessed. Finally, the adoption of remedial actions may be suggested. This may include modifications of the waste disposal strategy, alteration of the processing route, economical recovery of by-products and so on.

The adopted methodology consisted of:

(1) Analysis of the operational process of the industry;
(2) Sample collection (and radionuclide determination) from specific points of the operational process;
(3) Mass balance calculations and determination of the total activity accumulated in each step of the operational process and those deposited as wastes. The amount of radioactivity in the final product is also considered;
(4) Determination and quantification of the potential mechanisms involved on the mobilisation of the pollutants from the waste deposit areas (tailings dam/pile and waste dumps);
(5) Estimation of the environmental compartment concentrations associated to effluent releases;
(6) Risk assessment concerning the operational impacts of the facility and those associated to the facility close-out;

(7) Examination of the need for remediation concerning the contaminated area (waste deposit areas) for irrestricted use.

3. RESULTS

Table 1 shows the activity concentrations determined in samples from the run of mine collected in some industries.

It can be seen that, with the exception of gold ore sample, the radionuclides are not in equilibrium. The highest concentration of uranium was found in the Niobium II industry. In the other Nb-industry Th showed a higher concentration than uranium. The phosphate II industry showed higher concentrations of the natural radionuclides in comparison to the phosphate I industry.

The total inventory of radionuclide fluxes among the different industries is shown in table 2. These fluxes are obtained by multiplying the different radionuclide concentrations in the run of mine by the total mass of the run of mine entering the process. The highest values are observed for the phosphate industries and one of the investigated niobium industries.

Table 1. Activity Concentrations in some Ores of the Investigated Industries

Mining Industry	^{238}U	^{226}Ra	^{210}Pb	^{232}Th	^{228}Ra
Niobium I	930 +/- 62	805 +/- 97	1,330 +/- 231	6,390 +/- 655	5,176 +/- 716
Niobium II	4,550 +/- 300	3,390 +/- 319	7,890 +/- 1,121	904 +/- 94	2,040 +/- 312
Coal	359 +/- 24	457 +/- 57	754 +/- 167	33+/- 3	68 +/- 49
Gold	114 +/- 8	136 +/- 17	169 +/- 104	49 +/- 5	< 42
Phosphate I	114 +/- 8	330 +/- 41	800 +/- 172	204 _+/- 21	350 +/- 123
Phosphate II	880 +/- 58	700 +/- 85	990 +/- 192	753 +/- 77	1,550 +/- 255

Obs: Results refer to one composite sample. The analysed sample was composed by five sub-samples taken during five consecutive days by the mining operators (according to their quality control protocol).

Table 2. Fluxes of Radioactivity Associated to the Investigated Mining Industries

Industry	Total Radioactivity Flux (Bq/year)
Niobium I	1.8×10^{13}
Niobium II	6.4×10^{12}
Coal	1.5×10^{10}
Gold	3.3×10^{11}
Phosphate I	2.0×10^{13}
Phosphate II	2.7×10^{13}

The redistribution of the radionuclides along the operational process will cause that some of the radionuclides will be leaving the process in higher amounts associated to a specific waste. The redistribution will depend on the type of the operational process and on the mineralogical composition of the ore. Table 3 shows the redistribution of the radionuclides in the operational process of two of the investigated niobium industries.

By far, the highest concentrations are observed in the slags of both Nb industries and also in the barium sulphate residue of the Niobium I industry. However, the mass flux involved in these steps of the operational process (0.85 to 3.0 t/h) are very small if compared to the mass flux of the other steps. It means that these wastes may be disposed of in separated areas with proper preparation of the disposal area. Shielding against gamma radiation exposure shall be provided. Mobilisation of radionuclides from these wastes (with the exception of barium sulphate residue) will not be a major issue, once this material is very refractory. On the other hand, ground water bellow the barium sulphate disposal area shows (in the case of the Niobium I industry) Ra isotopes (226 and 228) concentrations as high as 5.0 Bq/L. These waters need to be pumped and treated with $CaSO_4$ to precipitate the dissolved Ra isotopes before being released to the open environment.

Table 3. Radionuclide Redistribution in the Different Steps of the Operational Processes of two of the investigated Niobium Industries

Operational Process Step	**^{238}U**	**^{226}Ra**	**^{210}Pb**	**^{232}Th**	**^{228}Ra**
Niobium I					
Magnetic Separation (22 t/h)	(1,091+/-74) 2.0 x 10^{11}	(340+/-43) 6.3 x 10^{10}	(720+/- 63) 1.3 x 10^{11}	(863 +/- 90) 1.4 x 10^{11}	(5,176+/-716) 6.9 x10^{11}
Disliming (17 t/h)	(1,265+/-83) 1.8 x 10^{11}	(1,381+/-158) 2.0 x 10^{11}	(2,029+/-311) 2.9 x 10^{11}	(8,995+/-924) 1.3 x 10^{12}	(5,278+/-720) 7.7 x 10^{11}
Floatation (90 t/h)	(770+/-50) 5.8 x 10^{11}	(990 +\- 120) 7.5 x 10^{11}	(2,440 +\- 360) 1.8 x 10^{12}	(3,100 +/- 320) 2.3 x 10^{12}	(1,440 +\- 243) 1.1 x 10^{12}
Slag (3 t/h)	(23,138 +/1520) 5.8 x 10^{11}	(3,290 +\- 313) 8.3 x 10^{10}	(2,400 +\- 355) 6.1 x 10^{10}	(117,600 +\- 12,000) 3.0 x 10^{12}	(20,200+\- 3,606) 5.1 x 10^{11}
Barium Sulphate (0.6 t/h)	(42 +/- 2) 2.1 x 10^{08}	(26,250+/- 3,100) 1.3 x 10^{11}	(7,400+/- 1,000) 3.7 x 10^{10}	(43 +/- 1) 2.2 x 10^{08}	(19,7300+/- 27,600) 9.9 x 10^{11}
Niobium II					
Magnetic Separation (13 t/h)	(843+/-56) 9.2 x 10^{10}	(941+/-112) 1.0 x 10^{11}	(1,730+/-276) 1.9 x 10^{11}	(293+/-30) 3.2 x 10^{10}	(315+/-120) 3.4 x 10^{10}
Disliming (8 t/h)	(6,700+/- 145) 4.5 x 10^{11}	(6,900+/-404) 4.6 x 10^{11}	(6,180+/-860) 4.2 x 10^{11}	(1,754+/-180) 1.2 x 10^{11}	(3,080+/-439) 2.1 x 10^{11}
Floatation (43 t/h)	(4,985+/- 327) 1.8 x10^{12}	(3,400+/-320) 1.2 x 10^{12}	(7,530+/- 1,065) 2.7 x 10^{12}	(1,040+/-107) 3.8 x 10^{11}	(1840+/-289) 6.6 x 10^{11}
Slag (0.83 t/h)	(34,819+/- 2,294) 2.4 x 10^{11}	(5,160+/-393) 3.6 x 10^{10}	(435+/-132) 3.0 x 10^{09}	(167,700+/- 1,713) 1.2 x 10^{11}	(6,450+/-900) 4.5 x 10^{10}

Obs: Concentration results in parenthesis

In both Nb industries the highest radioactivity mass fluxes are associated to the floatation step. However, the radionuclide concentrations in these wastes are different between both industries. ^{238}U concentration in the floatation wastes of the Niobium II industry is about 5,000 Bq/kg. The total flux of ^{238}U in these wastes is 1.8 x 10^{12} Bq/year which corresponds to 145 $t_{U\text{-}238}$/year. It means that 145 tons of ^{238}U are being lost as waste in the operational process. The obvious conclusion is that an economical feasibility study concerning the recovery of uranium from these wastes shall be commenced. This idea is even more plausible if one takes into account that the average production of the only uranium mining and milling facility to operate in Brazil until now was about 100 t_{U3O8} per year. The estimated production of a future Uranium mining and milling facility (located at Bahia state – Lagoa Real Project) is 300 t_{U3O8} per year.

Table 4 summarises the potential uranium recovery in some of the investigated mining industries. The data are very preliminary ones, however they have the potential to reveal that the recovery of uranium from the wastes of non-uranium mining industries may constitute an important source of uranium in the future.

One of the mining industries that is generally associated to major radiological problems is the phosphate industry. In Brazil, the total installed capacity for phosphate rock concentrate production is about 4.8 × 10^6 ton/year, being the mean national production about 3.4 × 10^6 ton/year. Differently from what is observed in the rest of the world, phosphates in Brazil are mainly associated to igneous rock. It is reported that 4 to 5 tons of phosphogypsum are generated in the production of 1 ton of phosphoric acid. It is estimated that by the year 2,000 about 80 million tons of phosphogypsum will be stocked in the country.
Table 5 shows radionuclide concentrations found in some phosphogypsum samples.

Table 4. Potential ^{238}U recovery in Different Industries Non-Uranium Industries

Mining Industry	Potential for Uranium Recovery (tons of ^{238}U per year)
Niobium I – industry	88
Niobium II – industry	200
Phosphate II – industry	400

Table 5. Radionuclide Concentrations is Some Phosphogypsum Samples

Radionuclide	n	Minimum Value	Maximum Value
^{238}U	62	5.52	116
^{226}Ra	62	28	319
^{210}Pb	31	20	513
^{232}Th	61	12	268
^{228}Ra	62	20	513

Source: Costa e Silva (1998) [3]

The wide range of concentrations for the individual radionuclides is caused by the different ore composition in respect to those radionuclides (see table 1). It may be said that the phosphogypsum is the most relevant aspect in terms of environmental radiological impacts associated to the phosphate cycle. It is reported that radon exhalation from the phosphogypsum piles may be represented by a generic value of 3,600 Bq/m^2/h, corresponding to a total input of 25 TBq/year. In addition to this, one has to consider the potential problems of groundwater contamination (especially by Ra isotopes) and the use of phosphogypsum for different purposes. Two works connected to this project have assessed the potential impacts of the use of phosphogypsum as building material and as a fertiliser in the agriculture. The first one [2] demonstrated that the use of phosphogypsum as building material would not cause undue exposures to members of the public in the considered scenario and that ^{220}Rn inhalation would account for 80% of the total dose. The second one [3] assessed the individual effective dose related to the consumption of different agricultural products cultivated with phosphogypsum being used as a fertiliser. The estimated dose values, for the examined situations, were lower than 2.3 μSv/year. A week point of this work was the fact that the collective dose associated to the use of phosphogypsum as fertiliser was not assessed. An alternative to the sulphuric route, to avoid the generation of phosphogypsum, is the nitric or chloridric route, as represented by equation 1.

$$\mathbf{Ca_{10}(PO_4)6F_2 + 14\ HCl + 3\ H_2O <=> 3\ Ca(H_2PO_4).2H_2O + CaCl_2 + 2\ HF} \text{ (equation 1)}$$

In this case, U, Th and Ra isotope dissolve and enter the waste stream. ^{226}Ra formed together with $CaCl_2$ (12 Ci_{Ra}/year per 1,000 ton_{ore}/day) may be precipitated with $BaSO_4$. Uranium can be recovered with OPPA or DEHPA-TOPO and the rare earths may also be recovered. In addition to these advantages, fertilisers relatively free of U, Ra and Th will be produced.
A last point to be observed is the exposure of workers to radon in the working places (especially in underground mines). As it will be showed in other contribution in this book [3] ^{222}Rn concentrations in the range of 10^4 to 10^5 Bq/m^3 were observed in some of the investigated mining sites.

Dose limits to be applied to these workers shall not be the same as those applied to workers in an uranium mining facility. As a consequence these workers must be faced as members of the general public and whenever the effective dose have the potential to exceed the value of 1 mSv/year, remedial actions shall be applied.

4. CONCLUSIONS

The investigation of several non-uranium mining and milling facilities revealed that radionuclides are remobilised and redistributed in the generated wastes reaching activity concentrations orders of magnitude higher than those observed in the run-of-mine material. The precise knowledge of the wastes composition and fluxes is of extreme relevance in aiding the adoption of adequate waste management strategies. As a general trend it must be proposed that the potential radiological problems are mostly associated to the solid wastes. The habitation of these areas and the use of these materials for house construction may lead to the undue exposure of members of the general public to radiation (external gamma exposure and radon inhalation). Operational impacts (by means of liquid effluent releases into the environment) were not found to be relevant. This was due to the fact that the chemical treatment applied to these effluents, to reduce the emissions of the non-radioactive pollutants, was effective to reduce the effluent concentrations of the radioactive ones. In as much, in some of the investigated industries process waters are recycled minimising the liquid effluent release into the environment. Natural processes like acid drainage generation may also mobilise significant amounts of radionuclides (mainly uranium) and must be properly managed. Changes in the operational process may reduce environmental problems and favour the economical recovery of products of interest, e.g., uranium and rare earth elements.

5. FUTURE STUDIES

Future studies to be developed comprise:

(1) Assessment of the present extension and situation of dump sites in all the mining industries where uranium and thorium occur associated to the main ore in significant amounts;
(2) Experimental and modelling studies on radionuclide migration from deposited wastes and assessment of the contamination of groundwater in the influence area;
(3) Development of methods to immobilise radionuclides in the wastes;
(4) Assessment of radon exhalation from dumpsites and experimental tests to reduce the gas exhalation (with emphasis on phosphogypsum piles);
(5) Priorization of studies involving radon exposure in working places (especially in underground mines).

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Radon parameters in outdoor air

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Abstract. For dose estimation by inhalation of the short lived radon progeny in outdoor air, the equilibrium factor (F), the unattached fraction (f_p), and the activity size distribution of the radon progeny were measured. Besides the radon parameter the meteorological parameter like temperature, wind speed, and rainfall intensity were registered. The measurements were carried out continuously for several weeks to find out the variation with time (day/night) and for different weather conditions. The radon gas, the unattached and aerosol-attached radon progenies were measured with an monitor developed for continuous measurements in outdoor air with low activity concentrations. For the determination of the activity size distribution a low pressure online alpha cascade impactor was used. The measured values of the equilibrium factor varied between 0.5–0.8 depending on weather conditions and time of the day. For high pressure weather conditions a diurnal variation of the F-factor was obtained. A lower average value (F = 0.25) was registered during rainy days. The obtained f_p-values varied between 0.04 and 0.12. They were higher than expected. The measured activity size distribution of the radon progeny averaged over a measurement period of three weeks can be approximated by a sum of three log-normal distributions. The greatest activity fraction is adsorbed on aerosol particles in the accumulation size range (100–1000 nm) with activity median diameters and geometric standard deviation values between 250–450 nm and 1.5–3.0, respectively. The activity median diameter of this accummulation mode in outdoor air was significantly greater than in indoor air (150–250 nm). An influence of the weather conditions on the activity of the accumulation particles was not significant. In contrast to the results of measurements in houses a small but significant fraction of the radon progeny (average value: 2%) is attached on coarse particles (>1000 nm). This fraction varied between 0–10%. 20%–40% of the activity is attached on particles in the nucleation size range (<100 nm). A diurnal variation was registered with a higher activity fraction during the day time caused by the higher particle number concentration of the atmosphere during the day hours.

Introduction

Not the radon gas ^{222}Rn but its short lived decay products ^{218}Po, ^{214}Pb, ^{214}Bi/ ^{214}Po, in the breathing air cause the greatest fraction of natural radiation dose of the human. The dominant parameter related to dose is the activity size distribution of the decay products in the air because the original deposition destination and amount of the inhaled activity deposited in lung depend on the particle size. For practical reasons related to measurements instead of the activity size distribution the characteristics

- equilibrium factor (F-factor),
- unattached fraction (f_p-factor),
- relative activity size distribution

for dose estimation were used.

The concentration of radon and its progeny in the atmosphere depends on the place, time, height above the ground, and meteorological conditions. The spread of radon in the atmosphere after their exhalation from the ground is mainly caused by turbulent diffusion and is limited only by the radioactive decay. In contrast to radon, the distribution of the decay products is also influenced by the removal into the earth's surface.

Jacobi and André [1] estimated the vertical airborne activity concentration of radon and its short lived progeny in model calculations. The results of such model calculations show the great variation of the radon concentration at ground level (about a factor 100) for different meteorological conditions (Table 1). Several investigators measured such great variations of the radon concentration and its progeny (e.g. [2] [3] [4] [5] [6] [7]) as predicted by model calculations.

Table 1. Radon concentration (C_o) and the equilibrium factor (F) in 1 m above the ground for different mixing conditions of the atmosphere after model calculations of Jacobi and André [1]. Assumed exhalation rate: 0.021 Bq m^{-2} s^{-1}

MIXING CONDITION	**^{222}Rn C_o [Bq/m^3]**	**EQUILIBRIUM FACTOR F**
INVERSION (INN)	103	0.71
WEAK MIXING (WNN)	14.5	0.54
NORMAL MIXING (NNN)	4.0	0.76
STRONG MIXING (SSN)	1.5	0.85

Table 2. Estimation of the unattached fraction (f_p), taking into account the attachment rate (X), obtained from measurements in the open air [8]

PARTICLE CONCENTRATION Z [x10^4 cm^{-3}]	ATTACHMENT RATE X [h^{-1}]	UNATTACHED FRACTION f_p
0.5	10	0.13
1	20	0.08
2.5	50	0.04
5	100	0.02

Theoretical considerations show, the dominant parameter, which influences the unattached radon progeny is the attachment rate to the atmospheric aerosol. The values of the unattached fraction of the free atmosphere can be estimated taking into account the attachment rate (X) as function of the aerosol particle concentration (Z) obtained from measurements with outdoor air [8]. After that a variation of the particle concentration outdoors between $1*10^4$ and $5*10^4$ particles/cm^3 corresponds unattached fractions between 8% and 2% (Table 2).

Simultaneous measurements of radon and its progeny for the determination of the F-factor and the measurement of unattached fraction (f_p) over a longer time period are scarce in the literature. Porstendörfer [9] reported a mean F-factor of about 0.6, with a variation of between 0.4–0.8 in a height of 1.5 m above the ground, and a mean value of the unattached fraction of about 2% [10].

The activity size distribution of the progeny aerosol C(d) and the number size distribution Z(d) of the aerosol are different, because the attachment probability ß(d) is a function of particle diameter d. The correlation between both size distributions can be expressed by [11]

$$C(d) = \frac{C}{X} \beta(d)\, Z(d)$$

C is the activity concentration and X is the attachment rate, which characterise the adsorption velocity of the decay product to the atmospheric aerosol. The equation above describes the activity size distribution for all four short lived decay products attached on aerosol particles, because the differences between the individual size distributions are small [12].

Only few data are available on the activity size distribution of radon progeny aerosol in the free atmosphere ([13] [14] [15] [16]) because of the difficulties encountered in measuring aerosol particles in a broad diameter range from 10 nm up to 10000 nm and at low activity concentrations outdoors.

The first direct measurements ([13] [14] [15] [17]) of activity size distributions could best be approximated by one lognormal size distribution with an activity median diameter (AMD) between 100–400 nm and geometric standard deviations between 1.5 and 3.0. The measurements of Becker et al. [14], Reineking et al. [16], and Zock [18] showed, that the AMD values of the outdoor air (300–400 nm) are significant greater than the values obtained in low-ventilated ($< 0.5\ h^{-1}$) rooms. In addition, Reineking et al. [16] and Zock [18] could show, that besides the accumulation mode with the greatest fraction of activity two further modes of the activity size distribution of the progeny exists. 10%–40% of the activity is attached on aerosol particles between 10 nm and 100 nm (nucleation mode) and 0–10% are adsorbed on particles > 1000 nm (coarse mode).

In the following the results of measurement campaigns over some weeks are reported. The aim was to find out the average values of F, f_p and the relative activity size distribution of the radon progeny in the free atmosphere and their variation with time (day/night) and for different weather conditions.

Measurement techniques

A monitor for measuring the concentrations of radon gas, the unattached and on aerosol attached radon decay products in air separately, simultaneously and continuously by α-spectroscopy has been developed.

Fig. 1 gives a schematic diagram of the monitor. The instrument is composed of a measuring head, an electronic-unit and a personal computer for data acquisition and analysis. The measuring head itself consists of three different units. An airflow of 600 l/h is sucked through the first two units by a pump and the unattached activities are sampled in the first unit on a screen and the attached ones in the second unit on a membrane filter. The number of α-decays of ^{218}Po and ^{214}Po-decays are measured with a surface barrier detector in front of the screen and another detector in front of the filter respectively. Furthermore the number of α-decays of ^{212}Po can be detected. With its amount the number of interfering ^{212}Bi-decays in comparison to the ^{218}Po-decays can be calculated.

After passing the first two units and the pump the flow of 600 l/h is divided in two single streams of 60 l/h and 540 l/h. The smaller one passes over an air drier ($CaCl_2$) into the third unit where the radon gas concentration is measured by the principle of electrostatic precipitation [19].

In all three units passivated implanted planar silicon (PIPS) detectors for α-spectroscopy are used. The signals of the detectors are feed in three preamplifier/amplifier combinations and a multi-channel analyser. The data are stored in form of an energy spectrum of 1024 channels and analysed with a personal computer.

For measuring the unattached radon progeny the on-screen measurement technique was chosen. The collected decay products on screen are measured directly by means of alpha-spectrometry. By selection of the right type and size of the screen and the flow rate the monitor was optimised to have a 50% penetration for particles with 3.5 nm diameters and low entrance losses (10%) for the unattached radon progeny clusters.

The disadvantage of the screen measurement technique is that not only the unattached but also a certain fraction on aerosol particles attached progeny were collected on screen. To avoid this error (for atmospheric aerosol outdoors up to 100%) all the obtained f_p-values were corrected as proposed by Reineking and Porstendörfer [10].

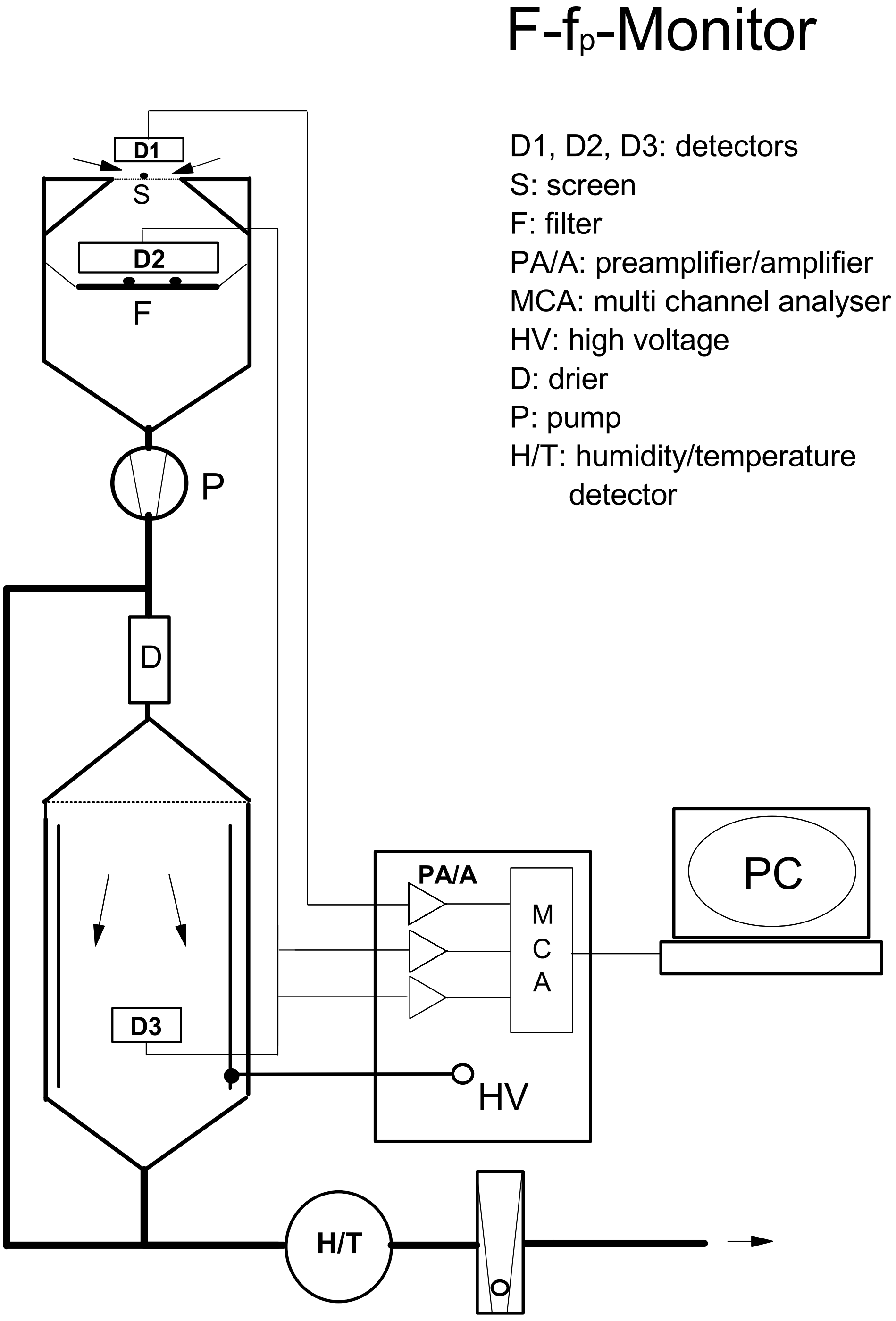

Fig. 1. Schematic diagram of the F-f_p-monitor.

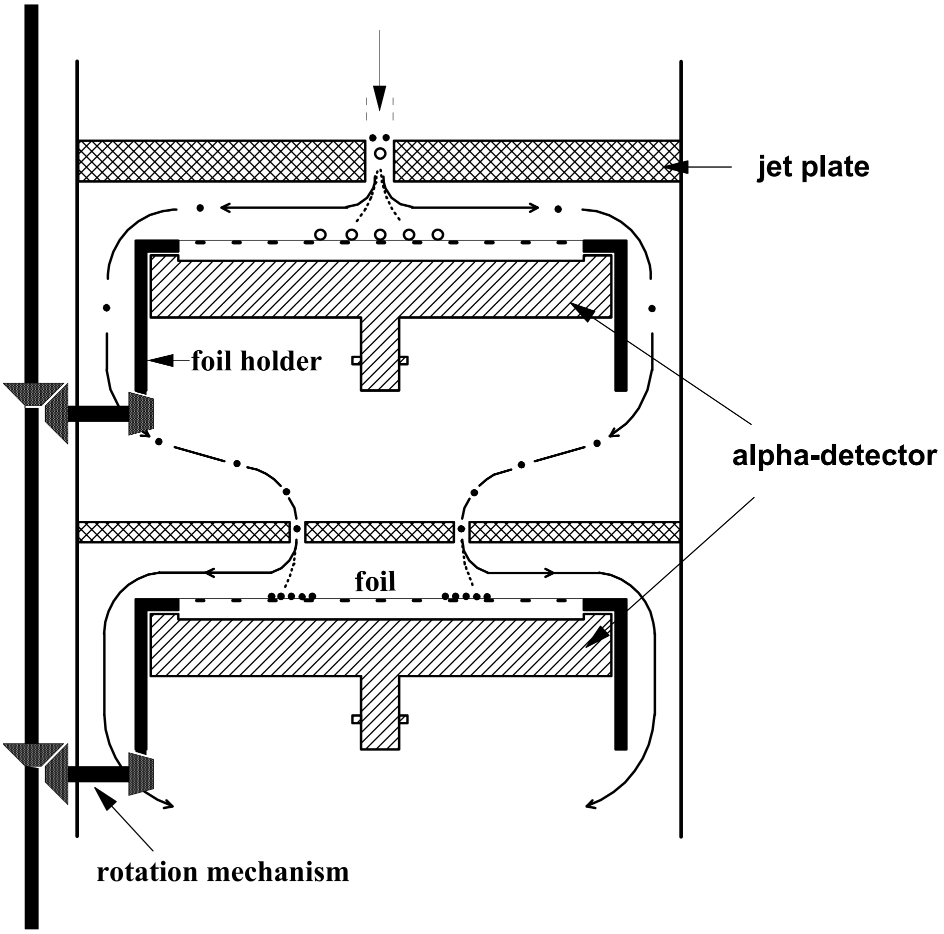

Fig. 2. The arrangement of jet plate collection foil and alpha detector of the online alpha cascade impactor.

The determination of the activity size distribution of the radon progeny was carried out with a low pressure online alpha cascade impactor (OLACI). This impactor was developed to measure continuously the size distribution of the radon progeny over longer time periods (1–2 weeks) [12]. The online impactor has nine stages with 50% cut-off diameters of 16000 nm, 8082 nm, 4242 nm, 2356 nm, 1135 nm, 589 nm, 292 nm, 150 nm and 60 nm. Particle sizes < 60 nm were collected and measured on a backup filter.

The aerosol particles of every impactor stage were collected on a thin aluminium-foil (4 μm) placed above an alpha detector (Passivated Implanted Planar Silicon (PIPS), active surface 2000 mm^2). Therefore the individual radon progeny can be measured by alpha-spectroscopy during air sampling. A rotating mechanism allows a homogenous activity and dust distribution on the foil (Fig. 2). In spite of the energy losses of the alpha particles in air and the collection foil, which cause an alpha spectra with an increased tailing, the energy separation between ^{218}Po and ^{214}Po was satisfactory. A tailing correction was made during data evaluation. The air sampling rate of 5.1 m^3/h made it possible to measure the activity size distribution also at low activity concentrations (1 Bq/m^3). For measurement of the size distribution of all three short lived radon decay products the alpha-counting during and after air sampling was carried out.

Besides the activity measurements the meteorological parameters like temperature, wind speed, and rainfall intensity were registered.

Results

The measurement campaigns were carried out in a suburban area of Göttingen. Each measurement campaign lasted for 2–3 weeks. The activity concentrations, the activity size distribution of the radon progeny, and the meteorological parameters like temperature, rain rate and wind velocity were measured continuously. For each quantity the results of only one measurement campaign are presented and discussed in the paper.

In Fig. 3 and Fig. 4 the measured values of radon, F and f_p as function of time are presented. The measurement period can be divided in two parts with different weather conditions. Some days with sunny weather and lower turbulent mixing during the night/morning hours follow cloudy days with higher turbulences during the whole day. This two different weather conditions are typically characterised by the diurnal variation of the radon concentration with higher activity concentration during the night/morning hours of a day (Fig. 4) [7] [9].

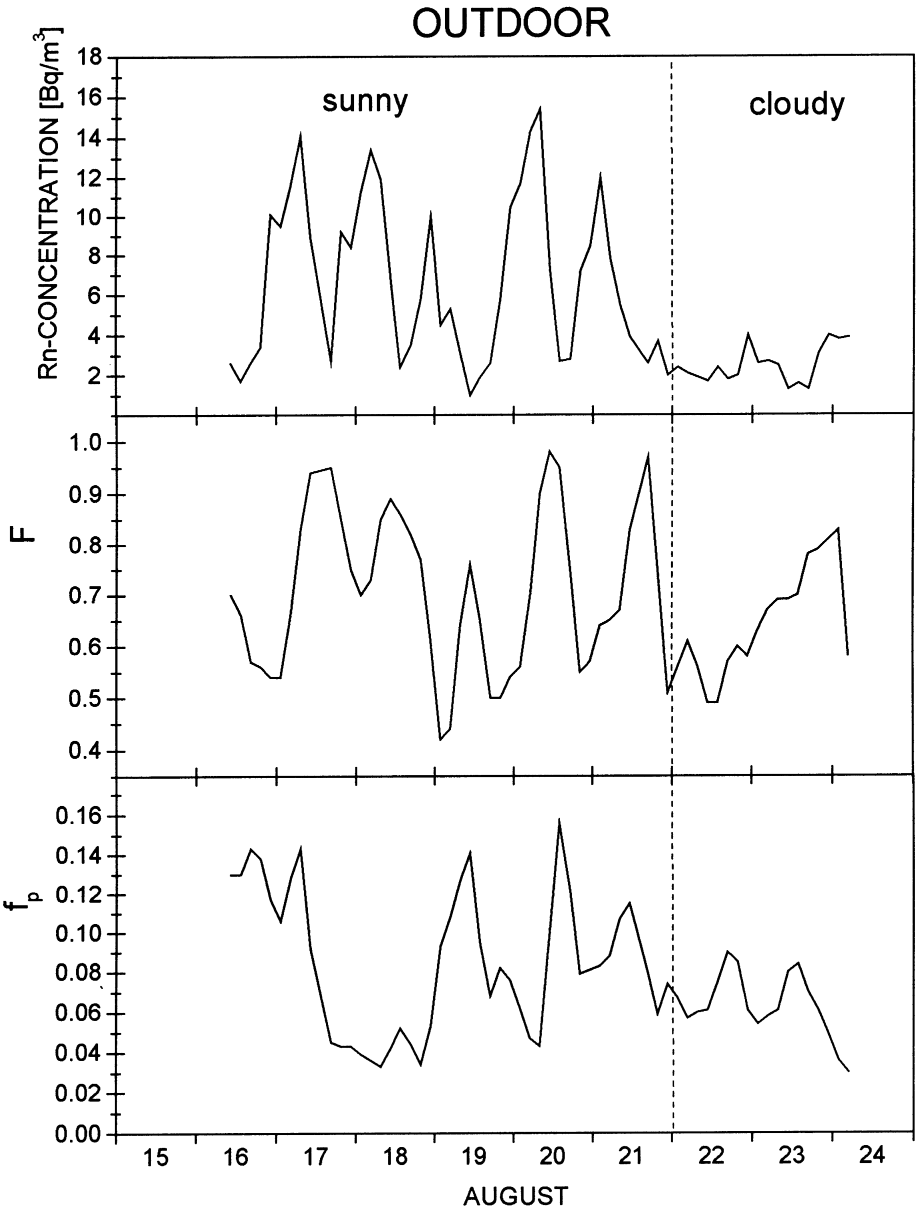

Fig. 3. Radon concentration, equilibrium factor (F), and the unattached fraction (f_p) in the atmosphere near the institute building 1 m above the ground.

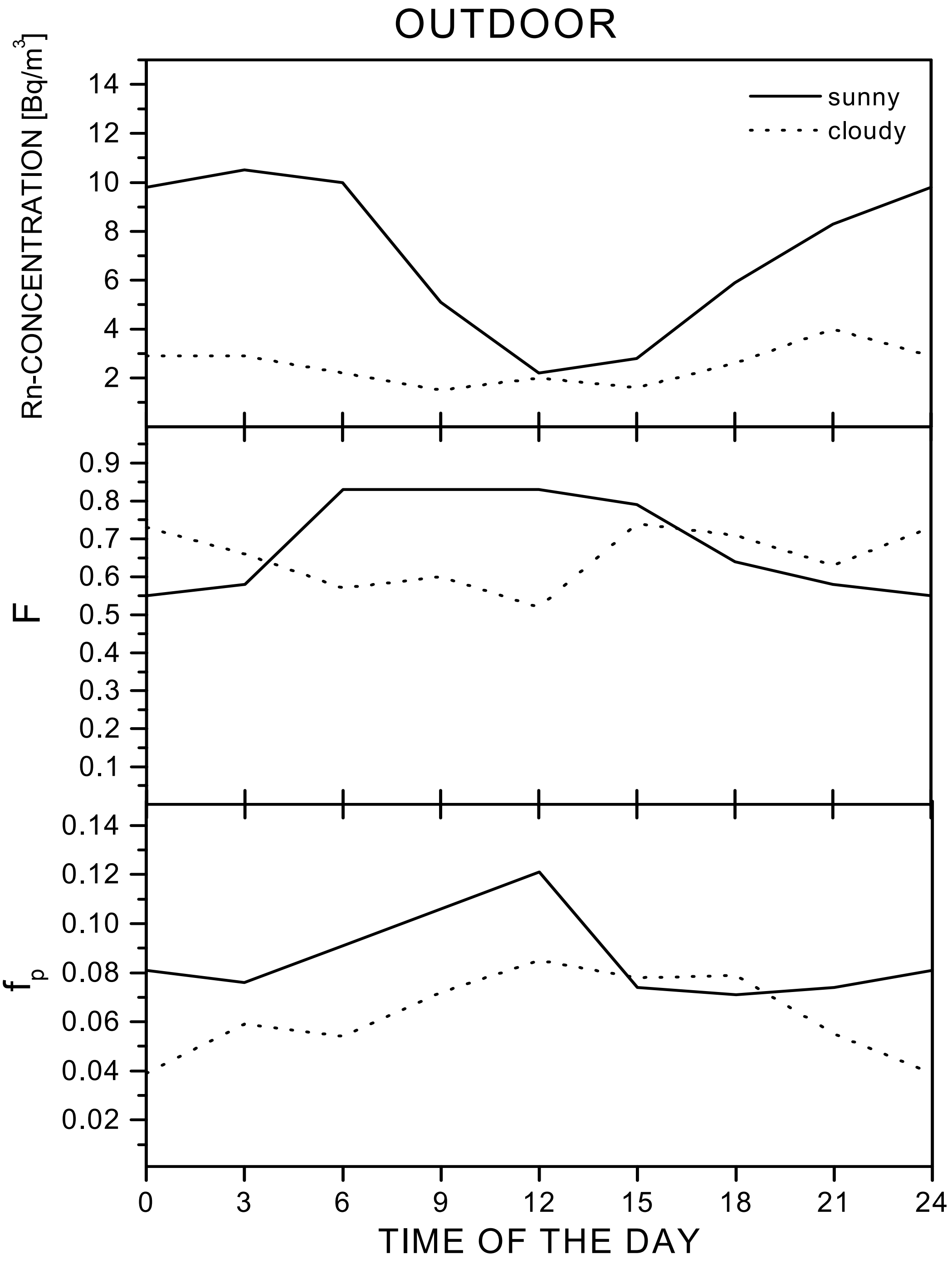

Fig. 4. Diurnal variation of the radon concentration, equilibrium factor (F), and the unattached fraction (f_p) obtain from measurements in the atmosphere near the institute building 1 m above the ground.

The results of the F-value vary between 0.5 and 0.8 with higher values during the day hours of the sunny high pressure days.

All f_p-values obtained from the measurements are fairly high (0.04–0.12) compared to the results of former measurements [10]. The maximum of the value during the sunny day hours cannot be understood. Because of the higher particle number concentrations during this daytime a minimum of unattached fraction should be expected. More measurements are needed. Especially the variation of the aerosol particle concentration should be registered to help the explanation of the results.

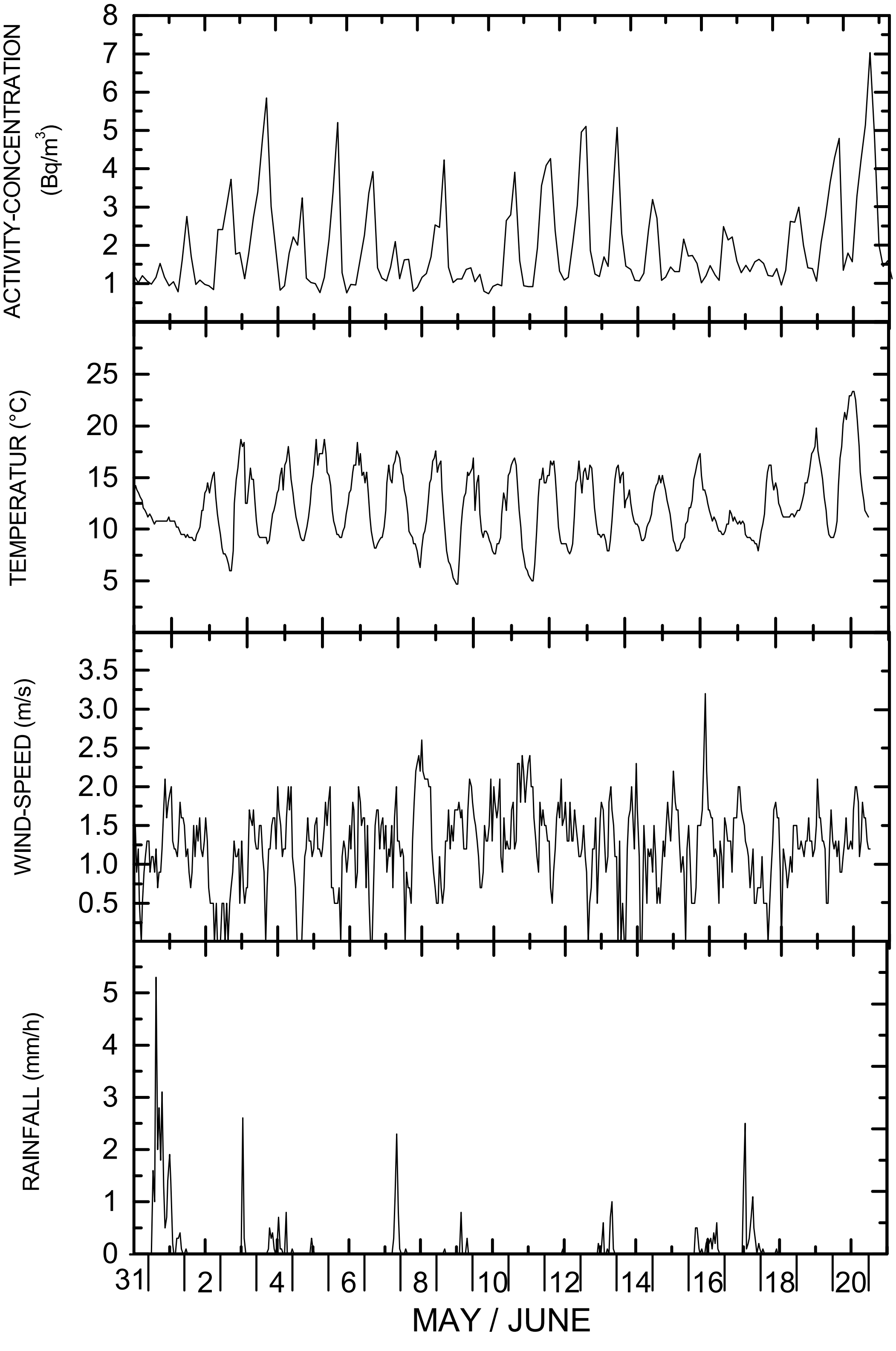

Fig. 5. The variation of the activity concentration, temperature, wind speed and rainfall intensity in the atmosphere during the measurement campaign.

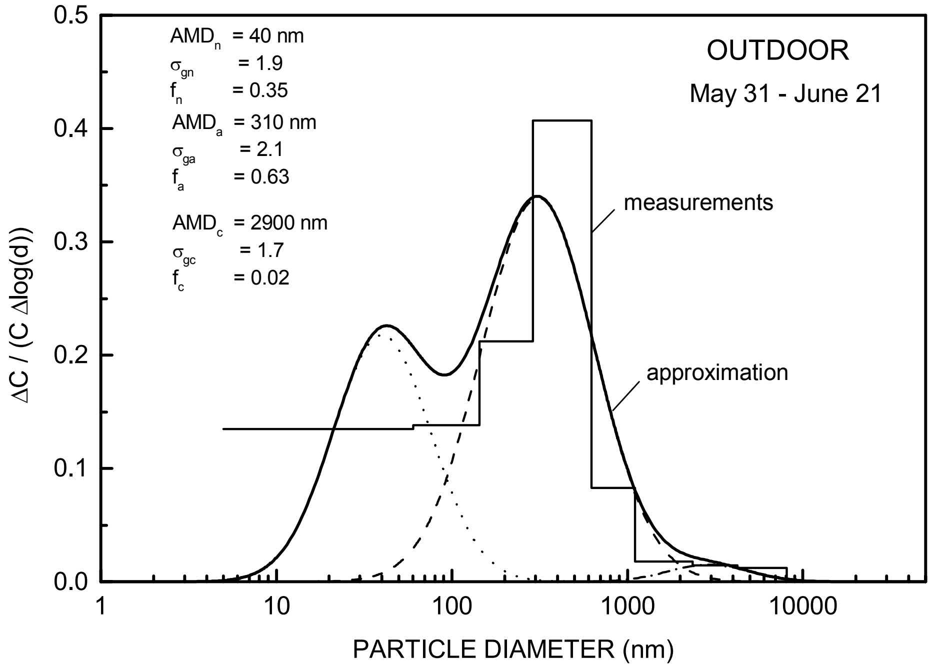

Fig. 6. The average activity size distribution of the radon progeny for the measurement campaign May 31–June 21.

The variation of the activity concentration of the ^{218}Po-aerosol and the meteorological parameters during the measurement campaign for determination the activity size distribution are presented in Fig. 5. The activity concentration of the progeny aerosol was obtained by the sum of the activities on all impactor stages and on the back up filter. Different weather conditions occur during the measurement period. The days with a high pressure weather are typically characterised by greater differences of temperature and activity concentration between day and night. In this case the night indicates a stable atmosphere with lower mixing and therefore higher activity concentration. During the rainy days there is higher mixing in the lower atmosphere, also during the night and morning hours. In this case no diurnal variation could be observed.

The relative activity size distribution of the radon progeny aerosol averaged over 22 days is presented in Fig. 6. The experimental data can be approximated by a sum of three lognormal distributions. Most of the activity (fraction $f_a = 63\%$) is adsorbed on particles of the accumulation mode with an activity median diameter $AMD_a = 310$ nm and a geometric standard deviation of $\sigma_{ga} = 2.1$. Remarkable is the fairly high amount of the activity on particles below 60 nm (collected on the backup filter). This activity fraction of the nucleation mode ($f_n = 35\%$) can be approximated by an AMD_n of about 40 nm. On average only 2% of the activity is adsorbed on coarse particles (>1000 nm) with an AMD_c value of about 3000 nm. The fraction of the coarse particle mode mainly generated by resuspension and dispersion processes varied between 0–10%.

To see the variation of the activity size distribution during the measurement period, the AMD_a value and the geometric standard deviation, σ_{ga}, of the accumulation mode and the activity fraction on the backup filter as function of time is presented in Fig. 7. The AMD_a and the σ_{ga} values vary between 250–500 nm and 1.8–3.0, respectively, but a diurnal variation and an influence of the weather parameters were not significant.

A high activity fraction of 20%–45% (average 32%) on the backup filter (sizes <60 nm) was registered with the online alpha cascade impactor (Fig. 7). This activity fraction showed also a diurnal variation (Fig. 8). For the explanation some measurements of the number size distribution of the atmospheric aerosol with a differential electrostatic mobility analyser (DMA) and a laser aerosol spectrometer (LAS) were carried out. The results of these measurements showed a higher particle concentration with diameters <50 nm during the day hours. This is caused by the higher aerosol generation by the combustion processes and photochemical reactions during the daytime.

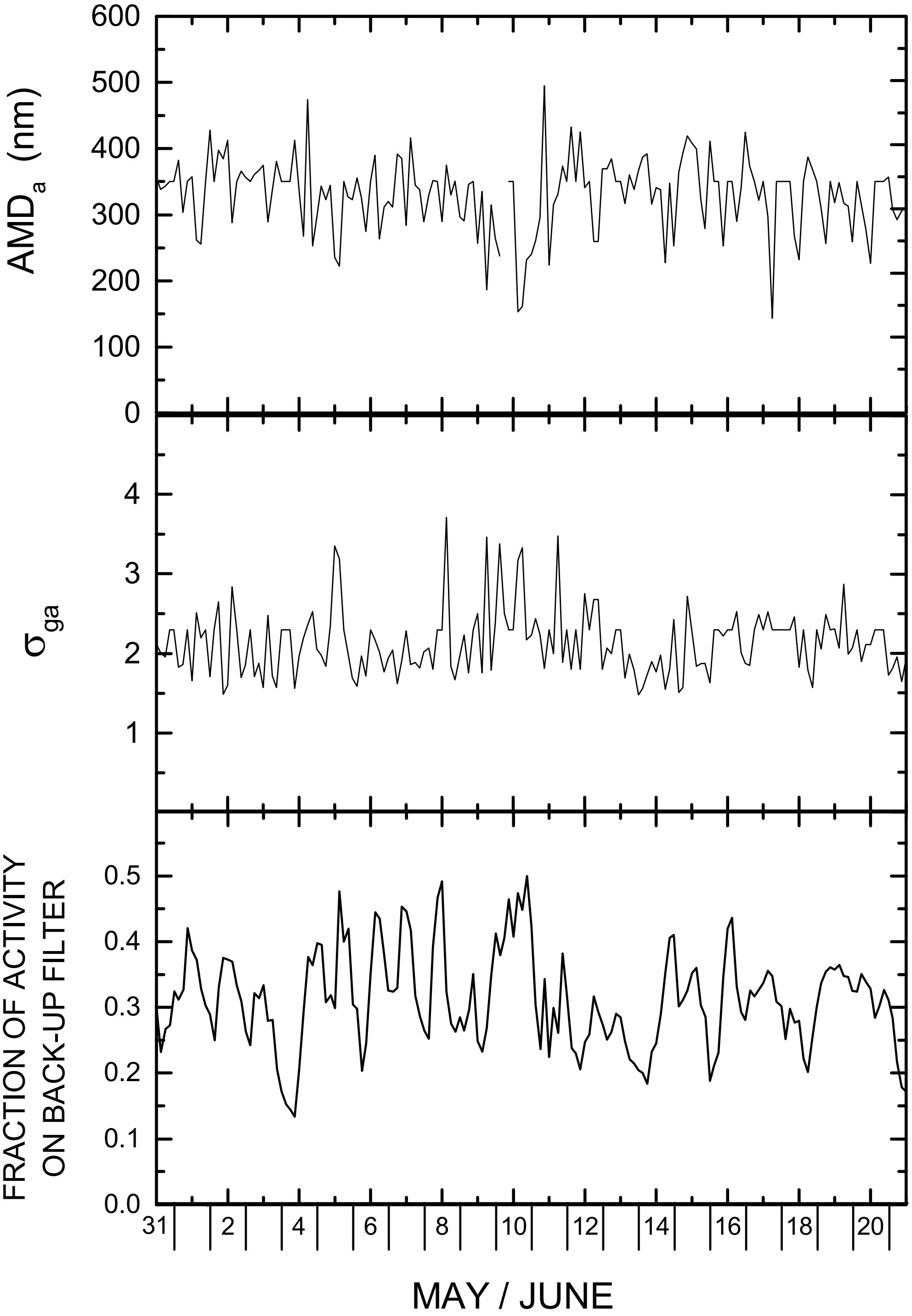

Fig. 7. The variation of the activity median diameter (AMD$_a$) and the geometric standard deviation (σ_{ga}) of the radon progeny in the accumulation size range and of the backup filter.

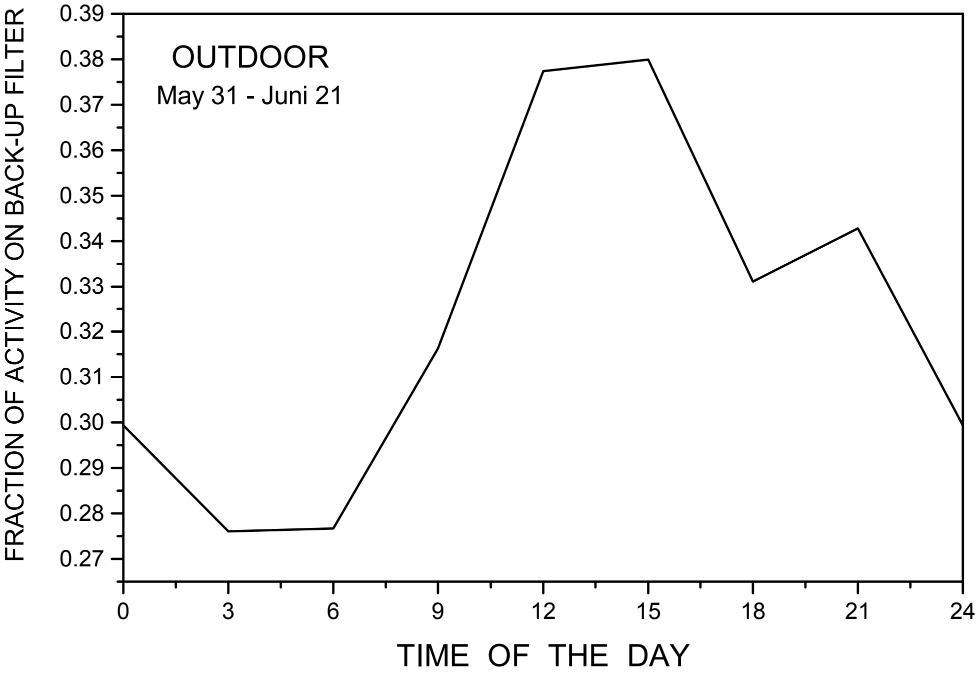

Fig. 8. The diurnal variation of the activity fraction on backup filter (<60 nm) averaged over the measurement campaign May 31–June 21.

Conclusion

The measured F-values vary between 0.5 and 0.8 in 1 m height above the ground depending on the daytime and the weather conditions. These are values which can be explained by model calculations.

The obtained f_p-values between 0.04 and 0.12 are higher than expected. In addition, the diurnal variation with a maximum during the sunny day hours cannot be explained.

The greatest activity fraction of the radon decay products is adsorbed on aerosol particles in the accumulation size range. The experimental data, approximated by a lognormal distribution give AMD_a and σ_{ga} values between 250–450 nm, and 1.5–3.0, respectively. This accumulation mode in outdoor air has significantly greater AMD_a values than in indoor air (AMD_a: 150–250 nm) in agreement with the results of former measurements [14] [16]. An influence of the weather conditions on the activity of the accumulation particles was not significant.

In contrary to the measurement values obtained in dwellings a small but significant fraction of the radon progenies (average value: 2%) is attached on coarse particles (>1000 nm). This fraction varied between 0 – 10% during the measurements.

The measurements with the online alpha cascade impactor yielt an activity fraction of 20%–40% in the nucleation size range (<100 nm). A diurnal variation was registered with a higher activity fraction during the daytime, caused by the higher aerosol particle concentration of the atmosphere during these day hours.

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Survey of radon in dwellings in area strongly affected by mining

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Abstract. Due to the Decree of the President of Polish Atomic Energy Agency [21], the permissible level of radon concentration in new houses is 200 Bq/m^3, while in existing houses -400 Bq/m^3. This Decree is valid since January 1, 1998. Till now, radon investigations in Poland were done on a small scale. Therefore Central Mining Institute started at first screening campaign and later long term measurements of radon concentrations were done in area of Upper Silesia. Usually measurements of radon concentration in dwellings are performed at two stages. On the first stage, a screening is made by means of short term methods of radon measurement, like activated charcoal canisters or grab sampling to find places with elevated radon risk. On the second stage a long term measurements have been done in dwellings chosen during screening campaign.The method of the radon measurement by means of charcoal canisters was developed in our Laboratory in early 90's. We designed our own detectors with the activated charcoal, after the exposure radon from the charcoal is washed out with toluene-based liquid scintillator and measured in the liquid scintillation counter. The reliability of the results was proved in many intercomparison runs. For long term radon measurements the method of track etched detectors was applied. As a detector the LR-115 strippable foil was chosen and as a reader the spark counter was applied. As predicted, the highest values in dwellings were found at the ground floor level in several towns in northern part of Upper Silesia. All these sites are situated in area without an overburden of impermeable Miocene clays. Moreover, these towns are located within a specific geological structure, known as Bytom Syncline. In the underlying strata, the dominant rocks are Triassic, strongly weathered formations, in form of carbonates. We supposed, that the influence of geology would be intensified by coal mining. The presence of abandoned workings, excavations and cavities on shallow depths should enable easy migration of radon gas and its penetration into houses. Moreover numerous faults and other tectonic dislocations occur in this area. Also tremors, caused with underground excavation, might increase radon exhalation.

1. Introduction

In 1975 Price, Fleisher and Walker [1] discovered a possibility of application of solid state nuclear track detector (SSNTD) for measurements of radon gas concentration in air. Since that time track detectors have a very wide applications in the radiological protection, geology, geophysics, biology, medicine, environmental protection etc. The application of the track detectors for measurements of radon concentration in dwellings is very common. A long time of exposure assures proper assessment of the average radon concentration and finally a calculation of the dose.

Upper Silesia, situated in southern part of Poland, is an industrial area, where over 50 coal mines are located as well as a couple of shallow lead and zinc mines. Geological structure of this area is very complicated [2]. In the southern part of the coal basin, the carboniferous strata are covered by thick layers of Miocene clays. In the north the carboniferous strata are covered by permeable limestone and Quaternary deposits. There are also numerous outcrops of coal strata. Such structure enables easy migration of gases.

Preliminary monitoring of radon concentrations in buildings in the Upper Silesian Coal Basin have been performed by Central Mining Institute in years 1993–1994. These measurements were carried out with use of activated charcoal detectors and liquid scintillator counter [3, 8]. During "screening" measurements we found that radon concentrations in buildings were in range between 7 Bq/m^3 up to 360 Bq/m^3. It was observed that radon concentrations in northern part of Coal Basin are higher than in the southern part.

As we needed a method for the long term measurements therefore a track detectors technique was implemented in our laboratory. We decided to use spark counting method because of it's relative simplicity. After implementation of this technique in our laboratory, in some of the dwellings, in which the screening procedure was applied, long term measurements of radon concentration by means of track etched detectors were done in period 1995–1996. Results were described earlier [18] — we found a good agreement with screening method what confirmed some of our preliminary conclusions.

Finally, we started another field campaign of radon measurements in dwellings in Upper Silesia in 1998 and the survey is still in progress. Till now we found no dwellings, in which radon concentration in habitable rooms were higher than 400 Bq/m^3. In several cases slightly elevated radon concentration was measured, but mainly in cellars. Results, achieved during the extended radon survey are described in this paper.

2. Investigation site

Geological structure

Upper Silesia, situated in the south of Poland is characterised by a very complicated and differentiated geological structure with numerous faults and other tectonic dislocations [2]. Moreover, Upper Silesia is an industrial region where over 50 coal and zinc and lead ore mines are located. The area is strongly affected by geodynamic events caused by mining. Numerous mining excavations and workings are quite close to the ground surface. According to Mennin [4] and Ball [5], radon indoor concentration is correlated with geological structure of investigated area. The southern and western Silesia is characterised by thick strata of sediments covering carboniferous formation. This overlay consists mainly of Miocene clays and silts. The thickness of this sediments is up to 700 m. Such strata makes the migration of water and gases almost impossible. In northern part of Silesia Miocene sediments do not occur. Carboniferous strata are covered by Mesozoic and Quaternary slightly compacted sands, gravel, sandstone. The oldest formation of 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.

Methods of investigation

During preliminary investigations, measurements of radon concentration in dwellings were performed at two stages. On the first stage, a screening was done, by means of short term methods of radon measurement, like activated charcoal canisters, grab sampling to find places with elevated radon risk. On the second stage a long term measurements have been done in dwellings chosen during screening campaign.

During current campaign, only track detectors are in use.

The method of the radon measurement by means of charcoal canisters was developed in our Laboratory in 1993–1994. We designed our own detectors — 5 grams of the activated charcoal is placed in the scintillation vial, after the exposure radon from the charcoal is washed out with toluene-based liquid scintillator [8]. Measurements are done in the liquid scintillation counter. The reliability of the results was proved in many intercomparison runs.

Later, we started to implement in our laboratory a method of track etched detectors, due to the fact that a decree of the President of the Polish Atomic Energy Agency was issued, concerning requirements for methods of measurement of indoor radon in dwellings. As a detector the foil LR-115 strippable from Kodak was chosen. It enables the detection of alpha particles with energy in a range from 0.1 MeV to 6 MeV. As a reader of tracks after chemical etching the spark counter was applied (from Italian MI.AM company).

Radon chamber

Our chamber was built of stainless steel sheets, and internal dimensions are: 3.7x1.6x1.8 m, so a volume of the chamber is equal to 7.25 m^3. The system of airlocks and valves ensures the leak-proof of the chamber and a stability of the conditions inside the chamber [7]. Additionally, in the chamber are placed two fans and outside the chamber is located a source of water aerosols. As a reference instrument, ratemeter AB-5 from PYLON is used.

Radon sources

Because of the need of a reference atmosphere for the proper calibration of track detectors two flow through sources of radon and thoron were bought from PYLON. Certified radon source (^{222}Rn) has the activity 256 kBq [Certificate RN-1025, 1992], while the thoron source (^{220}Rn) based on ^{228}Th had the initial activity 285 kBq [Certificate TH-1025, 1992]. Application of the flow through radon source in the chamber gives a possibility to reach the maximum concentration of ^{222}Rn of about 35 kBq/m^3.

3. Experimental section

Calibration of the track etched detectors

Before the application of the SSNTD for measurements in dwellings, it was necessary to gain some experience of the etching procedure, which is the key problem in handling of track detectors. Moreover, the calibration procedure of the detectors must be performed repeatedly, until we would rely on the results of measurements.

Accordingly with the instruction of the foil's producer (Kodak) all types of LR 115 foils should be etched in 10% (2.5N) solution of NaOH. The desired temperature of the etching solution is 60^{0}C and a time of the etching within the range 75–90 minutes. The optimal time should be chosen experimentally, depending on the different conditions like: geometry of the bath, number and total surface of etched foils, the temperature in the laboratory and so on [9]. At first the etching was done during period of 90 minutes but results of the read-out of detectors weren't stable. Therefore we exposed in radon chamber one big sheet of foil and later the analysis of the readout results for the stripes of foil etched in different time periods was done.

We found that for the time of etching between 120–130 minutes a kind of a plateau existed on the calibration curve. Therefore for the routine measurements the time of etching was set as 120 minutes. The calibration factor, calculated on the basis of results from this series was equal ~1.3 kBq*h/m^3*track. Even slightly longer time of etching than 120 minutes, didn't affected this value too much.

To ensure a good quality of radon measurements in dwellings, several calibration runs were performed in the radon chamber. As the diffusion chambers, in which detectors are placed, typical cups used for medical purposes (transparent polyethylene containers with a polyethylene lid). The average calibration factor, calculated from the results of these calibration runs was equal ~**1.44 kBq*h/m^3*track.**

4. Results of the field campaigns

Preliminary investigations

Preliminary investigations were performed in 1996 and 1997. Several dwellings were chosen for measurements, mainly those, in which in previous years screening measurements were made and elevated radon concentrations were found. The exposure time of track etched detectors was three or four months. We requested the owners to put detectors into the cellars and rooms on the ground floor (in each point two track detectors). Additionally, during that time, charcoal canisters for the short term measurements were used twice.

Within the frame of screening measurements, we have made slightly more than 200 measurements in 100 dwellings. The highest measured radon concentration was 362 Bq/m^3. The lowest concentration was 8 Bq/m^3, the arithmetic mean value was 56 Bq/m^3. The results obtained in cellars were higher than in the living areas in the same house. The highest result obtained in cellar was 679 Bq/m^3, while the average radon concentration in cellars was calculated as 81 Bq/m^3.

In the vicinity of several houses with the highest radon indoor concentration we performed measurements of radon in soil gas. Radon concentration measured in soil gas varied from 150 up to 45000 Bq/m^3.

Results of screening measurements showed a big difference between radon levels during summer and autumn. On the other hand, results of integrating measurements, performed with track detectors, could be stated in most cases as a good approximation of the average value for this period. The highest radon concentration, measured by track detectors, was as high as 66 Bq/m^3. The maximum permissible level of radon concentration in dwellings in Poland is 200 Bq/m^3, so there is no exceeds of this value in examined houses. Nonetheless, the highest radon concentration in cellars was 679 Bq/m^3.

Extended measurements

New radon campaign in Upper Silesia was started in autumn 1998. We wanted to measure radon concentrations in dwellings during winter, when radon level was usually higher. We chose few hundred dwellings for measurements, laying into different parts of Silesian Coal Basin. Typical time of the exposure was three months. In all cases detectors were placed in bedrooms, located at the ground floor and in cellars — two duplicate detectors at each sampling site. Another set of measurements was started in spring 1999, and is still in progress.

After a first set of exposures we retrieved detectors from of about 300 dwellings. These dwellings were located in different parts of the coal basin. Of about 100 dwellings were chosen in the southern part of the basin, and approximately 200 dwellings in the northern part. Results show a significant difference between both parts. The average concentration in the southern part is lower than the corresponding value in the northern part. Similar dependence was observed for the highest and lowest values. Only in few dwellings in the southern part slightly elevated radon values were found. In table 1 average values of radon concentration as well as maximum and minimum values are quoted.

Good correlation between elevated radon concentrations in dwellings and in cellars have been observed. But in several cases, mainly during spring/summer measurements, we found in basements lower concentrations as in dwelling. It was mainly due to better ventilation of cellars during hot days.

Table 1. Results of long term radon survey

	Northern part	Southern part	Whole area
Average value [Bq/m3}	45	27	39
Maximum value [Bq/m3]	267	125	267
Minimum value [Bq/m3]	10	5	5
Number of measurements	200	100	300

Assessment of dose equivalent for inhabitants

On the basis of the results of long term radon measurements the assessment of the dose equivalent was done for the inhabitants. Due to reports of UNSCEAR 1986 [10] and NCRP 1987 [11] the equilibrium factor between radon and progeny in dwelling F is equal 0.4 for our climatic zone. But in ICRP report [12] equilibrium factor in dwellings was set at level 0.5, which value is in agreement with the Decree of the President of Polish Atomic Energy Agency [13], concerning dose limits for ionising radiation and issued in 1995. Moreover, recent publication from the investigations made in Slovakia [14], shows that the value of the average equilibrium factor in schools there is 0.46–0.48. Therefore we decided to apply the equilibrium factor equal F=0.5.

Calculations of the potential alpha energy concentration Cα were done accordingly to the following equation:

$$C\alpha = 0.00059\ C_A + 0.00290\ C_B + 0.00213\ C_C\ [\mu J/m^3]$$

where C_A, C_C, C_C are concentrations of particular radon daughter products and for F=0.5. For instance, if radon concentration is equal 100 Bq/m^3, then $C\alpha = 0.28\ \mu J/m^3$ [15]. Later annual dose equivalents were calculated, taking into account the following equation from **Basic Safety Standards** [16]:

$$H\alpha = 0.0011 * C\alpha * t$$

where: 0.0011 - coefficient set in Basic Safety Standards

Hα - annual dose equivalent, mSv

Cα - concentration of radon progeny in the dwelling, μJ/m^3

t - occupancy time, 16 hours per day, 5840 hours/year.

Such assessment of the dose equivalents gives results within the range from 0.2 to 4.4 mSv per year. The average annual dose equivalent for whole area of Upper Silesia is roughly of about 0.7 mSv. Slightly different average values have been obtained for southern and northern parts of the Silesian Coal Basin – in the southern part the average dose equivalent was calculated as 0.5 mSv, while in the northern part – 0.8 mSv per year.

In comparison, investigations done by Jagielak and co-workers [17] give an average value of the annual dose equivalent from radon in Poland at level 1.7 mSv. Preliminary results of screening, quoted earlier, gave in average the similar value. Our results of long term measurements are two times lower. Of course, some of our measurements were done during spring and summer, so higher values of dose might be predicted on the particular areas of Silesia. Therefore short term measurements will be used for the searching of areas with potential radon risk and later long term measurement will be done to assess the real dose equivalent.

More detail analysis of geological structure of sites, where highest concentrations oh radon indoor and in soil gas were measured, have been done.

The highest concentration of radon were measured in area of occurrence of Triassic sediments filling synclinal forms of northern and eastern part of Coal Basin. This strata are formed mainly by dolomites and limestone. Triassic formation is strongly weathered with many fissures and caves being good way for migration of water and gases. Directly under thin layer of the soil (0.3–1.0 m) strongly weathered Triassic strata occur. Quaternary cover near investigated houses is reduced, Tertiary sediments do not occur. Beneath dolomites and limestone layer there is not isolating shale or clay layers. Under Triassic rocks with thickness up to 100 m carboniferous strata occur in which the exploitation of coal beds have been performed.

High concentrations of radon were also measured in places with different geological profile. In the area where structural deformations are present in a big number, carboniferous strata often occur under thin layer of Quaternary or directly on the surface in form of outcrops. These sites were being intensively exploited by small scale mining up to late 40's. Because of intensive exploitation the structure of bedrock were destroyed, cracked and fissured. Numerous of abandon workings and excavations are present just several meters beneath the surface. The excavations are backfield with different fillings such sand, waste-rocks, ash from power stations.

We predicted, that such transformations in bedrock caused by mining activity should enable very easy migrations of gases (radon, methane, CO_2) [19] and their penetration into houses. During screening measurements we found in several cases the enhanced exhalation of radon from the ground. But generally, results of extended survey don't prove our assumptions — only minor correlation between underground mining and elevated radon levels in dwellings were found. Possible explanation of that phenomenon is as follows. Enhanced exhalation of radon from underground abandoned working is more likely to be short term event, as a result of tremors or changes of the atmospheric pressure. Therefore during short term measurements, made by charcoal canisters, we were able to encounter such sudden releases.

The final conclusion can be drawn, that the most important factor, affected radon exhalation from the ground, is just a geological structure of the strata.

5. Summary

The method of radon measurements by means of track etched detectors LR-115 have been applied for long term investigations in dwellings on the area of the Upper Silesian Coal Basin.

Typical value of the annual dose equivalent from radon in Poland is at level 1.7 mSv. Our results of screening showed lower values, of about 0.7 mSv in average.

The influence of the geology structure of the Coal Basin on the radon level in dwellings is very important. Houses with highest indoor level concentrations are situated in northern part of Upper Silesia, where Miocene impermeable clay-silt cover do not occur. On this area dwellings are built on strongly fissured limestone or dolomites. In southern part of Silesia, where thick strata of isolating Miocene deposits occur, radon concentrations are lower. The influence of geology may be intensified by coal mines activity, but only on a small scale. Moreover numerous faults and other tectonic dislocations occur in this area.

The results of investigations allowed to characterise geological structure of regions where high concentration of radon can be expected:
- strongly weathered limestone-dolomite formations with numerous fissures, caverns and debris, covered with thin layer of soil
- outcrops of carboniferous strata with exploited coal beds under thin layer of soil and reduced Quaternary.

Carbonates, very common in bedrock in this area, are usually strongly weathered and a lot of fissures and emptiness can be found in rock body. Therefore easy migration of radon in soil gas is possible and high exhalation rates are predicted.

Additional factor, which enables easy migration of radon into buildings, is a high permeability of the soil and underlying Quaternary layers. Also mining activity in the past caused, that remains of old galleries and caverns at shallow depths can be stated as an extra source of radon Moreover seismic events, induced by mining activity, lead to the increase of emission of different gases, among them radon, from the ground.

The subsidence of the surface in area affected by mining, leads to smaller and bigger damages of buildings. Another reason of enhanced radon risk are fissures and cracks in walls - the easiest pathways of radon migration into buildings.

We would like to recognise this problem better, so further investigations are in progress.

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Comparing summer and winter indoor radon and radon daughters activity in Campinas, Brazil

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Abstract. We developed a technique — based on alpha particle track detection using CR-39 — where the activity originated from indoor radon can be potentially separated into three fraction: (i) radon in the air, (ii) radon daughters (RD), ^{218}Po and ^{214}Po, in the air and (iii) RD plated-out on the detector surface during exposure. In this work only a partial separation was carried out, then our results are limited to radon plus RD in the air and RD attached to detector surface. These activities can be separated if size and gray level of the round tracks are measured using an automatic optical microscopy system.Our group carried out an indoor radon and radon daughters (RD) survey in Campinas made up by a summer (November, 96 to May, 97) and a winter (May, 97 to November, 97) exposure, where the detectors were placed in the same rooms of the same dwellings (approximately 100) in both cases. Comparing winter and summer alpha activity for the detectors analyzed up to now, approximately 45 dwellings, we observed that: i) it seems that the source of radon is the material (brick and concrete mainly) making up walls, floor and ceiling of the dwellings, ii) there is no clear relationship between intensity of aeration and the activities measured in this work, and iii) the average ratio between winter and summer activity in the air (radon plus RD) is approximately equal to similar ratios observed in other countries, but for radon only.

Introduction

The radon gas has been intensively measured in the two last decades. Many experimental techniques have been employed [1], including etched track detectors [2]. One advantage of this technique is the long exposure, several months that is usually necessary. In this way, the tracks registered can be transformed in activity in the air that should be more realistic compared with the activity that people are actually submitted to.

We used in this work a well known track detector, CR-39, which is practically sensitive to all alpha particle´s energy range [3]. This sensitivity can be a problem if these particles cannot be separated concerning their energy and emission locus. We were able to carry out this separation, at least partially, as it is commented in the following. In this way, measurement results of the activity in the air, due to Rn-222 and RD, and due to the RD, plated-out on the detector surface during exposure are shown in the next sections, for a summer and winter survey (45 dwellings) performed in Campinas-Brazil.

The main goal of applying this technique in small a magnitude survey is to carry out a first evaluation of this new approach.

Methodology

Our group developed a technique where potentially the mean activity of Po-214 and Po-218, the RD that are alpha emitters, can be measured approximately free from the influence of environmental factors [4,6]. In this technique each assembly contains two CR-39 sheets: an internal detector used to measure radon and an external detector, exposed under a 2π geometry. The latter detector measures both the activity of radon plus RD in the air neighboring its surface and that one due to the RD plated-out on its surface during exposure. This work concerns only with the external detector. If only round tracks (eccentricity smaller than 1.10) are measured and if the gray level of each track is also measured — which implies the employment of an automatic microscopy system — the activity in the air due to radon plus RD can be separated from that due to RD plated-out on the detector surface [5, 6]. In the following sections the activity in the air is named Aw or As, where w and s mean winter and summer exposure, respectively, and the activity related to the plate-out of RD is named G_W or G_S.

Exposure

Detectors were exposed in dwellings selected by a weighted random process taking into account IBGE (Brazilian Institute of Geography and Statistics) annual income per capita. The unitary censual regions drawn in this way were constituted by approximately 200 families. To select a dwelling inside the unitary regions a new restriction was considered: the dwelling must be inhabited by a family where one of its members was professor or employee of UNICAMP (amounting approximately 16,000 families). Besides, the dwellings chosen had to present external aspects (building area, quality and conservation of the employed building material, etc.) similar to the neighboring houses. In the cases where this was not observed the dwellings were ruled out.

The advantage of this restriction was that we made a first contact with the chosen professors and employees at the Campus of our University, where the purposes of our research were explained and written texts about the matter were given to them. Usually some days after this first contact the correspondent dwelling was visited by members of our group and the exposure began. During this visit a questionnaire about characteristics of the dwelling (conditions of the floor, internal walls, ventilation, etc.) and some other useful information was filled and a plan of the dwelling was schematically drawn. It is worth to mention that detectors were exposed on a wall at the height of 2 m (to be out of the “children range”) usually in one of the bedrooms of the dwelling. Using this procedure the agreement with exposure was greater than 95% and after its end the return of the detectors was approximately 90%.

Our survey at Campinas was divided in two steps. A first 100 dwellings exposure covered the months between November of 1996 to May of 1997 (summer exposition). A second exposure started in May of 1997 and ended in December of 1998 (winter exposition). It was carried out in 89 of the 100 dwellings of the first exposition. The purpose of repeating the dwellings was to study whether there are differences between winter and summer exposition, analyzing assemblies placed in the same rooms in the same dwellings.

Measurements

Using an automatic microscopy system under a nominal magnification 10 × 63 (each observation field — the image sent by a CCD camera to the screen of the coupled TV monitor — has an area of 1.628×10^{-4} cm^2) the tracks contained in 1,600 observation fields were counted, for each detector. As quoted above only the tracks with eccentricity smaller than 1.10 — the round tracks — should be measured. To select them we employed the CRTRAN soft (developed in our laboratory) that measures, for each track, the major and minor diameters, the gray level of the track and of its neighboring area and calculates its eccentricity, product of the diameters and relative gray level.

Table 1. Data from the analyzed dwellings. Painting ages are expressed in years (a)

Dwelling	Aeration	Painting	A_S (Bq m^{-3})	A_W (Bq m^{-3})	G_S (Bq m^{-2})	G_W (Bq m^{-2})
2	Yes	Latex – 5 a	38.24 ± 7.68	53.75 ± 9.65	2.96 ± 0.45	2.27 ± 0.40
3	Yes	Latex – 2 a	87.21 ±	80.02 ±	5.97 ± 0.70	6.69 ± 0.76
4	Yes	Acrílic	24.72 ± 6.02	53.75 ± 9.65	2.09 ± 0.38	4.66 ± 0.61
5	Yes	Latex – 1 a	194.28 ±	117.05 ±	14.18 ± 1.30	8.36 ± 0.89
6	No	Latex – 10 a	45.95 ± 8.87	188.83 ±	2.30 ± 0.40	5.23 ± 0.65
8	Yes	Latex – new	33.91 ± 7.29	175.78 ±	2.37 ± 0.41	3.74 ± 0.53
11	Yes	Latex – new	96.75 ±	83.61 ±	8.84 ± 0.92	11.05 ± 1.08
12	-	Yes	88.38 ±	119.44 ±	8.00 ± 0.86	9.91 ± 1.00
13	Yes	Latex – 4 a	160.05 ±	163.63 ±	17.14 ± 1.49	14.39 ± 1.31
14	yes	Latex – 2 a	31.21 ± 6.87	38.22 ± 7.76	3.48 ± 0.51	4.60 ± 0.60
15	Yes	Latex – 5 a	20.41 ± 5.35	26.28 ± 6.19	1.38 ± 0.30	1.55 ± 0.32
16	Yes	Latex – 1 a	254.51 ±	152.88 ±	11.95 ± 1.14	11.76 ± 1.13
17	Yes	Latex – 3 a	127.25 ±	81.22 ±	6.18 ± 0.73	4.78 ± 0.62
18	Yes	Latex – 3 a	51.62 ± 9.41	45.39 ± 8.65	2.82 ± 0.45	3.52 ± 0.51
19	No	No	96.02 ±	151.16 ±	10.46 ± 1.04	10.03 ± 1.01
23	Yes	No	150.84 ±	193.94 ±	20.53 ± 1.73	13.32 ± 1.23
24	Yes	Latex – 2 a	48.97 ± 9.08	70.47 ±	4.12 ± 0.56	3.46 ± 0.51
25	Yes	Latex – new	113.47 ±	77.64 ±	11.82 ± 1.13	6.69 ± 0.76
26	Yes	Latex – 2 a	52.92 ± 9.19	83.61 ±	3.64 ± 0.53	3.34 ± 0.50
28	little	Latex – 4 a	31.37 ± 6.97	66.23 ± 9.82	3.04 ± 0.47	2.35 ± 0.41
31	yes	Latex – 2 a	224.14 ±	70.47 ±	6.79 ± 0.78	5.79 ± 0.70
33	yes	Latex – 7 a	70.60 ±	76.44 ±	9.41 ± 0.97	6.87 ± 0.78
35	yes	Latex – 3 a	49.54 ± 9.27	76.44 ±	5.64 ± 0.69	5.73 ± 0.69
36	yes	Latex – 2 a	170.93 ±	93.16 ±	4.83 ± 0.63	4.66 ± 0.61
37	yes	Latex – 1 a	84.23 ±	111.08 ±	5.76 ± 0.70	5.20 ± 0.65
38	yes	Latex – 2 a	115.80 ±	125.41 ±	12.76 ± 1.21	12.78 ± 1.20
39	no	Latex – 0.17	68.64 ±	82.84 ±	7.05 ± 0.80	5.52 ± 0.68
41	yes	Latex – 0.25	53.87 ± 9.19	80.22 ±	3.99 ± 0.56	5.67 ± 0.69
46	yes	Latex – 1 a	49.43 ± 8.87	77.95 ±	5.67 ± 0.70	4.72 ± 0.61
48	yes	Wall paper	172.43 ±	66.03 ±	3.71 ± 0.54	4.38 ± 0.58
49	yes	Latex – 0.5 a	124.60 ±	50.16 ± 9.22	4.59 ± 0.61	5.85 ± 0.70
50	yes	Latex – new	39.02 ± 8.02	47.78 ± 8.94	2.64 ± 0.44	4.00 ± 0.55
51	no	Latex – 4 a	42.79 ± 8.50	67.73 ±	4.28 ± 0.59	3.51 ± 0.51
56	no	Latex – bad	54.19 ± 9.82	105.49 ±	2.71 ± 0.45	4.04 ± 0.55
58	yes	Latex – 2 a	32.64 ± 7.29	82.20 ±	1.64 ± 0.34	3.15 ± 0.48
66	yes	Latex – 3 a	32.63 ± 7.29	35.83 ± 7.46	2.69 ± 0.45	1.85 ± 0.35
67	little	Latex – 3 a	39.93 ± 7.92	81.12 ±	3.17 ± 0.50	2.21 ± 0.39
74	yes	Latex – 5 a	28.14 ± 6.63	36.02 ± 7.50	2.49 ± 0.43	2.04 ± 0.37
80	yes	Latex – 2 a	33.26 ± 7.32	39.62 ± 7.95	1.92 ± 0.37	3.06 ± 0.47
82	yes	Latex – 1 a	53.62 ± 9.94	63.30 ±	4.58 ± 0.62	4.42 ± 0.59
84	little	Latex – 0.25	38.03 ± 7.61	34.64 ± 7.31	2.57 ± 0.44	2.57 ± 0.42
86	yes	Latex – 2 a	42.46 ± 8.24	96.02 ±	6.56 ± 0.78	2.28 ± 0.44
96	yes	Latex – 0.33	54.41 ± 9.92	69.63 ±	4.30 ± 0.59	6.66 ± 0.76
122	yes	Latex – 0.75	67.66 ±	64.50 ±	6.02 ± 0.75	5.32 ± 0.66
124	yes	Latex – 10 a	54.76 ±	72.86 ±	4.18 ± 0.60	4.66 ± 0.61

Discussion

Considering the measurements carried out on 45 dwellings (see Table 1 and Figure 1) the following results should be pointed out:

(a) The mean values for the ratios between the air (A_W/A_S) and selfplated-out (G_W/G_S) activities are different: 1.39 and 1.07, respectively. These results can be explained taking into account the fact that the main source of radon are the materials (floor, walls and ceiling) enveloping the indoor environments under measurement. The approximately unitary mean value of the G_W/G_S ratio is probably due to the short half-life of the radon daughters (mainly ^{214}Po), which suffer a weak influence from aeration and a strong influence from the "radon source" (the same in both exposures). In the case of the air activity, the long half-life of radon makes this ratio to be more influenced by aeration (certainly greater in the summer exposure). Consequently radon, that is homogeneously distributed through the air, can be partially carry out to outdoor by aeration.

(b) Dwellings without internal painting (detectors 19 and 23) presented activities (A_I, A_V, G_I and G_V) greater than the corresponding mean values. Only one dwelling was internally painted with acrylic paint (detector 4); it presented the lowest activities (A's and G's) among all the dwellings analyzed in this work.

(c) Analyzing 8 residences (detectors 6, 19, 28, 39, 51, 56, 67, 84) where aeration was practically absent or very weak – in accordance with information given by the dwellers — one observes that only detectors 19 for summer exposure and 6, 19 and 56 for winter exposure presented A's greater than the corresponding mean values ($\overline{A}_S$ and $\overline{A}_W$, respectively). Concerning the G's, only detectors 19 (summer) and 19 and 36 (winter) presented superficial densities greater than the corresponding mean values ($\overline{G}_S$ and $\overline{G}_W$, respectively).

(d) Four flats were analyzed (detectors 28, 66, 74 e 86). With the exception of detector 86, the other three presented A's and G's quite smaller than the corresponding average values. It is important to mention that in the case of flat 86 exposure took place in a room presenting an apparent concrete ceiling.

(e) In figures 1.1 and 1.2 one can see a roughly linear relationship between the G's and A's. This result is expected as the greater is the number of radon and RD in the air the greater also is the probability that RD can attach to the material surfaces making up a room (including the detector surface, also). Atypical results, residences presenting great activities in the air and low RD superficial activities, appear both in figure 1.1 (detectors 6 and 8) and 1.2 (16, 31, 36, 48 and 49). These results can be a consequence of a fall in the probability that RD become attached to the walls where these detectors were exposed due to the turbulence caused by air currents in these residences.

It is suggestive that detectors showing great G's and low A's are not observed in figure 1.1 and 1.2. If a result of this kind was observed the most part of the radon atoms penetrating the indoor air (from the floor/soil, walls and ceiling) should decay quickly and, then, close to the walls, what would lead to an increase in the G value. However, as mentioned above, the long half-life of radon makes very probable that before their radioactive decay occur the radon atoms have enough time to spread uniformly through the room.

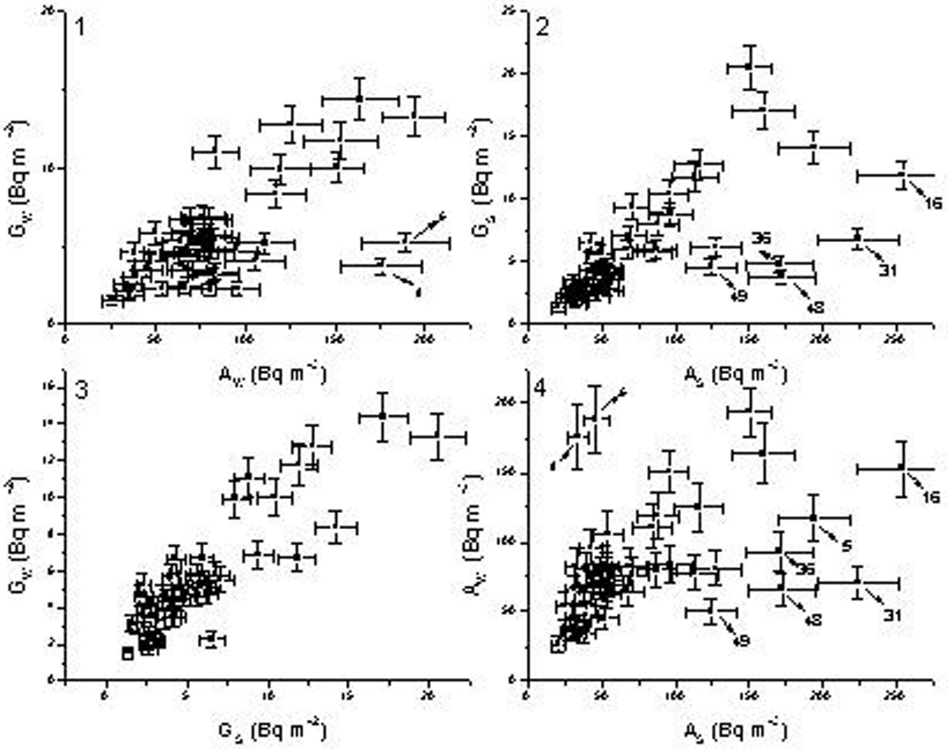

Figure 1. The activities of ^{222}Rn, ^{218}Po and ^{214}Po in the air for summer (A_S) and winter (A_W) exposures and of ^{218}Po and ^{214}Po plated-out on the detector surface, also for summer(G_S) and winter (G_W) exposures, were employed to build four plots: G versus A for winter and summer and G_W versus G_S and A_W versus A_S.

(f) In figure 1.3, one observes a clear linear dependence between G_W and G_S. The greater is G_W the greater is G_S for the corresponding residence. This indicates that the main factors determining the magnitude of the RD deposition rate should be associated with characteristics of the residences and not with factors that changed from the summer to the winter exposure, like the average temperature, ventilation rate, etc.

(g) In figure 1.4, if the points corresponding to the atypical residences (identified in figure 1.1, 1.2 and in this figure) are not considered, there is also a linear relationship between A_W and A_S, indicating again that the activity in the air is mostly influenced by the radon source, i. e. the residence.

Conclusions

Some results described in the previous section present coherence. Items a, b, c (observation about flat 86), f and g indicate that the “source of radon” comes from the material (brick and concrete are by far the most important materials used to build residences in Campinas) making up walls, floor/soil and ceiling of the dwellings. This is a partial result; only a half of our detectors were analyzed up to now. However, its confirmation can have an important consequence: indoor radon mitigation can be succeeded employing a proper internal wall painting. However, nowadays we can not go beyond this gross and generic statement. Our data are unclear if we search for more direct and detailed information at this respect. We did not found a relationship between age and conservation of the internal paintings usually utilized (latex) and a decrease of the measured activities. Only in one case (detector 4), this kind of decrease could be associated with the internal paint (acrylic). What means a proper internal painting (or even covering) is a matter that needs further investigation.

Our statistics concerning flats is very low: only four were analyzed. Then, it is difficult to state whether the low activities observed in these cases are due to their great distance to the soil, certainly also a source of radon, or to the lower amount of material — compared with houses — that is usually employed to build flats.

Our results (item c) also suggest that the activities measured in this work are not influenced by intensity of aeration. Although this intensity is only a rough and qualitative information given by the dweller owners.

The average A_W/A_S ratio found here is similar to winter to summer ratios carried out in other countries, but for radon only [7].

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Radon measurements in Rio de Janeiro

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Abstract. Few data are available on the dynamic of radon in the air for tropical climate conditions. The strong influence of the climatological characteristics on the transport of gases and particulates in air makes not adequate the use of data obtained at regions with different climate. Outdoor and indoor measurements of radon equilibrium equivalent concentrations (EEC) have been done for one-year period in Rio de Janeiro. Continuous measurements were performed using a radon monitor with an alpha spectrometry detector. Pluviometric index, temperature and humidity were registered. The paper presents the long term behaviour of outdoor radon equilibrium equivalent concentration results, their correlation with temperature and the influence of the pluviometric index. Maximum values were obtained during winter and minimum in summer, strongly influenced by the rain. A strong inverse correlation with temperature was found.

1. INTRODUCTION

The contribution of the natural source to the average annual effective equivalent dose of 2,4 mSv, about 1.2 mSv is due to radon and its decay products while the rest is due to cosmics rays, terrestrial gamma rays and radionuclides in the body (except radon). The average effective dose due to radon, as state above, corresponds to an average global population-weighted concentration of about 40 Bq.m^{-3} for indoors and 10 Bq.m^{-3} for outdoors [1].
Variations of radon concentration in air may depend on a number of factors, including geological and meteorological factors. Few data on long term variation of outdoor radon concentration for tropical climate are available. This information is very important to understand the behaviour of radon and short lived daughter products in air, to estimate dose and to interpret the results.

The radon can be estimated from potential alpha energy concentration (PAEC) based on measurements of individual progeny concentration [2]. In natural environment, PAEC change with time, with meteorological condition or life style of residents (ventilation of rooms).
A long term study on outdoor and indoor radon concentration was performed in 1996 [3]. Here, the results regarding long term variation of the radon outdoor concentration will be presented.

2. MATERIALS AND METHODS

This work reports the results of several measurements of outdoor radon equilibrium equivalent concentration (^{222}Rn EEC). The determination were made by potencial alpha energy concentration monitor (PAEC) in outdoor air in Barra da Tijuca, Rio de Janeiro, their correlation with temperature and the influence of the pluviometric index.

Long term variation of outdoor radon EEC was measured hourly from December 1996 to October 1997 with a Working Level – 200 plus equipment manufactured, by Tracelab Instruments from Germany. Averaged data are printed out and stored on magnetic disk for subsequent data evaluation. Temperature and humidity of air were investigated with a Thermo-Hygrograph (Ota Keiki Seisakusho Co) hourly and continuously recorded. The pluviometric index daily were obtained from the National Institute of Meteorology. The sampling station is located at Rio de Janeiro in the Instituto de Radioproteção e Dosimetria (IRD).

2.1. PAEC Monitor

The equipment used for measurements in this study consists of an air filter radon daughter sampler, a flow meter, a surface barrier detector, and an alpha spectrometer and associated electronics. An integrated microcomputer evaluates the data and prints the results. The printed results include the actual energy concentration, and activity concentrations of the radon daughters ^{218}Po, ^{214}Pb and ^{214}Bi (= ^{214}Po). The WLM-plus uses the ratio of different radon daughter concentrations and estimates the ^{222}Rn (gas) concentration and the equilibrium factor with an intrinsic calculation procedure [4].

2.2. Instrument

The PAEC is measured by pumping environmental air through a glass microfiber filter that collects the aerosol particles. The filter collects short half-lived decay products of ^{222}Rn on its surface. Simultaneously, the surface barrier detector of the sampler registers the alpha radiation from the filter. As shown in Figure 1, output signals from the detector are amplified by a charge sensitive pre-amplifier and a linear amplifier, and then, those are analyzed by multi channel analyzer.

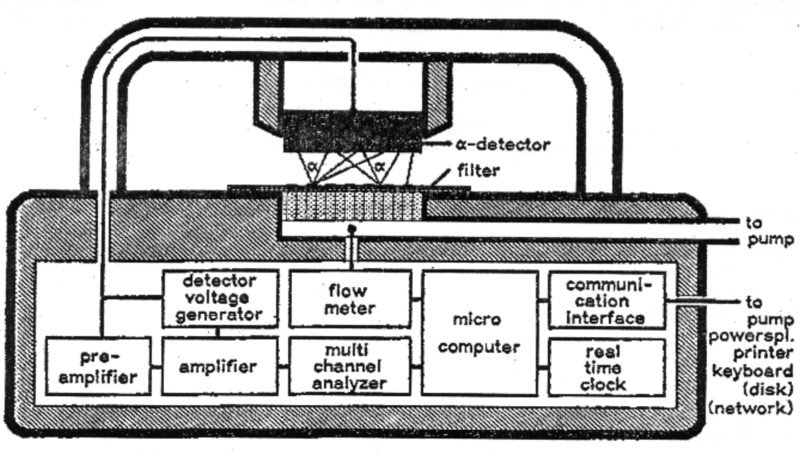

Figure 1. Schematic representation the radon daughter sampler.

3. RESULTS AND DISCUSSION

The results for the average diurnal variations of radon EEC during the period from December 1996 to October 1997 are shown in figure 2. Values from 0.5 Bq.m^{-3} in summertime to 50 Bq.m^{-3} in wintertime were found. It can be observed the strong variation of the average daily ^{222}Rn EEC as a function of the time in the year. Maximum values were observed during the months of winter (June, July and August) and minimum during summer (December and January).

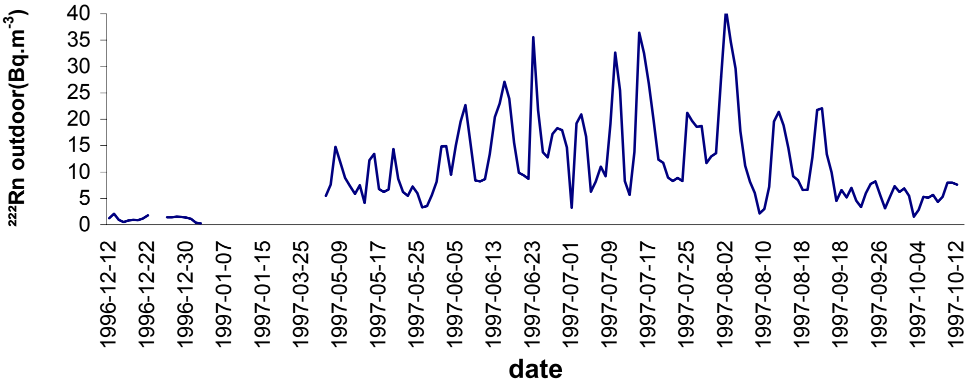

Figure 2. Average Daily Variation of Outdoor Radon concentration from December 1996 to October 1997.

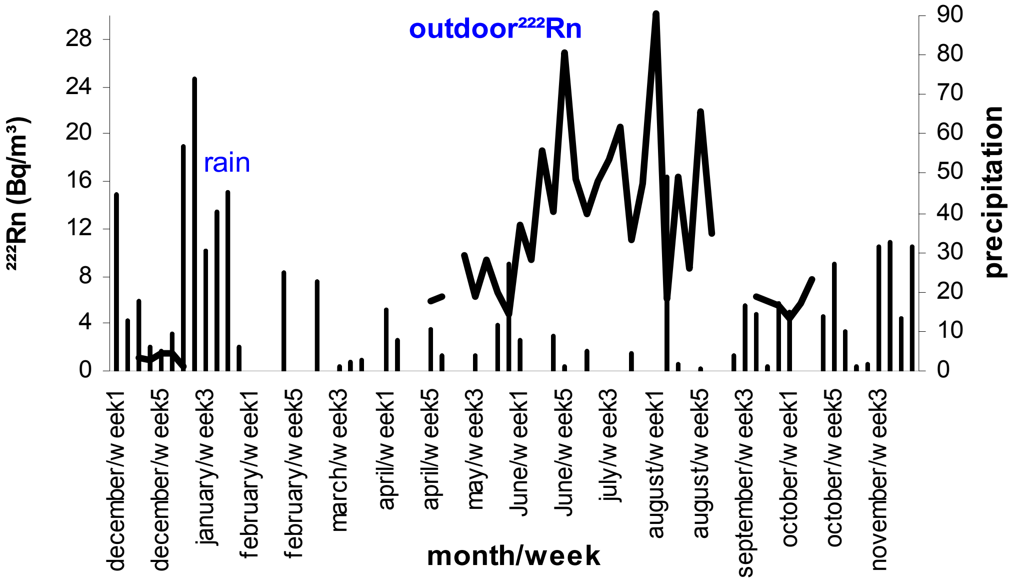

Figure 3. Weekly variation of radon Concentration and Rainfall rate.

The annual arithmetic mean ^{222}Rn EEC obtained during the sampling period is 12 Bq.m^{-3} ± 9,6 Bq.m^{-3} but better ajusted to a lognormal distribution (GM -7 Bq.m^{-3}; GSD - 3 Bq.m^{-3}). The values obtained are typical from normal low background areas. [1]. In United States an average outdoor radon gas concentration was estimated for normal areas in 9 Bq.m-3 [5].

Figure 3 presents the pattern of the radon EEC variation together with the rainfall rate during the same period. It can be observed that the lower values of radon concentration during the summer is related to the strong increase of the precipitation rate, characteristic of tropical climate. Consequently, there is an increase in the soil humidity, that blocks the soil pores and creates a physical barrier to radon diffusion, with the consequent reduction of gas exhalation. In addition to this and due to the high solubility of radon in water, the rain will transport the radon to deeper soil layers. In the other hand, during winter, when dry season occurs, radon concentration in air presents the highest values [3,6].

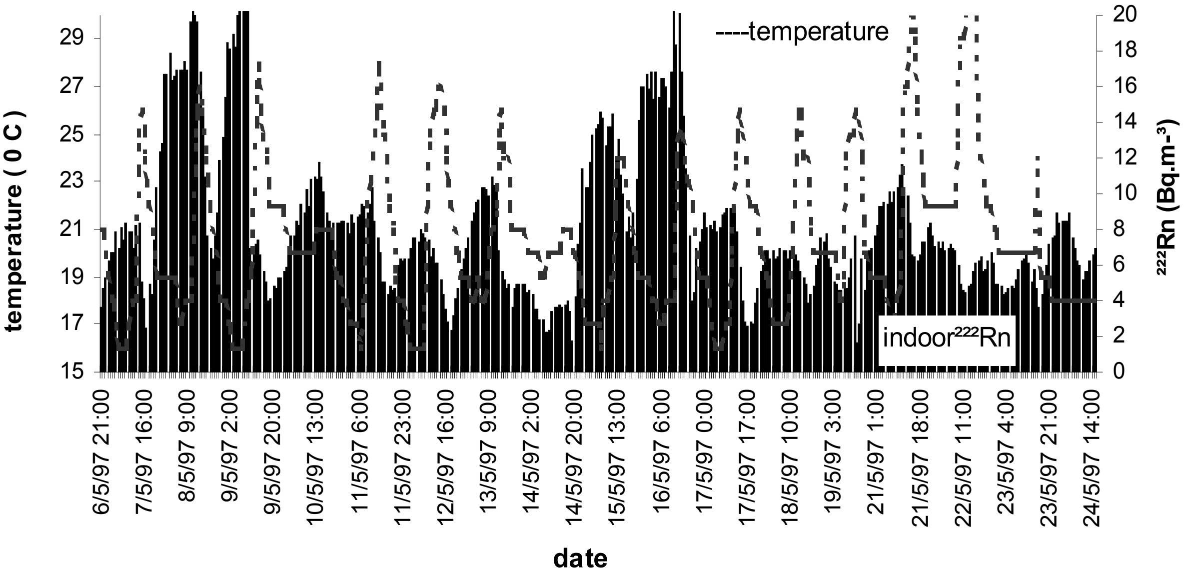

Figure 4. Daily variation of outdoor radon concentration and temperature.

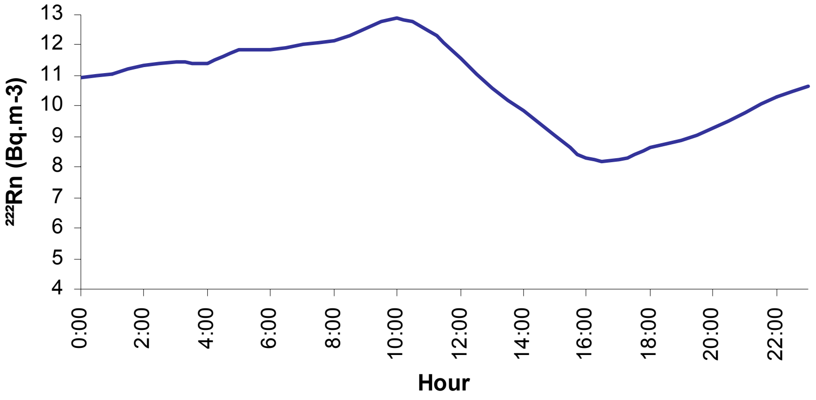

Figure 5. Hourly radon variation.

Figure 4 shows the daily variation of radon concentration and temperature. It is observed an inverse association between temperature and radon EEC, this pattern has already been proposed by Porstendörfer [7]. A Statistical correlation using time series analysis between radon concentration and temperature was applied. The observation of an inverse correlation with a delay of three hours was confirmed. Since most of the radon in air comes from soil exhalation, changes in meteorological conditions, such as temperature, need some time to generate in the soil changes in the emanation and exhalation rate and consequently on the radon in the air. This mechanism has an influence on the radon variability during the day as shown in Figure 5 [3], where the hourly mean values can be observed.

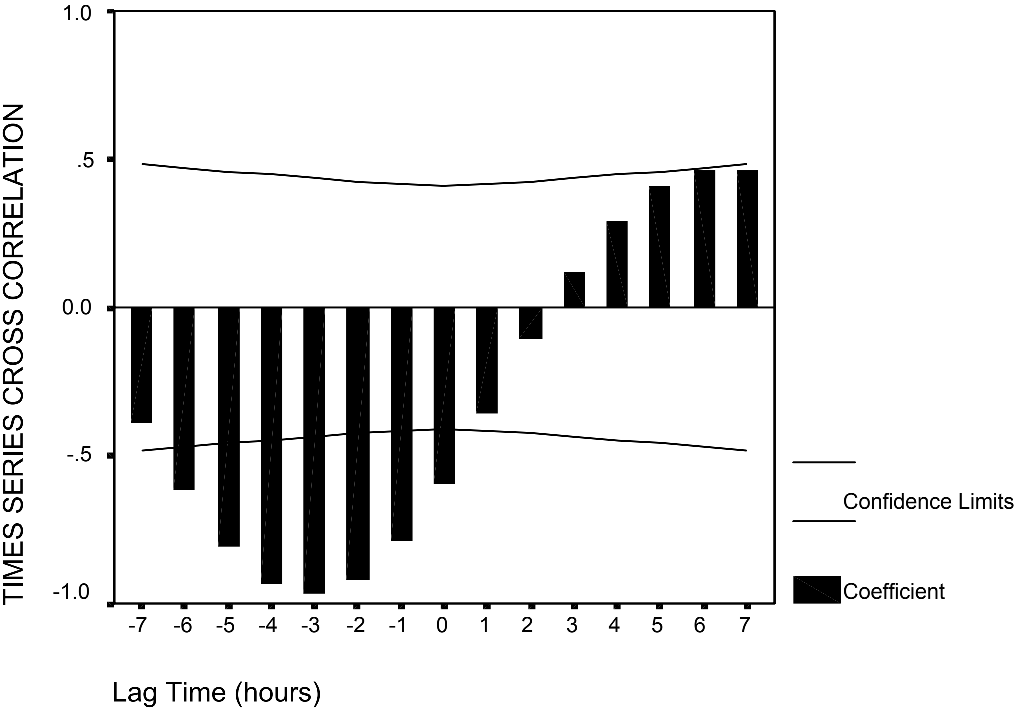

Figure 6. Times Series Correlation between radon and temperature.

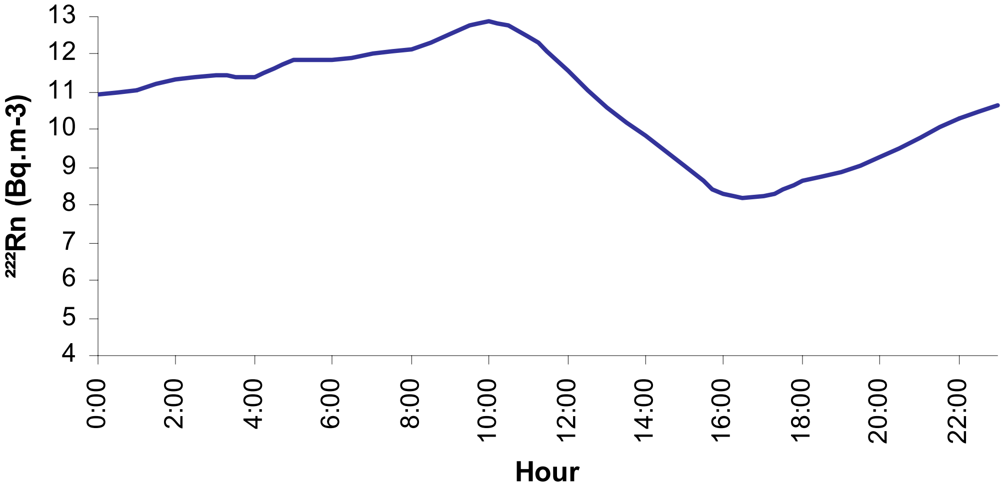

Figure 7. Hourly Radon Variation.

Radon concentration shows a maximum in the morning and a minimum in the afternoon. Generally speaking, early morning atmospheric temperature inversions lead to a stable atmosphere which restricts vertical mixing, consequently, maximum average radon concentrations occur at this period of the day. After sunrise, solar radiation heats the ground and causes the lower atmosphere warming. As a consequence, vertical mixing increases and leads to a decline in radon concentration in the afternoon [8].

CONCLUSION

The data are enough to give some information about the radon EEC behaviour under tropical conditions. A seasonal pattern, with higher values in winter and lower in summer was observed. It was also observed a strong inverse correlation of radon EEC with temperature.
This results are very important on the planning of measurements and dose assessment, however more data are still being collected.

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Radon exhalation from uranium mill tailings: Modelisation and in situ validation

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Abstract. TRACI, a model based on the physical mechanisms governing the radon transport in unsaturated soils, has been developped to evaluate the radon flux density at Uranium Mill Tailings (UMT) covers surface. First, moisture contents in the soil, induced by weather conditions, are calculated. Then, radon concentrations in the air-filled pore space, and radon flux density at the soil surface, are deduced from a transport model wich takes account for diffusion and convection in the pore space. To check the hypothesis used in TRACI and the efficiency of cover layers, an in situ study was launched in 1997 with the French uranium mining company, COGEMA. It consists of continuous measurements of moisture contents, suctions, radon concentrations at various depths inside an UMT cover, and flux density at its surface. The first analysis made on in situ observations shows that radon concentrations and flux density, calculated with a steady-state diffusion model using monthly averaged moisture contents, are in good agreement with monthly averaged concentrations and flux density measured.

1. Introduction

Mill tailings originating from the uranium ore treatment are stored in specific areas on the ground surface. They contain all the radium present in the original ore since physical and chemical processes used for the uranium extraction concentrate radium in the waste. Through radioactive decay, ^{226}Ra yields an inert radioactive gas, ^{222}Rn. Notwithstanding its comparatively short half life of 3.8 days, radon migrates through the tailings and a large quantity may reach the atmosphere. As a regulatory counter-measure, tailing piles are routinely covered to reduce radon release in the atmosphere.

In order to assess the long term environmental impact of Uranium Mill Tailings (UMT), the efficiency of the cover layer has to be determined, taking into account the change of its properties such as its thickness, porosity or permeability. Only models based on the physical mechanisms governing radon transport in soils, are able to predict the long term efficiency of the cover layer. Such a model, TRACI (Transport of Radon in the Unsaturated Zone), has been developped in the Institute for Nuclear Protection and Safety (IPSN – France). Its validation is one of the objectives of an in situ study carried out with COGEMA on the UMT covered pile of Bessines-sur-Gartempe, France. In the first part of this paper, the main mechanisms of radon transport in soils and a brief description of TRACI are given. In the second part, the in situ instrumentation is described. In the last part, monthly averaged radon concentrations and flux density are compared to radon transport model results.

2. Radon transport in soils — description

2.1. Source term – Radon emanation

Radon atoms are produced by the radioactive decay of ^{226}Ra atoms fixed on the solid particles of the soil. Only atoms of radon which escape from the solid grains to the free pore space can then migrate through the soil and reach the surface. The emanation power which is defined as the ratio between the number of radon atoms entering the free pore space and the total number of radon atoms formed [1], quantifies the effective radon source term.

When formed, radon atoms escape from the solid particle essentially by recoil and diffusion. But, if the kinetic energy received during their formation is too high, they can also go through the pore and be embedded in the opposite wall. This trapping effect depends on the pore geometry and on the amount of water in the pore space [2]. Studies of the emanation power of UMT show that it strongly increases with the moisture content of the porous medium [3, 4].

2.2. Radon transport mechanisms

Radon atoms migrate in the vadose zone lying between the aquifer and the soil surface, essentially by pressure and/or temperature induced convection, and molecular diffusion in the air– and water–filled pores. Water flow velocity is generally very low in the unsaturated zone and radon convection by water is often negligible. During its migration in the soil, radon gas can also be adsorbed on solid grains, particularly in clayey soils.

Convective transport by soil gas, diffusion in the pore space and adsorption, depend on the soil moisture content [5], and so does the radon flux density at the soil surface. Many authors have observed the effect of precipitations on soil radon concentrations. Atmospheric pressure appears also as a factor influencing radon transport in soils. Some authors mention a temperature and wind effect but their influence seems to be very low [6], [7], [8].

2.3. Water flow modeling

Thus, study of radon transport in soils requires the knowledge of the soil moisture profile and its evolution in response to changing meteorological conditions. Richards' equation is often used to calculate water flow in the unsaturated zone [9] but it assumes that the air phase is steady in the porous medium, whereas air flow must be taken into account to simulate atmospheric pressure effect on radon transport.

In the flow modeling, water is supposed to be uncompressible, air to behave as a perfect gas and porous medium to be undeformable. Flow equations are based on mass conservation and Darcy's law applied to each fluid phase [10]. The resolution of the non-linear system requires the retention characteristics of the soil to be incorporated in the model, which give an assessment of soil moisture content and permeability versus soil suctions [11].

2.4. TRACI, a model for radon transport in the unsaturated zone

The TRACI code includes a 1D water and air flow model and a 1D radon transport model based on the principles described in the previous paragraphs. It calculates moisture content, pore water and pore air velocity, radon concentrations, at different depths in the soil, and radon flux density at the surface. Input parameters are given in the Table 1.

The flow model results were first compared to published data and showed a fairly good agreement with the author's laboratory observations. Radon transport model was verified by comparing it to analytical solutions. Pressure effect on radon transport was also studied [12], but complete data for quantifying, with TRACI, the influence of meteorological parameters on radon flux density are lacking in the litterature. Therefore, an in situ validation was launched in 1997 in collaboration with COGEMA, the French uranium mining company.

Table 1. Input parameters of TRACI for an homogeneous soil layer I

Abbreviation	Définition	Unit
p	Porosity	$m^3.m^{-3}$
r_b	Dry bulk density	$kg.m^{-3}$
q_r	Residual water content	$m^3.m^{-3}$
K_s	Saturated hydraulic conductivity	$m.s^{-1}$
a	First Van Genuchten parameter	m^{-1}
b	Second Van Genuchten parameter	-
C_{Ra}	Radium content	$Bq.kg^{-1}$
E_a	Emanation factor for the dry material	-
E_w	Emanation factor for the wet material	-
S_{min}	Minimum moisture saturation of the emanation plateau	-
H	Thickness of the soil layer	m

3. In situ validation

3.1. Site description

The in situ instrumentation has been implemented since January 1998 on the covered COGEMA UMT of Bessines-sur-Gartempe, France. Two plots, with 15 m × 25 m and 15 m × 10 m areas, at 200 m from each other, were selected on the cover. The cover thickness spans from 4 to 5 m. The compacted cover material contains loamy sand as well as numerous blocks whose size can exceed one meter. Surface cover was sampled on ten spots evenly distributed on each zone to characterize the radon source term. Radium and corresponding emanation factor were measured by gamma spectrometry and the 21-day accumulation method, respectively. Table 2 displays the results of these analyses.

Table 2. Radium content and emanation factor measured on samples of the cover layer surface

	Number of measures	Mean	Standard deviation
Plot 1			
Radium content	10	947 $Bq.kg^{-1}$	464 $Bq.kg^{-1}$
Emanation factor	10	0.35 -	0.17 -
Plot 2			
Radium content	10	169 $Bq.kg^{-1}$	100 $Bq.kg^{-1}$
Emanation factor	2	0.53 -	0.03 -

3.2. In situ instrumentation

The in situ instrumentation consits of continuous measurements (every 30 minutes) of the soil suctions, with tensiometers at 15 cm, 50 cm, 100 cm and 130 cm depth, and of permittivities at the same depths. Permittivity and soil moisture are linked by a linear relation (from laboratory calibration). Such measurements give information on water flow in the cover.

Soil-gas radon concentrations at 25 cm, 50 cm and 100 cm depth in the cover, are monitored with a commercially available radon probe, which incorporates a solid-state silicon detector placed in a specially designed measurement chamber (BARASOL, Algade). Radon flux density at the cover surface are measured every three hours with an automated accumulation method: as soon as the accumulation volume is automatically laid on the soil surface, an ionisation chamber (Alphaguard, Genitron Instrument) monitors, every ten minutes during one hour, the radon concentration increase in the accumulation volume. The volume is then lifted up to expose the cover surface to normal weather conditions.

A meteorological station was added to measure precipitations, wind direction and speed, atmospheric pressure, air temperature, air relative humidity and sunshine.

4. Steady-state interpretation

Before interpreting transient phenomena using the flow model, radon transport model is implemented to calculate radon concentrations and flux density monthly averages. In this case, soil moisture contents are supposed to be constant during the month, and values are derived from the arithmetic mean of permittivities measured during this period. In this first step of the validation, the TRACI radon transport model is reduced to a steady-state non-uniform radon diffusion model, where radon diffusion factor relates to soil moisture content by [13] :

$$D = p \cdot D_0 \cdot \exp(-6 \cdot m \cdot p - 6 \cdot m^{14 \cdot p})$$

where D = radon diffusion coefficient of the soil pore space ($m^2.s^{-1}$)

p = soil porosity (-)

D_0 = diffusion coefficient of radon in air (1.1 10^{-5} $m^2.s^{-1}$)

m = fraction of water saturation of pores (-)

Table 3. Input parameters of the steady-state non uniform radon diffusion model for an homogeneous soil layer I

Abbreviation	Definition	Unit
p	Porosity	$m^3.m^{-3}$
r_b	Dry bulk density	$kg.m^{-3}$
q_{mi}	Mean water content of the soil layer	$m^3.m^{-3}$
C_{Ra}	Radium content	$Bq.kg^{-1}$
E_a	Emanation factor for the dry material	-
E_w	Emanation factor for the wet material	-
S_{min}	Minimum moisture saturation of the emanation plateau	-
H	Thickness of the soil layer	m

Table 4. Cover properties incorporated in the simulation

Parameters	Plot No 2
p	0.3 -
r_b	1520 kg.m^{-3}
C_{Ra}	400 Bq.kg^{-1}
E_a	0.5 -
E_w	0.5 -
S_{min}	-
H_1, H_2, H_3, H_4*	15cm, 35 cm, 50 cm, 1m

* H_1 referred to the top layer and H_4 to the lower one

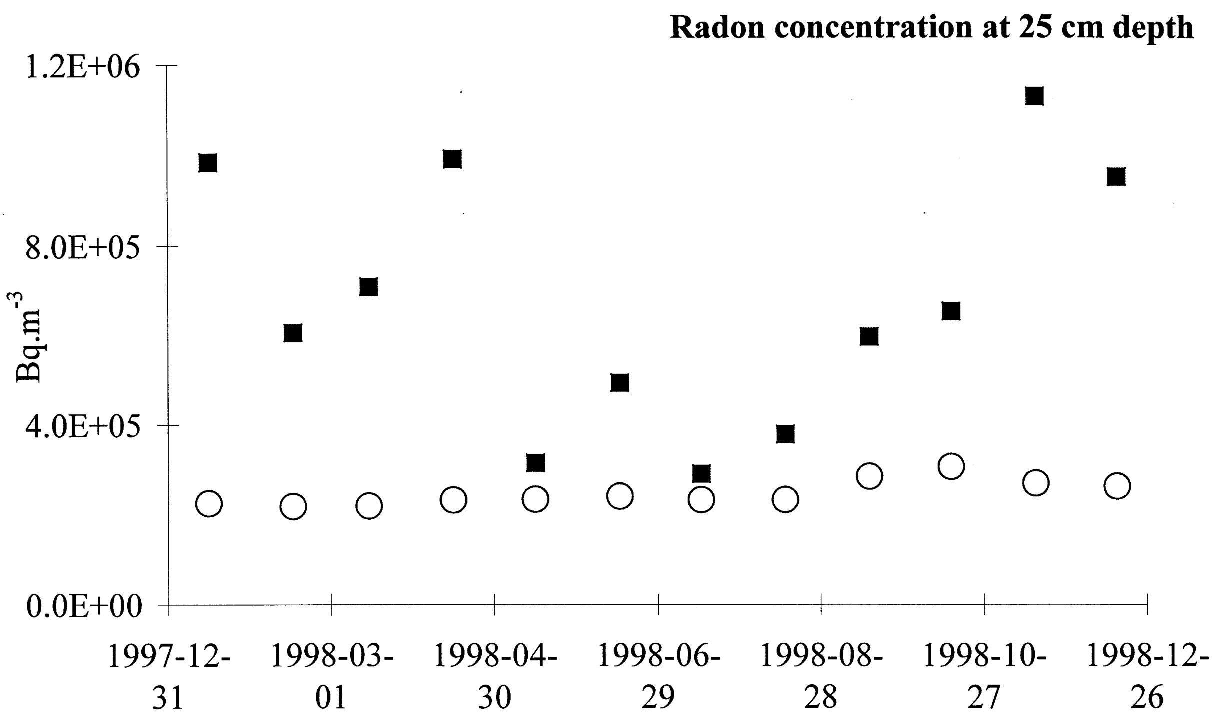

Fig. 1. Radon concentrations and flux density measured on the cover monthly averaged (■)and calculated (○) (Plot No. 2)

If another mechanism than diffusion dominates the radon migration in the cover layer, high discrepancies between calculations and observations would reveal themselves here. Table 3 lists input parameters for this type of simulation.

4.1. Intercomparaison between steady-state concentrations and flux density as calculated by TRACI and monthly averaged in situ measurements

Table 4 gives cover properties accepted for the simulation. Porosity and dry bulk density are deduced from the textural analysis. The emanation factor is deduced from surface sampling (see paragraph 3.1.) and the highest radium content measured on the plot is chosen for the simulation.

Figure 1 shows radon concentrations and flux density calculated on plot No 2 with the steady-state radon diffusion model by using measured and monthly averaged permittivities at the four measurement depths 15 cm, 50 cm, 100 cm and 130 cm.

4.2. Discussion

On average, calculated radon concentrations and flux density are in fairly good agreement with monthly averaged measurements despite the poor discretisation of soil moisture available and the uncertainties about cover properties. The same agreement is found on plot No 1.

Particularly, radon flux density measurements, which disturbs the cover very slightly, can be explained by this model. For the two plots under scrutiny, the variability of the calculated flux density is smaller than the obervations, since the radon transport model assigns to the uppermost layer the moisture measured at 15 cm depth, which varies less than the moisture at the surface.

Transport model calculations depend very strongly on moisture content measurements as an input parameter. A bad moisture content evaluation, particularly at the surface layer, can strongly affect the radon flux density estimation. On average, radon and moisture content measurements seem to be well correlated. Even if some discrepancies arise, they remain small when compared to the overall approximations used for the calculations.

5. Conclusion

A very simple non uniform diffusion model can well reproduce radon concentrations and flux density observed on the cover layer of an uranium mill tailing. Discrepancies and smaller variability can be explained by the lack of discretisation of the soil moisture vertical gradient. The good corrrelation between radon and hydric state of the soil gives confidence in the radon transport modelisation used in TRACI.

The next step of the validation will consist in analysing transient phenomena, *i.e.,* comparing observations to TRACI's results obtained before and after a rainfall. Questions currently raised are relative to the parametrization representation of a highly heterogeneous cover material, and to the interpretation of spot measurements.

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Occupational exposure to nickel, uranium and thorium in a nickel mine

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Abstract. The workers involved in mining and milling ores are exposed in the workplace to many hazardous agents that can cause a health detriment. In this work, the measurements obtained in a nickel mineral processing facility in the Brazilian Central-West are presented. One of the most important hazardous agents in this facility is the aerosol present in the air that contains nickel, uranium and thorium. The aerosol is inhaled or ingested, metabolised and deposited in the whole body or in specific organs. The surveillance of internal contamination of workers was performed by analysis of urine, fecal and hair samples. The ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) method was used to analytically determine nickel, uranium and thorium in these biological samples. Additional data were obtained by the collection of air samples in the workplace. A cascade impactor with six stages was used to collect mineral dust particles with an aerodynamic diameter in the range of 0.64 to 19.4 μm. The particles impacted in each stage of the cascade impactor were analysed by PIXE (Particle Induced X ray Emission), which permits the determination of elemental mass air concentration and the MMAD (Mass Median Aerodynamic Diameter). The concentrations of nickel, uranium and thorium were determined in the aerosol samples. All the results were analysed using statistical methods and biokinetical modelling was applied to evaluate the internal contamination and to make a risk estimation.

Introduction

In many regions of Brazil where ores of minerals with commercial importance are extracted, there is also an associated occurrence of the radioactive materials thorium and uranium. In the different steps of mineral processing, the aerosol is formed in the work place. This results in the inhalation of particles containing toxic and radioactive materials. In this work, internal contamination by nickel, uranium and thorium in a nickel extraction and processing facility is investigated. The choice of a nickel mine is supported by the high toxicity of refined nickel, which is classified as group 1 of priority by the International Agency for Research on Cancer [1]. The quantification of the nickel, uranium and thorium in the aerosol samples was made by PIXE (Proton Induced X ray Emission). To evaluate the internal contamination of the workers, biological samples: urine, feces and hair were collected and analysed by ICP-MS (Inductively Coupled Plasma – Mass Spectrometry). To determine the regional contribution due to food consumption, urine, feces and hair of local inhabitants (the worker's wives) were collected. Background values for nickel, uranium and thorium concentrations in urine were obtained by sampling and measuring urine and feces samples in the city of Rio de Janeiro.

Materials and methods

Methodology

The methodology used in this work was to collect samples of urine, feces, and hair of workers at the mining and milling facility and aerosols in the workplaces. Biological samples were also taken from the workers' wives. Biokinetical models were applied to determine the internal deposition and the intake, and the risk was estimated. Figure number 1 shows the applied methodology.

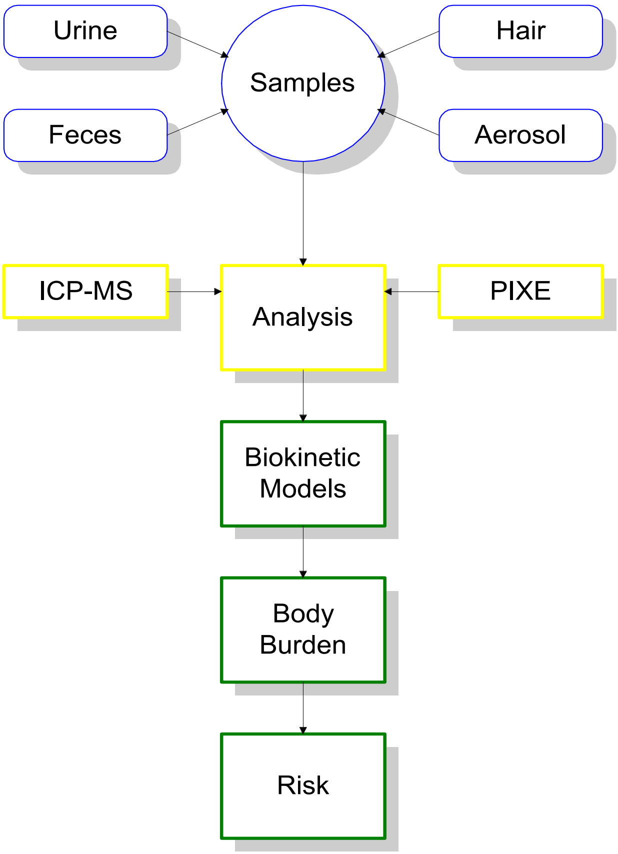
Sample collection

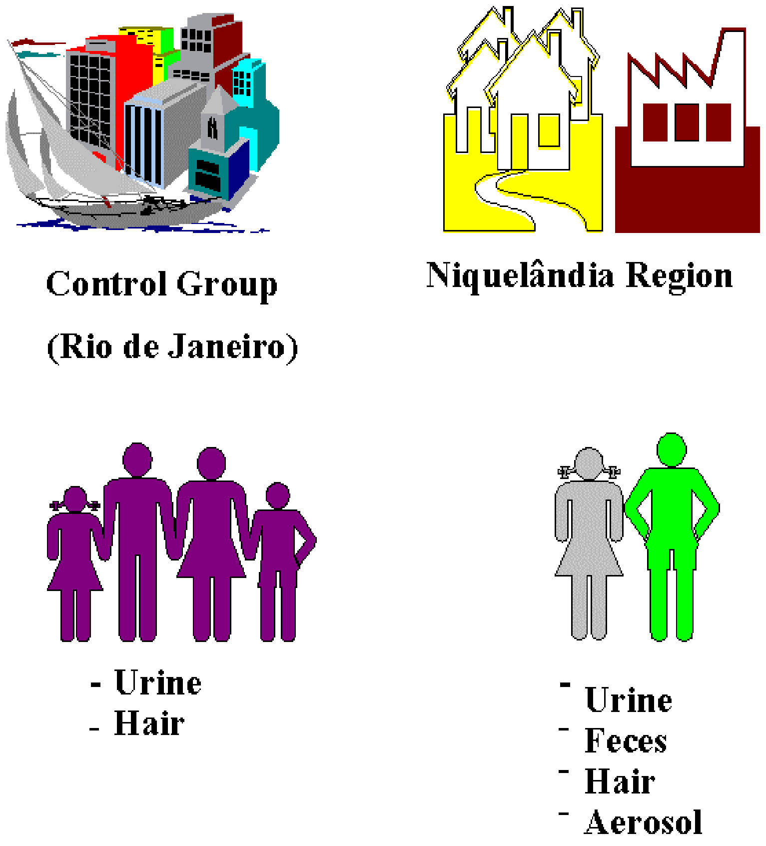
To measure the nickel, uranium and thorium concentrations in biological samples (urine, feces and hair) and in aerosols, a field expedition to the Region of Niquelândia was made, where the most important nickel extraction facilities of Brazil are located. In this expedition, urine, feces and hair samples of the workers occupationally exposed to aerosol in the workplace were collected, and also from their wives to obtain a regional factor for nickel, uranium and thorium excretion and amount in the hair. The collection of aerosol samples was performed with a cascade impactor to evaluate the air concentrations of Ni, U and Th. The results obtained in urine and hair were compared with the values found in the city of Rio de Janeiro. The Figure 2 shows the sampled groups and the samples collected in this work.

Sample preparation and analysis

Aerosol samples

By using a cascade impactor the air samples were collected to determine the aerodinamical behaviour of the aerosol [2]. A thin *Mylar* film covered with an emulsion of Vaseline/toluene was placed in each step of the impactor. The sampling time was adjusted to avoid membrane saturation. The air volume was determined using an integrator placed between the impactor and the vacuum pump. The qualitative and quantitative analysis of nickel, uranium and thorium in each step of the impactor was performed by PIXE (Proton Induced X ray Emission).





Biological samples
In this work, the urine, feces and hair were analysed by ICP-MS [3]. The urine was diluted 1:20 with HNO_3 1N, prepared from hyperpure HNO_3 and H_2O mili *Q*. The fecal samples were dry ashed initially at 400°C, homogenised and then dry ashed again at 600°C. From the residue 0,01g was taken and dissolved in 20 mL of 1N HNO_3 prepared from concentrated HNO_3 hyperpure and H_2O mili *Q*. The hair samples were obtained cutting 100 mg of the hair from the neck of the workers and their wives. The samples were washed in an ultrasound bath and dissolved in concentrated HNO_3 hyperpure in a microwave oven and diluted to 1N. In all the solutions which were analysed by ICP-MS, internal standards of In and Tl were added.

Results and discussion

Aerosol samples
The analysis of the X ray spectrum of the aerosol samples indicated that the uranium and thorium concentration in the respirable fraction of aerosol were below the detection limit of PIXE technique. Therefore the exposure to aerosols in this facility can be characterised as nickel exposure only. Figure 3 shows an X ray spectrum of particles impacted on the surface of the cascade impactor.

The nickel concentration in the respirable fraction of aerosol during the main steps of the facility are shown in table I

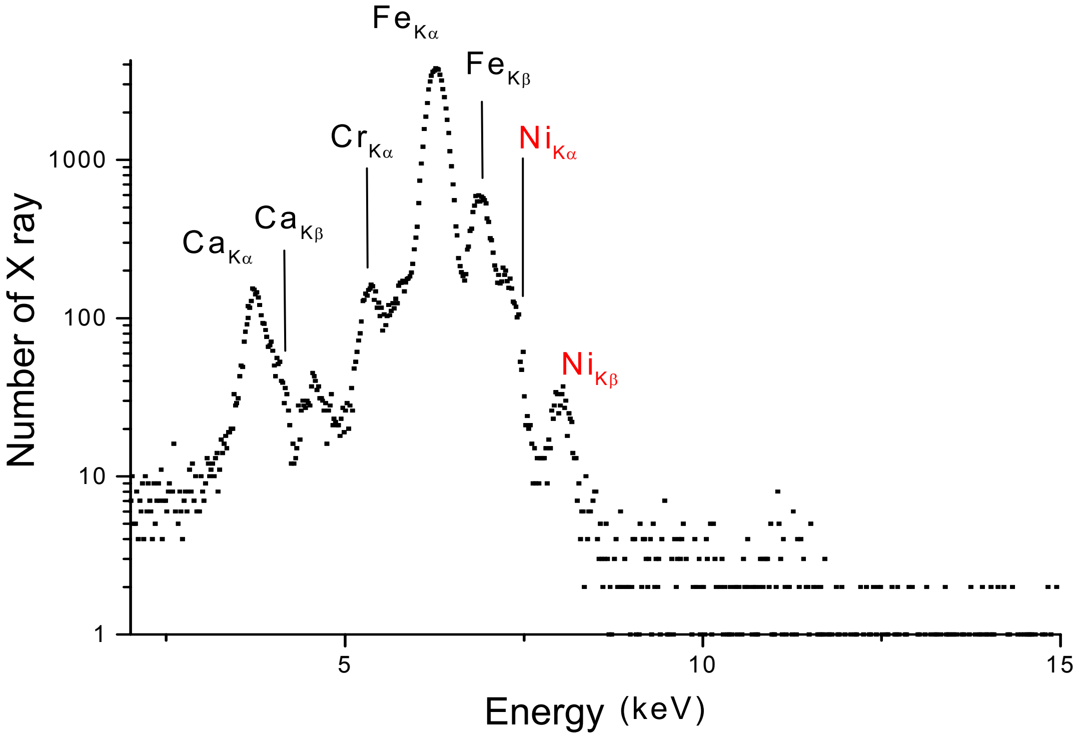


Table I. Nickel concentration in air samples

Step	Ni concentration (μg/ m^3)	MMAD (μm)	σ_g
Pneumatic crushing	0.86	1.0	2.4
Primary crushing	0.23	1.1	2.5
Secondary crushing	0.19	1.2	3.1
Pebbling	0.91	0.6	2.3
Sinter	0.22	1.2	2.3
Refine	0.30	0.9	3.0
Offices	0.02	1.4	2.2

$\sigma_{g=}$ geometric standard deviation

The values of MMAD (Mass Median Aerodynamic Diameter) indicate that the particles are in the aerosol respirable fraction.

Urine samples

In this work the nickel concentration in urine samples was determined for a group composed by workers from the nickel mine, and another group composed of inhabitants of the mine region, the workers' wives. To situate the magnitude of the obtained values was necessary obtaining nickel data in urine of a control group. The control group chosen was composed of 68 people from Rio, of both sexes and with ages from 7 to 51 y. The nickel concentration in urine was found to be in the interval of 2–16 μg/L. The concentration in the control group was compared to the international value of 7.9 μg/L [4]. The *t*-Student test was applied and no difference between the urine concentration in Rio de Janeiro and the international reference was found ($p>0.05$) [5, 6]. In the table II was represented the medium concentration of nickel in urine obtained in the three groups sampled: (a) group of Rio de Janeiro; (b) group of Niquelândia inhabitants (wives of mine workers); and (c) mine workers.

Table II. Nickel concentration in urine samples

Group	Age (y)	Ni concentration ± sd (μg/L)
Rio de Janeiro (n=68)	07–51	7.1 ± 3.1
Niquelândia inhabitants (n=26)	33–34	16.0 ± 6.5
Mine workers (n=24)	24–58	15.6 ± 5.7

sd= one standard deviation
n= sample size

As it can be seen, the average Ni concentration obtained in Rio de Janeiro (control group) was lower than the other two. The variance analyses showed that the three groups are different ($p<0.05$). The application of the *t*-Student test indicated that the Rio de Janeiro group is different from the others ($p<0.05$), and that there is no difference between the groups of local Niquelândia inhabitants and the mine workers.

The air sampling results also showed an absence of uranium and thorium, however the urine samples were analysed by ICP-MS and a concentration of uranium and thorium was measured. To situate the magnitude of the obtained values was necessary determining uranium and thorium data in urine of a control group. The control group sampled was the same as above. The results obtained for uranium excretion for the control group were in the interval 0.01–0.12 μgU/L The average value obtained of the group formed by the nickel mine workers was 0.10 ± 0.02 μgU/L. The application of the *t*-Student test indicated that is no significant difference between these groups ($p>0.05$) [5, 6]. Using the same methodology, the results obtained for thorium excretion for the control group were in the interval 0.08–0.28 μgTh/L. The average value obtained for the group formed by the nickel mine workers was 0.18 ± 0.04 μgU/L. The application of the *t*-Student test indicated that there is no significant difference between these groups ($p>0.05$) [5, 6]. The urine measurements therefore confirmed that the exposure to uranium and thorium in this nickel mine is not significant.

Fecal samples

To evaluate the nickel concentration in feces, two groups were sampled and compared: (a) group of Niquelândia inhabitants (wives of mine workers); and (b) mine workers. Table III represents the mean results obtained for the groups.

Table III. Nickel concentration in feces samples

Group	Age (y)	Ni concentration ± sd (μg/g)
Niquelândia inhabitants (n=26)	33–44	95 ± 28
Mine workers (n=24)	24–58	141 ± 51

sd= one standard deviation
n = sample size

The two groups were compared applying the t-Student test, and the result indicates that there is a significant difference ($p<0,05$). However the statistical test showed that the average fecal excretion of Niquelândia inhabitants (382 μg Ni/day) is not different ($p>0.05$) from the reference value (370 μg Ni/day) reported for reference man [4]. The comparison between the two Niquelândia groups didn’t show differences in the urine excretion. However there is an increment of nickel concentration in the fecal excretion of mine workers. This is due probably to nickel present in the air as insoluble compounds and the principal path of intake is probably the ingestion through mouth breathing.

Hair samples

The samples of hair from two groups were analysed in this work: (a) group of Niquelândia inhabitants (wives of mine workers); and (b) mine workers. The table IV represents the mean results obtained for the groups.

The *t*-Student test indicates that these groups are statistically different ($p>0.05$). The same statistical test was applied to compare each group with the reference value (0.06 μg/g) from people from Rio de Janeiro. The magnitude of the difference between the groups and the reference value makes it possible to conclude that this result comes from external sources rather than from systemic contamination. This idea is reinforced by the results of nickel concentration in urine that are 2 or 3 times the reference value, while the hair concentration is more than 100 times this value. A hypothesis of external hair contamination is reinforced by the good correlation obtained through the multiple regression between nickel content in feces and hair [5, 6].

Table IV. Nickel concentration in hair samples

Group	Age (y)	Ni concentration ± sd (μg/g)
Niquelândia inhabitants (n=9)	33–44	0.55 ± 0.34
Mine workers (n=11)	24–58	3.06 ± 1.36

sd= one standard deviation

n = sample size

Nickel exposure

The distribution of nickel in the organism of workers was estimated through the urine excretion using the metabolic model for nickel from ICRP publication 67 [7], together with the respiratory model of ICRP 66 [8]. The ratio urine/feces determined experimentally for the group of mine workers and Niquelândia inhabitants were compared to results obtained from 4 models for nickel entrance in the organism: (a) ingestion; (b) inhalation of type S (slow pulmonary clearance) compounds; (c) inhalation of compounds type M (medium pulmonary clearance); and (d) inhalation of compounds type F (fast pulmonary clearance). Table V resumes the values for the ratio urine/feces for nickel calculated experimentally and theoretically. The theoretical values are for the first and last days worked in a week. The experimental values are averages.

Table V. Theoretical and experimental ratio urine/fece

Ratio urine/feces					
Group	Ingestion	Inhalation (type S)	Inhalation (type M)	Inhalation (type F)	Experimental ±sd
Mine workers	1.08×10^{-1}	1.20×10^{-1}	7.42×10^{-1}	5.70	$(3.85 \pm 2.03) \times 10^{-2}$
	4.77×10^{-2}	7.05×10^{-2}	3.52×10^{-1}	2.30	
Niquelândia inhabitants	1.08×10^{-1}	1.21×10^{-1}	8.35×10^{-1}	6.72	$(5.86 \pm 2.94) \times 10^{-2}$
	4.77×10^{-2}	7.49×10^{-2}	4.13×10^{-1}	2.80	

sd = one standard deviation

The analysis of the obtained values suggests that for the workers and the Niquelândia inhabitants, the most probable path of nickel intake is the ingestion. The hypothesis of inhalation of type S compounds is also possible.

Through the ingestion model using the average excretion for workers and inhabitants of 15 μg Ni/L and 21 μg Ni/L, the daily intake of 0.47 mg Ni/day was estimated. This value is compatible with the 200–600 μg Ni/day suggested by ICRP 23 [4]. Using the inhalation model (type S) the expected excretion for workers would be 7.65×10^{-2} mg Ni/day for men and 5.27×10^{-2} mg Ni/day for women. These values are far from the 21 and 22 μg Ni/day determined experimentally. Applying the ingestion model over a time of 35 years, the total amount of nickel body burden will be 9.11 mg for workers and Niquelândia inhabitants.

To risk estimation was made using the oral reference dose (R_fD) for metallic nickel of 2.00×10^{-2} mg/kg/day [9, 10]. The reference dose was compared to the daily intake (D_E) of 0.47 mg/day. For the workers, it is acceptable to consider the weight of the reference man as 70 kg. For these individuals, the R_fD is 1.4 mg/day. The potential risk quotient (QR), defined as D_E/R_fD, then 0.34. This result indicates that for the workers, the appearance of adverse effects is unlikely due this exposure.

For the Niquelândia inhabitants, the group was composed of women, so the body weight of 58 kg was considered. For the risk estimation the oral reference dose (R_fD) was used for metallic nickel of 2.00×10^{-2} mg/kg/day [9, 10]. The reference dose was compared to the daily intake (D_E) 0.47 mg/day [11]. For these individuals, the R_fD is 1.16 mg/day. The potential risk quotient (QR), defined as D_E/R_fD, is then 0.41. This result indicates that for the Niquelândia inhabitants, the appearance of adverse effects is unlikely due this exposure.

Conclusions

In this nickel mine the coupled exposure due to radioactive and stable elements was not characterised, since uranium and thorium are present in background levels. On the other hand, Nickel is an element classified by the International Agency for Research on Cancer [1] in the first priority group due its high toxicity. It was verified that the mineworkers and the Niquelândia inhabitants have a nickel concentration in urine higher than Rio de Janeiro inhabitants, probably due to a dietary intake, through food and water consumption. The workers have an additional intake of aerosols predominantly through the gastrointestinal system and with a contribution of inhalation of nickel compounds with slow pulmonary clearance. Using the biokinetical model proposed by ICRP 67 [7] the nickel incorporation was calculated, and these values were compared to the nickel reference dose [9]. The potential risk coefficient calculated was low.

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