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DEVELOPMENT OF NEW NUCLEAR METHODS FOR THE ANALYSIS OF NATURALLY OCCURRING RADIONUCLIDES IN VARIOUS MATERIAL SAMPLES AND RESULTING RADIATION DOSES TO THE MEMBERS OF THE PUBLIC AND WORKERS

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Abstract

We developed three new and original methods based on the formalism of energy loss of alpha-particles inside different media for evaluating the ^{238}U, ^{232}Th, ^{222}Rn, and ^{220}Rn concentrations inside different liquid and solid material samples: rocks, soils, water, foodstuffs, plants, phosphates, tobacco, medical drugs….The first method is based on evaluating first the probabilities for alpha-particles emitted by the ^{238}U (8 alpha-particles) and ^{232}Th (7 alpha-particles) natural radioactive series inside a material sample to reach and be registered as bright holes on the LR-115 type II and CR-39 solid state nuclear track detectors, and secondly on measuring the alpha-particles track density rates registered on the detectors utilized. The second method consists of evaluating the mean critical angles of etching of the LR-115 type II and CR-39 solid state nuclear track detectors and measuring the resulting track density rates due to alpha-particles emitted by the ^{238}U and ^{232}Th radioactive families. The third new method is based on calculating the detection efficiencies of the LR-115 type II and CR-39 solid state nuclear track detectors for alpha-particles emitted by the nuclei of the ^{238}U and ^{232}Th radioactive series, by using a new Monte Carlo computer code, and measuring the resulting track density rates registered on the considered detectors. We also developed three new and original nuclear methods for measuring the concentrations of radon, thoron and their decay products inside various atmospheres: air of dwellings, cigarette smoke, air of work places, outdoor air and soil gas. We developed a new dosimetric model based on determining alpha- specific doses deposited by an activity of 1Bq of ^{238}U and an activity of 1Bq of ^{232}Th in different human organs and tissues and exploiting results obtained for the ^{238}U, ^{232}Th and ^{222}Rn measured inside the ingested waters and foodstuffs for evaluating the committed equivalent doses as well effective doses due to ^{238}U, ^{232}Th and ^{222}Rn in the human body from the ingestion of different foodstuffs and drinks. We developed a new dosimetric model based on evaluating the alpha specific doses deposited by 1Bq of ^{218}Po and 1Bq of ^{214}Po in the tissues of the human respiratory tract and measuring the concentrations of these radionuclides inside the air of various dwellings and work places for determining the committed equivalent doses and effective doses due to ^{218}Po and ^{214}Po after the inhalation of polluted and unpolluted air. We developed a new dosimetric model for evaluating the committed equivalent dose due to radon in different compartments of the human gastrointestinal system from the ingestion of drinking waters and medical drug preparations. We also developed a new dosimetric model for determining effective doses due to ^{238}U, ^{232}Th and ^{222}Rn from to the skin from the application of various black soap, plant oil and thermal water material samples by the members of the general public.

1. INTRODUCTION

Natural radionuclides exist ubiquitously in the environment and contribute significantly to external and internal doses to the population [1]. Among them, of particular importance are solid radionuclides belonging to the ^{238}U and ^{232}Th series. These radionuclides enter the human body mainly through ingestion and by inhalation to considerably smaller degree [1,2].

Due to their presence in soil and phosphate fertilizers, primordial radionuclides and their progeny are transferred via water to medicinal plants and then to foodstuffs and medical drugs

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which are ingested by individuals. It is necessary to measure the radionuclide content of foodstuffs, medical drugs and water samples to assess potential radiation doses and, if necessary, to take action to avoid the exposure of population to radiation. Uranium and thorium concentrations have been measured in various food and drink samples by using gamma-ray spectrometry [3]. Simultaneous determination of ^{238}U and ^{232}Th in some biological reference materials has been performed by using neutron activation analysis and radiochemical separation [4]. However, this technique is both destructive and expensive. ^{238}U and ^{232}Th have been analysed in different food samples using inductively coupled plasma mass spectrometry (ICP-MS) which is also destructive [5]. Committed effective doses to members of the public due to ^{238}U and ^{232}Th in different foods were evaluated by using the International Commission on Radiological Protection (ICRP) ingestion dose coefficients [6]. Radon (^{222}Rn) is a chemically inert and very mobile gaseous decay product of uranium (^{238}U) which is found in all rocks and soils. Inhalation and ingestion of radon and its progeny represent the main source of exposure to ionizing radiation for population in most countries.

In the present work, we used CR-39 and LR-115 type II solid state nuclear track detectors (SSNTDs) to evaluate uranium, thorium, radon and thoron concentrations in various solid and liquid material samples as well as the concentration of radon, thoron and their progenies in the indoor and outdoor air. We determined annual committed equivalent doses from intakes of ^{238}U, ^{232}Th and ^{222}Rn in different compartments of the human body of the members of the members of the public from the ingestion of the studied material samples. We also determined annual committed equivalent doses in the tissues of the respiratory tract due to the inhalation of radon short- lived daughters by the general public and workers.

2. METHODS OF STUDY

2.1. Determination of uranium, thorium, radon and thoron concentrations inside different liquid and solid materials

Disk shaped CR-39 (manufactured by Pershore Mouldings Ltd., U.K.) and LR-115 type II (manufactured by Kodak Pathe, France and marketed by Dosirad, France) solid state nuclear track detectors (SSNTD) of radius q=2cm have been separately placed in close contact with a homogeneous building material sample in a hermetically sealed cylindrical plastic container for one month (30days) [7]. During this exposure α-particles emitted by the nuclei of the thorium-232 and uranium-238 series bombarded the SSNTD films. After the irradiation, the exposed films were etched in appropriate NaOH solutions [7]. Resulting track densities registered on the SSNTD films were counted using an ordinary optical microscope.

2.1.1. Method based on the SSNTD probabilities

By calculating first the probabilities P_i^{CR} and P^{LR} for α-particles emitted inside a material sample by the nuclei of the uranium-238 and thorium-232 series to reach and be registered as tracks on the CR-39 and LR-115 type II SSNTD, and secondly by measuring the α-particles track density rates registered on the CR-39 (ρ_G^{CR} in tracks. cm^{-2}. s^{-1}) and LR-115 type II (ρ_G^{LR} in tracks. cm^{-2}. s^{-1}) one can evaluate the thorium C(Th) and uranium C(U) contents in the studied material sample by using a method described in detail by Misdaq and Satif [8]. Indeed, we have:

$$\frac{C(U)}{C(Th)}=\frac{A_{Th}}{A_U}\,\frac{6\,P^{LR}\Delta R\left(\frac{\rho_G^{CR}}{\rho_G^{LR}}\right)-\sum_{i=1}^{7}k_i P_i^{CR}R_i}{\sum_{i=1}^{8}k_i P_i^{CR}R_i-8\,P^{LR}\Delta R\left(\frac{\rho_G^{CR}}{\rho_G^{LR}}\right)} \tag{1}$$

and

$$C(Th)=\frac{\rho_G^{LR}}{2\,d_s\;\Delta R\left[4\frac{C(U)}{C(Th)}A_U P^{LR}+3\,A_{Th}P^{LR}\right]} \tag{2}$$

where A_U is the specific activity in 1 ppm (10^{-6} g/g) of ^{238}U, A_{Th} is the specific activity in 1 ppm (10^{-6} g/g) of ^{232}Th, C(U) and C(Th) are the uranium and thorium concentrations (10^{-6} g/g) of a considered sample, d_s is the sample density, R_i is the range of an α-particle of energy $E_{\alpha i}$ and index i in the sample, k_i is the branching ratio in %, and $\Delta R = R_{max}-R_{min}$ where R_{max} and R_{min} are the α-particle ranges in the building material sample. These ranges correspond to the lower and upper ends of energy window of the nuclear track detector and, therefore, depend on the residual thickness of the LR-115 SSNTD.

2.1.2. Method based on the SSNTD mean critical angles of etching

According to a method developed by Misdaq et al. [9], by measuring ρ_G^{CR} and ρ_G^{LR} track density rates and calculating the mean critical angles of etching of the CR-39 $\left(\langle\theta_c^{CR}\rangle\right)$ and LR-115 type II $\left(\langle\theta_c^{LR}\rangle\right)$ one can determine the thorium C(Th) and uranium C(U) concentrations in a given material sample by using the following equations:

$$\frac{C(U)}{C(Th)}=\frac{A_{Th}}{A_U}\,\frac{6\left(\sin\langle\theta_c^{LR}\rangle\right)^2\Delta R\left(\frac{\rho_G^{CR}}{\rho_G^{LR}}\right)-\sum_{i=1}^{7}k_i\left(\sin\langle\theta_{ci}^{CR}\rangle\right)^2 R_i}{\sum_{i=1}^{8}k_i\left(\sin\langle\theta_{ci}^{CR}\rangle\right)^2 R_i-8\left(\sin\langle\theta_c^{LR}\rangle\right)^2\Delta R\left(\frac{\rho_G^{CR}}{\rho_G^{LR}}\right)} \tag{3}$$

and

$$C(Th)=\frac{\rho_G^{LR}}{2\,d_s\Delta R\left[4\frac{C(U)}{C(Th)}A_U\left(\sin\langle\theta_c^{LR}\rangle\right)^2+3\,A_{Th}\left(\sin\langle\theta_c^{LR}\rangle\right)^2\right]} \tag{4}$$

2.1.3. Method based on the SSNTD detection efficiencies

By calculating first the detection efficiencies of the CR-39 (ε_j^{CR} and $\varepsilon_j'^{CR}$) and LR-115 type II (ε_j^{LR} and $\varepsilon_j'^{LR}$) SSNTD for α-particles emitted by the thorium-232 and uranium-238 series inside a material sample, and secondly by measuring track density rates (tracks.cm^{-2}.s^{-1}) registered on the CR-39 (ρ_G^{CR}) and LR-115 type II (ρ_G^{LR}) one can evaluate the thorium C(Th) and uranium C(U) concentrations (in 10^{-6} g/g) inside the considered material sample by using a method described in detail by Misdaq et al. [7]. Indeed, we have:

$$\frac{C(U)}{C(Th)} = \frac{A_{Th}}{A_U} \times \frac{\dfrac{\rho_G^{CR}}{\rho_G^{LR}} \sum_{j=1}^{7} k'_j \varepsilon_j^{'CR} R'_j - \dfrac{S'_d}{S_d} \sum_{j=1}^{7} k'_j \varepsilon_j^{'LR} R'_j}{\dfrac{S'_d}{S_d} \sum_{j=1}^{8} k_j \varepsilon_j^{CR} R_j - \dfrac{\rho_G^{CR}}{\rho_G^{LR}} \sum_{j=1}^{8} k_j \varepsilon_j^{LR} R_j} \qquad (5)$$

and

$$C(Th) = \frac{2 S'_d \rho_G^{LR}}{\pi q^2 d_s \left[A_U \dfrac{C(U)}{C(Th)} \sum_{j=1}^{8} k_j \varepsilon_j^{LR} R_j + A_{Th} \sum_{j=1}^{7} k'_j \varepsilon_j^{'LR} R'_j \right]} \qquad (6)$$

where S_d and S_d' are respectively the surfaces of the CR-39 and LR-115 II films, R_j and R_j' are the ranges, in the material sample, of an α-particle of index j and initial energy E_j emitted by the nuclei of the uranium and thorium series, respectively and k_j and k'_j are respectively the branching ratios corresponding to the disintegration of the nuclei of the uranium and thorium series.

The radon and thoron alpha- activities inside a material sample are given by [10]:

$$\frac{A_c(^{220}Rn)}{A_c(^{222}Rn)} = \frac{\dfrac{S'_d}{S_d} \sum_{j=1}^{8} k_j \varepsilon_j^{CR} R_j - \dfrac{\rho_G^{CR}}{\rho_G^{LR}} \sum_{j=1}^{8} k_j \varepsilon_j^{LR} R_j}{\dfrac{\rho_G^{CR}}{\rho_G^{LR}} \sum_{j=1}^{7} k'_j \varepsilon_j^{'CR} R'_j - \dfrac{S'_d}{S_d} \sum_{j=1}^{7} k'_j \varepsilon_j^{'LR} R'_j} . \qquad (7)$$

and

$$A_c(^{222}Rn) = \frac{2 S'_d \rho_G^{LR}}{\pi q^2 d_s \left[\sum_{j=1}^{8} k_j \varepsilon_j^{LR} R_j + \dfrac{A_c(^{220}Rn)}{A_c(^{222}Rn)} \sum_{j=1}^{7} k'_j \varepsilon_j^{'LR} R'_j \right]} . \qquad (8)$$

2.2. Determination of the concentrations of radon, thoron and their decay products inside different atmospheres

Disk shaped Pershore Mouldings CR-39 and Kodak LR-115 type II SSNTD of radius q=2cm have been placed in different atmospheres for 3 to 24 hours. During the exposure, α-particles emitted by radon (^{222}Rn), thoron (^{220}Rn) and their corresponding decay products bombarded the SSNTD films. After the irradiation, the exposed films were etched in appropriate NaOH solutions [7]. By calculating the probabilities P_i^{CR} and P^{LR}, mean critical angles of etching $\left(\left\langle \theta_c^{CR} \right\rangle\right)$ and $\left(\left\langle \theta_c^{LR} \right\rangle\right)$ and detection efficiencies (ε_j^{CR} and $\varepsilon_j'^{CR}$) and (ε_j^{LR} and $\varepsilon_j'^{LR}$) of the CR-39 and LR-115 type II detectors and measuring ρ_G^{CR} and ρ_G^{LR} track density rates one can evaluate α-activities (Bq.m^{-3}) due to radon, thoron and their progenies in indoor and outdoor air by using the methods described in detail by Misdaq et al. [11,11,12].

2.3. Evaluating of radiation doses due to ^{238}U, ^{232}Th and ^{222}Rn from the ingestion of various materials

The committed equivalent doses due to ^{238}U and ^{232}Th in the tissue T from the ingestion of a material sample are respectively given by [13]RM2006:

$$H_T(U) = \int_0^{50\,y} \dot{H}_T(U)\,dt \tag{9}$$

and

$$H_T(Th) = \int_0^{50\,y} \dot{H}_T(Th)\,dt\,. \tag{10}$$

Where HT and HT are Alpha-equivalent dose rate (Sv.s^{-1}) in the tissue T of the human body due to ^{238}U and ^{232}Th from the ingestion of a material sample, respectively.

The committed equivalent dose due to ^{222}Rn in the tissue T from the ingestion of a material sample is given by [14]:

$$H_T(^{222}Rn) = \int_0^{te} \dot{H}_T(^{222}Rn)(t)dt\,, \tag{11}$$

where H_T is the alpha-equivalent dose rate (Sv.s^{-1}) in a tissue T of the respiratory tract of an individual due to the inhalation of the j'th radon daughter and t_e is the exposure time.

2.4. Determining of radiation doses due to ^{214}Po and ^{218}Po from the inhalation of air

The equivalent dose in the tissue T of the respiratory tract for a radon decay product j' is given by [15]:

$$H_T(j') = \int_0^{t'_e} \dot{H}_T(j')(t)\,dt \tag{12}$$

where Alpha-equivalent dose rate (Sv.s^{-1}) in a tissue T of the respiratory tract of an individual due to the inhalation of the j'th radon daughter and t_e' is the exposure time of the tissue T.

2.5. Determination of radiation doses due to ^{238}U, ^{232}Th, and ^{222}Rn to the human skin from the application of different products

The committed equivalent doses to skin due to ^{238}U, ^{232}Th and ^{222}Rn from the application of a Moroccan black soap or plant oil material sample are respectively given by:

$$E_U = \frac{kK_U S_U Q}{2d_{skin} S_{skin}} \times A_C^{sample}\left({}^{238}U\right) t_e w_T \tag{13}$$

$$E_{Th} = \frac{kK_{Th}S_{Th}Q}{2d_{skin}S_{skin}} \times A_C^{sample}\left({}^{232}Th\right)t_e w_T \tag{14}$$

and

$$E_{Rn} = \frac{kK_{Rn}S_{Rn}Q}{2d_{skin}S_{skin}} \times A_C^{sample}\left({}^{222}Rn\right)t_e w_T \tag{15}$$

where K_U is the branching ratio for ^{238}U disintegration. K_{Th} is the branching ratio for ^{232}Th disintegration. K_{Rn} is the branching ratio for ^{222}Rn disintegration. d_s is the density of skin ($g.cm^{-3}$). $k = 1.6.10^{-13}$ ($J\ MeV^{-1}$) is a conversion factor. S_U is the stopping power of skin for the α-particles emitted by ^{238}U ($MeV\ cm^2\ g^{-1}$). S_{Th} is the stopping power of skin for the α-particles emitted by ^{232}Th ($MeV\ cm^2\ g^{-1}$). S_{Rn} is the stopping power of skin for the α-particles emitted by ^{222}Rn ($MeV\ cm^2\ g^{-1}$). $w_T = 0.01$ is the tissue weighting factor for skin [16]. t_e is the exposure time. $A_c^{sample}\left({}^{238}U\right)$ is the α-activity due to ^{238}U inside a material samle. $A_c^{sample}\left({}^{232}Th\right)$ is the α-activity due to ^{232}Th inside a material sample $A_c^{sample}\left({}^{222}Rn\right)$ is the α-activity due to ^{222}Rn inside a material sample.

3. RESULTS AND DISCUSSIONS

3.1. ^{238}U, ^{232}Th, ^{222}Rn and ^{220}Rn concentrations inside various liquid and solid material samples

The uranium ($C(^{238}U)$) and thorium ($C(^{232}Th)$) concentrations and radon ($A_c(^{222}Rn)$) and thoron ($A_c\ (^{220}Rn)$) alpha-activities per unit volume were evaluated inside different natural honey, medical drugs and black soap material samples. An example is given in Table 1 for natural honey material samples and their corresponding nectar solutions, plant flowers and soils. From the statistical uncertainty on track counting one can determine the uncertainty on track density production per unit time and then evaluate the uncertainty of the uranium, thorium, radon and thoron concentrations determination which ranged between 3.03% and 9.0%. We noted that the thorium concentration $C\ (^{232}Th)$ is higher than the uranium one $C\ (^{238}U)$ for all the honey material samples studied. This is because their corresponding soils contain more thorium than uranium (Table 1). Even though the thorium concentrations ($C(^{232}Th)$) are larger than those of uranium ($C(^{238}U)$), alpha-activities due to thoron are lower than those due to radon for the honey , nectar, plant flower, and soil samples studied. This is because radon has a higher half-life (3.82d) than thoron (55s). Positive correlations were found for the ^{238}U and ^{232}Th concentrations between soil and plant flower, plant flower and nectar, and nectar and honey, respectively. The uranium transfer coefficient $[\mathrm{TC}]_{\mathrm{PF/S}}^{\mathrm{U}}$ and thorium transfer coefficient $[\mathrm{TC}]_{\mathrm{PF/S}}^{\mathrm{Th}}$ between soil and plant flower, which are defined as the ratios of the plant flower to soil uranium and thorium concentrations, the transfer coefficients $[\mathrm{TC}]_{\mathrm{N/PF}}^{\mathrm{U}}$ and $[\mathrm{TC}]_{\mathrm{N/PF}}^{\mathrm{Th}}$ between plant flower and nectar, which are defined as the ratios of the nectar to plant flower uranium and thorium concentrations, and the transfer coefficients $[\mathrm{TC}]_{\mathrm{H/N}}^{\mathrm{U}}$ and $[\mathrm{TC}]_{\mathrm{H/N}}^{\mathrm{Th}}$ between nectar and honey, which are defined as the ratios of the honey to nectar uranium and thorium concentrations have been determined. We noted that 5% to 9% of ^{238}U and ^{232}Th are transferred from soil to plant flower, 48% to 88% are transferred from plant flower to nectar and 66% to 98% are transferred from nectar to honey (Table1).

3.2. Concentrations of ^{222}Rn, ^{220}Rn and their progenies inside various atmospheres

Alpha-activities due to radon, thoron and their decay products have been measured in indoor and outdoor air. An example is given in Table 2 for a cave visited by the members of the public. Alpha- and beta- activities per unit volume air due to the radon and thoron series have been measured in May 2005 between 11h and 14h in different locations of the studied cave. Data obtained are shown in Table 2. The radon alpha-activity per unit volume increases with the distance from the entrance of the studied caves and ancient mines. This is due to the fact that the ventilation rate decreases when penetrating inside the caves and ancient mines studied. We notice that alpha -and beta - activities due to radon and its decay products are higher than those due to thoron and its daughters for the caves and ancient mines studied. Indeed, due to its too short half-life (55s) thoron (^{220}Rn) has a diffusion length in air smaller than that of radon (^{222}Rn) which has longer half-life (3.82d).

3.3. Committed equivalent doses due to ^{238}U, ^{232}Th and ^{222}Rn in different compartments of the human body from the ingestion of various material samples

Committed effective doses due to ^{238}U [E_U] and ^{232}Th [E_{Th}] were evaluated in the human body of Moroccan adult patients from the ingestion of a medical drug preparation. Data obtained are shown in Table 3. Committed effective dose due to ^{222}Rn [E (^{222}Rn)] from the ingestion of the studied medical drug preparations by adult patients were evaluated by using our method (an ingestion dose coefficient of $0.74x10^{-8}$) and the NRC ingestion dose coefficient ($1x10^{-8}$ Sv Bq^{-1}) (NRC 1999). The difference between data obtained by the two methods is due to the fact that the NRC calculation models diffusion of radon into the stomach wall, while our calculations simply hold the radon in the stomach until it is absorbed from the small intestine.The maximum value of the global committed effective dose due to ^{238}U, ^{232}Th and ^{222}Rn from the ingestion of the studied drug preparations was found equal to (0.93 ±0.09) 10^{-6} Sv y^{-1}, obtained for patients consuming the (MD14+WW1) drug preparation, which is smaller than the mean world values for ingestion (ranging from 0.2 to 0.8 mSv) [17].

3.4. Committed effective doses due to radon short-lived alpha emitting decay products in the respiratory tract of the members of the public

Annual committed equivalent doses per hour of exposure due to the ^{218}Po (H_T(^{218}Po)) and ^{214}Po (H_T(^{214}Po)) radon short-lived alpha emitting daughters have been evaluated in the respiratory tract of different age groups of the members of the general public from the inhalation of air in different caves and ancient mines.

The annual effective dose (mSv y^{-1} per hour exposure) due to short-lived radon decay products to the visitors of the studied caves and ancient mines was evaluated by using the following equation:

$$E = 0.12[H_T(^{218}Po) + H_T(^{214}Po)] + 0.025\,[H_T(^{218}Po) + H_T(^{214}Po)] \qquad (16)$$

The annual effective dose (mSv y^{-1} per hour exposure) due to the radon progeny to the visitors of the studied caves and ancient mines was also estimated according to the following formula [18](ICRP, 1993):

$$E = A_c\,(^{222}Rn) \times F \times t \times D \qquad (17)$$

where A_c (^{222}Rn) is the average radon concentration inside a cave/ ancient mine (Bq m^{-3}), F=0.4 is the equilibrium factor between radon and its progeny in the cave, t =1hour per year and D=7.84 x 10^{-6} mSv (Bq m^{-3} h)$^{-1}$, is the dose conversion factor [18].

Annual effective doses due to radon progeny from the inhalation of air by the visitors of the studied were evaluated by using our model and the ICRP formula (Table 4). Data obtained for the average effective dose obtained by using our model for different age groups of individuals visiting the studied were found in good agreement with those obtained by using the ICRP model for the general public. The maximum value was found equal to 0.115 mSv y^{-1} for the 5 years children visiting the Wintimdouine cave 3 hours per week during the spring season (36hours per year) , which is smaller than the 1.15 mSv y^{-1} committed effective dose limit given by UNSCEAR [17] due to inhalation of radon decay products.

3.5. Committed effective doses to skin due to ^{238}U, ^{232}Th and ^{222}Rn from the application of different Moroccan black soap samples

Total annual committed effective doses to skin due to ^{238}U, ^{232}Th, and ^{222}Rn from the application of the black soap samples studied during 20 minutes per week (960 minutes per year) by different age groups of the Moroccan rural and urban populations were evaluated (Table 5). The maximum value was found to be equal to 0.88 μ Svy^{-1}cm^{-2}, obtained for individuals belonging to the 5 years age group from the application of the MBS1 black soap sample during 960 minutes a year, which is largely smaller than the dose limit for the members of the public to the skin which is of 50 mSv y^{-1} cm^{-2} [19]. Generally Moroccan women keep their black soap masks during 60 minutes (2800 minutes a year) inside traditional baths (Hammams): the maximum resulting effective dose to skin from the application of MBS1 black soap sample was of 1.11 μ Sv y^{-1} cm^{-2}. Total annual committed effective doses were also determined for the considered age groups of individuals from the application of the MBS1 polluted black soap samples during 20 minutes per week (960 minutes a year) inside traditional baths (Hammams). A maximum value of 0.24mSv y^{-1}cm^{-2} was found for individuals belonging to the 5 years age group from the application of the MBS1 black soap sample polluted by phosphate 2 dusts. Therefore, people in rural areas must avoid using polluted black soap material samples.

4. CONCLUSION

It has been shown by this study that by using CR-39 and LR-115 type II solid state nuclear track detectors (SSNTDs) one can determine uranium (^{238}U) and thorium (^{232}Th) concentrations as well as alpha-activities due to radon (^{222}Rn) and thoron (^{220}Rn) inside various liquid and solid material samples as well as alpha-activities due to radon, thoron and their corresponding decay products in indoor and outdoor air. Three new models have been used for evaluating radiation doses due to the uranium, thorium and radon from the ingestion of various foodstuffs and from the application of different black soap and plant oils to the skin of bathers and due to ^{214}Po and ^{218}Po from the inhalation of air by the members of the public and workers. It is concluded that pollution due to building material and phosphate dusts may increase radiation dose to the consumers of foodstuffs. This SSNTDs' technique which has the advantage of being inexpensive, sensitive, and accurate and does not need the use of any standard for its calibration is a good tool for assessing radiation-dose risk due to the ingestion of foodstuffs, inhalation of air and application of various products to the human skin.

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TABLE 1. VALUES OF THE ^{238}U AND ^{232}Th CONCENTRATIONS IN SOIL, PLANT FLOWER, NECTAR AND HONEY MATERIAL SAMPLES AND TRANSFER COEFFICIENTS BETWEEN SOIL AND PLANT FLOWER ($\left[\mathrm{TC}\right]^{\mathrm{U}}_{\mathrm{PF/S}}$ AND $\left[\mathrm{TC}\right]^{\mathrm{Th}}_{\mathrm{PF/S}}$), PLANT FLOWER AND NECTAR ($\left[\mathrm{TC}\right]^{\mathrm{U}}_{\mathrm{N/PF}}$ AND $\left[\mathrm{TC}\right]^{\mathrm{Th}}_{\mathrm{N/PF}}$), AND NECTAR AND HONEY ($\left[\mathrm{TC}\right]^{\mathrm{U}}_{\mathrm{H/N}}$ and $\left[\mathrm{TC}\right]^{\mathrm{Th}}_{\mathrm{H/N}}$).

Plant (Honey)	**Soil**		**Plant flower**		**Nectar**		**Honey**		$[TC]^{\mathrm{U}}_{\mathrm{PF/S}}$ **(%)**	$[\mathrm{TC}]^{\mathrm{Th}}_{\mathrm{PF/S}}$ **(%)**	$[\mathrm{TC}]^{\mathrm{U}}_{\mathrm{N/PF}}$ **(%)**	$[\mathrm{TC}]^{\mathrm{Th}}_{\mathrm{N/PF}}$ **(%)**	$[\mathrm{TC}]^{\mathrm{U}}_{\mathrm{H/N}}$ **(%)**	$[\mathrm{TC}]^{\mathrm{Th}}_{\mathrm{H/N}}$ **(%)**
	C(^{238}U) (ppm)	**C(^{232}Th) (ppm)**	**C(^{238}U) (ppm)**	**C(^{232}Th) (ppm)**	**C(^{238}U) (ppm)**	**C(^{232}Th) (ppm)**	**C(^{238}U) (ppm)**	**C(^{232}Th) (ppm)**						
Romarin (H1)	7.6 ± 0.4	9.6 ±0.5	0.58±0.03	0.76±0.04	0.41±0.03	0.59±0.04	0.39±0.02	0.56±0.02	8.0±0.5	8.0±0.5	71±4	78±5	95±5	95±5
Feuilno (H2)	7.8 ± 0.5	10.3±0.6	0.61±0.04	0.85±0.05	0.47±0.04	0.65±0.04	0.42 ±0.03	0.62±0.04	8.0±0.5	8.0±0.5	77±5	76±5	89±5	95±5
Herbe (H3)	6.2 ± 0.4	8.3 ±0.5	0.35±0.02	0.62±0.04	0.18±0.01	0.46±0.04	0.17 ±0.01	0.41±0.02	6.0±0.4	7.0±0.4	46±3	74±4	94±5	89±5
Ammi hella (H4)	5.9 ± 0.4	6.9 ±0.4	0.31±0.02	0.59±0.04	0.17±0.01	0.41±0.03	0.13 ±0.01	0.40±0.02	5.0±0.3	9.0±0.5	55±3	69±4	76±5	98±5
Sousi icinal (H5)	5.4 ± 0.4	6.5 ±0.4	0.28±0.02	0.49±0.04	0.15±0.01	0.33±0.02	0.12 ±0.01	0.28±0.01	5.0±0.3	8.0±0.5	54±3	67±4	80±5	85±5
Rue ousoudab (H6)	6.5 ± 0.4	8.5 ±0.5	0.43±0.02	0.67±0.03	0.31±0.02	0.48±0.04	0.25 ±0.02	0.46±0.03	7.0±0.4	8.0±0.5	72±4	72±4	81±5	96±5
Origon (H7)	6.1 ± 0.4	7.4 ±0.4	0.37±0.02	0.63±0.04	0.21±0.01	0.45±0.03	0.19 ±0.01	0.42±0.02	6.0±0.4	9.0±0.5	57±3	71±4	90±5	93±5
Chlorophyle (H8)	6.5 ± 0.4	9.1 ±0.6	0.43±0.02	0.69±0.05	0.28±0.02	0.51±0.03	0.25 ±0.02	0.48±0.04	7.0±0.4	8.0±0.5	65±4	74±4	89±5	94±5
Eucalyptus (H9)	5.3 ± 0.4	6.5 ±0.5	0.28±0.01	0.48±0.04	0.14±0.01	0.35±0.02	0.12 ±0.01	0.30±0.02	5.0±0.3	7.0±0.4	5±3	73±4	86±5	86±5
Thuya (H10)	6.3 ± 0.4	8.4 ±0.5	0.39±0.02	0.63±0.04	0.23±0.02	0.44±0.03	0.21 ±0.02	0.42±0.03	6.0±0.4	8.0±0.5	59±4	70±4	91±5	95±5
Lavande Officinal (H11)	6.7 ± 0.4	8.7 ±0.5	0.46±0.03	0.69±0.05	0.30±0.02	0.50±0.04	0.27 ±0.02	0.48±0.03	7.0±0.4	8.0±0.5	65±4	72±4	90±5	96±5
Euphorbe resinefere (H12)	7.6 ± 0.5	9.8±0.5	0.58±0.03	0.77±0.04	0.37±0.03	0.61±0.04	0.35 ±0.02	0.58±0.04	8.0±0.5	8.0±0.5	64±4	79±5	95±5	95±5
Nigelle (H13)	5.8 ± 0.4	6.8±0.4	0.31±0.02	0.54±0.04	0.15±0.01	0.38±0.02	0.13 ±0.01	0.33±0.01	5.0±0.3	8.0±0.5	48±3	70±5	87±5	87±5
Euphorbe cactoide (H14)	7.2± 0.6	9.5±0.6	0.55±0.04	0.75±0.04	0.39±0.03	0.58±0.04	0.35 ±0.02	0.54±0.03	8.0±0.5	8.0±0.5	71±4	77±5	90±5	93±5
Herbe (H15)	6.8 ± 0.6	9.3±0.6	0.49±0.03	0.72±0.03	0.35±0.03	0.57±0.04	0.30 ±0.02	0.52±0.04	7.0±0.4	8.0±0.5	71±4	79±5	86±5	91±5
Citronnier (H16)	6.5± 0.3	8.5± 0.5	0.41±0.02	0.65±0.04	0.35±0.03	0.57±0.04)	0.23 ±0.01	0.45 ±0.03	6.0±0.4	8.0±0.5	85±5	88±5	66±4	79±5

TABLE 2. DATA OBTAINED FOR THE VENTILATION RATE (V) AND ALPHA- AND BETA-ACTIVITIES PER UNIT VOLUME OF AIR DUE TO THE RADON AND THORON SERIES INSIDE THE WINTIMDOUINE CAVE (MAY 2005). F^{222} IS THE EQUILIBRIUM FACTOR BETWEEN RADON AND ITS DECAY PRODUCTS. F^{220} IS THE EQUILIBRIUM FACTOR BETWEEN THORON AND ITS PROGENY.

		Radon series						Thoron series					
Location	V(h^{-1})	$A_C(^{222}Rn)$ (Bq m^{-3})	$A_C(^{218}Po)$ (Bq m^{-3})	$A_C(^{214}Pb)$ (Bq m^{-3})	$A_C(^{214}Bi)$ (Bq m^{-3})	$A_C(^{214}Po)$ (Bq m^{-3})	F^{222}	$A_C(^{220}Rn)$ (Bq m^{-3})	$A_C(^{216}Po)$ (Bq m^{-3})	$A_C(^{212}Pb)$ (Bq m^{-3})	$A_C(^{212}Bi)$ (Bq m^{-3})	$A_C(^{212}Po)$ (Bq m^{-3})	F^{220}
L1	0.19	338±27	175±14	65±5	51±4	51±4	0.21	34±3	34±3	1.7±0.1	0.90±0.07	0.90±0.07	0.04
L2	0.164	415±32	215±17	81±6	64±5	64±5	0.21	40±3	40±3	2.1±0.1	1.3±0.1	1.3±0.1	0.05
L3	0.13	563±44	292±22	112±8	90±7	90±7	0.21	54±4	54±4	3.1±0.2	1.9±0.1	1.9±0.1	0.05
L4	0.13	565±45	293±22	113±9	91±7	91±7	0.21	54±4	54±4	3.1±0.2	1.9±0.1	1.9±0.1	0.05
L5	0.11	650±51	337±26	130±10	106±8	106±8	0.22	70±6	70±6	4.2±0.3	2.7±0.2	2.7±0.2	0.06
L6	0.10	706±56	367±29	142±11	116±9	116±9	0.22	74±6	74±6	4.5±0.3	2.9±0.2	2.9±0.2	0.06
L7	0.10	712±56	370±29	144±11	118±9	118±9	0.22	74±6	74±6	4.6±0.3	2.9±0.2	2.9±0.2	0.06
L8	0.10	758±60	394±31	153±12	126±10	126±10	0.22	77±6	77±6	4.8±0.3	3.1±0.2	3.1±0.2	0.06
L9	0.10	764±61	397±31	155±12	127±10	127±10	0.22	77±6	77±6	4.8±0.3	3.1±0.2	3.1±0.2	0.06
L10	0.10	766±61	398±31	156±12	128±10	128±10	0.23	77±6	77±6	4.8±0.3	3.1±0.2	3.1±0.2	0.06

TABLE 3. COMMITTED EFFECTIVE DOSES DUE TO ^{238}U [E_U], ^{232}Th [E_{Th}] AND ^{222}Rn [E (^{222}Rn)] FROM THE INGESTION OF THE (MD14 + WATER) MEDICAL DRUG PREPARATION BY ADULT PATIENTS.

Medical drug preparation	This method			NRC Ingestion dose coefficient
	E_U (10^{-8}Sv y^{-1})	E_{Th} (10^{-8}Sv y^{-1})	E(^{222}Rn) (10^{-6}Sv y^{-1})	E(^{222}Rn) (10^{-6}Sv y^{-1})
TW(Tangiers)+MD14	0.20±0.01	10.5±0.8	5.5±0.3	7.4±0.4
TW(Oujda) +MD14	0.18±0.01	6.7±0.5	4.5±0.3	6.1±0.4
TW (Tetouan) +MD14	0.19±0.01	6.9±0.5	4.6±0.3	6.3±0.4
TW (Rabat) +MD14	0.23±0.01	4.3±0.4	5.7±0.3	7.7±0.5
TW (Eljadida) +MD14	0.22±0.01	1.6±0.1	5.5±0.3	7.4±0.4
TW (Casablanca) +MD14	0.18±0.01	4.4±0.4	4.4±0.3	5.9±0.4
TW (Marrakech) +MD14	0.23±0.01	4.8±0.4	5.7±0.3	7.7±0.5
TW (Khouribga) +MD14	0.24±0.01	2.5±0.2	6.1±0.4	8.3±0.5
TW (Agadir) +MD14	0.25±0.01	1.4±0.1	6.3±0.4	8.5±0.5
TW (Meknes) +MD14	0.26±0.01	5.7±0.5	6.4±0.4	8.6±0.5
TW (Mohammadia) +MD14	0.16±0.01	6.0±0.6	4.1±0.3	5.6±0.3
TW (Nador) +MD14	0.22±0.01	4.2±0.4	5.4±0.3	7.3±0.4
TW (Guelmim) +MD14	0.38±0.02	3.8±0.3	9.4±0.6	12.8±0.8
TW (Laâyoune) +MD14	0.28±0.02	2.4±0.2	6.8±0.4	9.2±0.6
TW (Dakhla) +MD14	0.27±0.02	1.6±0.1	6.6±0.4	9.0±0.5
TW (Boujdour) +MD14	0.32±0.02	2.0±0.2	8.0±0.5	10.8±0.6
MinW1+MD14	0.25±0.01	4.0±0.4	6.3±0.4	8.5±0.5
MinW2+MD14	0.29±0.02	2.5±0.2	7.2±0.4	9.7±0.6
WW1+MD14	0.52±0.03	7.7±0.6	13.1±0.8	17.8±1.1
WW2+MD14	0.40±0.02	5.4±0.5	10.0±0.6	13.5±0.8
SW1+MD14	0.38±0.02	4.3±0.4	9.5±0.6	12.9±0.8
SW2+MD14	0.40±0.02	4.4±0.4	9.9±0.6	13.4±0.8

TABLE 4. . DATA OBTAINED FOR THE ANNUAL EFFECTIVE DOSE DUE TO RADON PROGENY TO THE ADULT MALE VISITORS OF THE STUDIED CAVES AND ANCIENT MINES BY USING THIS METHOD AND THE ICRP MODEL (ICRP, 1993).

Cave/ancient mine	Effective dose (Sv y^{-1} per hour exposure)					
	ICRP	This method				
	General public	Adult male	Adult female	Child 10y	Child 5y	Average
Wintimdouine	$1.9\ 10^{-6}$	$1.7\ 10^{-6}$	$1.3\ 10^{-6}$	$2.1\ 10^{-6}$	$3.2\ 10^{-6}$	$2.0\ 10^{-6}$
Ourika	$1.6\ 10^{-6}$	$1.4\ 10^{-6}$	$1.2\ 10^{-6}$	$1.8\ 10^{-6}$	$2.8\ 10^{-6}$	$1.8\ 10^{-6}$
Kettara	$1.5\ 10^{-6}$	$1.2\ 10^{-6}$	$1.1\ 10^{-6}$	$1.6\ 10^{-6}$	$2.6\ 10^{-6}$	$1.6\ 10^{-6}$
Koudia El Hamra	$1.0\ 10^{-6}$	$0.9\ 10^{-6}$	$0.8\ 10^{-6}$	$1.2\ 10^{-6}$	$1.8\ 10^{-6}$	$1.2\ 10^{-6}$

TABLE 5. DATA OBTAINED FOR THE COMMITTED EFFECTIVE DOSES TO SKIN DUE TO ^{238}U (E_U), ^{232}Th (E_{Th}), AND ^{222}Rn (E_{Rn}) FROM THE APPLICATION OF DIFFERENT BLACK SOAP SAMPLES BY INDIVIDUALS BELONGING TO THE 10 YEARS AND 5 YEARS AGE GROUPS IN TRADITIONAL BATHS (HAMMAMS). $S_{skin}= 1.12\times10^4$ cm^2 for 10 years. $S_{skin}= 0.78\times10^4$ cm^2 for 5 years [15]

Moroccan black soap sample	10 years				5 years			
	Effective dose (10^{-8}Sv.y^{-1}.cm^{-2})			E global (10^{-8}Sv.y^{-1}.cm^{-2})	Effective dose (10^{-8}Sv.y^{-1}.cm^{-2})			E global (10^{-8}Sv.y^{-1}.cm^{-2})
	E_U	E_{Th}	E_{Rn}		E_U	E_{Th}	E_{Rn}	
MBS1	55±3	1.5±0.1	4.5±0.3	61±4	79±5	2.2±0.1	6.4±0.4	87±5
MBS2	46±3	1.3±0.1	3.7±0.2	51±3	66±4	1.9±0.1	5.3±0.3	73±4
MBS3	34±2	1.01±0.06	2.8±0.2	38±2	49±3	1.46±0.09	4.0±0.2	54±3
MBS4	18±1	0.53±0.03	1.4±0.1	20±1	26±2	0.76±0.05	2.1±0.1	28±2
MBS5	47±3	1.4±0.1	3.8±0.2	52±3	67±4	2.1±0.1	5.5±0.3	75±5
MBS6	27±2	0.82±0.05	2.2±0.1	30±2	39±2	1.18±0.07	3.2±0.2	43±3
MBS7	40±2	1.21±0.06	3.3±0.2	45±2	58±3	1.73±0.09	4.7±0.2	64±3
MBS8	43±2	1.25±0.08	3.5±0.2	47±3	61±3	1.8±0.1	5.0±0.3	68±4
MBS9	31±2	0.87±0.05	2.5±0.1	34±2	44±2	1.25±0.07	3.6±0.2	49±3
MBS10	25±1	0.72±0.03	2.0±0.1	27±2	36±2	1.04±0.05	2.9±0.2	40±2
MBS11	35±2	0.92±0.06	2.9±0.2	39±2	51±3	1.32±0.09	4.1±0.2	56±3

DETERMINATION OF THE NATURAL RADIOACTIVITY IN BUILDING MATERIALS USED IN THE STATE OF QATAR USING HIGH-RESOLUTION GAMMA-RAY SPECTROMETRY

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1. INTRODUCTION

Building raw materials are products derived from rock, soil and industrial by-products such as coal fly ash from power plants, phosphogypsum and certain slags, beside the natural radioactivity in the soil and rock these additives contain also a trace amount of natural radionuclides.

Knowledge of natural radioactivity levels in building materials is a vital issue to assess the overall human exposure to natural radiation associated with radioactivity from ^{235,8}U, ^{232}Th (and their decay progeny), and the primordial radionuclide ^{40}K as most individuals spend 80% of their time indoors [1, 2]. It is also useful in order to set national standards in the light of global recommendations. The radionuclides present in the building materials are responsible for an external and internal radiation exposures of individuals living in dwellings which vary depending on the geology of the region and the geochemical characteristics of the building raw materials. The internal exposure is due to the inhalation of alpha particles emitted from the short- lived radionuclides radon (^{222}Rn, a daughter product of ^{226}Ra) and thoron (^{220}Rn, a daughter product of ^{224}Ra) . While the external exposure is a direct gamma radiation due to the radionuclides present in the building materials. These information will be also useful to assess any possible radiological hazard to human begins caused by the use of building materials.

The current research aims to measure such levels in the building materials used in the State of Qatar, help in establishing national standards for the levels of natural radioactivities in the building materials and determine the Gamma Dose Rate (D), Radium Equivalent (Ra_{eq}), External Hazard Index (H_{ex}), Internal Hazard Index (H_{in}), and Annual Effective Dose Equivalent (AEDE) for individuals living in Qatarian dwellings. The Radon mass exhalation rate (E_{Rn}) and Emanation Coefficient (C_{Rn}) for cement samples are measured as well. This short paper presents measurements of 28 samples of building materials collected from the

State of Qatar, Doha and discusses the analysis techniques used in the work.

2. EXPERIMENTAL ARRANGEMENTS

2.1 Sample preparation

About 16 samples of 4 different common buildings materials in the State of Qatar such Saudi cement, white cement, sand and washed sand were collected directly from houses and buildings under construction. Other samples from raw materials as main constituents and samples from the minor additives of the Qatarian cement were collected from the two main cement factories in the State of Qatar and from dwellings under construction. The samples were then filled into labeled polyethylene bags, sealed, packed in a box and shipped to the UK. The final sample preparation and all the gamma-ray measurements to determine the sample radioactivities were performed in the low-background radiation detection laboratories of the Centre for Nuclear and Radiation Physics, situated within the Department of Physics at the University of Surrey. Prior to final measurement in the laboratories in Guildford, As the collected samples are already in a powdered form, they were placed in a drying oven without any processing. The drying temperature was set to $60^{o}C$ for 24 hours to ensure that any significant moisture was removed from the samples. The samples were then weighed and transferred to 500 ml labeled Marinelli beakers and stored and kept sealed for about one month in order to reach radioactive secular equilibrium (> 7 half-lives of ^{222}Rn and ^{220}Rn). The cement samples were measured on the sealing day before reaching secular equilibrium in order to calculate radon mass exhalation rate and emanation coefficient.

2.2 Detector calibration

The building materials samples were analyzed using a high-resolution, low-background gamma-ray spectrometry system based on a coaxial hyper-pure germanium detector (HPGe). Each spectrum was acquired for 86,400 seconds (i.e. 24 hours). The absolute photo-peak efficiency calibration of the system were carried out using photopeak from standard sources of ^{226}Ra, ^{232}Th, ^{152}Eu and NG3 (a mixed source containing ^{241}Am, ^{57}Co, ^{60}Co, ^{85}Sr, ^{88}Y, ^{109}Cd, ^{137}Cs, ^{139}Ce, and ^{203}Hg) which have an identical geometry to the soil samples. The sources were placed surrounding the germanium detector with the radionuclides dispersed in gel matrices within marinelli beakers of identical geometries to the evaluated samples. The source activities of ^{226}Ra, ^{232}Th and ^{152}Eu were 3.10, 1.08, 3.02 kBq for active volume 550 ml respectively and they were spread homogenously in gel matrices of densities 1.1, 1.1, and 1.6 g/cm^3. These were taken to be representative of the density of the samples measured. Therefore, corrections for gamma-ray self-attenuation within the samples are accounted for in the initial efficiency measurements using these marinelli-housed sources. The calibration spectra were acquired for 86,400 seconds each. A range of discrete gamma-ray energies from 0.059 MeV (from the decay of ^{241}Am) up to 2.614 MeV (from the decay of ^{208}Tl) were covered using these standard sources. The absolute photopeak efficiency was determined using Equation (1). using the following polynomial fit suggested by Gray and Ahmad [3] cited in [4]:

$$y=(1/x)\times(a_0+(a_1\times\ln(x))+(a_2\times(\ln(x))^2)+(a_3\times(\ln(x))^3)+(a_4\times(\ln(x))^5)+(a_5\times(\ln(x))^7 \quad (1)$$

where the parameters, a_0, a_1, a_2, a_3, a_4, and a_5 were derived by applying the above mentioned equation for the ^{226}Ra, and ^{232}Th sources which were suspended in identical 1.1 gm/cm^3 density gel matrices within the marinelli beakers. A comparative efficiency measurement was also performed using the mixed source (suspended in a slightly higher density gel matrix) which showed little variation compared to the ^{226}Ra and ^{232}Th sources, particularly for energies above 200 keV.

2.3 Measurements of activity concentration

A Marinelli beaker with the same geometry filled with de-ionized water was used on a weekly basis during the measurements period to determine the background spectrum observed by the germanium detector. The counting time of the ambient background spectrum was also 86,400s.

The building materials samples were placed, in their marinelli beakers, directly on to the front face of the detector. The counting geometry of the samples and the standard sources used for efficiency calibration were kept constant. A wide range of different gamma-ray energy transitions lines ranging from ~100 keV up to 2.6 MeV, associated with the decay products of the ^{235,8}U and ^{232}Th decay chains were then analyzed independently to obtain more statistically significant overall results. These data were combined under the assumption of secular equilibrium of the radionuclides within these samples. The initial activity concentration of ^{238}U present in the samples was estimated using the γ ray transition at 186 keV, associated with the decay of ^{226}Ra. Several transitions from decays of shorter-lived radionuclides in the ^{238}U decay chain, such as ^{214}Pb and ^{214}Bi, were also used to estimate the activity concentration of ^{238}U. The activity concentration of ^{232}Th was determined using several gamma-ray transitions associated with the decay of ^{228}Ac, ^{212}Pb and ^{208}Tl. The gamma-ray peaks associated with decays from ^{40}K and ^{137}Cs at 1461 and 661 keV respectively, were used to determine the activity concentrations for these nuclei. Background spectra contributions were subtracted from the peak areas of the gamma-ray spectra peak area of gamma rays for the measured samples was subtracted from the background spectra using GF3 data analysis package in the RADWARE software suite [5]. The activity concentration of the radionuclide found in the soil samples were determined using Equation (2), and expressed in Bq/kg:

$$Ac = C_{net} / \gamma \times \varepsilon(E_\gamma) \times m \tag{2}$$

where C_{net} are the net peak counts, γ is absolute gamma decay intensity for the specific energy photopeak, $\varepsilon(E_\gamma)$ is the absolute photopeak efficiency of the germanium detector at this energy and m is the mass of the sample in kg.

3. RESULTS

Figure 1 shows the background-subtracted spectrum for the cement sample no. L00 7. Sample L007 shows ^{226}Ra, ^{214}Pb, and ^{214}Bi transitions associated with the decay of ^{238}U, as well as ^{228}Ac and ^{208}Tl decay lines associated with the ^{232}Th series. Figure 2 shows the activity concentrations of all the observed gamma-ray transitions which are expected from the equilibrium decays of ^{226}Ra, ^{214}Pb, and ^{214}Bi for ^{238}U series for sample L008. Early results show that we are obtaining mean activity concentrations of the radionuclides ^{238}U, ^{232}Th and ^{40}K for cement of 21.19 ± 1.06, 5.49 ± 0.25 and 321.15 ± 15.91 Bq/kg respectively. Details of gamma-ray spectroscopic analysis techniques will be presented, together with the preliminary values of the activity concentrations associated with the naturally occuring radionuclide chains for building materials samples collected from the Qatarian peninsula. This is part of a larger project aimed at providing a complete radiological map of Qatar [6].

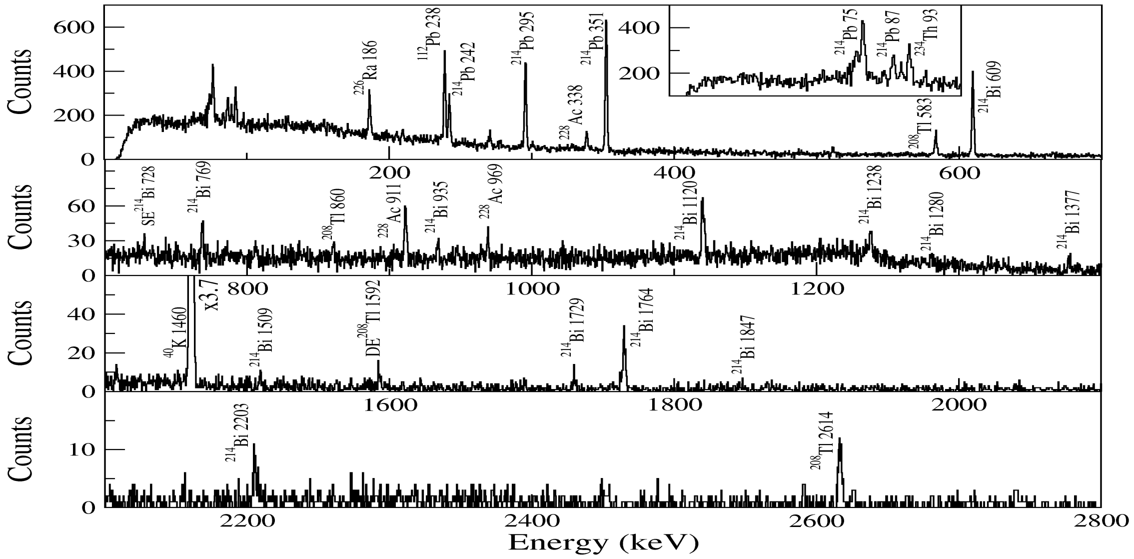

Fig. 1. Background-subtracted gamma-ray spectrum associated with Saudi cement sample L007

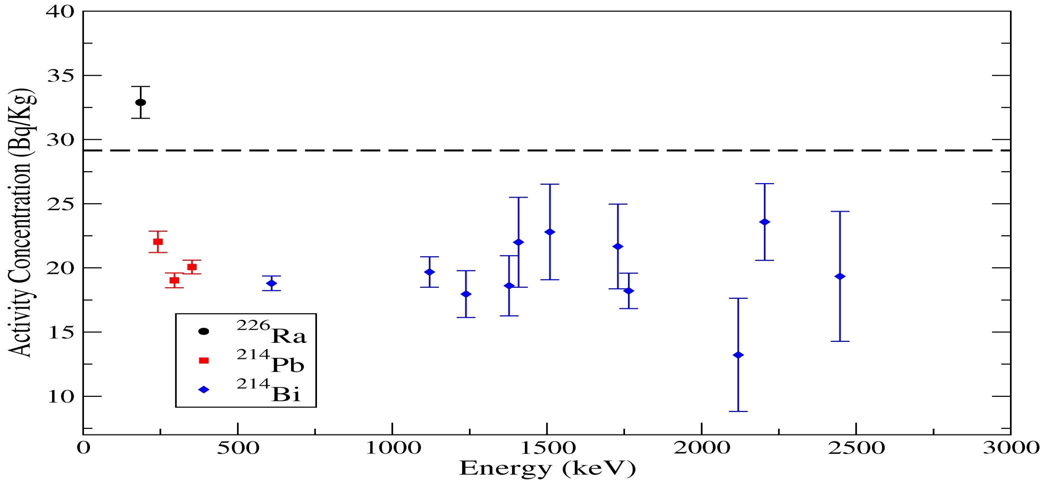

Fig. 2. The individual activity concentrations of the observed gamma-ray transitions from ^{226}Ra, ^{214}Pb, and ^{214}Bi from the ^{238}U series in sample L008. The horizontal line corresponds to the weighted mean of these individual data points

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NORM IN BRAZIL – A GENERAL OVERVIEW

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Abstract

There are many industries using NORM in the world today and they have been growing in a large scale. This growth has drawn the international community's attention. They have been discussing the importance of being aware of the existence or not of radiological risks associated with the exploration of ores containing both uranium and thorium, as well as, the treatment of these manufactured products. This fact led to the elaboration of TECDOC's, documents, Safety Reports Series produced by IAEA, and the elaboration of norms, normative instructions and regulatory guides, for the regulatory bodies organisms of the other countries. In Brazil the evaluation of the radiological occupational risks associated with the NORM industries has been accomplished without a centralized coordination doing with that there are diversified actions and discontinued actions. The necessity of a planned evaluation is related to the growing numbers of the Brazilian NORM industry. Therefore, this work has as objectives: (1) To consolidate information of previous projects, to quantify and to identify the mining company and treatment and to order them in groups; (2) To quantify the number of workers involved in the production and to identify the potential risk of process industrial areas; (3) To evaluate the industrial processing areas through direct measurements: dose rate, surface contamination radon monitoring and air samples collection and smear samples.

1. INTRODUCTION

In Brazil, the occupational radiological evaluations realized in NORM industries started in the 80's, being accomplished by research institutes that belonged to the National Commission of Nuclear Energy – CNEN.

The Fuel Cycle Division – DICCO, part of the Occupational Radiological Protection Department – DEPRO, from the Institute of Radioprotection and Dosimetry – IRD/CNEN, used to keep its scope of taking part in the routine inspection program designed for the installations which processed and manufactured products containing with uranium and/or thorium, associated. In the beginning, this program used to attend the following activities:

1) Minings with raw material of pyrochlore concentrated, where industrialized products of niobium are taken from;
2) Minings which produced phosphated fertilizers taken from ore, rich in apatite;
3) Minings with phosphate production obtained from ore compounded with phosphate oxide, iron, magnesium and calcium and;
4) Titanium mining, also explored, but not commercialized.

In the following years, there was another attempt to have the occupational evaluation program returned in minings which operated with uranium and/or thorium, associated, but it failed due to the difficulties encountered at that time, related to the fact that these installations cannot be classified as nuclear ones, and consequently, they cannot be inspected by CNEN.

In 1995, another attempt to evaluate and follow these installations was made, and because of this a new project called "Minings Project" was designed. This new project had as its main feature, an institutional project involving several divisions from IRD and other Institutes and Laboratories from CNEN as well.

The “Mnings Project” lasted three years and during this period very important results were generated. Although they were all related to radiological characterization (occupational and environmental) of the studied cycles, we hadn’t achieved its main objective yet, and this way, the continuity of the Project was fundamental.

The follow-up to the “Minings Project” would happen in a new phase, with greater emphasis on studies and more accurate radiological evaluations in the areas where potential radiological risks were identified with the development of specific projects to each area/installation.

Unfortunately we didn’t succeed and the “Minings Project”came to an end without the specific projects phase of each area/installation.

2. DEVELOPMENT AND RANGE OF THE PHASES

The inspection program for these areas/installations, which was adopted by the Fuel Cycle Division – DICCO in the 80’s, was continuous and composed of annual inspections accomplished “in loco” with the following purposes:

1. Evaluation of the industrial processing areas, identifying possible radiological risks;
2. Accomplishment of direct measurements of dose rate with beta/gamma monitoring system;
3. Collection of air samples and smears for posterior analysis in radiometry laboratories from DICCO through the total alpha counting technique and;
4. Radon measurements using the two-filter method.

In Table I are presented the codes used to identify the mineral processing cycles that were studied and also the quantity of installations involved during the studied phases.

Table I: Codes of the evaluated cycles and the quantity of installations

Code	Cycles Descriptions	Initial Project	Minings Project
01	Mining of pyrochlore concentrate as industrialized product ferro-niobium	01	01
	Mining of pyrochlore concentrate, apatite and phosphate	01	01
02	Phosphated fertilizers obtained from ore rich in apatite	01	01
	Phosphate production from ore composed basically of phosphate oxide, iron, magnesium, calcium and titanium	01	01
03	Coal mining and associated industries	----	02
04	Gold mining	----	01
05	Mining and milling of heavy mineral sands: monazite, ilmenite, zircon and rutile	02	----

Figures 1, 2 and 3 present some installations of the studied cycles with measurements and samples collection being realized.

Figure 1: Cycle 1 – Ferro-niobium

Figure 2: Cycle 3 – Coal

Figure 3: Cycle 5 –Heavy mineral Sands

In Table II are presented the analytic results found and also the measurements realized, in the initial phase between 1980 and 1988

Table II: Analytic results and measurements

Year	Code	Radionuclides concentration present in the air (Bq.m^3) daughters ^{222}Rn			^{212}Pb			Elem. T 1/2 longa			Dose rate (η Sv.h^{-1})		
		<	average	>	<	average	>	<	average	>	<	average	>
1980	01	----	----	----	----	----	----	----	----	----	1000	2250	6000
1988	01	7,70	8,42	12,12	0,76	2,42	66,78	0,01	0,06	1,27	1000	6700	20000
1988	02	----	----	----	----	----	----	----	----	----	200	450	1000
1988	02	3,10	3,70	4,99	0,18	0,64	1,30	0,01	0,01	0,02	200	700	1800

< lowest value found
> highest value found

The installations referring to mining and milling of heavy mineral sands (monazite, ilmenite, zircon and rutile – code 05) used to have a specific inspection program and a total of *sixty* inspections were realized during the period between 1980 and 1992. The average of these installations' analytic results is presented in Table III.

Table III: Analytic results of the installations that work with heavy mineral sands

Period	Radionuclides concentration present in the air (Bq.m^3) Daughters ^{222}Rn			^{212}Pb			Elem. T 1/2 longa			Dose rate (μSv.h^{-1})		
	<	média	>	<	média	>	<	média	>	<	média	>
1980 - 1992	----	----	----	0,59	12,07	63,42	0,01	8,71	148,74	40,00	21,83	670
1992 up to now	----	----	----	----	----	----	0,07	0,19	0,28	70,00	405,20	28000

The results of the radionuclides concentration present in the air were obtained through air samplings with a high flow sampler and the samples analyzed through the gross alpha counting technique. The measurements of the dose rate were obtained through direct measurements using beta/gamma monitoring system. Since the implementation and execution of the "Minings Project", whose initial objective was to gather the documentation and information already existing, adding new areas with different mineral processings and evaluation "in loco" of the industrial areas, it was possible to identify/classify the minings in cycles representing the industrial processes, as well as the total quantity of evaluated installations. The use of the final product or even its byproducts by manufacturing industries wasn't evaluated in this project. During the realization of the "Minings Prject", a multi-disciplinary group, composed of ten technicians with specialization in the areas which would be evaluated, went on *nine* trips. In this period, new measurements/equipments techniques were adopted by the IRD laboratories, allowing, this way, more meaningful samples collection and more accurate analysis.

The analytic results and the measurements of "Minings Project" are presented in Table IV.

Table IV: Analytic results and measurements of "Minings Project"

Code	Radionuclides concentration present in the air (Bq.m^3) Elem. T 1/2 longa			Radon (Bq.m^3)			Surface contamination (Bq.cm^{-2})			Dose rate (ηSv.h^{-1})
	<	average	>	<	average	>	<	average	>	average
01$^{(2)}$	0,060	2,250	6,98	3340	4500	5150	----	----	----	3900
01$^{(2)}$	0,023	0,187	0,352	34,00	65,33	118,00	0,002	0,043	0,136	1281
01$^{(2)}$	0,075	1,823	3,838	----	----	----	0,001	0,054	0,234	1717
02$^{(1)}$	0,010	0,016	0,029	----	----	----	----	----	----	280
02$^{(1)}$	0,009	0,012	0,014	----	----	----	----	----	----	150
03$^{(1)}$	0,005	0,013	0,022	22,00	36,81	65,80	----	----	----	100
03$^{(2)}$	0,300	0,533	0,700	----	----	----	----	----	----	20000
03$^{(2)}$	----	----	----	306	488	1424	----	----	----	500
04$^{(3)}$	----	----	----	780	1323,33	2300	----	----	----	165
04$^{(3)}$	----	----	----	----	----	----	----	----	----	325

(1) same cycle and different industries

(2) same industries and different periods

(3) same industries with two underground mines

3. BRAZILIAN MINERAL INDUSTRIAL PARK

According to the Brazilian Mineral Yearbook ("Anuário Mineral Brasileiro") [1] of 2006, referring to the mineral production in 2005, Brazil nowadays has a mineral industrial park of around *a hundred* companies and *fifty-five* out of those ones work directly in the production of gold, copper, nickel, phosphate, niobium and titanium, rare earths, thorium compounds, zircon, oil and gas, coal, and so forth.

According to the Safety Report Series [2] from IAEA as well as the evaluated bibliography proceeding from previous conferences (NORM IV and V) [3], these installations are classified as NORM industries and, this way, they must be evaluated concerning the radiological risks associated with its activities.

Nowadays, these *fifty-five* industries have mineral deposits of *twenty-three* billion tons of ores and from these deposits, *nineteen* billion can be explored.

These deposits led Brazil to have a gross production of minerals in 2005 of *five hundred and fifty* million tons of ore, with a milling production of *three hundred* million tons.

These industries accounted for *thirty-seven thousand* workers classified into: employees, third-parties and people from cooperatives.

4. CONCLUSION

The results compilation of several initiatives that have been happening since the 80's, has shown the necessity of having a more clear-sighted and standardized evaluation of the samples collection, analysis and measurements. The results presented here aren't conclusive due to the fact that they are not standardized for all areas/installations. Then, each cycle must be evaluated as being a continuous project in order to have comparable results among the industrial processing phases in the industries involved aiming at the dose estimate of the employees, third-parties and people from cooperatives. The results presented as being a dose rate are, in most of the cases, above the limit used for an individual who is a member of the public, cycles: *one, three and five.* A company of the cycle *three* and the ones of the cycle *five* are above the recommended limit for the individuals occupationally exposed – IOE's according to the norm of CNEN [4]. The results presented, referring to the radionuclides concentration present in the air, are above the limits of thorium and uranium ores dust in the cycles: *one and five.* The results presented, referring to the surface contamination, are under the determined limit imposed by CNEN [4]. But, these results are hindered by the reduced number of realized measurements – only one installation. The results for the determination of radon concentration are high for a company of the cycle *one, three and four.*

The quantity of industries and minings has increased as time goes by as well as the quantity of workers involved. This increase makes us believe that this project must be taken up again from the point it was paralyzed so that we could have a continuity in getting information, new evaluations because of the development of new technologies used in the mineral processing, new analytical laboratories' equipment and the update of the analytical techniques used. Workers from the oil and gas industries as well as the nuclear ones weren't counted for this work.

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TRANSPORT OF NORM: TANTALUM RAW MATERIALS

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1. TANTALUM

A non-radioactive transition group metal with many applications improving technology in our everyday lives. Its main application is in capacitors for compact electronics of high quality and reliability *e.g.* ABS and air bags for cars, or hearing aids and heart pacemakers. Other applications include bone joint replacements in medicine, high refractive index lenses for cameras, carbides for cutting tools in car manufacture, corrosion protection in the chemical industry, alloys for blades, discs and vanes in aircraft engines and turbines in energy generation from natural gas.

2. T.I.C.

An International Association representing the tantalum industry, with approximately 90 member companies around the world involved in mining, trading, refining / processing or end use of the metals niobium and tantalum.

3. TANTALUM RAW MATERIALS

The two main sources are tantalite mineral and tin slag, the latter a by-product of tin smelting. These materials are NORM due to naturally occurring thorium and uranium, in tantalite within the mineral matrix and in tin slag in a glass-like matrix, with 95% of the activities ranging between 5 and 50 Bq/g for the combined parent radionuclides. It is generally not possible to separate the Th/U easily from these minerals, requiring specialized digestion in *e.g.* hot HF/H_2SO_4 which is conducted by processors far from the mine sites, before the Th/U can be removed to waste.

Most tantalite is currently sourced from South America and Africa (Brazil, the DRC and Ethiopia), while tin slag comes mainly from Southeast Asia (Malaysia and Thailand). These are generally transported by sea to the processor industries in Asia, Europe and North America (China, Estonia, Germany, Kazakhstan, Thailand and the USA), which can separate the valuable tantalum from the waste thorium and uranium.

4. TRANSPORT AS CLASS 7

The transport exemption values in IAEA TS-R-1 are 1 Bq/g for Th(nat) and U(nat), *i.e.* the parent radionuclides, with a factor of 10 for NORM not extracted for the use of the radionuclides; this being a historical balance between radiological protection and the practical inconvenience of regulating large quantities of low activity materials. Above 10 Bq/g the transport is as Class 7 radioactive material, LSA-I, UN no. 2912.

5. DELAY AND DENIAL OF SHIPMENT

This classification has often resulted in delay or denial of shipment, a complex and global phenomenon where the burden of international and/or local regulatory requirements is perceived by carriers as being more than the transport is worth. Delay and denial of shipment has also arisen due to misinterpretation or application of local regulations by local authorities.

6. TANTALUM TRANSPORT STUDY

This led the T.I.C. to question whether the 10 Bq/g exemption level in TS-R-1 is appropriate to the risk posed by the transport of these materials, and to commission a study into the transport of tantalum raw materials which was completed in 2007. The objectives were to determine the radiological characteristics and exposures associated with normal transport and in the event of an accidental spill. The study included sampling, analysis and gamma radiation surveys of 67 shipments of tantalum raw materials. Exposure scenarios were established for several types of transport workers and for the public. Potential dose rates were assessed using measured radioactivity concentrations and Microshield modelling of the associated gamma radiation doses.

6.1. Main Results

- The tantalite and tin slag radioactivity concentrations (U-238 + Th-232 combined) showed a range of about a factor of 10 with an average of about 20 Bq/g for tantalite and about 25 Bq/g for slag. The majority (78%) of tantalite shipments and 45% of the slag shipments had concentrations exceeding 10 Bq/g.
- Radioactive equilibrium in the uranium (U-238) and thorium (Th-232) decay series was found to be a reasonable assumption for tantalum raw materials for dose assessment purposes.
- Based on an evaluation of potential internal and external exposure pathways, external exposure to gamma radiation was determined to be the only significant exposure pathway.
- Doses from exposure to spilled materials due to potential accidents were calculated and determined not to be a regulatory concern, as the resulting doses were less than 10 µSv/y.
- Doses to members of the public from the transport of these materials were found to be insignificant, much less than 10 µSv/y.
- The calculated doses to transport workers were well within the internationally accepted dose limit of 1 mSv/y for non-radiation workers.
- Truck drivers were found to be the most exposed transport workers. Assuming that the tantalum raw materials considered in this study reliably represent the likely range of tantalum raw materials in general, then the expected (mean) dose to truck drivers would be about 0.24 mSv/y from slag and 0.16 mSv/y from tantalite.

6.2. Conclusions

On the basis of the analyses of doses described in the report there is no apparent reason for an exemption value as restrictive as the current value of 10 Bq/g for these materials.

The study showed that there is considerable allowance for truck drivers who transport tantalum raw materials, to transport other materials containing elevated levels of naturally occurring radioactivity without exceeding a cumulative annual dose of 1 mSv. A higher exemption value of 30 Bq/g (U-238 + Th-232) would be unlikely to produce doses exceeding 0.3 mSv/y to the most exposed transport workers, based on conservative dose calculations. Irrespective of the exemption value, the radiological dose assessments described in the report provide assurance to the tantalum industry that the doses arising from the transport of tantalum raw materials are low and well within international norms for both transport workers and members of the public.

7. IAEA NORM CRP

This study and its conclusions was also put forward as a Canadian contribution to the IAEA Coordinated Research Programme on the “Appropriate Level of Regulatory Control for the Safe Transport of Naturally Occurring Radioactive Material (NORM)” which ran from 2006 to 2009.

SEQUENTIAL EXTRACTION AND MEASUREMENT OF ^{226}Ra, ^{210}Po, U AND Th ISOTOPES IN NORM MATRICES

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Abstract

Phosphate rock is a Naturally Occurring Radioactive Material containing high concentrations of radioisotopes from the ^{238}U and/or ^{232}Th natural decay series (up to $5\cdot10^{3}$ Bq•kg^{-1}). This is the reason why several products and by-products of the phosphate industry (e.g. phosphoric acid, phosphate fertilizers, dicalcium phosphate and phosphogypsum) retain large fractions of those radionuclides. A vast amount of radiochemical methods have been proposed in the literature to extract, concentrate and analyze the content of these natural radionuclides in those samples. Unfortunately, many of these methods were originally developed for their application in environmental samples, thus their application to highly complex industrial matrices often decreases their chemical performance. Hence it is advisable to develop radiochemical ad hoc methods for those samples. In this work a sequential chemical extraction method for the determination of ^{226}Ra, ^{210}Po, U-isotopes and Th-isotopes in raw material, products and by-products from the phosphate industry is presented. In a first step, ^{226}Ra is measured through Liquid Scintillation Counting following barium sulphate precipitation. Due to the difficulty of the matrices, recovery must be carefully controlled, thus ^{133}Ba ($T_{1/2}$ = 10.53 y) is used as internal tracer for ^{226}Ra. Afterwards, ^{210}Po, U and Th isotopes are determined using alpha spectrometry after a selective separation scheme which combines liquid-liquid extraction (TBP) and anion exchange techniques. The high concentration of uranium and thorium in those kinds of samples sometimes leads to crossover contamination after the radiochemical separation. For a successful uranium-thorium separation, after several anion exchange schemes trials, purification in hydrochloric acid media is suggested.

1. INTRODUCTION

The use of phosphate rock as raw material for the production of phosphoric acid and/or dicalcium phosphate generates products and by-products that are classified as NORM, together with the raw material. Thus all these materials involved in the phosphate industry, i.e. phosphate rock, phosphoric acid and phosphogypsum are subject to radiological control. In order to assess the radioactive content of these materials within short time scales, fast and robust methods that permit obtaining reliable results are required.

However, many of these methods were previously developed for environmental samples. Both the high natural radionuclide concentrations and the nature of sample matrices introduce a severe bias in the radiochemical performances and suitability of these methods when they're applied to NORM samples. Thus, the most widespread technique for thorium purification using AG 1-X8 anion exchange resin [1] [2] [3] produce a certain uranium crossover contamination into the thorium fraction [4], so thorium cannot be properly evaluated in samples having high U-contents. Indeed, common gravimetrical methods cannot be used for ^{226}Ra yield calculation prior to LSC measurement, because phosphate rock matrices are highly enriched in calcium and phosphorous, which easily precipitate together with barium. Hence, another way of quantifying Ra chemical yield should be used.

The aim of this work is to merge different environmentally oriented methods developed for the determination of specific radionuclides into one single robust procedure to allow their quantification in NORM-matrices. Thus, ^{226}Ra-barium-^{133}Ba sulphate precipitation, ^{210}Po self-deposition onto silver discs [5] and uranium and thorium sequential extraction using TBP and anion exchange resins were combined and modified [4] to adapt them to the measurement of NORM samples with phosphate rock origin.

2. MATERIALS AND METHODS

2.1. Samples description

Phosphate rock (PR) samples were provided by the phosphoric acid factories located near Huelva town (SW of Spain), and six different profiles of phosphogypsum (PG, three depths each) were collected from the PG wastes piles nearby. Dicalcium phosphate (DCP) samples were provided by the Departament de Salut de la Generalitat de Catalunya [6]. All the samples were stored for six months in order to allow ^{210}Po to reach secular equilibrium with ^{210}Pb.

2.2. Instrumentation

^{226}Ra and ^{133}Ba as internal tracer (internal and Auger electron emitter from electron caption decay) were measured by LSC techniques using a Perkin Elmer Quantulus 1220 [7]. The pulse shape analyser (PSA) function of this instrument was optimised to achieve separation and simultaneous counting of α- and β-events. The alpha emitting radionuclides, ^{210}Po, uranium and thorium isotopes were measured by alpha-spectrometry using PIPS detectors (Canberra). ^{209}Po, ^{232}U and ^{229}Th were used as internal yield tracers. All the measurements were done at CITIUS research facilities (Sevilla, Spain)

2.3. Radiochemical procedure

The radiochemical procedure developed for sequential extraction for ^{226}Ra, ^{210}Po, U- and Th- isotopes is displayed in Figure 1.

Briefly, the non-refractory fraction of the sample is extracted after a leaching using aqua regia. Ba^{2+} carrier was added following filtration. Ba-Ra-PbSO4 were precipitated using H_2SO_4 while Th, U and Po were remaining in the supernatant. The precipitate was re-dissolved using EDTA in ammonia medium and after selective re-precipitation of Ra-BaSO4 with glacial acetic acid; Ra-BaSO4 was re-dissolved with EDTA. The final sample volume was adjusted to 9 ml and then mixed with scintillator (Optiphase Hisafe 3) to completely fill the vial to avoid ^{222}Rn losses before LSC measurement [7]. Recoveries ranged 25-70 %.

Po, Th and U were extracted from the supernatant by solvent extraction using TBP (tributylphosphate). Po was first extracted with 8M HNO_3, and subsequently self-plated onto a silver disk [5]. After addition of Xylene to TBP, two back-extractions steps were applied: first with 1.5M HCl (Th), then with deionised water (U). A modification of the thorium purification method in nitric media [2] was implemented: the aqueous solution containing the thorium isotopes was evaporated and redissolved in 9 M HCl, and the solution was passed through Biorad AG1-X8 anion exchange resin to remove uranium impurities. Finally, U- and Th- isotopes were electroplated onto stainless steel discs [8]. Resolution of the peaks was found to be between 60 and 40 keV in all cases. Recoveries ranged 30-65 %.

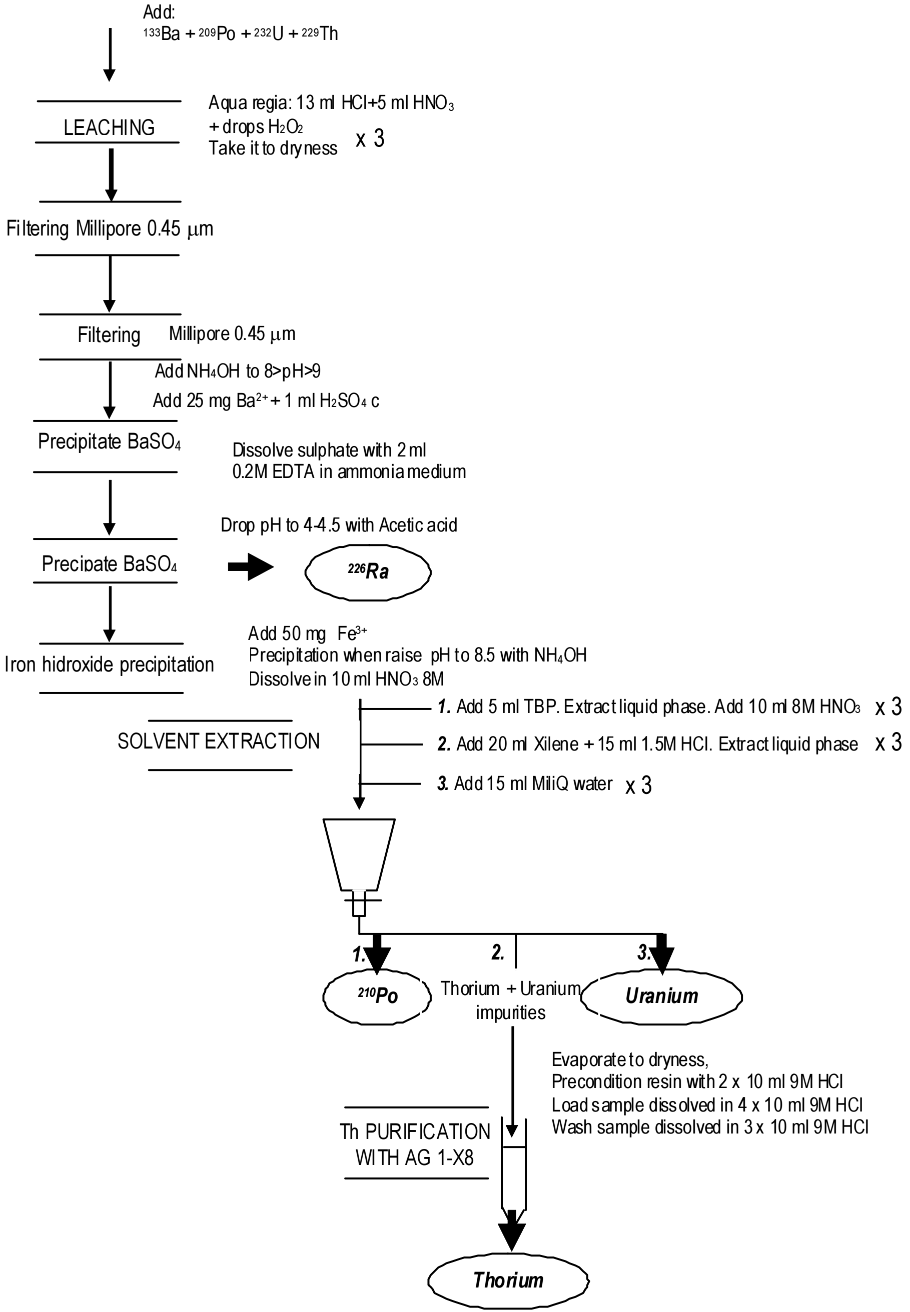

FIG 1. Sequential extraction procedure for the determination of ^{226}Ra, ^{210}Po, U and Th

3. RESULTS AND DISCUSSION

The scheme was applied to a PG sample previously used for a national proficiency test, Table 1. Our results were in good agreement with the reference values for all the nuclides, showing the suitability of the method in terms of accuracy and precision.

Results for phosphogypsum samples are displayed in Table 2. The results displayed a spatial variability of concentrations, in agreement with previous sampling campaigns in the area and showed the historic evolution of discharges [9]. Hence the concentrations of all isotopes reflected a well documented fact: ^{226}Ra and Po concentrations were systematically higher than uranium activities due to their different fractionation mechanisms along the industrial process [10]. The ^{238}U/^{234}U average ratio found was 0.97, in agreement with other measurements in the same area [11] and in *phosphorite* mineral [12].

In the phosphate rock (Table 3), all the radionuclides measured were in or near to secular equilibrium, as expected. The secular equilibrium found between ^{230}Th and ^{234}U confirmed that no uranium contamination was present in the thorium spectrum. The sample was also measured trough ICP-MS following an alternative Th-U separation method and gamma spectrometry (Table 1). Results were in agreement for all methods.

Concerning phosphoric acid, the low content of thorium measured in the sample pointed out that during the industrial process phosphate rock was wet acid digested using HCl [6]. This low thorium content, in comparison to uranium concentrations, confirms the quality of the thorium purification performed. The presence of U in the Th spectra was found to be negligible, while the thorium purification in nitric acid overestimated ^{230}Th concentration up to a 10%, due to U contribution to the Th spectrum. Low ^{226}Ra concentrations follow the usual pattern in phosphoric acid samples since most of the radium was partitioned during the industrial process from the phosphate rock to the phosphogypsum [10].

DCP samples (Table 4) presented high content of uranium and variable content of ^{230}Th; this variability was due to the different acids (hydrochloric and sulphuric) used in the wet-acid digestion to produce the DCP [6]. Samples SHA-3 and SHA-4 corresponds to monocalcium phosphate, for human consumption. Low contents of ^{230}Th in all samples, sometimes 2-3 orders of magnitude lower than ^{234}U, also confirmed that no contamination of uranium was found.

4. SUMMARY AND CONCLUSIONS

A sequential extraction method has been developed for the measurement of natural radioactivity of ^{226}Ra, ^{210}Po, U-isotopes and Th-isotopes in phosphoric rocks and its derivates from phosphate industry. ^{226}Ra is extracted by sulphate precipitation and measured together with ^{133}Ba as internal tracer. Afterwards ^{210}Po, Th and U are obtained from TBP solvent extraction. Thorium is purified through AG1-X8 resin using a modified method suitable for uranium enriched samples using concentrated hydrochloric media. The method is checked in a proficiency test, phosphogypsum, phosphoric acid, DCP and phosphate rock samples, providing reliable and fast results.

ACKNOWLEDGEMENTS

All the measurements have been performed in Universidad de Sevilla, Centro de Investigación, Tecnología e Innovación (CITIUS).

TABLE 1.NATURAL RADIONUCLIDES ACTIVITY CONCENTRATION, ^{226}Ra, ^{210}Po, ^{238}U, ^{234}U IN PHOSPHATE ROCK AND A NATIONAL PROFICIENCY TEST

	^{226}Ra (Bq/kg)				^{210}Po (Bq/kg)				^{238}U (Bq/kg)				^{234}U (Bq/kg)				^{232}Th (Bq/kg)				^{230}Th (Bq/kg)			
Phosphate rock	This method		gamma spectrometry		This method		^{210}Pb gamma spectrometry		This method		ICP-MS		This method		ICP-MS		This method		ICP-MS		This method		ICP-MS	
		± σ		± σ		± σ		± σ		± σ		± σ		± σ		± σ		± σ		± σ		± σ		± σ
	700	25	720	100	665	13	629	81	694	11	637	9	695	11	635	11.36	8.0	0.4	7.7	0.2	710	12	740	24
Phosphogypsum proficiency test	This method		Reference		This method		Reference		This method		Reference		This method		Reference		This method		Reference		This method		Reference	
		± σ		± σ		± σ		± σ		± σ		± σ		± σ		± σ		± σ		± σ		± σ		± σ
	600	20	573	18	720	20	678	8	53	2	55	2	53	2	56.0	0.2	7	2	6.1	0.1	390	10	332	6

TABLE 2.NATURAL RADIONUCLIDES ACTIVITY CONCENTRATION, ^{226}Ra, ^{210}Po, ^{238}U, ^{234}U IN PHOSPHOGYPSUM SAMPLES OBTAINED THROUGH SEQUENTIAL EXTRACTION METHOD

ID	^{226}Ra (Bq/kg)	± σ	^{210}Po (Bq/kg)	± σ	^{238}U (Bq/kg)	± σ	^{234}U (Bq/kg)	± σ	^{210}Po/^{226}Ra	± σ	^{238}U/^{234}U	± σ
Profile 1 0-30	818	88	588	13	166	3	171	3	0,72	0,08	0,97	0,03
30-60	810	87	513	11	175	3	178	3	0,63	0,07	0,98	0,03
60-90	1024	110	521	12	97	4	102	4	0,51	0,06	0,95	0,05
Profile 2 0-30	404	16	585	11	103	3	105	3	1,45	0,06	0,98	0,04
30-60	630	24	588	13	128	3	134	3	0,93	0,04	0,95	0,03
60-90	737	28	669	14	448	8	453	8	0,91	0,04	0,99	0,03
Profile 3 0-30	700	27	654	15	156	3	158	3	0,93	0,04	0,99	0,03
30-60	768	29	520	12	160	3	164	3	0,68	0,03	0,98	0,03
60-90	672	26	588	14	151	3	152	3	0,88	0,04	0,99	0,03
Profile 4 0-30	828	33	566	13	89	2	96	2	0,68	0,03	0,93	0,03
30-60	515	21	671	15	93	2	94	2	1,30	0,06	0,98	0,03
60-90	386	15	580	13	118	3	123	3	1,50	0,07	0,96	0,03
Profile 5 0-30	708	27	499	12	128	2	132	3	0,70	0,03	0,97	0,03
30-60	379	16	601	14	183	4	185	4	1,58	0,08	0,99	0,03
60-90	317	13	795	18	191	4	202	4	2,51	0,12	0,95	0,03
Profile 6 0-30	746	29	617	14	147	4	149	4	0,83	0,04	0,99	0,03
30-60	739	29	636	14	76	2	84	3	0,86	0,04	0,91	0,04
60-90	647	25	591	13	142	4	145	4	0,91	0,04	0,99	0,03

TABLE 3. NATURAL RADIONUCLIDES ACTIVITY CONCENTRATION, ^{226}Ra, ^{210}Po, ^{238}U, ^{234}U, ^{230}Th, ^{232}Th, IN FIVE PHOSPHORIC ACID SAMPLES (#2, #4, #6, #8, #12) AND A PHOSPHATE ROCK SAMPLE (#10)

ID	^{226}Ra		^{210}Po		^{238}U		^{234}U		^{230}Th		^{232}Th		^{238}U/^{230}Th		^{238}U/^{234}U	
	A (Bq/kg)	± σ	A (Bq/kg)	± σ	A (Bq/kg)	± σ	A (Bq/kg)	± σ	A (Bq/kg)	± σ	A (Bq/kg)	± σ		± σ		± σ
2	151	2	19	0,8	1203	19	1205	19	48	1	20	1	25,06	0,66	1,00	0,02
4	192	3	1529	30	1252	19	1057	16	19	1	44	1	67,31	2,40	1,18	0,03
6	160	3	93	3	1270	20	1254	19	86	2	58	1	14,77	0,41	1,01	0,02
8	164	4,5	14	0,6	300	5	297	5	21	2	6	1	14,29	1,38	1,01	0,02
12	309	8,1	1116	22	1236	19	1011	15	41	3	12	2	30,15	2,25	1,22	0,03
10	700	25	665	13	694	11	695	11	720	12	9	1	0,96	0,02	1,00	0,02

TABLE 4. NATURAL RADIONUCLIDES ACTIVITY CONCENTRATION ^{210}Po, ^{238}U, ^{234}U, ^{230}Th, ^{232}Th, IN DICALCIUM AND MONOCALCIUM (SHA-3 AND SHA-4) PHOSPHATE SAMPLES OBTAINED THROUGH SEQUENTIAL EXTRACTION METHOD.

ID	^{210}Po		^{238}U		^{234}U		^{230}Th		^{232}Th		^{238}U/^{230}Th		^{238}U/^{234}U	
	A (Bq/kg)	± σ	A (Bq/kg)	± σ	A (Bq/kg)	± σ	A (Bq/kg)	± σ	A (Bq/kg)	± σ		± σ		± σ
U-891-B	588	13	1500	13	1468	13	4512	109	27	6	0,33	0,01	1,02	0,01
U-896-B	513	11	1432	23	1418	23	2007	42	53	3	0,71	0,02	1,01	0,02
U-896-R	521	12	1450	16	1436	16	2286	47	27	2	0,63	0,01	1,01	0,02
U-897-B	585	11	1341	20	1369	21	1453	30	111	4	0,92	0,02	0,98	0,02
U-899-R	588	13	1494	15	1172	13	92	3	3	0	16,31	0,54	1,27	0,02
U-891-G	669	14	3128	31	3144	31	4512	109	27	6	0,69	0,02	0,99	0,01
U-893-G	654	15	1126	9	1106	9	63	2	<MDA		17,87	0,59	1,02	0,01
U-SHA-3	520	12	6.0	0.1	5.0	0.1	16	1	<MDA		0,36	0,03	1,10	0,09
U-SHA-4	591	13	2.0	0.1	2.0	0.1	53	6	<MDA		0,04	0,01	1,04	0,13

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DETERMINATION OF U AND Th ISOTOPES IN NORM SAMPLES BY TOTAL DISSOLUTION WITH ALKALI FUSION

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Abstract

Some raw materials commonly used in NORM Industries as phosphate rocks, ilmenite and Zircon sands , as well as some co-products or residues generated in the production processes from these minerals have a refractory behaviour, being impossible to put in dissolution all their uranium and thorium content by conventional acid leaching. This dissolution is essential in order to evaluate correctly the activity concentration of these elements in the mentioned samples by alpha-spectrometry. For that reason, we have adjusted in our laboratory a method for the total dissolution of NORM samples through their alkali fusion which allows the posterior application of a radiochemical method based in the use of extraction chromatographic resins for the isolation of the Uranium and thorium isotopes. Once they are isolated, the uranium and thorium fractions are electrodeposited onto stainless steel planchets, and the levels of ^{238}U and ^{234}U, as well as ^{232}Th and ^{230}Th are determined by alpha-particle spectrometry with PIPS detectors.

1. INTRODUCTION

There are in the bibliography different ways to carry out the total dissolution of a sample when it is needed. For instance, digestion with HF, and also fusion techniques among others. From them, we decided to set up a fusion technique already used in ICP-MS[1]or AAS[2] measurements that we have modified and readapted for the digestion of refractory samples followed by a separation process with solvent extraction for the determination of actinides (U and Th isotopes).

Different salts as Na_2CO_3, Na_2O_2, NaOH or H_3PO_4 have been used in fusion processes since the seventies [3,4,5,6] and the one chosen for us as melting salt was the $KHSO_4$. The whole process comes from the routine analysis carried out in the chemical controls and trace elements in raw materials and co-products from a NORM Industry. The original digestion method ends with the sample dissolved in H_2SO_4 but our U/Th separation process needs nitric acid solutions to work with, so that we have readjusted the methodology verifying that applied changes are corrects.

The method was checked in samples in which secular equilibrium could be supposed [7] in both natural chains (^{238}U and ^{232}Th). On these samples, gamma measurements were carried out and the results were compared to those obtained by alpha spectrometry via alkaly fusion. Furthermore, a second comparison exercise was made by digesting the same samples by usual leaching processes and checking that different results were found, which suggests that usual leaching only gets partial digestion of the sample matrix.

2. MATERIALS AND METHODS

2.1 Samples description.

The samples used to setup the method were a group of 10 aliquots of milled illmenite. These samples comes from a Titanium Dioxide plant located at the industrial area of Huelva City, at the south-west of Spain. Ilmenite rocks are classified as NORM [8] and used as raw material in the industrial process of Titanium Dioxide pigments. On a second stage, the fusion technique was also applied to sludges that comes from ilmenite's digestion with H_2SO_4 at the beginning of the TiO_2 industrial process. This sample contains the ilmenite solid fraction that was not dissolved with this sulphuric acid, implying that a high percentage of refractory matter forms this sample.

A third group of samples comes from the Huelva's surrounding industrial area where sediment samples were taken from the bottom of Tinto and Odiel Rivers. From a total amount of 19 samples in 2008 sampling campaign, the 4 more representative ones (Table 1) have been selected to check if there were any difference in results of activity concentration between alkali fusion technique or leaching digestion in sediment samples. This area (see FIG 2.) has been widely studied by our research group due to the enhancement of sediments in natural radionuclides coming from quite close factories generating phosphogypsum that either in an active or passive way, dumped NORM on this area.

Table 1. Location and brief description of selected samples sites in Tinto-Odiel framework

Sample's label	Description of sampling site
O4	Point in Odiel River, in front of phosphate factory where some years ago, phosphogypsum was dumped directly into the river.
T2	Point from Tinto River, in front of phosphogypsum piles.
OT1	Site located at the beginning of the confluence of both rivers.
OT5	Site far away from the beginning of rivers confluence and close to the sea.

2.2 Measurement systems

Most of measurements were carried out by alpha spectrometry, using PIPS detectors in an 8-chambers Alpha-analyst system from Canberra. The software used to work with spectra was Genie2K.

Regarding gamma measurement, used in ilmenite and sludge samples, a coaxial e**Xt**ended **Ra**nge germanium detector (XtRa) of 37.1% relative efficiency was used. This system works with a second detector (a Model BC-418 organic scintillator from Bicron) in anti-coincidence way [9], to reduce the environmental gamma background.

2.3 Methodology

2.3.1 Gamma Spectrometry

Samples were stored in cylindrical bakers and sealed to avoid radon gas emanations in order to achieve the secular equilibrium between Ra and daughters in both natural series. One month later, gamma measurements were carried out on these samples.

Furthermore, transmissions exercises with point sources were executed over each sample to correct efficiency differences (self-absorption effects) between real samples and standards used in our laboratory. ^{226}Ra (via ^{214}Pb and ^{214}Bi), ^{228}Ra (via ^{228}Ac) and ^{224}Ra (via

^{212}Pb and ^{212}Bi) activity concentrations can be determined with this technique and compared to those other results found via alpha spectrometry when possible.

2.3.2 Alpha spectrometry

Uranium (^{238}U, ^{234}U) and Thorium (^{232}Th,^{230}Th) activity concentrations in refractory matrices were estimated by alpha spectrometry. An usual radiochemical process for alpha spectrometry has three main stages: Sample's pre-treatment (where a sample is put onto a liquid solution), separation process (where U and Th fractions are separated) and source preparation (where each fraction is prepared in a thin layer to be measured in chambers with a determined degree of vacuum).

The alkali fusion technique (that belongs to the sample pre-treatment step) adjusted in our laboratory is described in detail as follows:

a) Smelt 25 g of $KHSO_4$ (using a quartz crucible) in a Bunsen's lighter for 10-12 minutes.
b) Remove the crucible and wait until the smelted salt get colder. Then, add 0.2 g of sample. Tracers (^{229}Th and ^{232}U) should be added as well.
c) Smelt again the compound in the Bunsen's until the mixing seems visible smooth (this step can vary from 5-15 minutes depending on sample's matrix).
d) Take the crucible directly from the Bunsen to a pre-heat oven to 800 ºC for 20 minutes.
e) After that time, take out the crucible form the oven and get colder. The fusion has been carried out.
f) Pre-heat 150ml of HNO_3 8M to 90ºC and immerse the crucible in it to dissolve the content. After some minutes, take the crucible out of the acid solution, leaving a clear yellowish solution with sample totally dissolved on it.

With sample totally digested, an actinide precipitation followed by a centrifugation process ends in some grams of solid precipitates. This solid fraction is easily re-dissolved onto 5ml HNO_3 3M to start the U/Th separation process by extraction chromatography [10, 11]. The solution that contain the sample is passed through a UTEVA column, and 5ml HNO_3 3M (twice) are passed through the resin to fix the actinides and for the elution of some interfering isotopes like Po. Later, Th isotopes are eluted passing 4ml of HCl 9M followed of 20ml of HCl 5M. The U isotopes are finally eluted passing 10 ml of HCL 0.01M.

At this stage, we have two independent solutions containing U and Th isolated isotopes. The U and Th are finally electroplated [12, 13] onto stainless steel disks. The samples are then prepared to be measured by alpha-spectrometry.

3 RESULTS AND DISCUSSION

The results are expressed in activity concentration ($Bqkg^{-1}$) for all the samples analyzed. Uncertainties are expressed with 1-σ criteria. Alpha measurements were made for 250.000 s what implies a Minimum Detectable Activity (M.D.A.) of 0.01 Bq/kg with a 95% of confidence level. On the other hand, gamma measurement depends on each emission but the M.D.A. values rise from 1.0 Bq/kg to 3.0 Bq/kg with measuring times surrounding 100.000 s.

3.1 Results in Ilmenite

Ten aliquots of the same ilmenite sample were labelled with letters from A to J (Fig 1) and treated with alkaline fusion. The last results in the X-axis from both graphics in this figure (represented with a dot line), corresponds to the average of each radionuclide measurement.

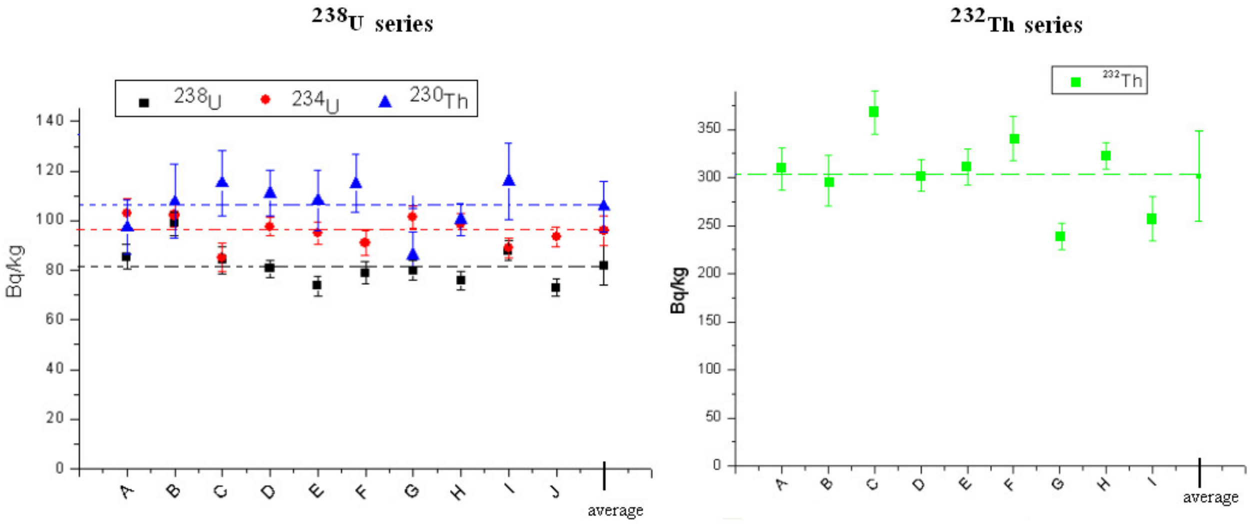

FIG. 1. Activity concentrations of U and Th Isotopes in ilmenite by alkali fusion.

Regarding the reproducibility, experimental results over ilmenite samples with alkaline fusion show agreement and secular equilibrium can be observed between ^{238}U, ^{234}U and ^{230}Th. This value could be established around 100 Bq/kg with an uncertainty of 10% for ^{238}U series with alkali fusion technique. In addition, the Table 2 shows another experimental value obtained via leaching digestion that could be set at 30Bq/kg. This result shows a partial ilmenite digestion when it is digested with aqua regia.

Table 2. Activity concentration of U and Th isotopes in ilmenite ore

Digestion technique	^{238}U (Bq/kg)	^{234}U (Bq/kg)	^{230}Th (Bq/kg)	^{232}Th (Bq/kg)
Leaching	28±1	20±1	33±1	205±7
Alkali Fusion[a]	83±7	96±6	107±8	301±48

[a] Represents the average of the 10 aliquots.

However, the found secular equilibrium with the alkali fusion does not assure that a total digestion of the samples was achieved. Trying to solve the last question, and using secular equilibrium assumption, the ilmenite ore was measured via gamma. The obtained results are shown in Table 3. They agree with the equilibrium value (100 Bq/kg) of ^{238}U series and moreover, they match up with a value of 300 Bq/kg in ^{232}Th series (instead of the 200Bq/kg found with leaching digestion) giving us confidence about the total dissolution of the samples.

Table 3. Ra and Th activity concentration by gamma spectrometry in ilmenite ore

^{238}U series (Bq/kg)		^{232}Th series (Bq/kg)		
^{226}Ra (via ^{214}Pb)	^{226}Ra (via ^{214}Bi)	^{228}Th (via ^{212}Pb)	^{228}Th (via ^{212}Bi)	^{228}Ra (via ^{228}Ac)
98±5	91±5	315±16	322±18	303±18

Regarding chemical yields, an average of 70% was obtained for U isotopes and a 60% for Th with alkali fusion technique. Besides, some of the aliquots (H, I, J) were traced after the 800ºC process to check if there were loses during the fusion time at the oven. We found that tracer recovery was hardly affected by this step.

Comparing this new method with a leaching digestion, we have to point out some additional advantages like the time needed to carry out the sample digestion. Alkali fusion takes no more than 2-3 hours while the leaching process take at least 16 hours. Additionally the fusion needs less reagents than the leaching.

3.2 **Results in Sludges**

Due to the origin of this sludge, no secular equilibrium can be supposed. When ilmenite is digested via sulphate at the beginning of the industrial process, mostly of the U and Th elements are put in the liquid fraction while the Ra falls associated to Radium sulphides in the solid fraction that becomes in sludge [14]. On the other hand, the high percent of refractory matter in this sample will make that a leaching process could hardly dissolve the remaining U and Th in sludge while the alkali fusion digestion is expected to do it.

We took 4 aliquots of the same sludge sample and a total dissolution process was applied to them. We wanted to check again the homogeneity of the sample and test the reproducibility of the experimental process. The results of these tasks are shown at Table 4.

Table 4. Results of activity concentration of U and Th isotopes in sludge (dry weight)

Digestion technique	^{238}U (Bq/kg)	^{234}U (Bq/kg)	^{230}Th (Bq/kg)	^{232}Th (Bq/kg)
Leaching	8.1±0.5	13.1±0.6	13.4±0.6	32.8±1.2
Alkali Fusion[a]	242±12	251±14	242±14	197±19

[a] Represents the average of 4 aliquots.

These results, support the hypothesis of that most of sludge are compound of refractory matter containing considerable quantities of U and Th. This situation makes useless a typical leaching process and, in doses assessments, wrong data would lead us to erroneous dosses evaluation in working environment related with this material.

3.3 Result in Odiel-Tinto estuary

The four selected samples were analysed, being found that the studied area was affected in different degree by natural radionuclides coming from phosphogypsum stacks. As a general trend, ^{238}U series isotopes (^{238}U,^{234}U,^{230}Th) are present in higher levels than those of ^{232}Th (Figure 2). Besides, as closer is the sample site from the source place, higher is the level of of radionuclide contamination. For the site far away from phosphogypsum sources, similar to non-affected levels of activities were found.

Aliquots of the sediment samples were treated in parallel by the alkaline fusion and the leaching digestion procedures. The results show that sediments with low refractory composition gives similar results regardless of the used digestion process, and the opposite effect happens when the refractory fraction is high. In this sense, the ratio between leaching to fusion activity concentration results, can give us an estimation of the quantity of refractory matter that would have each sample. In this sense, for example, for the OT5 sediment (quite sandy) the ratios $^{238}U_{leaching}/^{238}U_{fusion}=0.17\pm0.01$, $^{232}Th_{leaching}/^{232}Th_{fusion}=0.19\pm0.02$, indicate that 80% of U and Th were associated to the refractory matrix.

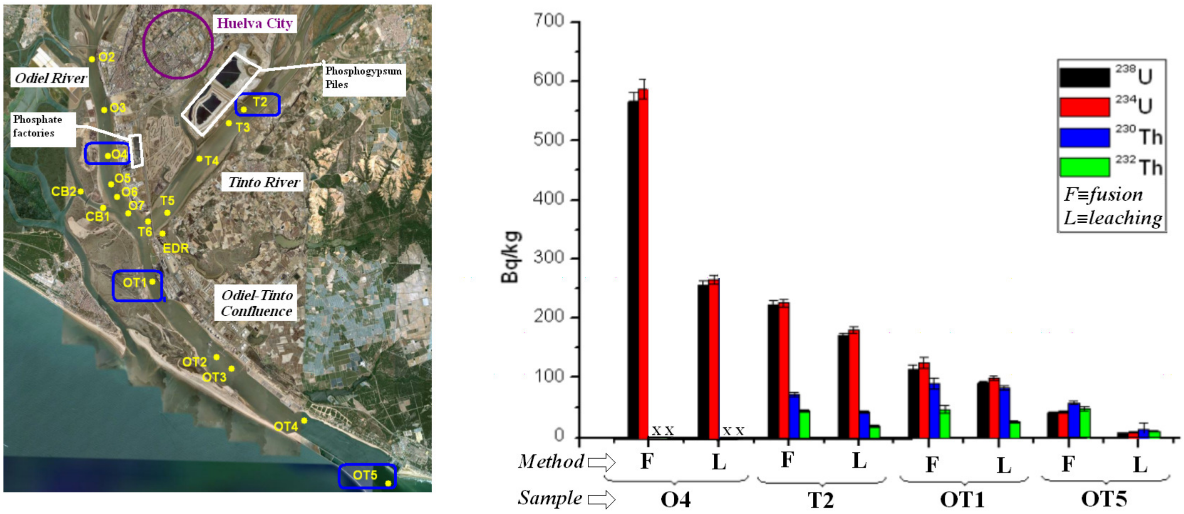

FIG.2.(Left) Sampling location map. (Right) Activity concentrations of U and Th Isotopes in sediments comparing leaching digestion with alkali fusion (Th fraction in sample O4 was not determined).

4 CONCLUSIONS

In this work, an alkali fusion technique (with $HKSO_4$) has been readapted and set-up in our laboratory in order to have a total dissolution in refractory samples. It has been applied over different groups of NORM samples. The behaviour of U, Th and Ra isotopes on these samples has been pointed out.

Alkali fusion method has been compared with a usual leaching process in many items concluding that alkali fusion technique works properly. In addition, it is a technique easy to carry out, less time-consuming and need as well less reagents than leaching digestions. For all these aspects we can indicate this technique as a good option for U and Th determination in refractory matrices.

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RADIOLOGICAL IMPACT DURING THE EXTRACTION, PROCESSING AND USE OF PHOSPHATE MINERALS IN CUBA

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Abstract

The use of phosphates for the production of fertilisers is a practice broadly diffused in the world. Their wide use is associated to the contribution of this material to formulation of NPK fertilisers. It is known in turn that phosphates have in their composition appreciable quantities of radioactive elements of natural origin. For this reason the use of phosphates in the composition of fertilizers can cause a radiological impact to both workers and public during all the phases of extraction and processing of phosphates, as well as during the production and application of these fertilizers. Finally the transfer of radionuclides contained in the fertilizers to the products of human consumption (vegetables, milk, meat) can produce an additional radiological impact on population. In Cuba there exist six locations of phosphoric rocks, located in the counties of Pinar del Río, Havana, Matanzas, Sancti-Spíritus and Holguín. From these deposits there were studied the two ones which are in exploitation: "La Pimienta" deposit, located in the West part of the country and "Trinidad de Guedes" deposit, located in the Centre-West of Cuba. Paper shows the results obtained by the Center for Radiation Protection and Hygiene (CPHR) in the determination of radionuclides concentrations in collected in the sites samples. Based on these results and taking into account both the features of routine works carried out in the sites and the later use of collected mineral as fertilizer, doses to mining workers and to members of the public were estimated. Estimated doses are in the range 0.3 – 2.70 mSv per year for workers and in the range 1.3 – 17 µSv per year.

1. INTRODUCTION

The use of phosphate minerals as raw material for the production of fertilizers is a practice broadly diffused in the world. Their wide use is associated with the phosphorus that this material contributes for the preparation of NPK formulas. It is known in turn that phosphate minerals can have in their composition appreciable quantities of radioactive elements of natural origin. By this reason the potential radiological impact of the use of these minerals in the elaboration of fertilizers for cultures that are object of human consumption constitutes a topic of study of diverse research groups.

In 1963 start the geological investigations for localization of phosphoric rocks deposits in the whole territory of the Republic of Cuba. The conditions of the calculation of reservations for each location vary according to the use for which they were studied. In Cuba there are six locations of phosphoric rocks at the present time, studied in different grade of detail. These deposits are located in the counties of Pinar del Río, Havana, Matanzas, Sancti - Spíritus and Holguín. As part of the studies carried out by the Center for Radiation Protection and Hygiene (CPHR) to evaluate the doses due to different technological modifications introduced by man to natural sources of radiation, a study was carried out to evaluate the radiological impact of the use of Cuban phosphate minerals in the elaboration of fertilizers.

Of the six locations of phosphoric rocks existing in the country, the location "La Pimienta", in Pinar del Río, was studied in a previous investigation [1]. The attention was put hence in the location "Trinidad de Guedes" that is the only location of the country that is in exploitation at the present time for obtaining phosphoric rocks for use in fertilizer production. The location "Trinidad de Guedes" is an open mine and occupies a small area near the village of Alacranes, in Matanzas. The extension of the location in the layer foreseen for the exploitation is of 312 m of wide and 435 of long in a varied way. The mine is in exploitation since 1994 and the production has reached the 4352 tons of mineral.

The material obtained as a result of the extraction of the mineral after being dried and milled in a plant located near the deposit is sent to the fertilizers factory of Rayonitro, in the city of Matanzas. The fertilizer produced is used for application in field used for potato, tobacco and sugar cane cultivations. The mineral is also used in the preparation of mineral salts for the livestock, mixing 60 % of phosphoric rock, 30% of common salt, 5 % of magnesit and 5% of sodium sulphide. These salts are added to the drinking water of the livestock and the forage to compensate salts balance in the animals. These salts are used mainly in cattle farms located in the East of Havana, as well as in the counties of Villa Clara and Granma, but they find use in general in the whole country.

2. MATERIALS AND METHODS

For the characterization of the phosphoric material it carried out a campaign of collection of samples in the place of the deposit. Samples of the phosphoric material of the deposit were collected and additionally samples of vegetation of the place and of sugar cane cultivated in place were collected, in order to see local possible impacts. Finally samples of the product obtained in the local plant processing the phosphoric mineral were also collected.

Once classified, the samples underwent the processes of drying and incineration for preparing them for the measurements, according to the pre-treatment of samples procedures of the Laboratory of Radiological Environmental Surveillance of the CPHR. The radioactivity determinations were carried out for Ra-226, Th-232, K-40 and complementarily for Cs-137 that appears as a consequence of the radioactive global precipitations (fallout). After pre-treated, the samples were measured for determining the radionuclide content by high resolution gamma spectrometry using a hiperpure germanium detector.

With evaluation purposes, using the measurements results a dosimetric estimation was made for the public using a simple and extremely conservative model, described below.

3. RESULTS AND DISCUSSION

The results of the determinations of the concentration of the radionuclides of interest are shown in the table I. From the results it can be observed that, as expected, only Ra-226 appears in significant concentrations, which is a characteristic of this type of geological formations and which constitutes the fundamental object of this investigation. In the case of the concentrations of Th-232, although the detection limits are high in the case of the vegetation, the values estimated in soils allow to wait not significant concentrations in vegetation.

In results obtained for mineral samples taken it is possible to observe that the Ra-226 concentration is forty times superior to the average for soils reported for Cuban soils in other studies [2]. The results obtained for vegetation are as expected, starting from the values of transfer coefficients soil-vegetation calculated in previous works [3] for these species or similar and based on Sr-90, which has a similar chemical behaviour in the environment as Ra-226.

Table I: Radionuclide concentrations in collected samples.

Sample Code	Sample type	Radionuclide concentration (Bq/kg)			
		Ra-226	Th-232	K-40	Cs-137
71/00/EGE	soil	135±9	14±3	140±14	<2.7
72/00/EGE	soil	800±50	5.8±0.1	80±7	<3.6
73/00/EGE	soil	75±5	<2.8	27±3	<3.3
74/00/EGE	soil	92±6	<4	ND	<5.0
75/00/EGE	grass	160±14	<16	<412	<13.8
76/00/EGE	sugar cane leaf	<36.8	<16	<226	<15
77/00/EGE	sugar cane stem	<23.9	<11	<390	<11.7

For the estimation of the doses extreme conditions were considered that make the estimation extremely conservative. The concentration value considered for Ra-226 in the mineral was the maximum measured value. The pattern of used land was of a soil with the maximum concentration of Ra-226 found for the soils of non anomalous areas in Cuba (43 Bq/kg), increased in 75% by the use of the fertilizer, percent that is assumed of the results obtained previously [1]. The values of the transfer coefficients were assumed for sugar cane and potato cultures and for the milk (starting from the consumption by livestock of grass grown in floors with the same concentration of salts and containing 30% of mineral). The individual doses obtained by groups of ages assuming average annual rates of consumption of 183 kg/year and 26 kg/year of milk respectively for children and adults, 0.025 kg/year of sugar cane and 50 kg/year of potato. The conversion coefficients to dose were those recommended by OIEA [4] for each group of ages.

The dose weighted by the Cuban population's distribution was 1.3 μSv/year. The fundamental contribution is given by potato's consumption: 0.9 μSv/year. This value doesn't represent a significant contribution to the doses that the Cuban population receives by incorporation of radionuclides via ingestion.

4. CONCLUSIONS

In the frames of the present study the material coming from the country’s main mine of phosphoric mineral was characterized.

The determinations of Ra-226 in the taken mineral samples evidence high concentrations of this radionuclide that potentially should be reflected in the soils fertilized with this material. The estimates made, even when they were carried out with a high grade of conservatism, show that the increments in the doses to the population due to ingestion of the products benefited with this fertilizer are not significant.

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EXTERNAL QUALITY CONTROL FOR SPANISH ENVIRONMENTAL RADIOACTIVITY LABORATORIES: RESULTS FOR A PHOSPHOGYPSUM TEST SAMPLE (CSN-CIEMAT-2008)

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Abstract

Within the proficiency test programme for the laboratories supporting the Spanish radioactive environmental monitoring (REM), a phospogypsum material was used as a test sample, in an attempt to evaluate the performance of the laboratories analyzing NORM (Naturally-Occurring Radioactive Materials). The results of the exercise were computed for 34 participating laboratories, and their analytical performance was assessed using the z-score approach. Robust statistics of the participant's results was applied to obtain the median and standard deviation and to verify the Reference Values. The exercise has shown an homogeneous behavior of laboratories, being statistical parameters from the results close to the assigned Reference Values. A raised percentage of satisfactory laboratory performance has been obtained for all radioanalysis, also gross alpha and gross beta produced a homogeneous distribution. The study has shown that participant laboratories perform radioactive determinations in phosphogypsum (NORM) samples with satisfactory quality levels.

1. INTRODUCTION

Continuous monitoring programs are imperative to survey radioactivity levels in the environment (REM), the reliability of the assessment obtained from these programs requires the laboratories producing the analytical data to be able to provide results traceable to international standards, and for their quality to be adequately demonstrated and documented. To assist laboratories in meeting those quality requirements, CIEMAT and CSN established in Spain (since 1985) periodical intercomparison exercises or proficiency test (PT), using samples similar in composition and activity levels to the ones routinely analysed in the programs. These exercises should provide laboratories with an external quality assessment, by which they can demonstrate the quality, comparability and traceability to SI of their results.

The surveillance of the environment includes all radioactive elements present in the biosphere; natural long-lived radionuclides (potassium, uranium, thorium and any of their decay products), give rise to a much larger radiological dose to the public compared with that caused by man-made activities. Radioactive materials which occur naturally occur widely, and are known by the acronym "NORM". Exposure to NORM is often increased by human activities, e.g. burning coal, making and using fertilizers, oil and gas production, etc.. Phosphate rock used for fertilizers is a major NORM due to uranium and thorium series, in Southern Spain, a large industrial waste disposal site (near Huelva Figure 1), from phosphate rock processing plants (originating mainly from Morocco), was partially undergone restoration works, as the wastes released to the area lead to a clear enhancement of radionuclide concentrations from U-series in different compartments of the site [1-3]. Social impact generated not long ago by the restoration operations in this area, produced certain concern over the potential environmental radiological impact.

Several years ago, the exposure from natural radioactivity became part of radiological protection regulations (EURATOM'96/29 transposed to Spanish legislation as RD 783/2001) and the CSN, as a regulatory Body, developed radiological criteria to implement the specific recommendations regarding NORM. Within this context, the CSN being aware of the need to appraise the competence of laboratories in analyzing natural radionuclides, selected as a test sample, a phosphogypsum material collected at the referred site in Huelva. The outcome of the exercise, CSN/CIEMAT-2008, is described in this paper.

2. ORGANIZATION OF THE EXERCISE

The scheme was organized according to ISO-43&13528 recommendations and the international protocol ISO/IUPAC/AOAC [4], the use of these guidance for evaluation, provides participants an external and independent assessment of the quality of their results when analyzing radionuclides in NORM.

From a total of 38 environmental radioactivity laboratories that were asked to participate, 34 reported results. CIEMAT prepared the documentation to be distributed among participants: technical bases recommended performing for each analysis the number of determinations carried out routinely, and inform the final result. In case of making several determinations by analysis, it should be reported the mean value of activity concentration (weighted mean) and its expanded uncertainty, stating whether it was informed the internal or external variance.

2.1. Test material

Test material was obtained during the second half of January 2008, from a specific area at the Fertiberia dumping site, where accumulated deposits were old enough as to ensure their stability and the secular equilibrium of the existing natural radioactive series. The phosphogypsum contains naturally occurring radionuclides which activity concentration levels are modified due to the industrial manufacturing process that undergoes the raw material (phosphate rock). [5-7].

The bulk material (70 kg) was sent to the University of Barcelona to undertake the preparation of the samples. The material was dried (30º- 40º C during 180 h); as the pH of the phosphogypsum was 2.6, it was to be washed repeatedly, to increase the pH up to 6.7. The decanted material was dried in consecutive steps (25º-30º-40º during 110 h.), crushed, homogenized (during 130 hours with a mechanic mixer) and sieved (through 2mm mesh and later 125 μm nylon sieve). The homogeneity was checked according to Protocol recommendations [1]. Elemental composition of the sample was determined using X-Ray Fluorescence, major component was found to be CaO.

After ensuring global homogeneity, the sample was bottled in polyethylene units containing 300 g of phosphogypsum: one bottle was sent to the University of Seville, to estimate the initial radioactivity content and subsequent verification of the Pb-210/Po-210 equilibrium.

Five bottles were sent to CIEMAT, to confirm the final radionuclide homogeneity; once verified, four of these bottles were shipped to International expert Laboratories (IAEA Seibersdorf, IAEA-MEL, IRSN-Orsay and ENEA-Sta.Teresa), to obtain reliable radionuclide activity results, for later use in establishing the Assigned Values for the PT. The rest of bottles were directly shipped from Barcelona University to participant laboratories on a regular basis, at the end of November 2008

2.3 Establishing the Assigned Value

The results from the 4 expert-laboratories were combined to establish the Assigned Values (AV); the weighted mean was obtained and its expanded uncertainty.

The AV for each analysis was established according to the *consensus of expert laboratories* method [1]. For some radionuclides, a relatively high uncertainty was estimated, thus the initial information provided by the Universities of Barcelona and Sevilla, to establish the orders of magnitude and intervals of activity, was also used to extend and contrast the results that sent the reference laboratories. Besides, the parameters from the robust statistics applied to participants 'results (median, ML and robust standard deviation, RSD) have been employed to further refine the AV and the performance criterion [8].

2.4 Scope of the exercise

The analyses to be performed in the phosphogypsum sample were: U-238, Th-234, U-234, Th-230, Ra-226, Pb-214, Bi-214, Pb-210, Po-210, Th-232, U-235, gross alpha and gross beta.

Laboratories were requested to inform the results of activity, uncertainty, detection limit from each determination, and relevant information on the procedure's methodology and calculations. Activity results from analyses should be expressed as dry weight, due to the hygroscopic characteristics of phosphogypsum, it was recommended to determine the moisture content of the sample prior to analysis (weight loss by drying at 85 ° C for 24 h), and decay corrected to 01/01/2008, except for Po-210, that should be referred to the date of separation.

The results provided by laboratories were checked for consistency at the CSN and a code was assigned to ensure confidentiality, afterwards the set of all participants' results was sent to CIEMAT for statistical analysis and performance assessment.

2.5 Data Treatment. Statistical Analysis

Statistical study of the results was performed following the last recommendations of International Committees and Organizations, compiled in the ISO/IUPAC/AOAC Protocol [1]. Because the test sample is not a reference material, the robust statistics has also been applied for a more objective analysis of the results (ML and RSD) [8]. The RSD enabled comparison of individual laboratory uncertainties with those of the whole data populations, providing a good evaluation of the assigned values.

The Protocol recommends performing a *"fitness for purpose"* evaluation, based on the conversion of participants' results into z-scores. The performance criterion, has been set so as to ensure that the routinely analysis is of a quality that is adequate for the purpose of this exercise.

2.5.1 Formation of the z-score

A participant's result, ***x***, is converted into a z-score according to the equation:

$$z = \frac{(x - X)}{\sigma_p} \tag{1}$$

where, $\boldsymbol{X}$, is the AS (the scheme provider's best estimate of the value of the measurand, $\boldsymbol{x_{true}}$) and $\boldsymbol{\sigma_p}$ is the fitness-for-purpose-based "standard deviation for proficiency assessment", which has been established by covering an interval wide enough to include the possible uncertainties or trends in the results from expert-laboratories.

The interpretation of z-scores is founded in an assumed model based on the fitness-for-purpose criterion (represented by $\boldsymbol{\sigma_p}$): a normal distribution $\boldsymbol{x} \sim N(\boldsymbol{x_{true}}, \boldsymbol{\sigma_p}^2)$, the Protocol recommends the following classification of proficiency:

— SATISFACTORY: $|\mathbf{z}| \leq 2$
— ACCEPTABLE[1] : $2 < |\mathbf{z}| < 3$
— UNSATISFACTORY : $|\mathbf{z}| \geq 3$

Since the frequency distribution of the scores (apart from outliers) in the exercise, was found to be alike normal, the assessment of proficiency has been carried out in agreement to this criterion.

3. RESULTS AND DISCUSSION

The global results of the exercise are presented in Table 1, the number of participants/analysis, the proficiency score and the comparison of the assigned value (AV) to the participants' median (ML). A good agreement is evidenced; the cases of raised difference have been evaluated with the ML (highlighted in the Table). Some laboratories informed more than one result by analysis (i.e. different method or type of detector, analyst, etc.), each result has been considered independent for the participants' total account in the evaluation.

TABLE 1. GLOBAL RESULTS OF THE EXERCISE, HIGHLIGHTED ROWS ARE ANALYSIS ASSESSED BY THE ML

Analysis	Number of participants	Proficiency classification			AV (Bq/kg_{dry})	ML (Bq/kg_{dry})	% Diff ML-AV
		S	A	U			
U-238	21	21	0	0	55	55.4	0.7
Th-234	25	20	1	4	49	55.6	13.5
U-234	21	21	0	0	56	56.5	0.9
Th-230	18	18	0	0	332	386	16.4
Ra-226	33	30	3	0	573	594	3.6
Pb-214	36	33	2	1	519	563	8.5
Bi-214	34	31	2	1	511	530	3.6
Pb-210	31	29	1	1	783	734	-6.3
Po-210	15	14	0	1	678	748	10.3
Th-232	18	15	2	1	6.1	5.6	-7.7
U-235	28	19	0	9	2.3	2.5	9.3
gross α	17	15	1	1		2887	
gross β	18	14	1	3		1635	

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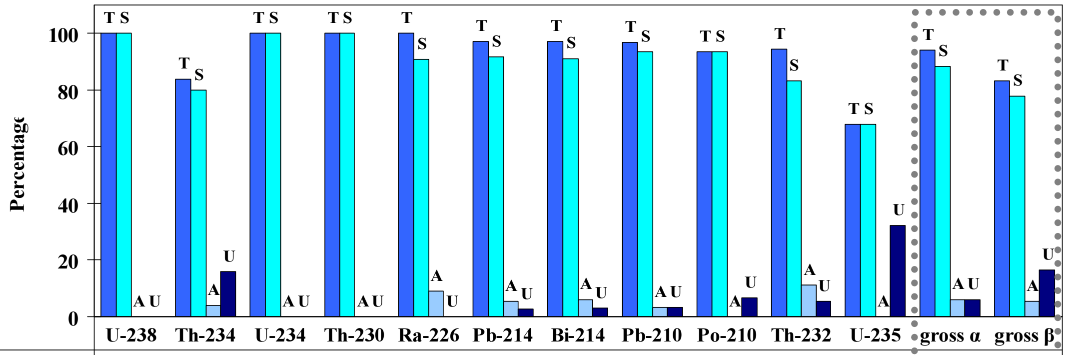
[1] - The recommendation of the Protocol to designate the interval, $2 < |\mathbf{z}| < 3$, is: *"... Scores in this class are sometimes designated "questionable"....*", but the authors would consider ACCEPTABLE, as a more suitable expression for designating the proficiency in this interval.

Figure 1 shows the percent of laboratories being classified as satisfactory, acceptable or unsatisfactory by radionuclide/analysis; the analytical proficiency was found to be Satisfactory in most analyses, ranging from 68 (U-235) to 100 %.



	U-238	Th-234	U-234	Th-230	Ra-226	Pb-214	Bi-214	Pb-210	Po-210	Th-232	U-235	gross α	gross β
🟦 Total (S+A)	100	84	100	100	100	97	97	97	93	94	68	94	83
🟦 Satisfactory	100	80	100	100	91	92	91	94	93	83	68	88	78
🟦 Acceptable	0	4	0	0	9	6	6	3	0	11	0	6	6
■ Unsatisfactory	0	16	0	0	0	3	3	3	7	6	32	6	17

Figure 1. Percentage of laboratory performance by analysis (gross alpha and beta evaluated by ML)

Results from the three first elements of the U-238 series, appeared 100% Satisfactory, except for Th-234 (68% assessed by z-score), whilst by using the ML the percentage raises up to 80%. The theoretical situation of equilibrium for these three nuclides, seems to be better represented in the laboratories' ML, that in those of the experts (obtained from only 2 laboratories).

Regarding the rest of the analyses, a high level of satisfactory performance has been estimated, still some practical difficulties have been found:

Ra-226. From 33 informed results, the majority 27 were quantified by gamma spectrometry and the 6 remaining by radiochemistry. Figure 2., presents the results grouped by methods:

- 15 laboratories measured directly the gamma emission of the Ra-226 by solving the multiplet (EGRaU), show a symmetrical distribution,
- 12 laboratories, measured the emission of its descendants Pb-214 and Bi-214 at the secular equilibrium Ra-226/Rn-222 (EQBi/Pb), from which, 6 combined the activities of both nuclides, 3 informed the activity through the emission of the Bi-214 and the other 3 informed by the Pb-214 gamma emission. The results in this group are slightly biased below the AV and ML.
- the 6 radiochemical determinations (SR) show a trend to inform values above AV and ML

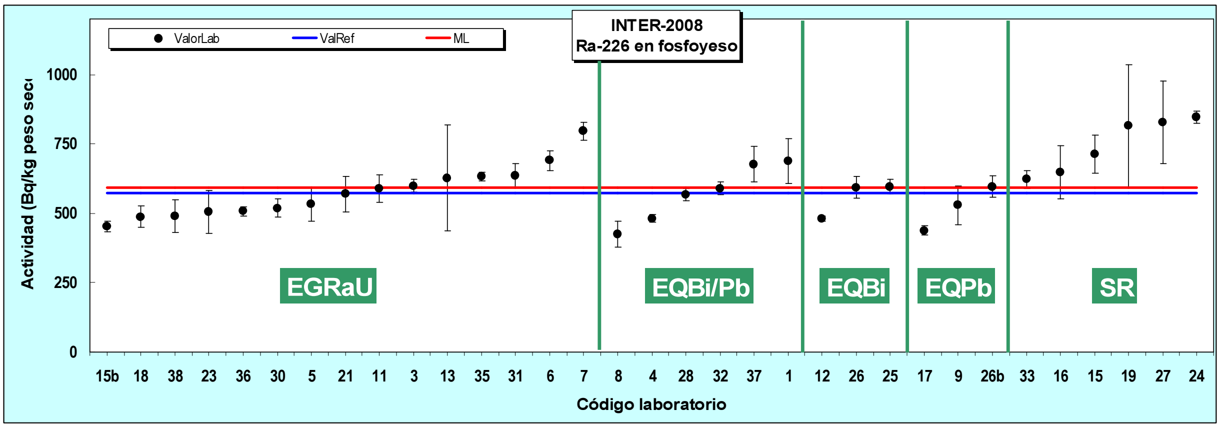


Figure 2. Results from Ra-226 grouped by method.

U-235. 28 results were informed, from which 19 were determined by radiochemistry (only two behaved unsatisfactory) and 9 by gamma spectrometry, being classified as satisfactory 2 values, 4 as unsatisfactory (z> 3) and 3 results were informed as limit of detection (see Figure 2.).

Certainly, the determination of U-235 by radiochemistry provides better quality of results than the measurement by gamma spectrometry. There is an increased uncertainty at the "troubled zone" (combination of numerous peaks from natural series), producing in most cases an unsatisfactory result, or else the impossibility of detection/quantification of the nuclide at environmental activity levels (as it is the case of the test sample). Regardless, two laboratories behaved satisfactory by gamma spectrometry.

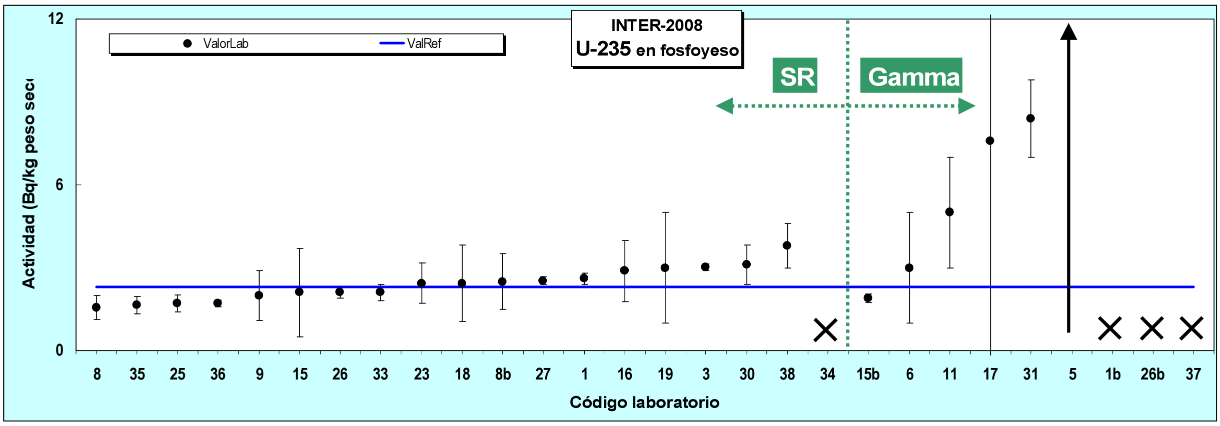


Figure 3. Results from U-235 grouped by method

The exercise has shown a homogeneous behaviour of laboratories, being statistical parameters from the results close to the assigned values; the established σ_p were compared to the calculated laboratories' RSD, being remarkably always been found coincident.

A raised percentage of satisfactory laboratory performance, ranging from 100 % for the determination of U-238, U-234 and Th-230, to 68 % for the determination of U-235 (due to the high uncertainty in the gamma "troubled zone"). Nevertheless, in this zone Ra-226 has the highest probability gamma emission being the proficiency of the laboratories 100 % satisfactory. This point to the experience acquired over the years by participant laboratories in the determination of this nuclide (since it is a "common- nuclide" in the exercises organized by the CSN).

The study has shown that participant laboratories perform natural radionuclides determinations in phosphogypsum samples (NORM) with satisfactory quality levels. Finally the scheme has also allowed examining the capability of laboratories to determine the activities of natural radionuclides at the equilibrium.

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RADIOACTIVITY IN ARC WELDING WITH CONSUMABLE ELECTRODES

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Abstract

Arc welding is one of several fusion processes for joining metals but perhaps is the most widely used. The processes produce smoke containing particles of various types of oxides. The particles tend to influence the toxicity of the fumes, with smaller particles presenting the greater danger. In particular ^{238}U, ^{232}Th, ^{210}and ^{210}Po are present in many materials used in the manufacture of the electrodes and consequently evaporate in the welding process being a potential danger for the user.

1. INTRODUCTION

Arc welding with consumable electrodes is perhaps the most popular and widely used method to weld metals. The idea is to create an electric arc between an electrode and the base material to melt the metals at the welding point. The current can be either direct or alternating with a potential of no more than 70-80 Volts and intensities up to 200 Amps.Two methods are widely used: single electrodes covered with a flux and a flux cored tubular wire. Millions of electrodes and kilometres of tubular wire are used daily by workers in a wide variety of industries. In Spain about three million electrodes are used daily together with several kilometres of tubular wire.

One of the most common types of arc welding is the so called shielded metal arc welding (SMAW), which is also known as manual metal arc welding (MMA) or stick welding. The electrodes are rods that consist of a core wire of low carbon steel and a flux covering. The electrode rod is made of a material that is compatible with the base material being welded and the covering flux protects the weld area from oxidation and contamination. The electrode core itself acts as filler material, making separated filler unnecessary. The process is very versatile, requiring little operator training and inexpensive equipment, but is slow because the electrodes must be frequently replaced and the residue from the flux must be chipped away after welding.

The electrode in the so called flux cored arc welding (FCAW) is actually a fine metal tube filled with powdered flux materials. Flux cored electrodes are manufactured from a flat metal strip that is passed through a mill where forming rolls progressively shape it into a U-shaped section. The flux is added and then passes through the closing rolls, forming the strip into a tube and tightly compressing the core material. Flux cored tubular wire generates an effective gas shield precisely at the weld site. The system is more expensive than the rods and requires more expensive equipment and trained personnel, but is much faster and can be used in a semi-automatically form.

In the manufacture of the cover of the electrodes and in the flux in the tubular wire a variety of many NORM materials are used, some of them with substantial amount of Uranium, Thorium, Potassium and their descendants. The welding process evaporates almost all the cover of the electrodes and the whole flux core of the tubular wire producing smoke containing particles of various types of oxides. The size of the particles has an influence in the radio-toxicity of the smoke, being the smaller the most dangerous. Welders are exposed to these potentially dangerous gases because they don't use any special protection to prevent the inhalation. These gases could be dangerous if ventilation is inadequate. Only an eye protection is commonly used.

There are thousands of different electrodes; each manufacturer has its own specific type with a well kept mixture of materials. Within a project to study the radiological implications of these welding systems we have studied the prime materials used in the manufacture of electrodes and wires. To start, we have analyzed 63 prime materials used by the manufacturers for the flux of the cover of the electrodes and the core of the tubular wires.

2. RESULTS

We have analyzed first of all, by gamma spectroscopy, different coated electrodes. In Figures 1 and 2 we present the gamma spectra of the flux of the cover of two electrodes that show the presence of radioisotopes from the natural chains of ^{238}U, ^{232}Th and from ^{40}K.

The gamma spectrometry has been performed on a low background extended range Canberra Germanium detector with 43,7% efficiency and 1,77 keV resolution (FWHM 1332 keV).

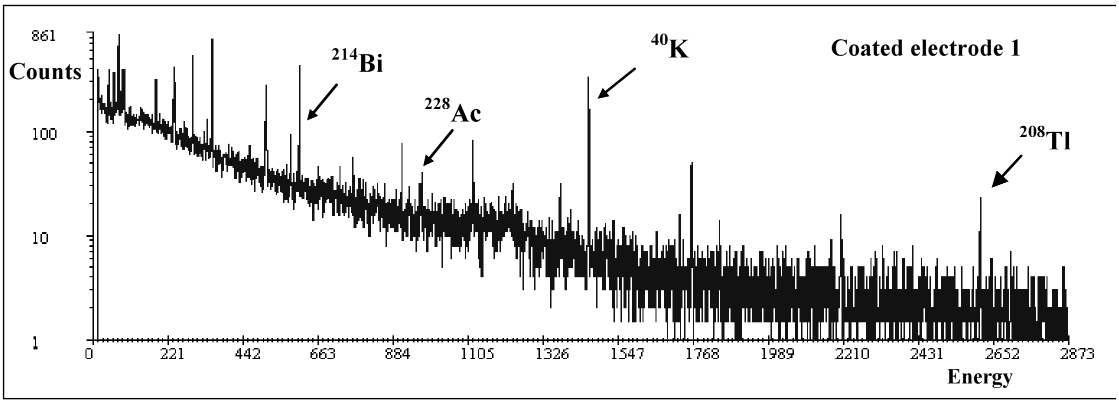

Fig 1: Gamma spectra of covering flux of a coated electrode.

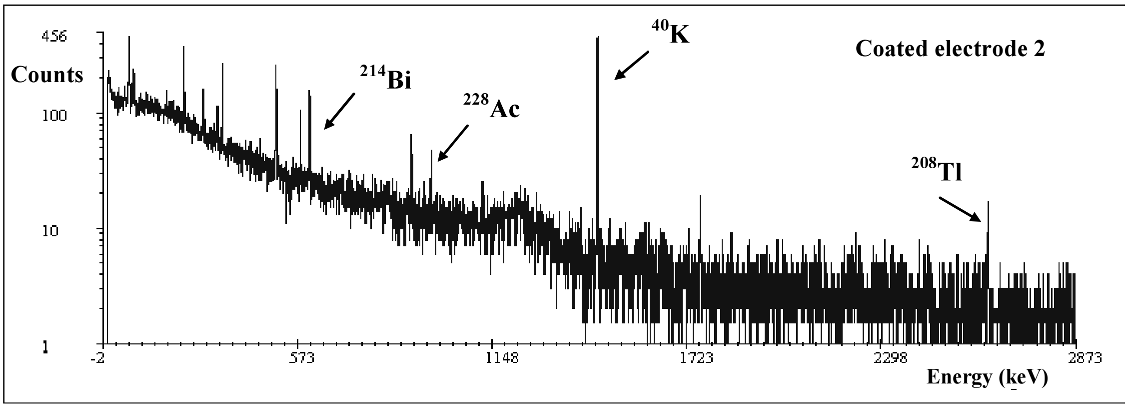

Fig 2: Gamma spectra of covering flux of a coated electrode.

As a result of these analyses we decided to collect prime materials used in the manufacture of the electrodes. Samples were placed on Brand polypropylene boxes of 7,3 cm diameter, 120 ml. capacity.

We have detected considerable activity in 38 of the 63 analyzed materials. The results for four gamma emitter isotopes representatives of the family chains of ^{238}U and ^{232}Th as well as the activity of ^{40}K are shown in Table I. For instance activities in ^{226}Ra are ranging from 2,08 ± 1,6 Bq/kg (k=2) for Chrome powder up to 5.182 ± 44,84 Bq/kg (k=2) in Zirconium silicate. Note that the most used material, Rutile has an ^{210}Pb activity around 183,50 ± 8,85 Bq/kg (k=2) for the Australian Rutile and 97,95 ± 6,72 Bq/kg (k=2) for the African one. Activities for ^{40}K varies between 6,64 ± 2,15 Bq/kg in Oligiste to 3.849 ± 69,10 Bq/kg in Potassium Titanate.

TABLE I. ACTIVITY IN Bq/Kg OF ^{226}Ra, ^{208}Tl, ^{228}Ac, ^{210}Pb AND ^{40}K FOR 38 OF THE PRIME MATERIALS ANALYZED BY GAMMA SPECTROSCOPY

Prime material	**Activity ^{226}Ra (Bq/kg)**	**Activity ^{208}Tl (Bq/Kg)**	**Activity ^{228}Ac (Bq/Kg)**	**Activity ^{210}Pb (Bq/Kg)**	**Activity ^{40}K (Bq/Kg)**
Alumine	11,53				
Aluminium	10,25	0,38		10,06	
Arabic gum					79,15
Barium Carbonate	19,22	1,17	2,80	17,30	
Bentonite	304,2	50,88	159,20	160,30	145,20
Calcium carbonate	11,94			8,11	7,92
Chrome	2,08			1,37	2,74
Coconut Flour					51,02
Dolomite	22,17		2,21	10,40	
Ferric Oxide	303,2	2,60	9,22	106,80	197,30
Ferrosilicium	7,57	1,54			
Ferrous carbonate	22,09	0,97	3,08		60,67
Fluorine Espate	5,33	1,38	3,52	3,52	14,99

TABLE I. ACTIVITY IN Bq/Kg OF ^{226}Ra, ^{208}Tl, ^{228}Ac, ^{210}Pb AND ^{40}K FOR 38 OF THE PRIME MATERIALS ANALYZED BY GAMMA SPECTROSCOPY (cont.)

Prime material	**Activity ^{226}Ra (Bq/kg)**	**Activity ^{208}Tl (Bq/Kg)**	**Activity ^{228}Ac (Bq/Kg)**	**Activity ^{210}Pb (Bq/Kg)**	**Activity ^{40}K (Bq/Kg)**
Graphite	24,13	1,35		16,06	18,34
Ilmenite	116,20	46,61	140,10	20,51	
Kaolín	65,22	12,12	27,80	37,24	211,60
Mica I	131,60	10,10	30,89	95,80	1.463,00
Mica II	61,25	3,66	10,32	44,42	2.630,00
Mica III	61,24	3,80	11,67	29,35	2.805,00
Nefelite Sienite		1,70	2,37	3,11	1.343,00
Nickel Oxide	30,89	0,58	1,2	1,11	
Oligist	31,99	0,63	1,70	4,63	6,64
Phonolite	131,6	5,58	16,05	136,90	2.004,00
Potassium feldespate	11,90	1,94	6,89	3,95	2.815,00
Potassium carbonate					15.920,00
Potassium Feldespate	79,15	4,90	14,05	39,99	1.180,00
Potassium Titanate	772,20	32,85	87,92	296,90	3.849,00
Rutile(ground)	797,70	46,05	132,80	196,40	40,01
Rutile (Africano)	482,70	35,54	105,05	97,95	
Rutile (Australian)	884,70	8,57	24,39	183,50	
Silica	20,16	3,26	9,51	14,31	21,41
Silica (Neubourg)	24,36	7,81	21,28	17,73	87,85
Silicium carbure	6,51	1,45	2,14	2,05	
Talc	112,30	9,66	26,78	70,68	
Titanium Dióxide	12,39			10,88	81,36
Wollastonite	26,56	0,53		15,26	22,72
Zink.Fritte	26,21	3,62	10,53	18,50	1.261,00
Zirconium Silicate	5.182	247,76	730,3	296,40	

To check the ^{232}Th presence we have measured the activities of ^{208}Tl and ^{228}Ac, and for the family of ^{238}U the presence of ^{226}Ra has been checked. The natural isotope ^{40}K has been detected in 27 prime materials with activities ranging from 6,64 Bq/kg in Oligiste to 15.920 Bq/kg in Potassium carbonate..

In principle the ^{238}U and ^{232}Th families should be in radioactive equilibrium but in order to check this we have analyzed by alpha spectrometry ^{210}Po in two widely used coating materials, Zirconium Silicate and Rutile (Australian). Alpha spectrometry has been performed in Alpha PIPS detectors with 450 mm2 of active area and10 keV resolution (FWHM 5.486 keV).

The results for ^{210}Po are:

- Zirconium Silicate Activity A = 92,74 ± 4,00 Bq/kg (k=2), MDA= 0,70 Bq/kg.
- Rutile (Australian) Activity A = 8,62 ± 1,26 Bq/kg (k=2), MDA= 0,73 Bq/kg.

The apparent discrepancy between ^{210}Pb and ^{210}Po could be due to an evaporation of ^{210}Po from the prime material in the sample preparation for alpha spectrometry.

3. CONCLUSIONS

Gamma spectra of coated electrodes and core of the tubular wires used in arc welding show the presence of radioisotopes from the natural chains of ^{238}U, ^{232}Th as well as ^{40}K. We have analyzed by gamma spectroscopy the radioactive content of 63 ingredients used in the manufacture of the electrodes, most of them are NORM materials. Almost all the coating for the rods and the entire core in the tubular wire is evaporated in the welding process and usually the operators do not have any special protection. Our results point the possibility that the inhalation of gases in real situations could be a radiological risk for the workers. Measurements in real cases with different electrodes and welding installations in order to evaluate its possible consequences for the operators and public in the surroundings are on the way.

ACKNOWLEDGEMENTS

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There is not available literature on the radioactivity in arc welding with consumable electrodes or in the prime materials used in the flux. For the general characteristics of Arc Welding and electrodes there are many books and web pages.

ENVIRONMENTAL HAZARD ASSESSMENT OF PHOSPHOGYPSUM WASTE STOCKPILE MATERIAL FROM JORDAN

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Abstract

Phosphogypsum (PG) is a by-product of the chemical reaction called the "wet process" whereby sulphuric acid is reacted with phosphate rock (PR) to produce phosphoric acid, needed for fertilizer production. Through the wet process, some impurities naturally present in the PR become incorporated in PG, including U decay-series radionuclides are the main important concern which could have an effect on the surrounding environment and prevent its safe utilization. In order to determine the distribution and bioavailability of radionuclides to the surrounding environment we used a sequential leaching of PG samples from Aqaba and Eshidiya Fertilizer industry. The results show that ^{226}Ra and ^{210}Pb radionuclides fractionate likely in PG, where percentages in the corresponding to PR of 85% of the ^{226}Ra and 85% of the ^{210}Pb were presented. The sequential extraction results exhibit that most of ^{226}Ra and ^{210}Pb are bound in the residual phase (non-CaSO4) fraction ranging from (45-65% and 55-75%) respectively, whereas only 10-15% and 10-20% respectively of these radionuclides are distributed in the most labile fraction. The results obtained from this study that radionuclides are not incorporated with gypsum itself and may not form a threat to the surrounding environment.

1. OBJECTIVES

(1) to measure the activity concentrations of ^{226}Ra, ^{210}Pb and the uranium and thorium isotopes in Jordan PG and the ore rocks from which it is derived;
(2) to determine the fractionation between these radionuclides during processing of the ores; and
(3) to evaluate the availability of radionuclides (^{226}Ra and ^{210}Pb), rare earth elements Ba and Sr to the surrounding environment of the stacks.

2. MATERIAL AND METHODS

2.1. Sampling

Forty eight PG samples were collected from Aqaba and Eshidiya facilities. The samples were selected from 12 sites corresponding to piles of different ages depending on their formation;

20 kg from each site were collected. All samples were dried, homogenized, sieved and ground into three particle size ranges: Course > 32 #; Medium – 32 # + 270; and Fine – 270 #.

2.2. Experiments

A **Partial Extraction**: 50 mg of each dried sample was put in a 15-ml centrifuge tube—5 ml of nitric and hydrochloric acids were added. The tube was shaken and left for 24 hours. Afterward, the tube was shaken and left an additional 24 hours. The supernatant solutions were then prepared for chemical analysis by ICP-AES. X-ray diffraction analysis was also performed on composite samples to determine the mineral compositions of PG. In addition, SEM was also used to identify the texture and structure as well as simultaneous elemental analysis maps.

B **Total Extraction**: 0.2 g of composite samples were put in teflon beakers—3 ml HCl, 2 ml HNO_3, 1 mL $HCLO_4$ and 2 ml HF were added. Samples were dried on a hotplate overnight. 1 ml $HCLO_4$ was then added and allowed to dry. The dried samples were removed from the hotplate and cooled, 1 ml Aqua Regia was then added. A pre-set volume of 1% HNO_3 was added to each beaker. The solutions were analyzed for U and trace metals by ICP-MS.

C **The sequential extractions** performed in this study; similar undertaken by Burnett et al. (1999). The following sequence for analysis of radionuclides and heavy metals released from PG fraction was followed: Double Deionized Water (DDW), (2) Exchangeable 16 mL of 1 M $MgCl_2$ for 1 h (3) Carbonates16 mL of 1 M NaOAC/HOAC adjusted to pH 5.0 for 1 h, (4) Oxides and hydroxides 40 mL of 0.04 M ($NH_2OH.HCl$) in 25% acetic acid at 96±3 0C, (5) Organic matter (a) 6 mL of 0.02 M HNO_3 and 10 mL of 30% H_2O_2 adjust to pH 2 at 85±2 0C for 2 h (b) 6 mL of 30% H_2O_2 at pH 2 at 85±2 0C for 3 h, (6) Residual 5:1 mixture of HNO_3 and HF; and then dissolve with 12 M HCl sequentially

D Activity concentrations of radionuclides were measured in 10 each samples of ground composite phosphogypsum by γ-spectromentry at USGS, Denver, USA. About 20 g all samples were packaged in clear acrylic petri dishes (8.5 cm diameter X 3.8 cm high). The dishes were sealed with black electrical tape to inhibit loss of radon gas, and stored for three weeks to establish radioactive equilibrium between ^{226}Ra and its relatively short-lived daughters (^{222}Rn, ^{218}Po, ^{214}Pb, ^{214}Bi, ^{214}Po) within the ^{238}U decay series

3. CONCLUSIONS

The activity concentrations of the radionuclides in the U-decay series, including ^{226}Ra and ^{210}Pb, and the uranium and thorium isotopes, were determined in Aqaba and Eshidiya PG and the ore PRs from which it is derived. The results show that ^{226}Ra and ^{210}Pb fractionate preferentially to the PG, where percentages (to ore PRs) of 85% for ^{226}Ra, 85% for ^{210}Pb were presented. The distribution of thorium isotopes and uranium isotopes are predominantly incorporated in phosphoric acid as uranyl phosphate, sulphate or fluoride complexes. The activity concentration ranges for ^{226}Ra (12 to 16 pCi/g and 14 to 22 pCi/g) and ^{210}Pb (11 to 15 pCi/g and 15 to 22 pCi/g) in Aqaba PG and Eshidiya PG respectively are in good agreement with results found in the literature for PG from other locations.

Most ^{226}Ra and ^{210}Pb are found in the residual phase (non-$CaSO_4$) fraction ranging from (45-65% and 55-75%) respectively, and that only 10-15% and 10-20% respectively of these radionuclides are variable distributed in the iron oxide, ion exchangeable, organic matter and carbonate fractions

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MONITORING ANTHROPOGENIC AIRBORNE NATURAL RADIONUCLIDES IN THE VICINITY OF A TENORM INDUSTRY USING LICHEN AS BIO-INDICATOR

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Abstract

This paper aims to study the viability of using lichen species from the family *Parmeliaceae* as bio-indicator of air pollution by natural radionuclides of the U and Th series (^{238}U, ^{226}Ra, ^{210}Pb, ^{232}Th and ^{228}Ra) in the surroundings of a tin and lead industry. The raw material used is the cassiterite, which presents in its composition concentrations of U and Th up to 60 kBq kg^{-1}. The radionuclides ^{226}Ra, ^{228}Ra and ^{210}Pb were determined by radiochemical separation followed by gross alpha and beta counting using a gas flow proportional counter. Uranium and thorium were determined by instrumental neutron activation analysis. Concentration values obtained for lichen samples varied from 19 Bq kg^{-1} to 473 Bq kg^{-1} for ^{238}U, 21 Bq kg^{-1} to 265 Bq kg^{-1} for ^{226}Ra, 401 Bq kg^{-1} to 1083 Bq kg^{-1} for ^{210}Pb, 16 Bq kg^{-1} to 574 Bq kg^{-1} for ^{232}Th, from 175 Bq kg^{-1} to 389 Bq kg^{-1} for ^{228}Ra; therefore, they can be used as a fingerprint of contamination by the operation of a TENORM industry.

1. INTRODUCTION

It is well known that the operation of TENORM (Technologically Enhanced Naturally Occurring Radioactive Material) industries may affect the surrounding environment. The amount of natural radionuclides discharged to the atmosphere from a TENORM industry depends on a number of factors such as the composition of the raw material and final residue formed and the chemical process involved. The tin industry is a typical example of a TENORM industry, since the high temperatures used in the smelting and refining processes may lead to concentrations of natural radionuclides, mainly in the precipitated dust and in slag, which are stored in piles in open air. Lead-210 can also be released to the atmosphere during the combustion, depending on the efficiency of the emission control devices. All the process can increase the doses to such an extent that radiation measures may be needed to protect workers and members of the public.

The most important Brazilian company that produces tin and metallic lead is located in the city of Pirapora do Bom Jesus, in the state of São Paulo. This industry is responsible for the production of about 7,500 ton year^{-1} of tin and 120 ton year^{-1} of lead. The raw material used in this facility is the cassiterite (SnO_2), which is found together with other ores such as cryolite (Na_3AlF_6), niobium minerals (Nb_2O_5) and tantalum (Ta_2O_5) [1], [2]. It comes from a mine located in Pitinga, Amazon, where the rock is concentrated (55%). The concentrate presents in its composition concentrations of U and Th up to 60 kBq kg^{-1} [3].

Although in the raw material the radionuclides from the uranium and thorium series are almost in equilibrium, during the processing this equilibrium is disrupted and the radionuclides migrate according to their chemical properties. The high temperatures used in the melting and refining of tin may increase the levels of these radionuclides, mainly in the final slag, which is stored in open air and in the emission from the stacks. The amount of residue stored is about 54,000 tons per year. Since this facility has been in operation for more than 20 years, it is expected an environmental impact due to re-suspension of the residue, atmospheric dispersion and deposition in the soil; and due to the emission of gaseous and particulate effluents from the stacks. The approximate height of the stacks is 10m.

The environmental atmospheric impact of such facilities can be monitored by using lichen as bio-indicator. The lichen species chosen in this study is from the family *Parmeliaceae*, which is foliose lichen, with large thallus (5 to 20 cm in diameter) and radial growth, found on tree trunks or even on rocks, in several regions in Brazil [4]. The central part of this species is the oldest and it is the part that was exposed to the pollutant for a long period of time. The dust particles that penetrate in lichens thallus accumulate in their intercellular space, due to their mechanism of obtain nutrients for growth and metabolism from wet and dry precipitates [5], [6].

There are few data in the literature concerning the use of this lichen for the air quality evaluation in urban regions in Brazil [7], [8], [9], however none of them is related with atmospheric pollution from natural radionuclides. The main objective of this paper is to study the viability of using lichen species from the family *Parmeliaceae* as bio-indicator of atmospheric pollution by natural radionuclides of the U and Th series (^{238}U, ^{226}Ra, ^{210}Pb, ^{232}Th and ^{228}Ra). The radionuclides ^{226}Ra, ^{228}Ra and ^{210}Pb were determined by radiochemical separation followed by gross alpha and beta counting using a gas flow proportional counter. Uranium and thorium were determined by instrumental neutron activation analysis.

2. MATERIALS AND METHODS

2.1 Sampling

The lichen samples were collected in the tree barks, at about 1.5 m from the ground level. The samples were removed using a plastic knife and stored in paper bags. In the laboratory the lichens were cleaned using distilled water to remove dust and the unwanted materials such as barks and insects were separated manually. The samples were then dried at 60^{o}C and pulverized in a glass mortar. Nine lichen samples were collected in the sites depicted in Fig. 1, at distances from 480 m to 1 830 m from the facility, at altitudes ranging from 700m to 760m. The installation is located at an altitude of 760m.The prevailing wind directions in this area are South Southeast (34%), Southeast (20%) and Northeast (10%).

A one meter long soil core was collected in sampling point 2, which was considered impacted. The core was sliced each two centimeter and the samples were dried at room temperature and sieved.

2.2 Determination of ^{226}Ra, ^{228}Ra and ^{210}Pb in soil samples by gamma spectrometry

The concentration of the natural radionuclides ^{226}Ra, ^{228}Ra and ^{210}Pb in the soil samples were carried out by non-destructive gamma-ray spectrometry. Soil samples were packed in 100 ml PVC cylindrical containers and they were kept sealed for 30 days in order to reach radioactive equilibrium between ^{226}Ra and ^{222}Rn and their progenies. A coaxial Be-layer HPGe detector with 25% relative efficiency, 2.09 keV resolution at 1.33 MeV and associated electronic devices were used, with live counting time of 80 000 s. The activity concentration of ^{210}Pb in the samples was corrected for self absorption [10]. The detector was calibrated using the Standard Reference Material IAEA 300 - Baltic Sea Sediment.

Figure 1. Map of industrial area with sampling sites, stacks and wind prevailing direction

2.3 Determination of ^{226}Ra, ^{228}Ra and ^{210}Pb in lichen samples by radiochemical separation

500 mg of lichen, in duplicate samples, were dissolved in mineral acids in a microwave digestor and submitted to a sequential radiochemical procedure for ^{226}Ra, ^{228}Ra and ^{210}Pb determination. The procedure consists in an initial precipitation of Ra and Pb with 3M H_2SO_4, dissolution of the precipitate with nitrilo-tri-acetic acid at basic pH, precipitation of $Ba(Ra)SO_4$ with ammonium sulphate and precipitation of $^{210}PbCrO_4$ with 30% sodium chromate. The ^{226}Ra and ^{228}Ra concentrations were determined by measuring the gross alpha and beta activity of the precipitate $Ba(Ra)SO_4$ and the concentration of ^{210}Pb was determined through its decay product ^{210}Bi, by measuring the gross beta activity of the precipitate of $^{210}PbCrO_4$. Both radionuclides were measured in a low background gas flow proportional detector for 200 minutes. The activity concentration of ^{226}Ra and ^{228}Ra were measured after 21 days of the radium precipitation and the concentration of ^{210}Pb after 10 days of the precipitation of Pb as chromate [11].

2.4 Determination of ^{238}U, ^{232}Th, Hf and Ta in lichen and soil samples by instrumental neutron activation analysis

Approximately 200 mg of lichen and 150 mg of soil (duplicate samples), and about 150 mg of reference materials were accurately weighed and sealed in pre-cleaned double polyethylene bags, for irradiation. The samples and reference materials were irradiated for 16 hours, under a thermal neutron flux of 10^{12} n cm^{-2} s^{-1} in the IEA R1 nuclear reactor at IPEN. Two series of counting were carried out: the first, after one week decay and the second, after 15 days. The counting time was 1.5 hours for each sample and reference material. Gamma spectrometry was performed using a coaxial Be-layer HPGe detector with 22% relative efficiency, resolution of 2.09 keV at 1.33 MeV and associated electronic devices. The accuracy and precision was performed by measuring the reference materials lichen IAEA-336, IAEA-Soil 7 and MAG from USGS.

3. RESULTS AND DISCUSSION

The results of measurements of radionuclides (Bq kg^{-1}) and the elements Ta and Hf (mg kg^{-1}) in the raw material, residue and lichen samples; and the distances from the sampling points to the installation are presented in Table 1. It can be seen that the elements Ta, Hf, and the radionuclides ^{238}U, ^{226}Ra, ^{232}Th and ^{228}Ra are enriched in the residue whereas ^{210}Pb is not, due to the industrial process. It should be emphasized that the piles stored at open air are not the only source of environmental pollution, since the atmospheric discharges from the stacks can also release particulates and gases such as radon, which decays to ^{210}Pb. The lichen samples collected in points 3, 4 and 7 presented the lower concentrations for all elements analyzed when compared with the other samples (Fig. 2).

The cluster analysis for the radionuclides concentration, Hf and Ta (Fig. 3) shows the separation of the lichen samples in two main groups: group A formed by lichen samples 3, 4 and 7 collected in distant points or not directly under the influence from the installation due to the local topography and considered as the *background* of the region; and group B collected more close to the installation in the prevailing wind directions, which can be considered as contaminated (points 1, 2, 5, 6, 8 and 9).

TABLE 1. CONCENTRATION OF Ta AND Hf (mg kg^{-1}) AND RADIONUCLIDES (Bq kg^{-1}) IN RAW MATERIAL (RM), RESIDUE (RS), LICHEN SAMPLES (LI) AND DISTANCES FROM TO INSTALLATION (m)

	(m)	**Hf**	**Ta**	**^{238}U**	**^{226}Ra**	**^{210}Pb**	**^{232}Th**	**^{228}Ra**
LI 5	740	$(5.3 \pm 0.5) .10^1$	$(7.9 \pm 0.8) .10^1$	$(4.7 \pm 0.7) .10^2$	$(2.7 \pm 0.1) .10^2$	$(1.1 \pm 0.1) .10^3$	$(5.7 \pm 0.6) .10^2$	$(3.1 \pm 0.1) .10^2$
LI 2	570	$(3.8 \pm 0.4) .10^1$	$(6.3 \pm 0.7) .10^1$	$(3.6 \pm 0.5) .10^2$	$(1.0 \pm 0.1) .10^2$	$(5.7 \pm 0.2) .10^2$	$(3.7 \pm 0.4) .10^2$	$(6.6 \pm 1.0) .10^2$
LI 8	470	$(3.7 \pm 0.4) .10^1$	$(5.2 \pm 0.5) .10^1$	$(2.9 \pm 0.4) .10^2$	$(1.2 \pm 0.1) .10^2$	$(5.2 \pm 0.6) .10^2$	$(3.3 \pm 0.4) .10^2$	$(3.8 \pm 0.1) .10^2$
LI 9	1250	$(2.9 \pm 0.2) .10^1$	$(3.7 \pm 0.5) .10^1$	$(3.4 \pm 0.8) .10^2$	$(1.3 \pm 0.2) .10^2$	$(7.1 \pm 0.4) .10^2$	$(3.1 \pm 0.2) .10^2$	$(5.3 \pm 0.1) .10^2$
LI 6	650	$(2.6 \pm 0.2) .10^1$	$(2.7 \pm 0.4) .10^1$	$(2.6 \pm 0.6) .10^2$	$(1.1 \pm 0.1) .10^2$	$(1.0 \pm 0.2) .10^3$	$(3.2 \pm 0.2) .10^2$	$(5.3 \pm 0.6) .10^2$
LI 1	480	$(2.0 \pm 0.2) .10^1$	$(2.8 \pm 0.4) .10^1$	$(2.6 \pm 0.6) .10^2$	$(7.1 \pm 0.9) .10^1$	$(7.8 \pm 2.0) .10^2$	$(2.4 \pm 0.2) .10^2$	$(5.3 \pm 0.4) .10^2$
LI 3	1010	$(1.7 \pm 0.2) .10^1$	$(2.5 \pm 0.3) .10^1$	$(1.6 \pm 0.2) .10^2$	$(5.3 \pm 0.3) .10^1$	$(9.9 \pm 0.7) .10^2$	$(1.6 \pm 0.2) .10^2$	$(2.4 \pm 0.2) .10^2$
LI 7	1450	5.4 ± 0.4	6.7 ± 0.9	$(6.4 \pm 0.2) .10^1$	$(5.0 \pm 1.3) .10^1$	$(5.8 \pm 0.6) .10^2$	$(6.1 \pm 0.5) .10^1$	$(4.1 \pm 0.3) .10^2$
LI 4	880	1.7 ± 0.1	2.5 ± 0.2	$(1.9 \pm 0.2) .10^1$	$(2.1 \pm 0.3) .10^1$	$(4.0 \pm 0.1) .10^2$	$(1.6 \pm 0.1) .10^1$	$(1.8 \pm 0.1) .10^2$
RM		$(6.4 \pm 0.3) .10^3$	$(3.4 \pm 0.6) .10^3$	$(2.3 \pm 0.7) .10^4$	$(2.9 \pm 0.1) .10^4$	$(3.9 \pm 0.2) .10^3$	$(5.0 \pm 0.4) .10^4$	$(5.3 \pm 0.2) .10^4$
RS		$(1.1 \pm 0.1) .10^4$	$(5.7 \pm 1.0) .10^4$	$(4.7 \pm 1.4) .10^4$	$(6.2 \pm 0.2) .10^4$	$(1.9 \pm 0.1) .10^3$	$(9.8 \pm 0.8) .10^4$	$(9.7 \pm 0.3) .10^4$

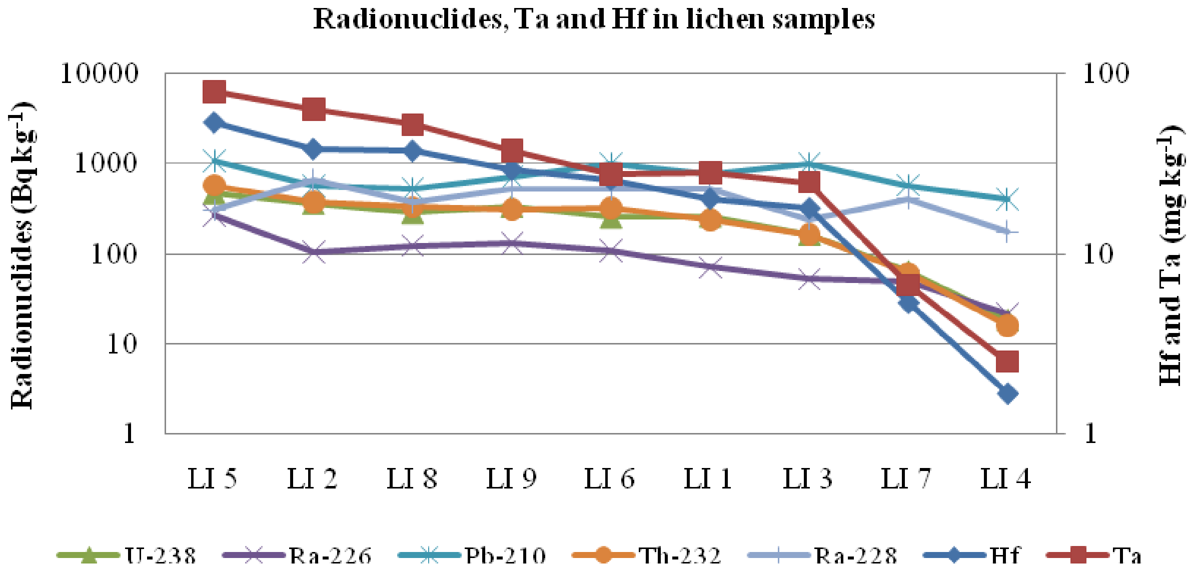

Figure 2 – Concentration of Hf, Ta and radionuclides (^{238}U, ^{226}Ra, ^{210}Pb, ^{232}Th and ^{228}Ra) in lichen samples as a function of the sampling points

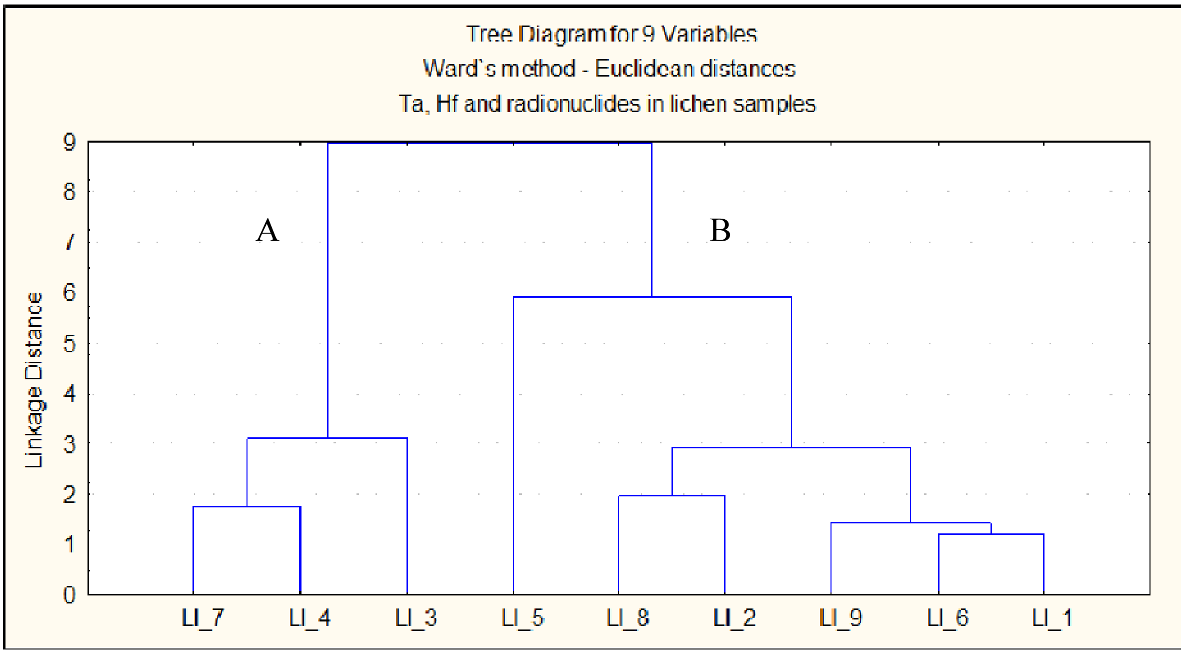

Figure 3 – Dendrogram of concentration of Hf, Ta and radionuclides (^{238}U, ^{226}Ra, ^{210}Pb, ^{232}Th and ^{228}Ra) in lichen samples as a function of the sampling points

Figure 4 presents the results obtained for the elements Hf and Ta in mg kg^{-1} and the radionuclides ^{238}U, ^{226}Ra, ^{210}Pb, ^{232}Th and ^{228}Ra in Bq kg^{-1} in the soil profile collected in point 2. It can be observed that the elements and the radionuclides concentrations decrease with depth giving evidence of anthropogenic contribution from the installation. After 18 cm, the concentrations can be considered as the base line.

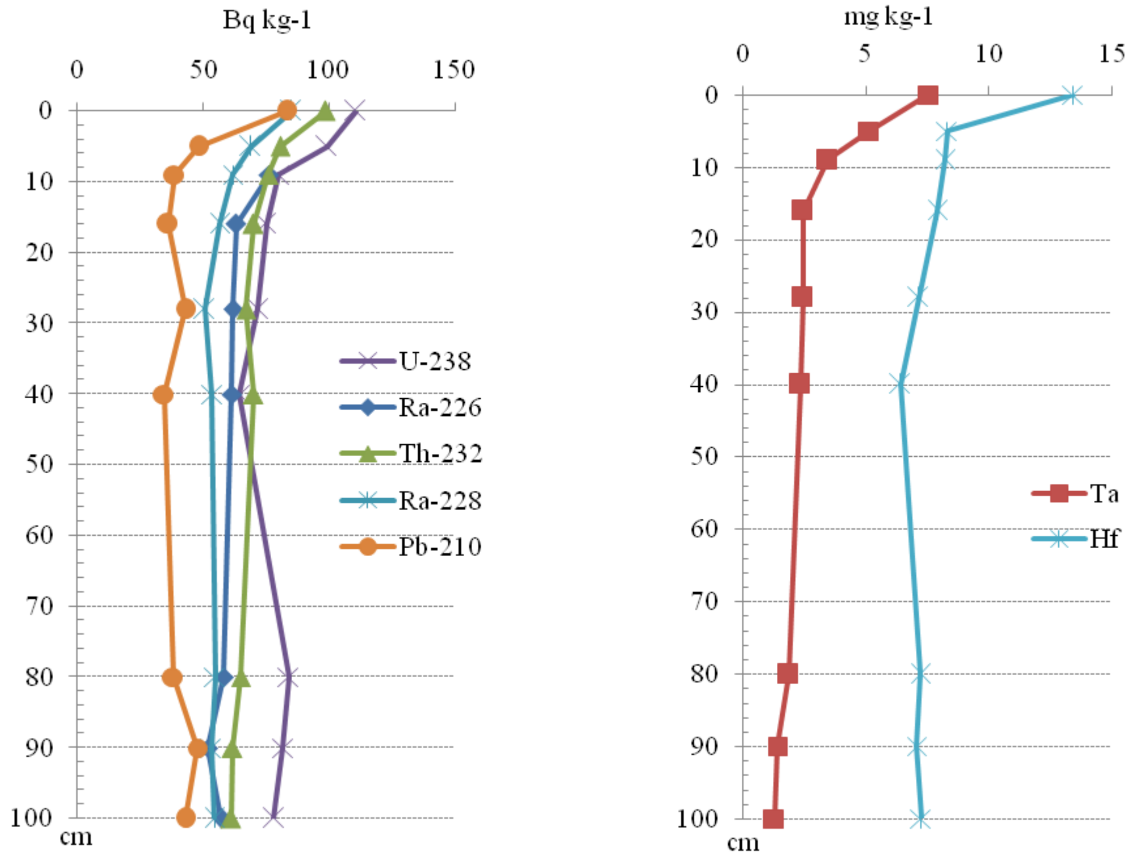

Figure 4 – Concentration of Hf, Ta and radionuclides (^{238}U, ^{226}Ra, ^{210}Pb, ^{232}Th and ^{228}Ra) in the soil profile collected in point 2

4. CONCLUSION

The residue of the tin industry stored in open air and the emission from the smokestacks cause contamination of the surrounding environment. The lichen samples concentrate radionuclides, Hf and Ta and therefore they can be used as a fingerprint of contamination by the operation of the tin industry. It was observed that the lichens more exposed to atmospheric deposition presented higher accumulation of these elements.

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EQUIVALENT DOSES OF INDOOR RADON-222 IN SOME DWELLINGS AND ENCLOSED AREAS IN MOROCCO

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Abstract

In this work, some volumetric activities of indoor radon-222 in some dwellings and enclosed areas in Morocco have been measured and their effective equivalent dose have been calculated. The obtained results show that the effective equivalent dose measured in indoor dwellings are inferior to the admissible annual limit fixed by ICRP for population except in two towns situated in regions rich in phosphate deposits where the calculated doses are slightly higer. The results obtained for enclosed areas are inferior to the admissible annual limit fixed by ICRP for workers except in one cave at depth of –12 meters where the obtained value don't present any risk for workers health because workers pass only a few minutes by day in this cave. The risks related to the volumic activities of indoor radon could be avoided by simple precautions such the continuous ventilation.

1. INTRODUCTION

The principal source of exposure to radiation for public in built-up areas is known to be the inhalation of radon and its short-lived daughters. Most of this exposure occurs inside homes, where many hours are spent each day and where the volumic activity of radon is usually higher than outdoors.

The compelling effects of radon and its short-lived decay products spread slowly but surely through a wide range of biological problems encountered in such areas as the mortality rates and lung cancer in uranium mines, the results of experimental work with animals, and the discovery of unusually high levels of radon in the living environments of the general population.

The human environment is one in which ionizing radiations are present at all time and at all places on the earth from the deepest caves to the highest mountains and on into space. Radon and its decay products are present wherever radium and thorium exist in the earth or in any planetary material. In the terrestrial environment, the inhaled radon isotopes and their daughter products make up almost two-thirds of the total dose to living tissue. Attention is directed now to a more detailed description of radiations from natural radionuclides and their effects upon living tissues.

In this work, we report the results of experiments conducted to calibrate the used cellulose nitrate films LR-115 type II, the volumetric activities measured by means of theses films in some dwellings and enclosed work areas in Morocco and we give the calculate doses of these activities received by population exposed to the radon effects.

2. EXPERIMENTAL

The passive time–integrated method of using a solid state nuclear track detector (LR-115 type II) was employed. These films, cut in pieces of 3.4×2.5 cm^2, were placed in detector holders and enclosed in heat-scaled polyethylene bags. Calibration measurements were made giving a calibration factor of 0.58 tracks.cm^{-2}/kBq.h.m^{-3} at the reference “removed thickness” of 6 µm (1,2). After exposure, the films were chemically etched in sodium hydroxide (2.5N) at 60°C for 120 minutes. The tracks produced were counted with an optical microscope and the background was then subtracted. After normalizing the track density to a removed thickness of 6 µm, the number of tracks per cm^2 was correlated to the volumic activity of radon. Figure 1 show the relationships established between the volumic activity of ^{222}Rn and the density of counted tracks.

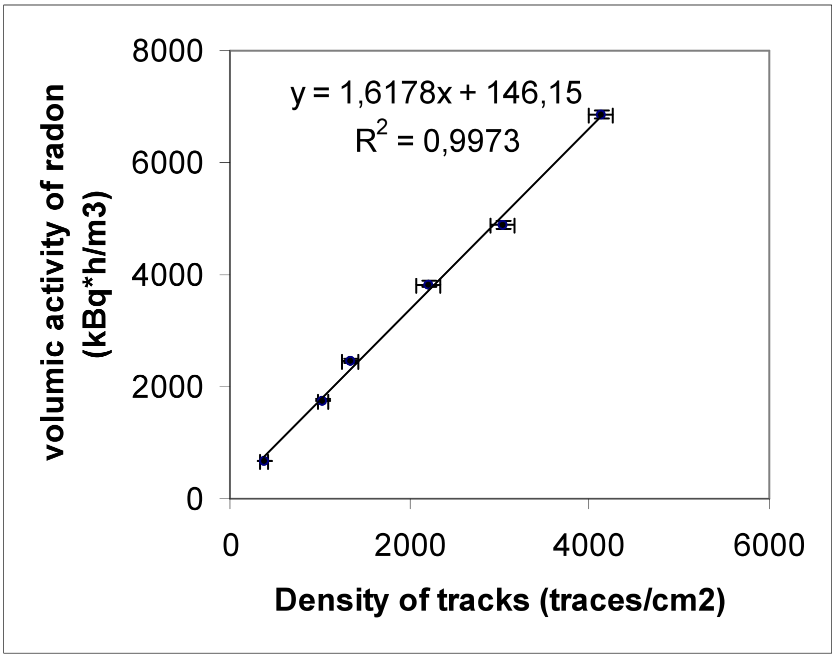

Figure 1: Calibration curve of cellulose nitrate films LR-115 type II

3. RESULTS AND DISCUSSION

The preliminary measurements were performed in 9 dwellings and 7 enclosed work areas in different regions of Morocco. Results for dwellings are given in table 1 and these for enclosed work areas are given in table 2. The exposure period of films in dwellings and in enclosed work areas varied between 2 and 4 months. The equivalent dose of ^{222}Rn volumic activity have been calculated using the conversion factor of 20 Bq/m^3 for 1 mSv/year (3).

TABLE 1: VOLUMETRIC ACTIVITIES OF ^{222}Rn AND EQUIVALENT OF ANNUAL DOSES IN INDOOR DWELLINGS

Town	Volumetric activity of ^{222}Rn (Bq/m^3)	Equivalent of annual dose (mSv/year)
Berchid		3.20 ± 0.25
Casablanca	31 ± 3	2.95 ± 0.3
El Jadida	47 ± 4	1.55 ± 0.15
Ouarzazate	99 ± 5	2.35 ± 0.2
Oujda	83 ± 7	3.80 ± 0.4
Rabat	64 ± 5	4.95 ± 0.25
Kénitra	59 ± 6	4.15 ± 0.35
Youssoufia	124 ± 8	6.20 ± 0.40
Khouribga	136 ± 9	6.80 ± 0.45

TABLE 2: VOLUMETRIC ACTIVITIES OF ^{222}Rn AND EQUIVALENT OF ANNUAL DOSES IN ENCLOSED WORK AREAS.

Enclosed work area	Volumetric activity (Bq/m^3)	Equivalent of annual dose (mSv/year)
Laboratory of nuclear physics (Rabat)		3.0 ± 0.2
Local for practical nuclear studies (Faculty of Sciences, Rabat)	68 ± 6	3.4 ± 0.3
Factory 1	435 ± 4	21.8 ± 1.4
Factory 2	142 ± 15	7.1 ± 0.8
Geophysical Observatory of Berchid (Ground level)	63 ± 5	3.1 ± 0.3
Geophysical Observatory of Berchid (Cave at –12 meters)	1541 ± 64	77.1 ± 3.2

Table 1 show the relatively higher volumic activities of ^{222}Rn in Youssoufia and Khouribga towns. The equivalent doses corresponding to these activities are slightly superior to the admissible annual limit fixed by ICRP for population (5 mSv/year). These values are obtained because Youssoufia and Khouribga are situated in regions rich in phosphate deposits. Measurements at the geophysical observatory of Berchid show that the volumic activity of radon increases with depth, this is most probably due to decreased ventilation. The reached value of above 77 mSv/year is higher than the admissible annual limit fixed by ICRP for workers (50 mSv/year). This value don't present any risk for workers health in the geophysical observatory of Berchid because workers pass only a few minutes by day in cave to control and reregister data.

Estimation of public exposure to radioactivity is not a precise process as there are a number of sources of uncertainty and variability in the radiation dose. Uncertainty reflects the current degree of knowledge and the level of accuracy in estimating doses. Variability relates to the differences in environmental transfers and people's habits, and variations in uptake between individuals. Estimated doses to members of the public from radioactive discharges are therefore subject to uncertainty and variability and may cover a significant range of possible values. Uncertainty in the assessed dose/ risk should also be communicated effectively and clearly to members of the public to enable them to make informed decisions about their exposure.

Most countries have their own systems of radiological protection which are generally based on the recommendations of the International Commission on Radiological Protection (ICRP).National radiation protection standards are based on ICRP recommendations for both Occupational and Public exposure categories.

Other measures not presented here (2,4,5) have confirmed the relationships between volumic activities of indoor radon and ventilation, depth and seasonal variations.

4. CONCLUSION

The obtained results show that the measured volumic activities of ^{222}Rn in some dwellings and enclosed areas in Morocco are comparable to those reported in previous works for different regions in the world (2). The calculated equivalent doses corresponding to these activities are slightly superior to the admissible annual limit fixed by ICRP for population (5 mSv/year) in regions rich in phosphates as Khouibga and Youssofia. We can not generalize the obtained results because of the limited analyzed samples number.

Measurements at the geophysical observatory of Berchid show that the volumetric activity of radon increases with depth, this is most probably due to decreased ventilation. The reached value of above 77 mSv/year is higher than the admissible annual limit fixed by ICRP for workers (50 mSv/year). This value don't present any risk for workers health in the geophysical observatory of Berchid because workers pass only a few minutes by day in cave to control and reregister data.

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NATURALLY OCCURRING RADIOACTIVE MATERIAL IN THE NETHERLANDS: DOSE ESTIMATES TO THE PUBLIC OVER THE LAST TWENTY YEARS

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Abstract

In 1983 in the Netherlands, an environmental survey revealed elevated radionuclide concentrations above the background level. The source was identified as an industrial plant producing elemental phosphorus, by means of the thermal process. Within a few years a permit for emissions of radionuclides to the environment was requested, and granted. The plant reports yearly since 1987 its radiological emissions to the Dutch Ministry of the Environment. In the subsequent years permits were granted to a primary steel production plant and to a titanium dioxide plant. This permit was granted following legislation which is specific to NORM, and was first promulgated in 2004.

1. INTRODUCTION

In 1983, elevated concentrations of NORM were detected by the monitoring network associated with the site of a nuclear power plant in the Netherlands, a single unit operating on the left arm of the Scheldt estuary since 1973. The source was identified as the industrial plant (Hoechst, currently Thermphos) producing elemental phosphorus by means of the thermal process [1]. The problem of enhancement of natural radioactivity and the associated emission was thus recognized [1]. Within a few years, an application for a permit for emissions of radionuclides to the environment was submitted to the relevant authorities, and granted in December 1985, under the only legislative framework available at the time: the Nuclear Energy Act, dating back to 1963. Since 1987 this industrial plant reports its emission data to the Dutch Ministry of the Environment. Thus did the policy concerning industries processing NORM in the Netherlands take shape, predating by a decade the first European legislation on NORM [2].

In the subsequent years, operating permits were granted to an industrial plant with blast-furnaces for primary steel production and two phosphoric acid (wet process) plants. Both these phosphoric acid plants terminated production in 2000 and have been dismantled; the phosphogypsum was discharged, under permit, into the North Sea.

A new ordinance regulating exclusively work activities involving NORM came into force in 2004. In 2005, based on this ordinance, a permit was granted to a titanium dioxide plant for discharges to water.

These three industrial plants, which have been granted a permit for emission of radionuclides, report yearly the activity which has been released to the environment. The plant with the highest release of Po-210 to air is the elemental phosphorus plant, with a release in the order of 500 GBq per year. Recently its emissions of Pb-210 have increased to over 200 GBq per year. Over the years, both the elemental phosphorus plant and the steel plant have drastically reduced their discharges to water.

The RIVM institute collates these reported releases and performs dose assessments, in order to monitor the stress added by human activities to the environment. Information is made available on http://www.rivm.nl/brs (in Dutch).

2. OVERVIEW OF NORM EMISSIONS IN THE NETHERLANDS

2.1. Elemental phosphorus plant

The elemental phosphorus plant (thermal process) is located on a river estuary.

This industrial plants reports its releases to the environment on a yearly basis. A measurement plan is defined and carried out the following year. In 2008 the phosphorus plant revised upwards the values of the Pb-210 activity to air which had been reported since the year 2003. These revised values, shown in Figure 1, are thus larger than those reported in [3].

The thermal phosphorus plant is the only one of its kind in Europe. Worldwide there are currently only a few plants processing elemental phosphorus operating with the thermal process. Besides Thermphos in the Netherlands, we may name Monsanto in Soda Springs, Idaho, USA, and Kazphosphate in Kazakhstan.

The measurement plan of the elemental phosphorus plant includes activity measurements of the feed stock, inside the stack, and air concentration and deposition in fixed receptor points in the vicinity of the stack. It is difficult to identify the enhanced activity due to the plant, because this is in the same order of magnitude of the background level. The regular measurements at the RIVM institute, which lies at over 100 km distance from the phosphorus plant, can give an indication of the background level of Pb-210 activity from natural sources. The yearly average for 2007, which lies within the same range of other years, is for example 372 ± 6 microBq/m^3 [4]. The reference value of UNSCEAR is 500 microBq/m^3 [5].

For a comparison with this background value, the emission of the plant can be modelled by an air dispersion model [6]. Assuming a continuous annual emission of 500 GBq activity bound to aerosols of size less than 1 micron, at 3.5 km distance from the source (where the nearest dwellings are located), the modelled activity concentration varies from 450 to 750 microBq/m^3, depending on yearly weather variations [7].

2.2. Iron and primary steel furnace plant

The primary steel furnace plant in the Netherlands is located near the dunes overlooking the North Sea. This plant was granted the first permit for discharges to the environment in 1992.

The discharges of radionuclides to air from the steel furnace plant (Figure 2) are in general a fraction of the emissions of the phosphorus plant. The emissions to water are currently below the exemption level, but are reported yearly nonetheless. The maximum effective dose outside the perimeter of the factory is estimated to be below the permitted 10 microSv per year.

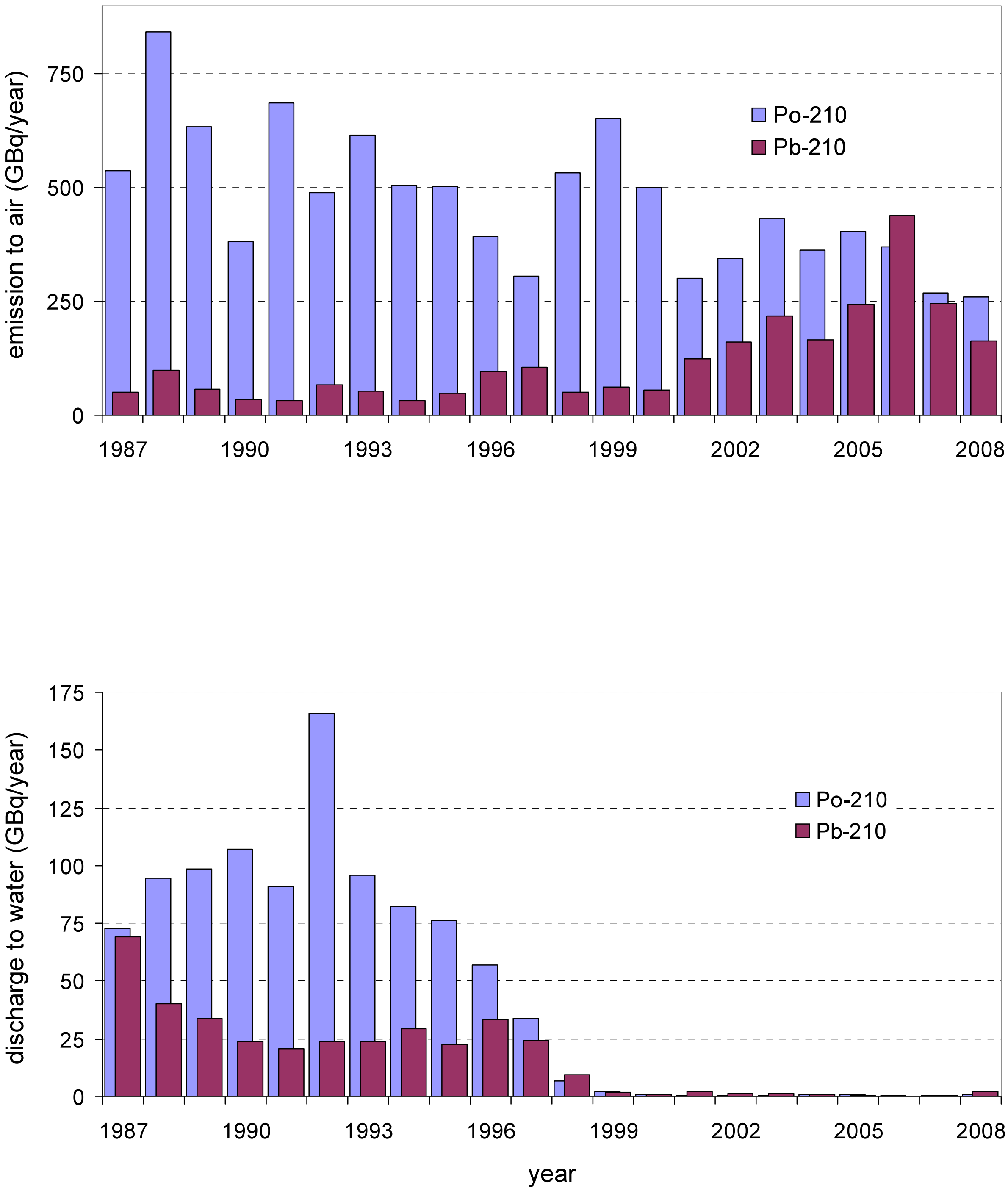
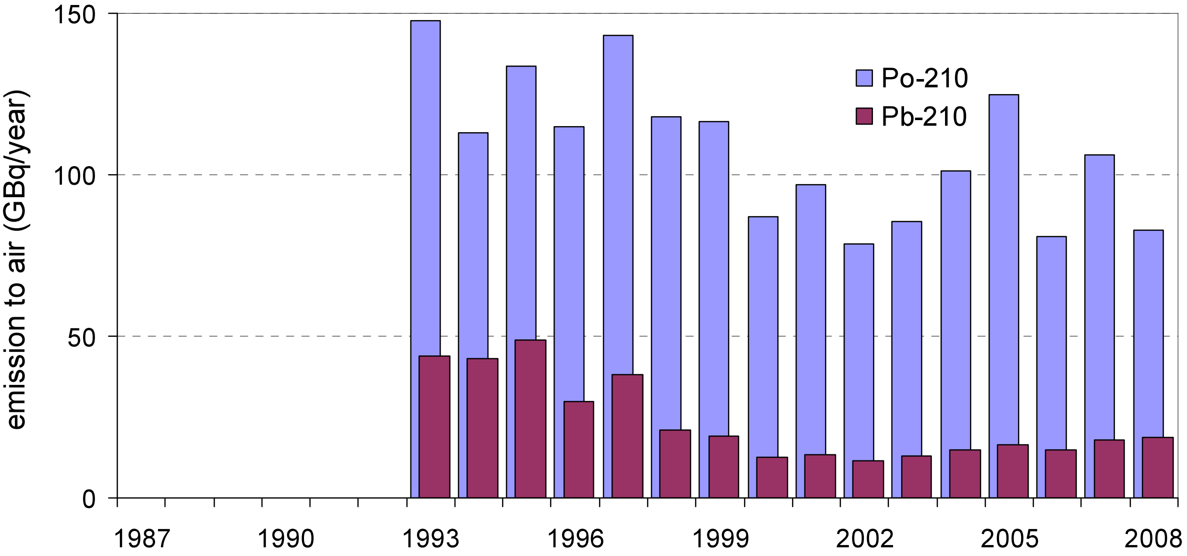


Figure 1 Emission to air and water of the thermal phosphorus industry in the Netherlands.



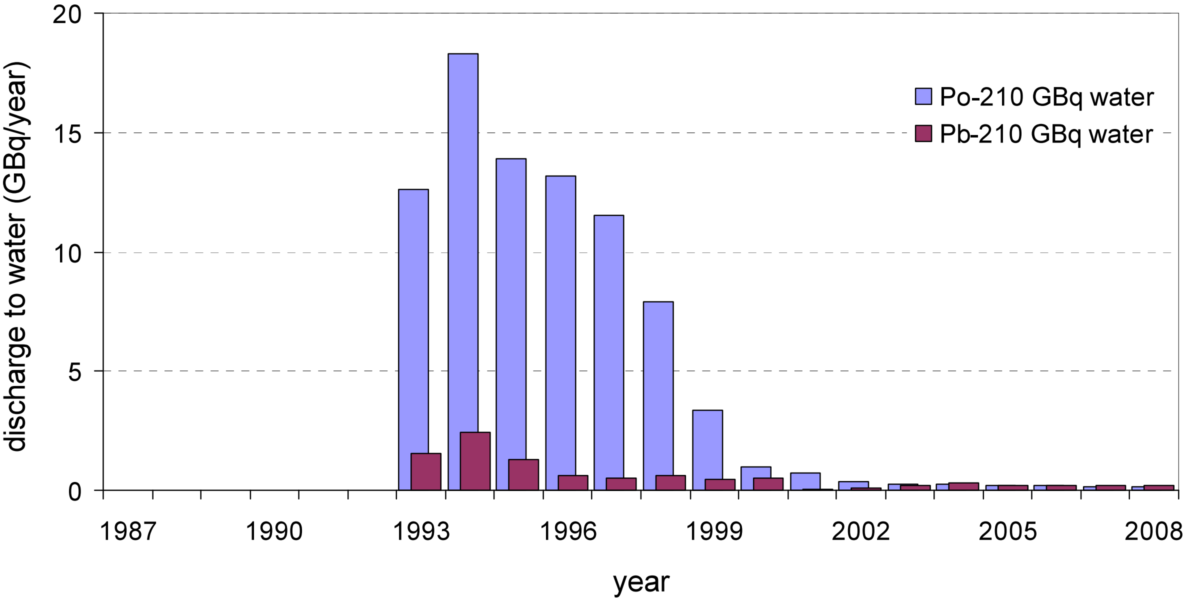


Figure 2 Emission to air and water of the steel furnace plant in the Netherlands.

2.3. Titanium dioxide pigment factory

A permit has been granted in 2005 to a titanium dioxide plant for discharges to water, in a canalized river some 15 kilometers from the coast. In 2007, the plant's annual capacity was 90,000 tonnes. The plant operates by means of the chloride process

The discharges to water, both of the thorium and uranium series, are yearly reported to the ministry since 2005. The reported activity of each discharged nuclide, or decay series (as specifically mentioned in the permit), was below 10 GBq/year over all reported years.

3. RESULTS AND DISCUSSION

RIVM carries out assessments of the effective dose to members of the general public. The reported yearly activity discharged to water for each relevant nuclide has been, since 2000, less than 10 GBq/y, which is the clearance level for Pb-210, Po-210 and Ra-226 discharged during NORM activities. The clearance level for all other discharged nuclides is higher than 10 GBq/y. For this reason, only releases to air are discussed here, with emphasis on the thermal phosphorus plant, which releases the highest activity to the environment.

For the estimate of the effective dose, the screening approach of IAEA [8] is followed (see also [9] and [10]). This means that for the ingestion of contaminated farmland produce the following assumptions are made for the dose associated to each calendar year: the industry starts its emission 25 years before that calendar year, at an emission rate equal to the rate reported in that calendar year. The concentration in the soil of Pb-210 is thus smaller than its corresponding equilibrium value, which is actually reached after a far longer period. The ingrowth of Po-210 from the deposited Pb-210 in the soil is also calculated for a residence time of 25 years.

The collective dose per one million inhabitants is shown in Figure 3. This is in order to allow a direct comparison of the industrial emissions, as the population of the Netherlands has increased over this time span. The year 2006 showed a peak in the Pb-210 emissions: the calculated effective dose for that year is comparable to that of 1988, which is the year with the peak Po-210 emissions to air (shown in Figure 1). It should be noted that, according to the model, deposition of the emitted nuclides is expected as far as Belgium [10].

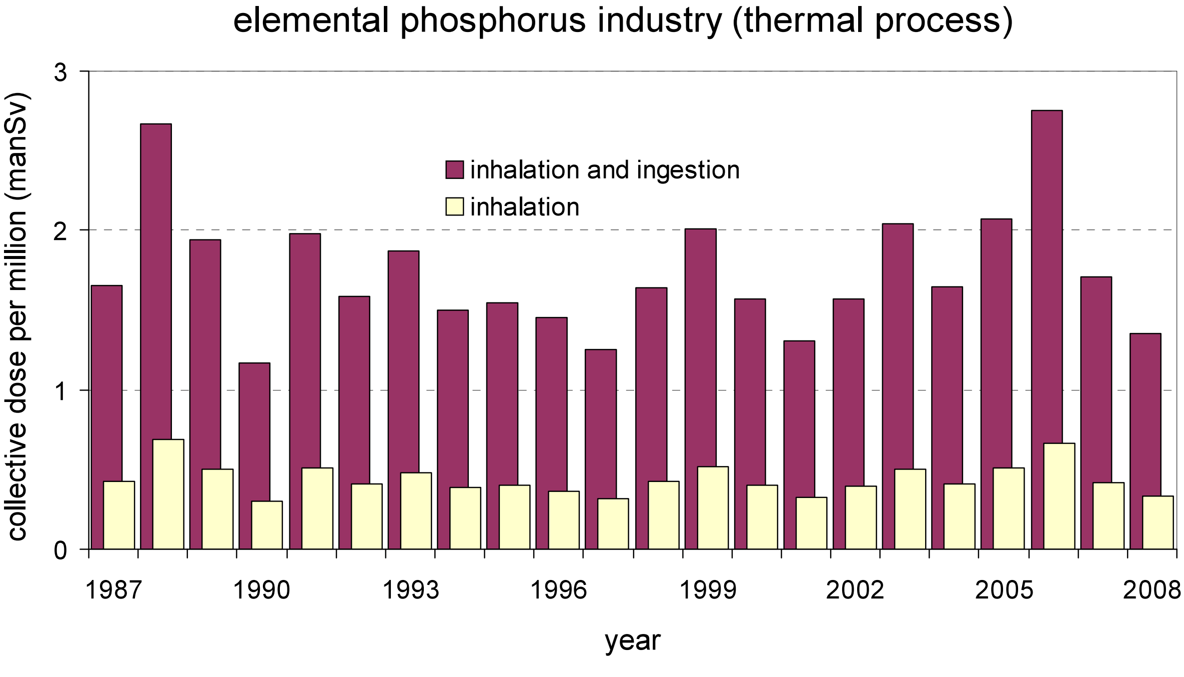


Figure 3 Collective dose given by the thermal phosphorus industry in the Netherlands. The model for the collective dose is as described in [10]. The population of the Netherlands has increased in these 21 years. In 2008 the total number of inhabitants was 16.4 million.

Figure 4 shows a map of the individual dose for both the thermal phosphorus plant (South-West) and the primary steel factory (on the coast to the North). In this map, the contribution of the ingrowth of Po-210 is not shown.

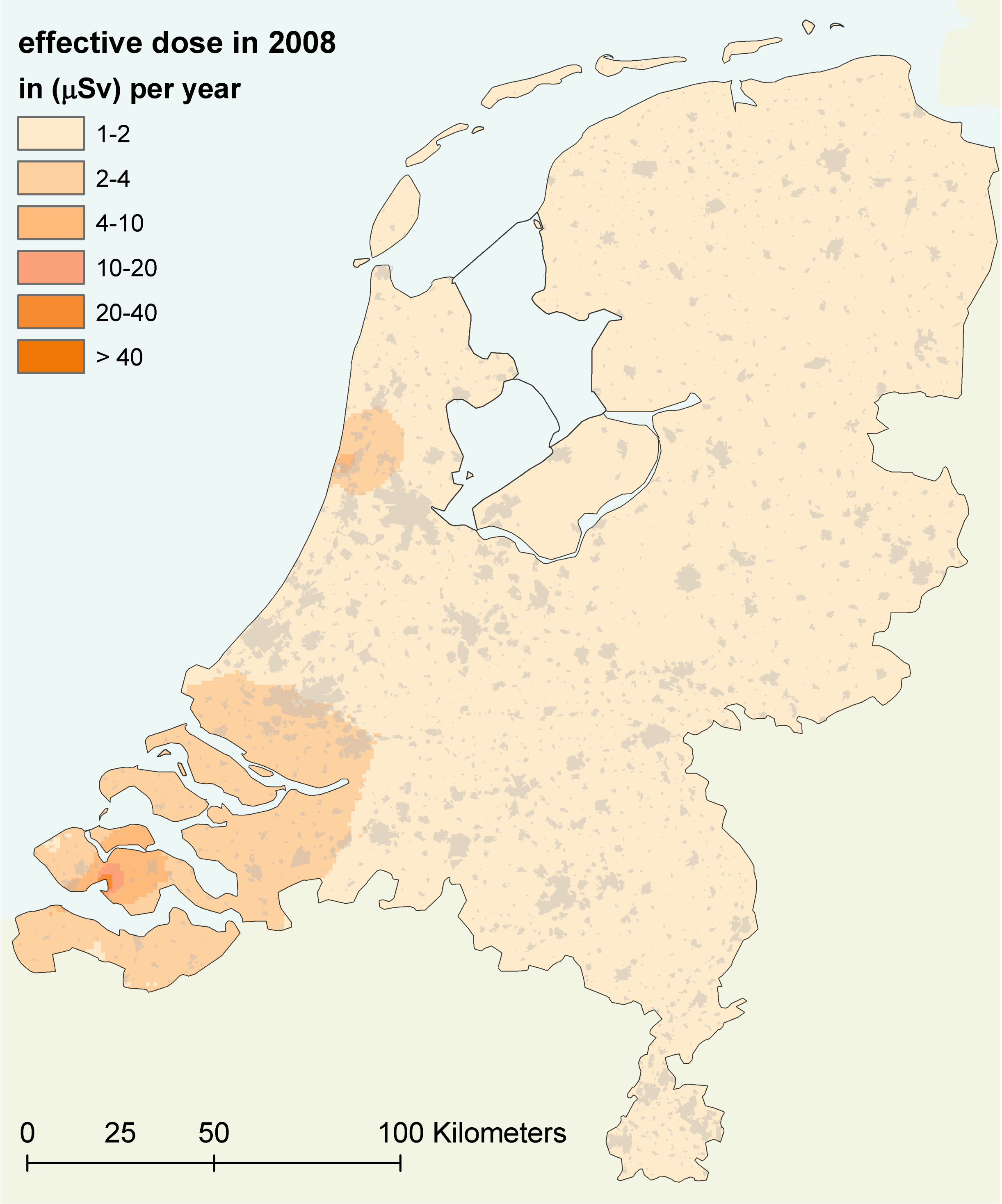


Figure 4 Effective dose given by the thermal phosphorus industry (in the South-West) and the primary steel industry (on the coast to the North) in the Netherlands. Residential areas are in grey.

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CHARACTERIZATION OF TENORM FORMATION IN FACILITIES AS BASIS OF RADIATION PROTECTION

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Abstract

Several industrial processes are known to enrich naturally occurring radionuclides resulting in TENORM (Technologically Enhanced Naturally Occurring Radioactive Materials). In order to assess such processes regarding their radiological concern, the basic processes and the key factors causing this enrichment have to be addressed. For that reason a unique model for the characterisation of TENORM formation in different industrial processes was developed. The model is based on mass and activity balances in industrial processes. It characterises the radionuclide enrichment of a residue in relation to the input materials according to three principal parameters (mass transfer factor MTF, activity transfer factor ATF and enrichment factor EF). The model demonstrates that a high enrichment is only possible if TENORM are generated in such a way that a significant amount of activity is transferred into a small amount of mass. Using basic process parameters like mass streams and physical or chemical process parameters, the prognoses of radioactivity content in residues and in products can be derived as well. This gives the possibility for assessing radiological properties of materials in individual facilities in such cases where raw materials are changed or processes are modified resulting in changed mass streams. The modelling of TENORM formation becomes particular important if residues are re-used in other processes and process chains have to be assessed.

1. INTRODUCTION

The occurrence of Technologically Enhanced Naturally Occurring Radioactive Materials (TENORM) has been described in the last 10 to 20 years in many papers (see for instance [1-4]. Most of these papers are focussed on radionuclides, their activities and the exposure of persons caused by them. Some papers have analysed the kind of materials, the ways they are formed in technical processes and the activity they contain in a very detailed manner [5,6]. Meanwhile, a lot of experience has been gained that allows to assess the occurrence of TENORM in many industries in a general way. This experience covers a diversity of materials, processes and industries, which are related to the term TENORM. For reducing this diversity it is desirable to identify a manageable number of physical or chemical key processes that are responsible for TENORM formation. Furthermore, there are some questions regarding the quantification of TENORM amounts or activity concentrations, which are difficult to answer only from experience. One such question is; what specific activities have to be considered in processes that are planned but not yet in operation. Another issue refers to the role of feedstocks used as a factor in TENORM formation. This is closely connected to the question of whether there are any possibilities for mitigating or avoiding the formation of a certain level of activity concentrations for a specific technological process. And last but not least the question may arise what effects on the radioactivity have to be expected, if TENORM-wastes produced in one facility are further processed in another facility. Such process chains are common in a modern economy with an increasing role reuse and recycling of wastes. This paper presents a possibility to find answers to these questions by a straightforward model describing several processes of TENORM formation in a unified approach.

2. KEY PROCESSES OF TENORM FORMATION

In Table 1 the formation of TENORM is attributed to ten physical or chemical processes that play the pivotal role in technological enrichments of the radioelements uranium, thorium and radium or certain radionuclides like Pb-210 or Po-210. Additionally, the most relevant parameters determining the efficiency of radionuclide enrichments at these processes are compiled.

These basic processes of TENORM formation are helpful if process steps that most likely require attention within a particular industrial facility have to be identified. Furthermore, they may be useful in order to check new developments in processing of bulk amounts of materials regarding their risk regarding the formation of TENORM.

3. KEY FACTORS OF RADIONUCLIDE ENRICHMENT

Any TENORM consists of two components - natural radionuclides and a non-radioactive carrier. The latter one is an inherent part of any TENORM and determines the activity concentration in a similar degree as the radionuclides do. Therefore, one has to consider radioactivity and mass transfer at equal footing in order to describe the processes of TENORM formation, whereby a straightforward modelling of radionuclide redistributions in technical processes can already be achieved by regarding solely activity and mass balances.

The model approach introduced in a former research report [7] simplifies any industrial processing as a redistribution of masses and activities from the feedstocks (“raw material” index “M”) and additives (index “A”) to the output fluxes “Residues” (index “R”) and “Product” (“P”) (see Figure 1). In this process the activity inventories of the materials are split between the residues (wastes) and the products. This process can be described by the following balance equations [8]:

Mass flux: $$J_M + J_A = J_R + J_P \tag{1}$$

Activity flux: $$\dot{A}_{M,r} + \dot{A}_{A,r} = \dot{A}_{R,r} + \dot{A}_{P,r} \tag{2}$$

Here J is the mass flux (kg/s), the total activity flux (Bq/s), the indices M, A, R, P stand for materials described above, and the index “r” denotes a specific radionuclide.

The mass and activity balances can be characterised by four parameters.

The **mass transfer factor**

$$MT\mathrm{F} = \frac{J_R}{J_M + J_A} \tag{3}$$

describes which part of the total mass flux is transferred into the residue and is independent of the degree of radioactivity of the materials. Analogously, the **activity transfer factor**

$$ATF_r = \frac{\dot{A}_{R,r}}{\dot{A}_{M,r} + \dot{A}_{A,r}} \tag{4}$$

describes, which part of the activity of radionuclide “r” is transferred from the input mass flux into the residue. This factor is usually different for all radioelements involved.

The enrichment of the activity concentration “a” is characterised by the **enrichment factor**

$$EF_{RM,r} = \frac{a_{R,r}}{a_{M,r}} = \left(\frac{ATF_r}{MTF}\right) \cdot AIF_r . \tag{5}$$

Here AIF_r quantifies the influence of the additives in the activity balance of the radionuclide r. This “additive impact factor” is given by

$$AIF_r = \frac{1 + \dot{A}_{A,r} / \dot{A}_{M,r}}{1 + J_A / J_M} . \tag{6}$$

TABLE 1. KEY PROCESSES RESULTING IN NORM/TENORM RESIDUES

Processes	**Residue (examples)**	**Parameters affecting the radionuclide enrichment**
Physical mineral separation processes without or only with low enrichments (NORM)		
Mining of minerals, ores or other materials with naturally enhanced radioactivity	Waste rock	No enrichment of radionuclides
Mechanical processing of ores or minerals (breaking, cutting, milling)	Unusable debris	Grain size Mineral density
Hydro-mechanical processing of ores or minerals (Flotation)	Fine grained materials (tailings)	Specific characteristics of minerals (density, surface tension, …)
Physical processes of significant radionuclide enrichment (TENORM)		
Thermal volatilisation	Filter dust (from mineral sintering, blast furnace smelting or other thermal processes)	Temperature, Mass fraction of dust, Vapour pressure of lead and polonium (Pb-210, Po-210), Content of other volatile components
Partitioning of (trace) elements at phase separation during metal melting	Slag	Grade of ore; Partition coefficients of radioelements between metal-phases and slag
Sorption of dissolved radionuclides on ion exchangers (e.g. oxide hydrate surfaces)	Filter sands in water treatment	Radionuclide concentration of water; Chemical composition of raw water; Useful life of filter
Chemical processes (chemical reactions) resulting in radionuclide enrichments (TENORM)		
Oxidation of carbon (combustion or incineration)	Ashes, slags	Ash content of used fuels; TOC of incinerated materials
Precipitation of insoluble salts (e.g. Ba-Sr-sulfates)	Scales, sludges (oil or gas production; geothermal plants, etc.)	Concentration of metal ions (e.g. Ba-Sr-Ca) in water or brine
Wet chemical extraction processes of non-radioactive minerals	"Red mud" (residue of bauxite treatment with alkaline solutions) Phosphogypsum (residue of wet phosphor processing)	Grade of bauxite ore Grade of phosphate rock
Selective chemical extraction of radioelements	Uranium-mill tailings	Grade of uranium ore Type of leaching (acidic / alkaline)

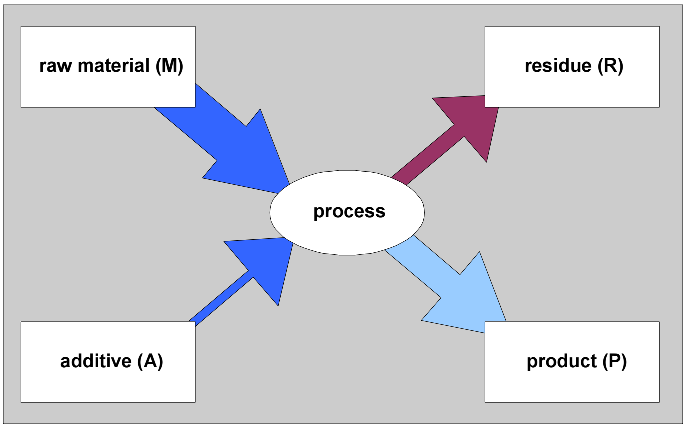

Fig. 1. Schematic diagram of a general TENORM formation process.

Some exemplary values of MTF, ATF and enrichment factors EF for typical processes of TENORM formation inferred from the analysis of a large body of data are given in Table 2.

TABLE 2. EXEMPLARY MODEL PARAMETERS OF SELECTED TENORM FORMATION PROCESSES

Physical or chemical elementary process	**MTF**	**Radioelement* (-nuclide) "r"**	**ATF$_r$**	**AIF$_r$**	**EF$_r$**
Physical processes					
Vaporisation of volatile elements at high temperatures (example: filter dust from blast furnace process of pig iron production)	0.005	Pb-210	0.9	1.4	250
		U, Ra, Th	. 0.005		1-2
Partitioning of radio-elements between metal and slag phases in smelting facilities (example: blast furnace slag)	0.4	U, Ra, Th	0.95-1	1.4	3.5
		Pb-210	0.1		0.3–0.4
Sorption of dissolved radionuclides on oxide hydrate surfaces (example: Fe-Mn-coated filter gravel in water treatment facilities; for illustration the coatings without the carrier mass are referred here as the residue)	<1E-5	Ra	0.8-0.99	1	>1E+5
		U	0.05		5E+3
Chemical processes					
Oxidation of carbon (combustion or incineration; the parameters given represent bottom ash from coal as residue)	0.3 – 0.1	U, Ra, Th	1	1	3-10
		Pb-210	0.1 –0.5		0.3-1
Precipitation of insoluble salts (e.g. Ba-Sr-sulfates from water or brines; residue = scales, sludges)	1E-5	Ra	. 0.1	1	1E+4
Dissolution of minerals by alkaline solutions (here: red mud from NaOH treatment of bauxite)	0.3	U, Th, Ra, Pb-210	1	0.8	2.7
Dissolution of minerals by acid solutions (example: sulphuric acid treatment of phosphate rock; residue = phosphogypsum)	0.72	Th, Ra, Pb-210	0.9	0.44	0.55
		U	0.1(a)		0.06

*The term "radioelement" is used in order to characterise the radioactive elements uranium, thorium and radium as a mixture of several individual radionuclides. (a) uranium is enriched in the phosphate fraction; (b) Pb-210 is depleted due to thermal volatilisation

This process analysis allows to conclude that any enrichment of radioactivity in a technical process results simply from the mass and activity transfer. A considerable enrichment of at least one radionuclide in the “residue” fraction occurs only if the activity transfer is significantly different from the split ratio of the masses. High enrichment of radionuclides requires both

- a low mass transfer factor MTF (i.e. the part of the total mass flux which represents the residue is small) and
- a high activity transfer factor ATF as well (i.e. that a large amount of the total activity is transferred into the residues).

The key factors that determine the activity concentration of wastes produced in a technical facility are:

- The activity concentrations in the feedstocks.
- The mass fraction of an individual residue (waste) stream referred to the mass of feedstocks.
- The efficiency of activity transfer from the feedstocks to the waste.

A more detailed consideration of technical processes with respect to these key factors lead to the conclusion:

- The radioactivity of residues is only partially determined via the radioactivity of raw materials. The transfer of radionuclides into mass streams, which constitutes the residue may result in activity concentrations of wastes which cannot be disregarded from the radiation protection point of view.
- Because high radionuclide enrichments are attributed to (very) low mass transfer factors, residues with high activity concentrations occur usually in mass streams of technological processes, which constitute a small fraction of the mass streams in a certain facility.
- Processes with mass ratios of products and residues in the same order of magnitude are less sensitive with regard to changes of activity concentrations in the wastes. Here the activity of wastes can be well estimated from the activity concentration of feedstocks. A typical example of such process is the alumina production from bauxite.
- Activity concentrations in residues arising from processes with high enrichment factors are very sensitive with regard to any changes of masses in the process. That is why the activity concentrations of scales in oil and gas production vary in different facilities in a poorly predictable degree.

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A COST-BENEFIT ANALYSIS OF THE USE OF PHOSPHOGYPSUM IN THE BRAZILIAN SOUTH REGION AGRICULTURE

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Abstract

In Brazil, about half of the phosphogypsum generated by the phosphoric acid production is used in agriculture as amendment of acid soils and, in less extension, in the cement industry. The advantages of using phosphogypsum in agriculture, as a source of sulphur and calcium and as an amendment for acid soils with high levels of aluminium are well known. In addition, studies on economic–environmental aspects of the use of phosphogypsum in agriculture have shown higher crop yields and best quality of vegetable products. This paper addresses a cost benefit analysis to evaluate the impact of this practice on corn cultivation on the Brazilian state of Rio Grande do Sul. Information regarding all costs and benefits (increase in yield of crops due to phosphogypsum use) were compared. A radiological and chemical characterization of the phosphogypsum used was performed and information regarding all costs and benefits (increase in yield of crops due to phosphogypsum use) were compared. The radiological assessment is carried out by calculating the individual effective dose due to ingestion of these products.

1. INTRODUCTION

Phosphogypsum is a by-product of the phosphoric acid and fertilizers industry, produced on millions of tons per year in several countries by the acid leaching of phosphate rock [1]. Its parental material, the phosphate rock, has in its constitution significant levels of uranium, thorium and radionuclides from their radioactive decay chain, and so does the phosphogypsum. The American Environmental Agency (USEPA) consider phosphogypsum as a reject with low-level radioactivity [2], and the International Atomic Energy Agency (IAEA) included it in the list of materials known as TENORM (technologically enhanced naturally occurring radioactive material) [3].

As natural gypsum, phosphogypsum is mainly compounded by calcium sulphate ($CaSO_4$) and has many uses on agriculture, to reduce high toxic aluminium (Al^{3+}) levels, excess of exchangeable sodium and to supply calcium and sulphur to crops [4,5,6]. Therefore, the application of phosphogypsum in agricultural soils may cause an increase in dose of ionizing radiation [7], due to various types of exposure, but also can improve the harvesting of economic crops, as it promotes an improvement on the root zone and increase on the crops productivity. Due to its great solubility, phosphogypsum penetrates into the deeper layers of soil (sub-surface), complementing the benefits of lime, which acts only in the surface layer (0-25 cm). Increasing the porosity of the soil and neutralizing the toxic aluminium, the phosphogypsum allows a better development of the roots, which are in contact with nutrients and water for crop development and to withstand periods of drought.

In Brazil, about half of the phosphogypsum generated by the phosphoric acid production is used in agriculture as amendment of acid soils and, in less extension, in the cement industry. The advantages of using phosphogypsum in agriculture, as a source of sulphur and calcium and as an amendment for acid soils with high levels of aluminium are well known. In addition, studies on economic–environmental aspects of the use of phosphogypsum in agriculture have shown higher crop yields and best quality of fruits, cereals, sugar cane, soybeans, beans, coffee and pasture [8].

Farinelli and Loboda [9], studying the effects of phosphogypsum on soils cultivated with peanuts, in an area previously limed and high content of calcium in the soil, proved that the addition of phosphogypsum had a positive effect on number of pods per plant, the weight of grain and the crop yield. The physiological quality of seeds was also affected positively with the application of phosphogypsum, with respect to germination.

TABLE 1: EFFECTS OF THE USE OF PHOSPHOGYPSUM ON THE PRODUCTIVITY OF ANNUAL CROPS [10].

Crop	Corn	Wheat	Soybean
	(tons.ha^{-1})		
Without phosphogypsum	3.2	2.2	2.1
With phosphogypsum	5.5	3.5	2.4

Once phosphogypsum is produced in limited amounts and is stockpiled near to the phosphoric acid and fertilizers industrial plants, its use may be not viable due to the expense of transporting it until the farms.

The production of grains in Brazil on 2009-2010 period was drafted in 143.09 million tonnes, thanks to the stability of rainfall in the main producing states, unlike the previous period which was marked by drought climate in the Southern states, causing significant reduction in the harvest, especially soybeans and corn. In addition, the corn area reduced, and the use of natural gypsum or phosphogypsum might contribute to increase the productivity.

Previously research of the assessment of intake dose due to consumption of vegetables have shown that due to the high values of their soil to plant transfer factors as well their committed effective dose per unit intake via ingestion, ^{228}Ra, ^{210}Pb and ^{226}Ra are the main contributors to the intake dose [8,11].

Taking as an example the corn production, the objective of this paper was to evaluate the economic viability of the use of phosphogypsum on agriculture by Brazilian farmers from the states of the south region of Brazil, based on cost from Rio Grande do Sul and to estimate the increment of the individual dose due consumption of vegetables cultivated with its use.

2. MATERIAL AND METHODS

To assess the economic impact of the use of phosphogypsum in the production of corn, were used data from the cost of production provided by CONAB (Companhia Nacional de Abastecimento, Brazilian National Supply Company) [12] to the agricultural market of Passo Fundo, on the state of Rio Grande do Sul, that is a city used as reference on economical studies by CONAB. The method of calculation adopted search all the items of expending, explicit or not, that are supplied by farmers, from the early initial preparing of the agricultural area until the initial marketing of the product. In addition, the cost of acquisition, transport and application of phosphogypsum were added, plus the cost of harvest of the increase in production caused by phosphogypsum and post harvest costs.

The cost of production depends on the technological level of the farmers and the average prices from each production region, know by the term *vector of prices*. The *vector of prices* used by CONAB is obtained by marketing researches on the productive region, as the cost of some items as agrochemicals and agricultural inputs vary on accordance with the market. The surveyed data is treated statistically, by calculating the arithmetic means of prices in the sampled regions (in cases of discrepant data, the extremes are excluded). Only after this process the values are used in the calculation of production costs.

The phosphogypsum used on this study is the one produced on the Brazilian State of Santa Catarina. The material was stockpiled next to the production plant, which ended the production on the last decades of past century, and next to one of the most important highways of the region, that allows the distribution of the product to the state of Rio Grande do Sul and others, besides the own state of Santa Catarina. Actually, it is used on crops of corn, soybean and wheat as main annual crops of Brazilian south states.

In economic terms, the cost components are grouped according to their function in the production process, in the categories of variable costs, fixed costs, operating cost and total cost. On the variables cost are grouped all the components involved in the process as long as the productive activity is developed, i.e., those that affect or occur only if there is production. This includes the costing items, the post-harvest cost and the financial costs. The fixed costs include the charges that are incurred by the producer, regardless of the volume of production, such as depreciation, insurance, regular maintenance of machines and others. The operating cost consists of all items of variable costs (direct expenses) and fixed costs directly associated with the implementation of the crop. The total cost of production comprises the sum of operating cost plus compensation paid to factors of production.

When calculating the cost of production of a crop, basic information as the combination of inputs, services and machinery and implements used during the production process should be included, with reference to one unit area (hectare) and can be expressed in tons, kilograms or liters (lime, fertilizer, seeds and pesticides), in hours (machinery and equipment) and working days (human or animal).

In 2010, each ton of phosphogypsum costs US$ 21.56 in wholesale, not considering the transport expenses. The mean distance between the cities of Imbituba and Passo Fundo is 633 km, what makes a transportation cost of, in an average, US$43.13/ton Passo Fundo (quotation of Brazilian Central Bank on February 9, 2010: US$1.00 = R$1.86). As phosphogypsum is physically very similar to the limestone, the cost of limestone was adopted as a reference (US$ 21.83/ton and also its transportation cost: US$ 43.13/ton), to permit a comparison of a cultivation with and without phosphogypsum. An amount of 5 tons of limestone was chosen as a reference value, and an amount of 2 tons of phosphogypsum was used in this study, based on EMBRAPA [10].

Phosphogypsum is distributed in the soil through the same equipment that distributes the limestone. The cost of this operation was estimated assuming the use of a distributor of limestone pulled by a tractor involving a tractor driver and a helper. The incorporation of gypsum in the soil is accomplished by diskings, made with a tractor, disks and only operates the tractor driver.

As a result of increased productivity caused by the use of phosphogypsum, an additional quantity of agricultural products is generated and the cost of harvesting must be computed. For this, estimated costs and procurement costs in the purchase of bags for packing of grains. We considered the harvest is performed by harvester operated by a harvester drive.

Due to the concentration of natural radioactive elements on phosphogypsum, was investigated the levels of ^{226}Ra on this material sampled. This radioisotope was the only considered because the USEPA defined a criteria to agricultural use of phosphogypsum based on the concentration of this radioisotope on the material. To this, samples of the material were analyzed by gamma spectrometry on an HPGe detector. The concentration obtained allows the calculation of the concentration of ^{226}Ra on soil is based on the equations 1 [13]:

$$C_{s,i} = \frac{C_{f,i} \times a_f \times \left(1 - e^{-\lambda_{E,i} \times t_d}\right)}{P \times \lambda_{E,i}} \tag{1}$$

where

$C_{s,i}$ is the concentration of the radionuclide *i* on the soil (Bq.kg^{-1})
$C_{f,i}$ is the concentration of the radionuclide *i* on the phosphogypsum (Bq.kg^{-1})
a_f is the rate of phosphogypsum applied on soil, per year (kg.m^{-2}.y)
$\lambda_{E,i}$ is the constant of effective remove of the radionuclide *i* from the root zone ($\lambda_{E,i} = \lambda_i + \lambda_s$) (y^{-1})
t_d is the period of time of phosphogypsum application on soil (year, y^{-1})
P is the superficial density of the soil (kg.m^{-2}), that is a multiplication of the density of the soil (1.8 g.dm^{-3}) by the depth of the root system (1.5 m), estimated on 270 kg.m^{-2}

On the equation above, the $\lambda_{E,i}$ (constant of effective remove of the radionuclide *i* from the root zone) is obtained by the use of an remove factor, exponential to the deposition rate. On these constant two mechanisms are involved: the radioactive decay (λ_i) and the infiltration of the radionuclide on the soil profile (λ_s) [13]. To ^{226}Ra, the λ_i is 4.34E-04.year^{-1} and λ_s is 18.25.y^{-1} .

To estimate the concentration of certain radionuclide on vegetable sample (in the case, corn grains), the equation 2 [13] was utilized:

$$C_{v,i} = C_{s,i} \times TF_{v,i} \times \left(e^{-\lambda_{i \times} t_d}\right) \tag{2}$$

where

$C_{v,i}$ is the concentration of the radionuclide *i* on the edible part of the vegetable (Bq.kg$_{wet}^{-1}$)
$C_{s,i}$ is the concentration of the radionuclide *i* on the soil (Bq.kg^{-1})
TF is the soil-to-vegetable transfer factor for the radionuclide *i*
λ_i is the constant of radioactive decay of the radionuclide *i*
t_d is the period between the harvesting and the consumption of the vegetable (year)

The FT is the factor that represents the transference of the radionuclide from the soil to vegetable, by root uptake, and is defined as the relation between the concentration of the radionuclide on the edible part of the vegetable and the concentration of the radionuclide on soil. The $e^{-\lambda_{i \times} t_d}$ term corrects the concentration of the radionuclide on the vegetable, considering the time from the harvesting and the consumption and the constant of radioactive decay.

The individual dose by the consumption of corn tilled with phosphogypsum is finally calculated by the following equation 3 [13]:

$$E_v = C_{v,i} \times U_v \times DCF_{ing,i} \qquad (3)$$

where

E_v	is the effective dose due the consumption of the vegetable tilled with phosphogypsum ($Sv.y^{-1}$)
$C_{v,i}$	is the concentration of the radionuclide i on the edible part of the vegetable ($Bq.kg_{wet}^{-1}$)
U_v	is the rate of ingestion of the vegetable ($kg.year^{-1}$)
$DCF_{ing,i}$	is the dose factor conversion (by ingestion) of the radionuclide i ($Sv.Bq^{-1}$)

The $DCF_{ing,i}$ to ^{226}Ra is $2.25x10^{-7}$ $Sv.Bq^{-1}$ [11]. The rate of ingestion of the vegetable (U_v) to corn at the Rio Grande do Sul was estimated by the IBGE [14] as 2.459 $kg.y^{-1}$.

3. RESULTS AND DISCUSSION

The data on production costs collected by CONAB is shown on table 2. Limestone and phosphogypsum are use on each 3 years. It is estimated a productivity of 5.4 tons of corn grains per hectare without phosphogypsum. As showed on table 1, the corn production with phosphogypsum is increased on almost 70%, resulting in almost 9.2 tons of grains per hectare.

Assuming the producing, harvesting and transport/storage cost of the production, the crop without phosphogypsum costs of US$1204.16 per hectare, and produced 5.4 tons of grains, or 90 bags of 60 kg. The cost pf production of a 60 kg bag of corn, at Passo Fundo and just with liming is estimated on US$13.78. Considering the sell price of a 60 kg bag of corn on the market of Passo Fundo as US$ 14.50, the producer receives as net profit US$1.30 per bag, and U$117.00 per hectare.

The production of corn with phosphogypsum costs US$1360.75 per hectare, or US$167.47 more than the produce without phosphogypsum. With the increase of productivity, 153 bags of 60 kg are produced. Each bag has a production cost of U$9.00 and sold by U$14.50, the producer receives a net profit of US$5.5 per bag and U$841.50 per hectare. The difference on the net profit is enormous: with phosphogypsum, the profit is almost seven times higher than without it, even considering an increase on the costs of harvesting and post harvesting, transporting and commerce.

The concentration of ^{226}Ra obtained by gamma spectrometry varied from 60 to 130 $Bq.kg^{-1}$. Even the upper value is lower than the 370 $Bq.kg^{-1}$ of ^{226}Ra concentration considered as a limit by the U.S. Environmental Agency [15]. To a conservative approach, the highest value was used. The concentration of ^{226}Ra on soil tilled with phosphogypsum, calculated by the equation 1 is 52.76 $Bq.kg^{-1}$. The concentration of ^{226}Ra on corn grain was calculated on 0.06 $Bq.kg^{-1}$, and considering a TF of $0.12x10^{-2}$ the individual dose by ingestion of corn, considering a per capita consumption of 2.459 $kg.y^{-1}$ was calculated on 0.033 $\mu Sv.y^{-1}$. The IAEA consider on the Basic Standard Series 115 [16] the value of 10 $\mu Sv.y^{-1}$ as one of the requirements for a practice to be exempt of control under the radiological point of view, it is 0.33% of this value.

TABLE 2: ESTIMATED PRODUCTION COST OF CORN CULTIVATION AT RIO GRANDE DO SUL STATE (average values on September 30th, 2009) to a 1 hectare area, with and without phosphogypsum (adaptation of CONAB/DIGEM/SUINF/GECUP).

Production Factors Cost	Without phosphogypsum	With phosphogypsum
	(US\$.ha^{-1})	(US\$.ha^{-1})
I - Operating cost of the crop		
Operations with machines	101.15	151.15
Temporary manpower	6.39	30.39
Fixed manpower	17.51	30.51
Seeds	89.72	89.72
Limestone (plus freight) 5 tons.ha^{-1}	174.62	174.62
Phosphogypsum (plus freight) 2 tons.ha^{-1}	0.00	69.59
Fertilizers	226.62	226.62
Agrochemicals	91.42	91.42
Total operating cost of the crop (A)	*707.43*	*864.02*
II - *Pos harvesting expenses*		
Insurance	15.75	15.75
Technical assistance	10.66	10.66
Harvesting transport	69.1	69.1
Storage	46.95	91.80
Total of post harvesting expenses (B)	*142.46*	*153,34*
Variable cost (A+B = C)	*849.89*	1017.36
III - Depreciation		
Facilities	39.32	39.32
Equipments	23.40	23.40
Machines	43.58	43.58
Total of Depreciation (D)	106.30	106.30
VI- Other fixed costs		
Regular maintenance of machinery/implements	24.65	24.65
Social security costs	10.33	10.33
Insurance of fixed capital	3.47	3.47
Total of other fixed costs (E)	38.45	38.45
Total fixed costs (D+E = F)	*144.75*	*144.75*
Operational costs (C+F = G)	994,64	1162.11
V – Income of factors		
Expected return on fixed capital	32.10	32.10
Agricultural area	177.42	177.42
Total Income of factors (H)	209.52	209.52
Total costs (G+H = J)	*1204.16*	*1371.63*

4. CONCLUSIONS

The use of phosphogypsum on the cultivation of corn at the city of Passo Fundo, used as reference to the states of Southern Brazil, is viable on the economic point of view. In a first assessment the production of corn with phosphogypsum costs US$1360.75 per hectare, or US$167.47 more than the produce without phosphogypsum. With the increase of productivity (70%), 153 bags of 60 kg are produced resulting in a net profit of US$841.50 per hectare. It increase almost seven times the net profit, and the most expensive cost to its utilization on agriculture is the transport.

Considering the ingestion dose of ^{226}Ra the estimated maximum individual effective dose is 0.033 μSv.y^{-1}, corresponding to less than 1% of the exemption level established by the International Atomic Energy Agency (10 μSv.y^{-1}).

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NATURAL RADIOACTIVITY IN PRODUCED AND IMPORTED PHOSPHATE FERTILIZERS IN TUNISIA

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Abstract

Tunisia is the fifth phosphate producer in the world. Many types of phosphate fertilizers are produced in the country and many others are imported and used in agriculture. It is known that natural radioactivity content (NORM), due to ^{226}Ra, ^{232}Th and ^{40}K isotopes in phosphate industry can be elevated. This work consists on a study of the concentration of these radionuclides in some produced phosphate fertilizers in Tunisia and sum exported ones. The study concerns the most used fertilizers in the country. It was found that generally the Tunisian fertilizers contain the highest activity concentrations of radium and thorium isotopes with the exceptions for ^{40}K. TSP contains the highest concentration of ^{226}Ra (186.2±14.5 Bq/kg) and of ^{232}Th (33.7±3.5 Bq/kg). The highest amount of ^{40}K was found in one type of NPK (9969.5±123.6 Bq/kg). The radium equivalent index was calculated for all the analysed fertilizers and was found to be the highest in imported NPKs samples (the maximum value was about 775 Bq/kg) because of their high content of ^{40}K. For the Tunisian fertilizers the maximum radium equivalent index was about 238 Bq/kg in TSP.

1. INTRODUCTION

Phosphate industry is known to be a subject of possible naturally occurring radioactive materials [1]. In fact, phosphate fertilizers could contain a high concentration of some natural radioactive isotopes due to uranium and thorium series. In the phosphoric acid process, the phosphate material is acidified with sulphuric acid which results on the gypsum precipitation which is separated from phosphoric acid by filtration. Triple Super Phosphate (TSP) is then obtained by reacting phosphoric acid with phosphate material. NPK fertilizers are obtained by adding potassium to MAP. MAP is the Monoammonium phosphate and is the result of reacting ammonia with phosphoric acid [2]. Using these fertilizers in agriculture introduces uranium, thorium and radioactive potassium to the surface soil and could cause an exposition to radiation and/or could be transferred to agriculture products. That's why it is very important from radiological point of view to survey the concentration variation of especially ^{226}R, ^{232}Th and ^{40}K isotopes concentrations during all the industrial processes concerning the phosphate industry, from the extraction to the production of this material and its related derived substances, such as fertilizers which as the subject of this study. The proposed study is also important to a country like Tunisia because it is an important producer and consumer of phosphate fertilizers (the fifth phosphate producer in the world). This work consists on the measurement of the above cited natural radionuclides concentrations in Tunisian phosphate fertilizers (the most used ones in agriculture) and also in some other imported ones. We used gamma spectrometry with HPGe crystal for the measurement. The presented results could be an interesting resource for a NORM identification and study in Tunisia.

2. MATERIAL AND METHODS

Ten samples were collected from the local markets of phosphate fertilizers in Tunisia during 2009. Three of them are Tunisian and are TSP (triple superphosphate), DAP (diammonium phosphate) and phosphoric acid with 30% concentration. The seven other fertilizers are imported and are NPKs. NPK is the abbreviation of the expression Nitrogen-Phosphorus-Potassium. The fertilizers were in two forms, granules and powder. Phosphoric acid was of course in liquid form. The solid samples were transferred into polyethylene bottles with 100 ml capacity and tightly sealed for more than one moth to reach secular equilibrium between natural radionuclide series. An HPGe detector of 80% relative efficiency and 2 keV resolution at 1332 keV gamma line of ^{60}Co was used. For the phosphoric acid sample a polyethylene container of 1 litre volume was used. An other HPGe of 35 % relative efficiency and 1.9 keV resolution at 1332 keV gamma line of ^{60}Co was employed to measure radionuclide concentrations in this liquid sample. The efficiency calibration of the 35% efficiency detector was realized using a solid mixed source containing the artificial radionuclides ^{241}Am, ^{109}Cd, ^{57}Co, ^{139}Ce, ^{203}Hg, ^{113}Sn, ^{137}Cs, ^{54}Mn, ^{88}Y and ^{60}Co (IAEA 74414-767) with the same geometry as the sample. The HPGe 80% efficiency detector was calibrated using a reference material consisting of a lake sediment provided by the IRSN (The French Institute of Radioprotection and Nuclear Safety) through an inter-comparison exercise realized in 2005 (IRSN n^{o} 77 SR 300) for the measurement of the natural radioactivity due to thorium and uranium series. It is important here to note that Because of the fact that our used reference material contains the same natural radioactive series as the one of the samples and not artificial radionuclides, the only difference between the samples and the reference material are the density and chemical composition. This means that coincidence summing effects act approximately identically during the tow procedures of the detector calibration and the samples measurement. Errors due to this effect in the detector calibration procedure and the samples measurement are then very close. This means that errors contribution due to coincidence summing affect on the samples measured activities is very low compared to a calibration realized with another reference material containing artificial radionuclides, which is generally the case for many laboratories. For this reason we used the natural lake sediment reference material for the detector calibration and we did not correct coincidence summing effect. The difference between the samples (prepared samples) and reference material densities are also an important factor which could cause significant errors on the activity measurement results. This error increases as a function of the volumes of the used geometries and as a function of the density differences between the samples and the reference material. It increases also as the concerned emission energy of the gamma ray decreases, because this enhances the attenuation of the gamma radiation which is related to the high photoelectric effect occurring at low energy. The used cylindrical geometry in our study has a volume of order of 97.5 cm^3 which is placed directly above the crystal having a volume of 430.6 cm^3. Because of the smallness of the samples geometry compared to the crystal volume we expect a very low contribution of the density effect to the errors on the activity measurement results. This expectation is also supported by the fact that all the prepared samples densities that we measured are very close to the one of the reference material (With a relative deviation from the reference density lower than 10 %). Statistical uncertainties on the measurement are considered for the net area (lower than 10%) and for the calibration efficiencies (lower than 10%). They are expressed with expending factor equal to 2 and are calculated as the sum of the statistical and systematic quadratic errors. The acquisition times of the samples and the background were respectively equal to 100000 and 250000 s. The gamma line transitions used for specific activity calculations were 351.9 keV of ^{214}Pb; 609.3, 1120.3 and 1764 keV of

^{214}Bi for ^{226}Ra; 338.4, 911.1 and 968.9 keV of ^{228}Ac for ^{228}Ra (^{232}Th); and 1460.8 keV for ^{40}K.

3. RESULTS AND DISCUSSION

The specific activities of ^{226}Ra, ^{232}Th(^{228}Ra) and ^{40}K in the studied samples are shown in table 1 with the radium equivalent activity index (Ra_{Eq}) which is defined as [3] :

$$Ra_{Eq} = C_{Ra} + 1.43C_{Th} + 0.077C_K \tag{1}$$

This index serves to compare specific activities of samples containing different concentrations of these radionuclides. It is expressed in Bq/kg and defined based on the hypothesis that 10 Bq/kg of ^{226}Ra, 7 Bq/kg of ^{232}Th and 130 Bq/kg of ^{40}K produce the same gamma dose rate. C_{Ra}, C_{Th} and C_K in the equation (1) are the coefficients corresponds to the specific concentrations of radium, thorium and potassium isotopes, respectively. As seen in table 1, ^{40}K concentration values are generally higher than the ones corresponding to ^{226}Ra and ^{232}Th with the exception of the DAP sample. The highest value is 9969±32 Bq/kg for the NPK 15-3-35 (imported fertilizer) which is due to its highest content of potassium compared to the other analysed NPKs. ^{232}Th activity concentration varies between 0.3±0.1 Bq/kg (for NPK 20-20-20) and 34.0±2.5 Bqkg-1 (for TSP) and ^{226}Ra activity concentration varies between 0.3±0.1 Bq/kg (for NPK 13-40-13) and 186.2±12.5 Bq/kg (for TSP).

TABLE 1: RADIUM, POTASSIUM AND THORIUM RADIONUCLIDES ACTIVITY CONCENTRATIONS AND Raeq OF THE ANALYSED PHOSPHATE FERTILIZERS

Fertilizer	^{226}Ra (Bq/kg)	^{40}K (Bq/kg)	^{232}Th (Bq/kg)	Raeq (Bq/kg)
DAP[a]	20.2±1.9	47.6±3.5	18.0±2.1	50
TSP[a]	186.2±12.5	53.0±2.5	34.0±2.5	239
NPK 20-20-20	<LLD	5305±35	0.3±0.1	410
NPK 15-3-35	4.4±1.5	9969±32	2.2±1.1	775
NPK 1-60-20	2.8±1.1	5279±24	0.6±0.2	410
NPK 13-40-13	0.3±0.1	3875±29	<LLD	299
NPK 9-35-9	1.1±0.5	3417±28	<LLD	264
NPK 23-10-10	1.9±0.5	3413±30	2.3±0.2	268
Phosphoric acid[a]	<LLD	15.9±1.9	14.2±1.5	21

[a] Local fertilizers

Ra_{Eq} values were found to be higher than the limit value of 370 Bq/kg corresponding to a radiation dose of 1.5 mSv/y for the following analysed fertilizers, NPK 20-20-20, NPK 15-3-35 and NPK 1-60-20, which are imported products. For the local fertilizers, the highest Ra_{Eq} corresponds to the TSP (235 Bq/kg) which is lower than the maximum value of 370 Bq/kg. It is important to note that for the phosphoric acid the activity corresponding to ^{226}Ra radionuclide was under our detection limit. This could be due to the fact that this radionuclide behaves chemically like calcium and then appears at the end of the phosphoric acid process in the gypsum and in the material deposit on the tubes. As we expect to find measurable concentrations of ^{226}Ra in the phosphoric acid (local product) and in the imported NPK 20-20-20 sample because this isotope belongs naturally to the ^{238}U series, we can suppose that during the processes of production of these fertilizers a high amount of ^{226}Ra was transferred (by precipitation for the case of phosphoric acid for example) to the production equipment as tubes and tanks. ^{226}Ra activity concentration measurements have to be performed at the level of the deposited substances in the material production to confirm this hypothesis which, if real, could expose workers in the corresponding factories to high level of radiation.

4. CONCLUSION

Natural radioactivity content of local and imported phosphate fertilizers commonly used in Tunisia was measured using HPGe gamma spectrometry. It was found that Tunisian fertilizers (TSP, DAP and phosphoric acid) have a Ra_{Eq} which de no exceed the maximum recommended value of 370 Bq/kg. Although, three samples from the imported fertilizers which consists on NPKs were found to exceed this value due to their high content on ^{40}K. It was also found that the phosphoric acid which is a local fertilizer contains a very low concentration of ^{226}Ra which was lower than our lower limit of detection. Possible hypothesis explaining this finding were proposed.

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RECYCLING OF METALLIC RESIDUES WITH NORM CONTAMINATION BY MELTING

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Abstract

A lot of branches dealing with raw material generate NORM contaminated scrap from the decommissioning of their facilities. The naturally occurred radioactivity results from the decay of uranium and thorium which is concentrated in scales or sludges on the surface of components and tubes. Scale is formed in gas and oil field equipment due to the precipitation of alkaline earth metal sulphates and carbonates, particularly $CaCO_3$ and $Sr/BaSO_4$ which also contain Uranium and Radium. Depending on the region of the oil and gas field, specific activity is amounting to some hundred Bq/g, often cross-contaminated by mercury and hydrocarbons. Scrapped components from phosphor plants show well detectable activity in scales up to some 10 Bq/g. The welding rod and filament industry generates thoronated tungsten waste with thorium activities between 10-15 Bq/g. Other branches like coal mining, rare earth or non-ferrous metal are to be considered, too. In order to avoid radioactivity input in the steel and non-ferrous metal cycle, scrap yards and steel mills are equipped with gate detectors. Scrap loads with radiation levels above background are rejected at the entrance. Most detections result from NORM contamination in the scrap. For this rejected scrap, Siempelkamp offers the service to decontaminate it in a special melting plant, licensed according to the federal law on protection against environmental pollution (BImSchG). The annual dose exposure to workers does not exceed 1 mSv/a in the plant. In accordance with the European Basic Safety Standard and the German Radiation Protection Ordinance, no licensing nor radiation surveillance or protection is required. Authorized recycling and underground dumping is assured for the waste resulting from the melting process, like slag and dust, in which radioactivity is accumulated. The paper will present experiences and results from melting projects for different industries.

1. INTRODUCTION

Since 1998 Siempelkamp Nukleartechnik operates a melting plant in Krefeld, Germany, to treat steel scrap contaminated with NORM, mercury, asbestos or hazardous organics. The so called GERTA facility was a spin off of a melting facility for slightly radioactive metal scrap from nuclear power plants and is licensed in accordance with the German BImSchG (Federal Law on protection against environmental pollution).

GERTA facility is able to treat steel scrap contaminated with NORM from oil and gas extraction operations, fertilizer plants, paper mills or to recycle tungsten-thorium residues. The generated steel ingots are almost free of detectable radioactivity and other impurities and can be reused in the conventional steel cycle.

Concerning the processing of NORM contaminated scrap the annual dose exposure to workers does not exceed 1 mSv in the GERTA plant and therefore no licensing nor radiation surveillance or protection is required according to the GRPO (German Radiation Protection Ordinance) [1] [3]. But nevertheless the process is controlled by the own radiation protection team.

2. PROCESS AND RADIOLOGICAL ASPECTS

2.1 Licensing and Specification for Incoming Material

The specification for incoming steel scrap originates from restrictions based on foundry processing, on safety regulations and on specific threshold values related to the different contaminations.

The radiological acceptance limit is depending on the threshold values for the release of slag and will be discussed in chapter “Handling of metal ingots, slag and filter residues” below.

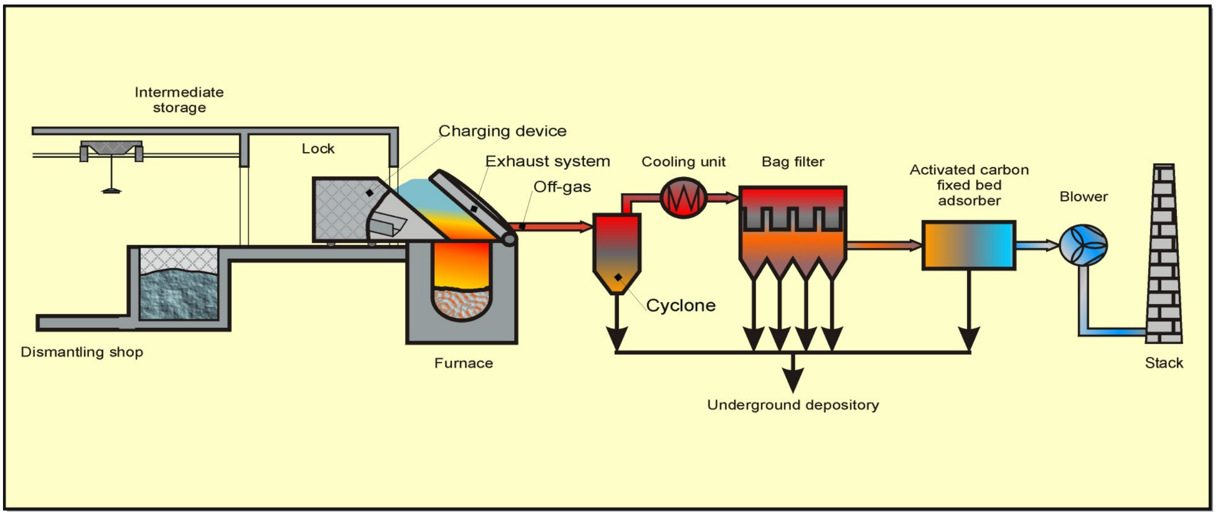

FIG 1. Recycling process in the GERTA-plant including off- gas processing (schematically)

Organics like plastics and rubber are limited to 5 wt-%. Mercury is limited to 1 wt-% of the steel mass. Asbestos is restricted to 0,1 %. PCB´s are restricted to 50 mg/kg. The sum of PCDD/F is restricted to 10,000 ng/kg (according to the international toxidic equivalent) averaged over the total steel mass. The total annual throughput of the plant is currently limited to 2,000 t.

2.2 Process

The decontamination process can be divided into three steps: dismantling, melting and off-gas-processing. Figure 1 shows schematically the three steps, dismantling/storage, melting and off gas processing.

2.3 Entrance check, dismantling and storage

All incoming material first has to pass through a gate detector for radiological check, before it enters the dismantling area, located in the GERTA hall. In advance, additional spectroscopic analyses have to be performed by authorized laboratories. Chemical contaminations have to be proved by corresponding analyses.

To cut incoming material down to chargeable sizes a hydraulic guillotine shear and an encapsulated thermal cutting chamber are available. Components up to 15 m length, Ø 3,5 m and a weight of approx. 25 t can be handled.

In case of any mercury evaporation, the air in this area is filtered by an exhaust system with a capacity of 13,500 m^3/h.

2.4 Melting

The melting process takes place in a net-frequency-induction-furnace with a capacity of 8 t liquid iron per batch. The furnace can be operated in the temperature range up to 1,580 C.

The scrap is taken from the interim storage bunker and is filled into a charging device which moves through a lock to its end position above the furnace, where the device is closely connected to the top of the furnace so that the off-gas can be extracted and conveyed to the filter system.

During the melting process, contaminations of the scrap behave in different ways. NORM behaves differently depending upon the kind of radionuclides. The oxides of Radium, Uranium and Thorium isotopes are transferred into the slag which is separated from the melt. Volatile isotopes like lead (Pb-210) and polonium (Po-210) remain with the dust in the filter system (see Tab. 1). Elementary mercury evaporates completely and is partly absorbed by lime powder which is added to the exhaust gas or by the dust. Other impurities like Asbestos, PCB´s and organics get totally destroyed at the high temperatures.

TABLE 1. PATHS OF RADIONUCLIDES AFTER MELTING

Nuclide	**Melt**	**Slag**	**Dust**
U-238, U-235	1 %	98 %	1 %
Th-232, Th-234	< 1 %	> 98 %	1 %
Ra-226, Ra-228	-	98 %	2 %
Pb-210	-	7 %	93 %
Po-210	-	2 %	98 %

2.5 Off-gas-processing

Dust and off-gas evaporate from the melt and pass through the exhaust cover to a second off-gas and filter system with a capacity of 15,000 m³/h. This filter system consists of four steps, a cyclone, a cooler, a bag filter and a fixed-bed-absorber.

The cyclone is ensuring the separation of furnace sparks as well as of large hot particles. Additionally lime powder is added to the off gas to bind a part of vaporised mercury. Through the air cooling system, where the off-gas is cooled down to lower temperatures to enable optimum efficiency of the following devices, the gas reaches a bag filter, which is separating dust as well as a large part of the mercury adherent to the dust and the lime. The fixed-bed-absorber with activated carbon is doped with sulphur and serves for the separation of mercury and regenerated cyclic chloridic hydrocarbons.

This combination of filters prevents the mercury concentration in the chimney stack from exceeding 50 µg/m³, which is only ¼ of the permitted value.

As NORM scrap is processed, vaporised Pb-210 and Po-210 condense and are absorbed by the dust and retained in the bag filter.

Dust emissions do not exceed 20 mg/m³ according to BImSchG.

2.6 Handling of Metal Ingots, Slag and Filter Residues

Output of the recycling process are metal ingots (amounting to 90-95 wt-%). For the slag (4-10 wt-%), the German authorities require a recycling path in accordance with the 1 mSv/a criteria for workers and population. Only the dust (1-2 wt-%) has to be disposed underground.

The melt is almost free from any radioactivity. Further on the metal is free of any chemical contamination. So far 100 % of the produced ingots, amounting to almost 16,000 t could be reused in the steel cycle.

The slag is free of any toxic impurities but contains a certain amount of the radioisotopes.

The German Radiation Protection Ordinance postulates the monitoring of NORM-contaminated residues according to appendix XI, § 96 respectively § 102, if the dose exposure to the public may exceed 1 mSv per year. To check this limit value, exposure calculations for the slag from NORM melting campaigns were carried out by an accredited radiological expert team and all possible paths of exposure for the slag processing, were taken into consideration [1]. The calculation based on the assumption of 100 Mg slag production from NORM-contaminated scrap melting of 1,000 Mg per year. Table 2 shows the results of the calculation as specific activity values for the slag to be sent for recycling. A common practice is recycling of slags from induction furnace process to road construction material, but for the 100 Mg of NORM slag the recycling was licensed under the conditions that

- the slags are mixed on site in a quota of 1:4 with slags free of NORM.
- processing is contracted with a recycling company of an annual throughput of approx. 100,000 t/y
- recycling to construction material for landfill sites like temporary roads etc.

Since starting operation of GERTA melting plant, 100% of the slag could be recycled by this path. Based on that fact the acceptance limits for scrap can be calculated related to the mass and specific activity of each batch of incoming material.

Only 1-2 wt.-% of the input-material is dust retained in the bag filter and in the cyclone. Both kinds of dust are mixed with quick lime and are then filled into storage drums. Underground storage in rock salt mines up to a depth of 200 metres offers a disposal solution for hazardous waste in Germany, that has long been regarded as safe for the environment. The radiation exposure to the mine workers and to the public has to be less than 1 mSv/a, which Siempelkamp also proved by an expert opinion. Additionally, the filter dust must not be radioactive in the sense of the former ADR regulation for transport, that means the total activity of Pb-210/Po-210 must be below 70 Bq/g [2].

3. EXPERIENCES

3.1 NORM and Mercury Contaminated Scrap from Oil and Gas Industry

Depending on the deposit, oil and natural gas carries a freight of NORM and/or mercury, which remains mostly encapsulated in a $CaCO_3$ or $Sr/BaSO_4$–scale (in case of NORM) or condenses in case of mercury in tubes, pipelines or components.

So far 2,710 t of NORM or NORM/Hg contaminated scrap from North sea on- and offshore installations have been processed for several Dutch and German producers [FIG. 2].

TABLE 2. NUCLIDE SPECIFIC ACTIVITY LIMITS FOR SLAG
TO BE SENT FOR RECYCLING

Nuclide	**Specific activity [Bq/g]**
U-238sec	21
Th-232sec	15
Ra-226+	25
Pb-210++	40

Additionally 7,355 t Hg contaminated scrap from onshore gas installations have been processed.

The experience of Siempelkamp varies between < 1 Bq/g up to 250 Bq/g specific activity in the scale and a maximum of 1 wt-% of mercury related to the steel mass. The activity results mostly from the Uranium decay series where Ra-226 is the main radionuclide.

3.2 Tungsten Thorium Scrap

Filaments and welding rods are made of an W-Fe-Th alloy. Up to 4 wt.-% of radioactive ThO2 and a certain amount of molybdenum are sintered with tungsten powder to enhance the properties of tungsten for the use in filaments and welding rods. This leads to activity levels of up to 65 Bq/g Th-232sec for the particular alloy. The average activity of the residues, which have been processed at Siempelkamp was 12 Bq/g.

Concerning the high melting point of tungsten (3,410°C), Siempelkamp uses the eutectic of the tungsten–iron alloy to be able to melt the tungsten at temperatures suitable to a net frequency induction furnace. During the melting process the W-Fe-Th-alloy is solved and the main elements and components behave in different ways. Tungsten remains in the melt. The thorium and its non volatile daughter products are transferred into the slag. Volatile isotopes from the thorium decay chain remain with the dust in the filter system.

The transfer of the radionuclides into the slag results in a decontaminated melt, which is reusable. The produced ferro-tungsten (17-25 wt.-% W) is used as an additive for alloyed steel. So far Siempelkamp recycled successfully 530 t of Tungsten scrap [4].

FIG. 2. Components from oil and gas industry

FIG. 3. Scale in a tank of a phosphate plant

3.3 NORM from Phosphate Industry

Fertilizer producing facilities using phosphate rock as raw material also show contamination with radionuclides of the Uranium decay series. The radioactive isotopes are found in an encapsulated form in fluorides, calcium sulphates or phosphates which form the scale [5] [FIG. 3].

The specific activity of the scale is between 10 and 130 Bq/g. So far Siempelkamp got experience in several projects with material from The Netherlands, Greece, Northern Africa and Germany amounting to a total weight of 300 t. Scrap from fertilizer plants consists mainly of stainless steel, which also can be processed without any problem in the induction furnace.

4. SUMMARY

Siempelkamp offers a complete recycling service for NORM contaminated metal scrap including dismantling, decontamination and recycling/disposal of melting process residues. For this purpose Siempelkamp operates a dismantling and melting facility in Krefeld, Germany. Components up to 25 t weight and 12 m length can be handled in a sealed dismantling shop. Several kinds of metals (carbon steel, stainless steel, tungsten) can be decontaminated by melting. Cross contaminations with mercury exist especially in pipes and components of the oil and gas industry. The mass distribution of scrap from served industries is shown in FIG. 4. The produced metal ingots are reusable in the conventional steel cycle. The slag can be processed due to the 1 mSv/a criteria within certain thresholds. Dust can be stored in an underground disposal.

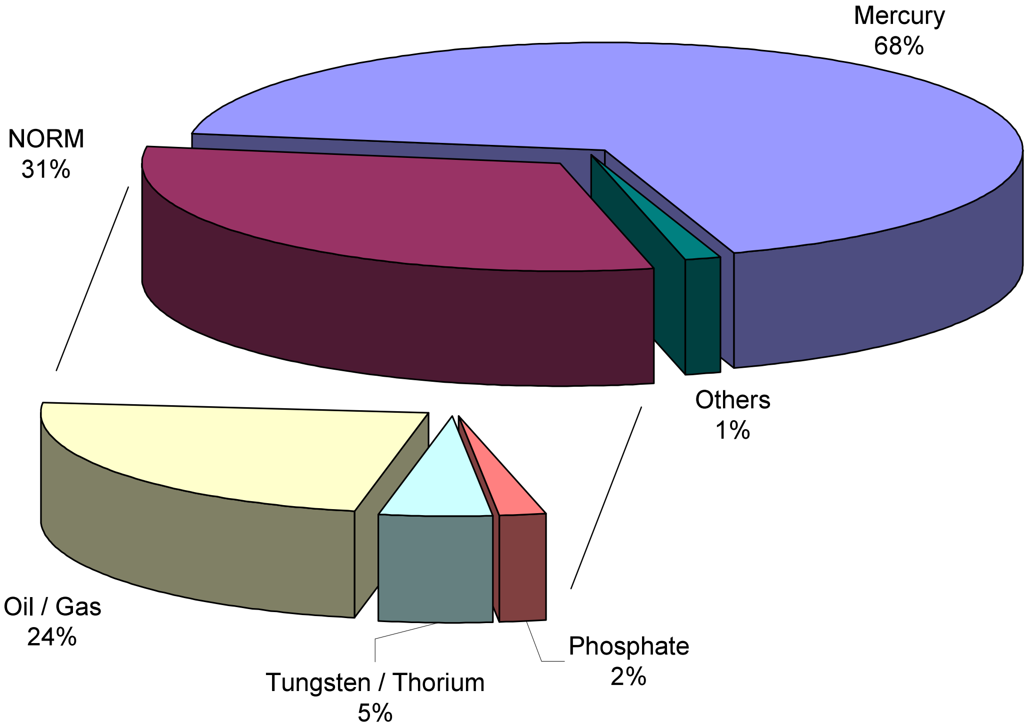

FIG. 4. Mass distribution of scrap from served industries

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LEVELS OF NATURAL RADIONUCLIDES IN CEMENTS AND CLAY BASED BUILDING MATERIALS USED IN SOUTH WEST COASTAL REGION OF INDIA

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Abstract

Building materials are one among the potential sources of indoor radioactivity. Naturally occurring radio nuclides in building materials are sources of gamma radiation exposure in dwellings. The internal radiation exposure occurs due to the short-lived daughter products of radon, which exhales into room air from building material. Natural clay is the most widely used raw material for the production of bricks and tiles. Use of industrial waste materials like fly ash for the manufacture of cement and cement bricks are increased manifold in the recent years. The south west coastal region of India is known to have high natural back ground radiation mainly because of the thorium rich monazite sand available in plenty in the region. There are several dwellings in the region with unusually high levels of indoor radiation levels. After subsoil emanation of radio nuclides into the indoor atmosphere, the second major radiation contributor is the building materials namely cement, bricks and tiles. In the present study samples of cement, bricks, floor and wall tiles have been analysed for their uranium, thorium and potassium levels. Gamma ray spectrometry using NaI(Tl) scintillation detector has been used. Levels of uranium, thorium and potassium were found to vary widely depending on the building materials. Radium equivalent activities for the samples to assess the radiation hazards arising due to the use of these materials in the construction of dwellings, gamma dose rate, effective dose equivalent, internal and external hazard indexes are also presented.

1. INTRODUCTION

Naturally occurring radioactive materials (NORM) are found everywhere including soil, rock, vegetation, air, and water. Radioactive material has been ubiquitous on earth since its creation and therefore, we inhale and ingest radionuclides every day of our life. Radioactive elements which can be found in nature are generally categorized in two distinct classes, namely ‘cosmogenic’ and ‘terrestrial’. The most commonly encountered radionuclides are ^{238}U and ^{232}Th and their subsequent radioactive decay products and ^{40}K [1, 2]. Building materials are either part of the environment or derived from naturally occurring materials. Cement, Bricks and other clay based building materials like tiles are used extensively for the construction of buildings. Use of industrial waste materials like fly ash for the manufacture of cement and cement bricks are increased manifold in the recent years. The reasons for the use of industrial wastes products as admixtures in building materials are cost reduction, saving of natural resources and recycling. Fly ash is known to contain elevated levels of long lived radio nuclides like uranium [3]. Owing to its relatively small size and hence large surface area, fly ash has a greater tendency to absorb trace elements that are transferred from coal to waste products during combustion [4]. Human population is directly exposed to the radiation from building materials. Knowledge of natural radioactivity in them becomes an important aspect while assessing the health effects of NORM. Materials derived from rock and soils contain mainly natural radioisotopes of the uranium (^{238}U) and thorium (^{232}Th) series, and the radioisotope of potassium (^{40}K). These radionuclides constitute natural sources of indoor and outdoor radiation exposure as well as internal and external radiation exposure. Natural radioactivity and the associated external exposure due to gamma radiation depend primarily on the geological and geographical conditions, and appear at different levels in the soil of each region in the world. The activity concentrations of radionuclides in the building materials and its components are important in the assessment of population exposures as most individuals spend about 80% of their time indoors. The south west coastal region of India is known to have high natural back ground radiation mainly because of the thorium rich monazite sand available in plenty in the region. There are several dwellings in the region with unusually high levels of indoor radiation levels. In the present study samples of cement, bricks, floor and wall tiles have been analysed for their uranium, thorium and potassium levels.

2. MATERIALS AND METHODS

There are a large variety of building materials being used for construction of dwellings in the region. Most commonly used brands of cements and ceramic tiles were selected for the study. For manufacturing bricks clay is collected from local fields. There are several brick factories in the district of Kollam and therefore it was difficult to analyze all brands of bricks available. Therefore, the selection of brick samples was at random. Samples of cement, bricks and tiles were collected from the construction sites situated in the coastal region of Kollam district in the state of Kerala. The samples include six brands of most commonly used cement, four brands of clay based wall and floor tiles, and bricks from different sources. Two to four samples of each brand and category was collected for the analysis. Altogether sixty samples were collected and analyzed. Cement samples were dried in hot air oven, sieved and stored in the polyethylene cans of specific size (70 mm diameter and 80mm height). While collecting samples, external gamma dose rates were also measured using a GM tube based survey meter. The collected samples of tiles and bricks were crushed to small pieces and ground to fine grain size and sieved with a sieve of about 100 size mesh in order to homogenize it and remove big size particles. The samples were then dried at 110^0 C for 24 h to ensure that moisture is completely removed. The homogenised samples were packed in standard polyethylene cans and were hermetically sealed with adhesive tape and left for 6 weeks, in order to ensure that the daughter products of ^{226}Ra up to ^{210}Pb and of ^{232}Th up to ^{208}Pb are in secular equilibrium with their respective parent radio nuclides, before analyzing by gamma spectrometry. Analysis of the sample for determining the levels of ^{238}U, ^{232}Th and ^{40}K were done using a flat type 3”x3” NaI(Tl) detector, housed in a 3” thick graded lead shield, PC coupled 8 K MCA. The energy resolution of the detector was 1.95 keV at 1332 keV of a ^{60}Co source. A cylindrical source (having homogeneously distributed activity with constant volume and shape) was placed coaxially with the detector for efficiency determination and the same procedure was applied for sample measurements. The activity of ^{40}K was evaluated from the 1460 keV photo peak of its own gamma, the activity of ^{238}U from 1764 keV gamma ray of ^{214}Bi and that of ^{232}Th from 2614 keV gamma ray of ^{208}Tl. Each sample was counted for 18000s. Background counts were deducted for obtaining the net activity. In the uranium series the decay chain segment starting from radium (^{226}Ra) is radiologically the most important and, therefore, reference is often made to radium instead of uranium.

3. CALCULATION OF RADIOLOGICAL EFFECTS

3.1 Radium equivalent activity (Ra_{eq})

Distribution of ^{238}U, ^{232}Th and ^{40}K in environment is not uniform, so that with respect to exposure to radiation, the radioactivity has been defined in terms of radium equivalent activity (Ra_{eq}) in Bq/kg to compare the specific activity of materials containing different amounts of ^{238}U, ^{232}Th and ^{40}K. An index called the 'radium equivalent activity' to obtain the sum of activities for comparison of the specific radio activities of materials containing different radionuclides like Ra, Th and K. It has been estimated that 370 Bq/kg of ^{226}Ra, 260 Bq/kg of ^{232}Th and 4810 Bq/kg of ^{40}K produce the same gamma ray dose rate. Thus the radium equivalent activities (Ra_{eq}) were estimated using the equation (1) of Ref. [5]

$$Ra_{eq} = C_U + 1.43C_{Th} + 0.077C_K \tag{1}$$

where C_U , C_{Th} and C_K are activity concentration in Bq/kg of ^{238}U, ^{232}Th and ^{40}K, respectively.

3.2 External hazard index (H_{ex}):

The ultimate use of the measured activities in building materials is to estimate the radiation dose expected to be delivered externally if a building is constructed using these materials. The external hazard index (H_{ex}) is given by the following equation: [6,7]

$$H_{ex} = C_{Ra}(370)^{-1} + C_{Th}(259)^{-1} + C_K(4810)^{-1} \tag{2}$$

where C_{Ra}, C_{Th} and C_K are the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in Bq/kg, respectively . The value of this index must be less than unity in order to keep the radiation hazard to be insignificant. This is the radiation exposure due to the radioactivity from a construction material, limited to 1.5 mGy/yr. The maximum values of H_{ex} equal to unity corresponds to the upper limit of Ra_{eq} 370 Bq/kg [8].

3.3 Internal hazard index (H_{in}):

The internal exposure to ^{222}Rn and its radioactive progeny is controlled by the internal hazard index (H_{in}) which is given by [9,10]

$$H_{in}= C_{Ra}(185)^{-1} +C_{Th} (259)^{-1}+ C_K(4810)^{-1} \tag{3}$$

For the safe use of a material in the construction of dwellings, index (H_{in}) should be less than unity[11]

3.4 Absorbed Dose (D)

Gamma dose rate (D) in air at 1 m above the ground level has been calculated with the equation:

$$D = 0.427 C_U + 0.662 C_{Th} + 0.043 C_K \tag{4}$$

where 0.042, 0.666 and 0.430(nGy/h per Bq/kg) are the dose conversion factors for ^{238}U, ^{232}Th and ^{40}K respectively [7]

3.5 Annual Effective Dose Equivalent (EDE)

In order to estimate the annual effective dose rate from absorbed dose, the conversion coefficient of 0.7 Sv/Gy has been used as suggested by UNSCEAR 2000 [7] The indoor occupancy factor which is about 0.8 is given in the same reference. The annual effective dose equivalent in the indoor environment is given by the following equation:

$$EDE(\mathrm{m}Sv\,/\,y) = D(nGy\,/\,h \times 8760(h\,/\,y) \times 0.8 \times 0.7(Sv\,/Gy) \qquad (5)$$

Therefore, the annual effective dose equivalent in the outdoor environment with the occupancy factor of 0.2 is given by:

$$EDE(\mathrm{m}Sv\,/\,y) = D(nGy\,/\,h \times 8760(h\,/\,y) \times 0.2 \times 0.7(Sv\,/Gy) \qquad (6)$$

4. RESULTS AND DISCUSSION

The results of radiometric analysis of the samples are summarized in the Tables 1-3. Table 1 shows the measured specific activity concentrations of the ^{238}U, ^{232}Th, and ^{40}K in the Cement samples (C1-C6), Floor tiles (FT1-FT4), Wall tiles (WT1-WT4) and Bricks (B1-B8) analyzed. Table 2 depicts the results of the calculated radiological effects namely radium equivalent activity (Ra_{eq}), external hazard index (H_{ex}), internal hazard index (H_{in}), Gamma dose (D) and effective dose equivalent (EDE) of the samples investigated. Table 3 summarizes the statistics of the results of radioactivity analysis of the building materials. The measured specific activity concentration of ^{238}U, ^{232}Th, ^{40}K and radium equivalent activity in cement samples were found to have mean values of 54±15.06, 66.03±12.10, 490.66±105.63 and 186.20±35.50 Bq/kg, respectively. The activity concentration of ^{238}U, ^{232}Th, ^{40}K and radium equivalent activity in floor tiles were found to have mean values of 46.94±9.67, 60.78±3.84, 482.58±28.09 and 171.01±13.50 Bq/kg, respectively whereas for wall tiles these values were 45.42±9.3, 56.84±3.72, 494.37±46.82 and 164.77±14.69 Bq/kg, respectively. The specific activity concentration of ^{238}U, ^{232}Th, ^{40}K and radium equivalent activity in bricks were found to have mean values of 20.54±4.52, 23.49±4.35, 289.51±20.02 and 76.34±10.76 Bq/kg, respectively.

The present study has been carried out to establish baseline data regarding concentration levels of naturally occurring radionuclides of ^{238}U, ^{232}Th, and ^{40}K in cements and clay based building materials used in the region. The data generated here may be useful for the introduction of radiation safety standards by the authorized organizations for the protection of general population from radiation hazards owing to terrestrial sources. Table 3 indicates that the concentrations of uranium and thorium are slightly more than the world average of these isotopes in soil samples. The worldwide concentrations of the radionuclides ^{238}U, ^{232}Th and ^{40}K in soil have averages 40, 40, and 580 Bq/kg respectively [7]. The radium equivalent activity values for all samples of cements, bricks and tiles are lower than the safe limit value (370Bq/kg) recommended by OECD[12].

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TABLE 1. THE MEASURED SPECIFIC ACTIVITY CONCENTRATIONS OF THE ^{238}U, ^{232}Th, AND ^{40}K IN THE SAMPLES

Sample No	Number of samples	^{238}U (Bq/kg)	^{232}Th (Bq/kg)	^{40}K (Bq/kg)
C1	3	56.76	67.89	567.33
C2	3	77.45	68.24	612.67
C3	3	48.62	80.43	438.84
C4	3	62.42	72.75	566.24
C5	3	44.24	62.22	410.22
C6	4	34.48	44.65	348.68
FT1	3	45.33	62.44	448.24
FT2	4	37.65	58.46	496.43
FT3	3	60.52	65.34	472.98
FT4	4	44.26	56.88	512.65
WT1	3	42.88	52.66	523.88
WT2	2	36.89	59.6	468.74
WT3	3	58.66	60.33	542.64
WT4	3	43.26	54.77	442.23
B1	2	20.18	20.68	283.14
B2	2	18.45	20.44	264.22
B3	2	25.45	28.34	276.54
B4	2	15.67	19.45	320.69
B5	2	27.33	30.11	289.45
B6	2	23.56	27.45	318.32
B7	2	15.32	21.25	277.45
B8	2	17.66	20.23	286.28

TABLE 2. THE CALCULATED VALUES OF RADIUM EQUIVALENT ACTIVITY (Ra_{eq}) EXTERNAL HAZARD INDEX (H_{ex}), INTERNAL HAZARD INDEX (H_{in}), GAMMA DOSE (D) AND EFFECTIVE DOSE EQUIVALENT (EDE) OF THE SAMPLES UNDER INVESTIGATION.

Sample No.	Ra_{eq} (Bq/kg)	H_{ex} (Bq/kg)	H_{in} (Bq/kg)	D nGy/h	EDE mSv/y
C1	197.53	0.53	0.69	93.57	0.46
C2	222.21	0.60	0.81	104.59	0.51
C3	197.43	0.53	0.66	92.88	0.46
C4	210.05	0.57	0.74	99.16	0.49
C5	164.80	0.45	0.56	77.72	0.38
C6	125.18	0.34	0.43	59.27	0.29
FT1	169.13	0.46	0.58	79.97	0.39
FT2	159.47	0.43	0.53	76.12	0.37
FT3	190.38	0.51	0.68	89.44	0.44
FT4	165.07	0.45	0.57	78.60	0.39
WT1	158.52	0.43	0.54	75.70	0.37
WT2	158.21	0.43	0.53	75.36	0.37
WT3	186.72	0.50	0.66	88.32	0.43
WT4	155.63	0.42	0.54	73.75	0.36
B1	71.55	0.19	0.25	34.48	0.17
B2	68.02	0.18	0.23	32.77	0.16
B3	87.27	0.24	0.30	41.52	0.20
B4	68.18	0.18	0.23	33.36	0.16
B5	92.67	0.25	0.32	44.05	0.22
B6	87.32	0.24	0.30	41.92	0.21
B7	67.07	0.18	0.22	32.54	0.16
B8	68.63	0.19	0.23	33.24	0.16

TABLE 3. MEASURED MAXIMUM, MINIMUM, MEAN AND STANDARD DEVIATION OF THE LEVELS OF ^{238}U, ^{232}Th, ^{40}K AND THE RADIUM EQUIVALENT ACTIVITY IN THE FOUR TYPES OF BUILDING MATERIALS

		U (Bq/kg)	Th (Bq/kg)	K (Bq/kg)	Ra_{eq} (Bq/kg)
Cement 19 samples	Maximum	84.02	82.43	614.66	225.46
	Minimum	30.08	40.67	346.22	123.47
	Mean	54	66.03	490.66	186.20
	Std. Deviation	15.06	12.10	105.63	35.50
Floor tiles 14 samples	Maximum	68.54	66.64	510.06	192.28
	Minimum	34.66	55.26	444.82	154.46
	Mean	46.94	60.78	482.58	171.01
	Std. Deviation	9.67	3.84	28.09	13.50
Wall Tiles 11 samples	Maximum	62.08	61.42	544.68	187.62
	Minimum	34.86	52.48	440.62	153.42
	Mean	45.42	56.84	494.37	164.77
	Std. Deviation	9.3	3.72	46.82	14.69
Bricks 16 samples	Maximum	28.88	31.12	324.42	93.87
	Minimum	13.68	18.84	260.88	66.08
	Mean	20.54	23.49	289.51	76.34
	Std. Deviation	4.52	4.35	20.02	10.76

STATUS OF INDUSTRIAL USE OF NORM AND THE REGULATION POLICY IN JAPAN

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Abstract

The amount and types of the minerals or ore for industrial use imported to or produced in Japan were investigated. Exposures to workers who are engaged in use of the materials were estimated from the information of the field measurements and usage of the materials. The annual exposures to the workers were found to range from level as low as those for natural background to less than 1 mSv/y. Among NORM contained consumer products, ship bottom paint, clothes, bedclothes, etc. were also investigated. The examination revealed that some of the goods caused users to receive external exposure of more than 100 µSv/y under the normal conditions of the use. Under these results, General Administrative Group of the Radiation Council in Japan discussed issues for exemption level related to control of the industrial use of NORM. From the result of discussions, the policy on the regulation with categorization of NORM according to controllability and degree of artificialness were shown. The guideline for voluntary regulation of NORM according to the policy was also published last year.

1. INTRODUCTION

In Japan General Administrative Group of the Radiation Council examined exemption of NORM, in connection with the introduction of BSS exemption levels into national laws. Through this examination, the current status of industrial use of NORM in Japan was surveyed and the policy of the regulation of NORM was mentioned in the same report in 2004 [1].

For the implementation of the regulation policy, a guideline for voluntary regulation of NORM according to the policy was also published and explanatory meetings for the involved industry were held in 2009 [2]. The categories of materials which are possibly subject to voluntary regulation were designated in the guideline. In this report the current status of industrial use of NORM and the regulation policy were summarized with reference to published documents [1,2].

2. SURVEY ON INDUSTRIAL USE

2.1. Materials and methods

Japan is a country with few natural resources and is dependent on imported raw materials from overseas for its industrial activities. Among those raw materials, the survey on current industrial use of NORM were conducted for monazite, phosphate ore, titanium minerals, bastnaesite and zircon, which may contain NORM with relatively high concentration through literature survey and an actual condition survey. Also coal was surveyed for its large amount of import, and samarium oxide, for which activity concentration in pure metal exceeds 1 Bq/g IAEA exemption levels [3,4].

Ambient radiation dose rates were measured with NaI(Tl) scintillation survey meter at the surface and at 1m away from the NORM. Samples of NORM containing material were corrected and measured concentrations of uranium, thorium and samarium with inductively coupled plasma mass spectrometer (ICP-MS). The activity concentrations of ^{238}U, ^{232}Th and ^{147}Sm were then determined using the specific activity of each nuclide. The effective dose to worker was estimated with the annual working time and the workplace radiation dose rate subtracted background dose rate from the measured one at 1m away.

2.2.Results

The survey results shown in Table 1 indicate the activity concentrations of the minerals depend on the producing countries. For phosphate ores from Jordan and Morocco exceeded 1 Bq/g of IAEA exemption level [2]. Since monazite, zircon and bastnaesite are not chemically processed and their chemical components remain unchanged, the materials are marketed directly or as products mixed with other substances. The waste arising from these minerals in the separation processes is normally treated as industrial waste, and the activity concentration in the waste that exceeded the IAEA exemption level was not found. This may be due to the fact that the concentration is diluted in these processes. As the result of measurement of ambient radiation dose rates, the case was found where even the raw materials of low activity concentrations sometimes gave a relatively high dose rate at the surface, even at 1m away from NORM, due to the adhesion of scales to the process stream. However, in consideration of actual working hours, the annual dose exposure to workers is estimated to be about 0.40 mSv/y at most for the work at a bastnaesite product yard. When workers handle raw material powders and other powdery substances, the amount of dust inhaled by the workers are estimated to be small because they usually wear dust protective masks. Furthermore, an ambient radiation dose rate at the site boundary was found to be almost equivalent to the natural radiation dose rate of 0.004 to 0.11 μSv/h (except for cosmic radiation) across the country. Thus the external dose should cause no particular risks to the general public.

Samarium oxide is converted into metal to be alloyed with cobalt for magnet materials. Since samarium contains ^{147}Sm, a natural radionuclide that emits only α rays, it is necessary to consider internal exposure. During the process of producing alloys and magnets, dust occurs in the pulverization and sintering processes. Hence, airborne concentration of samarium during each process at a workplace was measured to determine an effective dose due to the inhalation of samarium. As a result of maximum concentration $1.7\text{x}10^{-8}$Bq/cm^3 at magnet production place, assuming 1.2 m^3/h as a breathing rate and 2,000 hours as an annual working time, for the inhalation of the dust of particle diameter of 1μm, the annual dose was estimated 380μSv. These values were calculated on a conservative assumption. Being evaluated in consideration of mask-wearing (mask protection factor: 10) and actual working hours, the dose would be lower. For these reasons, the annual dose could not exceed 1 mSv.

TABLE 1. SURVEY RESULTS OF ACTUAL STATE OF APPLICATION OF MINERALS INCLUDING URANIUM AND THORIUM [1]

Minerals	Nuclide analysis concentration (Bq/g)			Mesured radiation dose rate (uSv/h)		Estimated effective dose(mSv/y)
	Sample	U-238	Th-232			
Monazite	Monazite	About 40	About 300	Monazite warehouse	Surface: 100 (Th concentration 7 %)	0.3 (work at product fabrication place)(Annual working time: About 360 hours, workplace dose rate: 0.75uSv/h)
				Product fabrication place	1 m: 0.8	
Phosphate ore	Phosphate ore (Jordan)	0.74	0.0078	Phosphate ore warehouse	Surface:0.32-0.46, 1m:0.19-0.22	0.28. (Work at phosphate ore warehouse) (Annual working time: About 1,600 hours, workplace radiation dose rate: 0.18uSv/h)
	Phosphate ore (Morocco)	1.2	0.0084	Phosphate ore storage	Floor surface: 0.26 1m: 0.17	
	Phosphate ore (China)	0.10	0.0019	Phosphate ore (Morocco)	Surface: 4.6	
	Enriched phosphate	0.8	0.0038	Product warehouse	Surface: 0.05 1m: 0.05	
	Diammonium hydrogen phosphate	0.73	0.0044			
Titanium	Titanium mineral (South Africa)	0.074 - 0.44	0.13 - 0.16	Raw material minerals yard (South Africa)	Surface: 0.20-0.40 1 m: 0.15-0.25	0.27(work at minerals yard)(Annual working time: About 1,400 hours, workplace radiation dose rate: 0.19uSv/h)
	Titanium oxide products	0.018	0.0013	Still standing tank	Surface: 0.30 1 m: 0.15	
	Industrial waste	0.21	0.23	Industrial waste yard	Surface: 0.30 1 m: 0.15	
Bastnaesite	Bastnaesite raw materials	1.1	5.8	Raw material yard	Surface: 1.9 1 m: 0.6	0.40 (Work at product yard) (Annual working time: About 480 hours, workplace radiation dose rate: 0.84uSv/h)
	Solid separated through a filter	1.0	4.9	Raw material input hopper	Surface: 2.0 1 m: 0.10	
	Abrasive products	1.4	7.1	Product yard	Surface: 3.6 1 m: 0.88	
Zircon	Raw material (zircon sand)	4.2	0.77	Raw material yard (zircon flour for firebricks)	Surface: 2.7 1 m: 1.0	0.14 (Work at product yard) (Annual working time: About 120 hours, workplace radiation dose rate: 1.13uSv/h)
	Firebricks (zircon 100 %)	3.5	0.81	80 % zircon-content refractor	Surface: 1.8 1 m: 1.2	
	Dust collected at waste provisional storage yard	0.17	0.037	Waste temporary storage yard	1 m: 0.15	
Coal	Coal (China)	0.015	0.018	Coal-storage yard	Surface: 0.03 1m: 0.03	0.13 (work at clinker warehouse) (Annual working time: About 1,100 hours, workplace radiation dose rate: 0.12uSv/h)
	Clinker	0.097	0.072	Clinker warehouse	Surface: 0.15 1 m: 0.15	
	Fly ash	0.095	0.091		Surface: 0.15 1 m: 0.10	

3. CONSUMER GOODS

3.1. Materials and methods

NORM containing minerals are chemically or physically processed and often used in living environment as consumer goods. They are utilized for various purposes ranging from the products with which few people would come in contact in daily life such as pigment for painting the bottom of ships and catalyst applied to automobile mufflers to those which people could touch with their skin in the daily life such as clothing materials and bedclothes. From a viewpoint of external exposure, there are consumer goods such as wallpaper and paint pigment that provide lower dose per unit area when they are applied to walls though they have high activity concentrations per unit mass. On the other hand, there are consumer goods such as ornaments in which localized exposure should be considered even at their low activity concentrations. For this reason, samples of major consumer goods were analysed. Dose evaluation on some of the samples was conducted under their normal use conditions.

3.2. Results

Uranium and thorium contents of samples were measured with an inductively coupled plasma mass spectrometer (ICP-MS). ^{238}U and ^{232}Th concentrations were then determined by multiplying the results by specific activity of each nuclide. The measured concentrations were shown in Table 2. From the table, some consumer goods were found to exceed IAEA exemption level. In addition, a user's external exposure dose was determined employing a calculation code with modelling the normal conditions and the time of use of the consumer goods and their source geometry [5]. As the results of dose evaluation, an external annual dose 110 μSv/y was assessed for a radon spa bathing element A, 220 μSv/y for underclothes, 90 μSv/y for bedclothes, and 10 μSv/y for wallpaper painted odor-eating paint [5]. The external annual dose may not exceed the public dose limit 1 mSv/y, when a person uses these consumer goods. However, if the person would use several consumer goods at the same time, the annual dose might exceed the limit.

4. REGULATION OF NORM

4.1. Policy of Regulation

According to the published report in 2004 titled "Exemption of NORM from Regulations" by General Administrative Group of the Radiation Council in Japan, the policy of the NORM regulation is described as follows [1].

Industrial activities using NORM containing raw materials and use of NORM containing consumer goods can be controlled, cause exposure of workers and the public, and are selected to make some benefits, so those activities are considered in a category of "Practice" like the use of artificial radiation sources according to ICRP Publ.60 [6]. Since exposure to NORM is no difference from that due to artificial radiation sources, it can be considered that exposure to NORM should be subject to regulation for radiation protection. However, most of NORM containing raw materials that are used for industrial applications are not produced as radioactive substances, not used for the radioactive purposes.

TABLE 2. ACTIVITY CONCENTRATIONS IN CONSUMER GOODS [1]

Sample	Analysis results (activity concentration): (Bq/g)	
	U-238	Th-232
Radon spa bathing element A	34	270
Ship bottom paint pigment	12	81
Radon spa bathing element B	10	81
Bracelet/necklace (ceramics)	1.7-8.8	12-71
Health appliances (containing powders)	5.4	34
Refractory fire brick	2.9-3.5	0.49-0.57
Muffler catalyst	3.3	210
Clothes (incorporating NORM in fabrics)	1	8.8
Supporter/wristband (incorporating NORM in fabrics)	0.011-0.94	0.093-8.5
Odor-eating paint	0.4-0.82	2.9-5.5
Socks (incorporating NORM in fabrics)	0.7	6.2
Seat (incorporating NORM in fabrics)	0.67	5.4
Shoe socking (containing powders)	0.085-0.42	0.63-6.2
Bedclothes (incorporating NORM in fabrics)	0.043-0.26	0.01-2.3
Abrasive	0.2	0.7
Phosphate fertilizer	0.038-0.073	0.0014-0.0015
Sinter or mineral encrustations left by hot springs	0.00084-0.012	0.00081-0.029

(Surveyed by the Nuclear Safety Technology Center and other organizations in fiscal 2002)

From the above viewpoints, General Administrative Group of the Radiation Council in Japan discussed and published the policy on the regulation with categorization of NORM according to controllability and degree of artificialness was shown in Table 3 to classify NORM containing substances and review the measures for individual regulation.

Category 1 in the table shows the substances to be subject to "Exclusion". Category 2 shows substances that should be subject to "Intervention" since long-term exposure from past practices (e.g., mining surplus soil and residues generated from industrial use) was not controlled as "Practice". NORM in Category 3 is contained in substances that are used as raw materials in general industries such as energy production. Industrial activities for those NORM are not subject to "Practice" due to that their activity concentrations are generally well below the BSS exemption levels. Products (coal ash, scale, etc.) generated through the process of these industrial applications are those that are not intended to contain radioactive substances. The products are not produced for radiation purposes, and their activity concentrations and activities are distributed in a wide range. For this reason, Category 3 should also be subject to "Intervention". However, the products are included in Categories 4 and 5 when they are disposed of or reused. In addition, they are included in Category 6 when they are used as consumer goods. Category 4 and 5 is basically considered to be involved in "Practice" when exposure dose from the activity is significantly increased. In most cases, however, these residues are not perceived to contain radioactive substances while their activity concentrations widely vary. For this reason, it is difficult to set an exemption level for the residues and regulate them in the same manner as doing artificial radiation sources. Furthermore, these residues are often disposed of in the same manner as substances from past activities. Since industrial use and mining of these raw materials have a longer history than that of radiation regulation, their exposure pathways may be already existing.It may be difficult to distinguish the residues from the substances when they are disposed of. Therefore, there are some possibilities that the residues can be subject to "Intervention".

TABLE 3 CLASSIFICATION OF NORM-CONTAINING SUBSTANCES AND PROPOSED RESPONSE TO THE SUBSTANCES[1]

	Category	Cases required for review *1	Exclusion, Practice or Intervention	Law-based regulation	Action to be taken	Dose target/ Criteria for action
1	Substances that are not treated to increase a ratio of NORM-containing minerals and ores (Excluding Categories 2, 3, 4, 5, 6)	Garden stone, mineral samples for research and education, mineral samples owned by museums, ores from construction sites and rivers	Exclusion	Not Subject	_	_
2	NORM-containing residues that were disposed of in the past	Residues disposed of from titanium plants or illegally dumped	Intervention	Not Subject	Measures level	Future review (1 to 10 mSv/y)
3	Ash and scale generated from industries (raw material substances whose concentration is below an exemption level)	Coal ash (including fly ash), scale from gas and oil fields, slag from steelmaking plants	Intervention	Not Subject	Measures level	Future review (1 to 10 mSv/y)
4	Surplus soil form operating mines, residues after industrial use (disposal)	Monazite, bastnaesite (abrasive), zircon, tantalite, phosphorus ore, samarium, uranium ore, thorium ore, titanium ore, coal ash (including fly ash), other raw materials for consumer goods	Practice/ Intervention *2	Subject	･Identify substances whose concentration could exceed a certain level. ･Require proper control for radiation protection in proportion to dose received by workers or the public when specific substances are used.	1mSv/y (Review regulation or intervention if this level is exceeded.)
5	Industrial raw materials (fabrication, energy production, mining)(excluding Category 7)	ditto	Practice/ Intervention *2	Subject	Same as in Category 4	1mSv/y (ditto)
6	Consumer goods (use)	Spa bathing element, health appliances, bedclothes, clothes, paint, mantel, automobile catalyst, refractor, abrasive, fertilizer, flowers of sulfur	Practice	Consider whether substances are subject to Practice by commodity.	The BSS exemption level is basically applied.	10uSv/y
					Review a system equivalent to type approval.	1mSv/y
7	Nuclear fuel substances and radium sources that were refined for radiation use and substances used as radiation sources	Nuclear fuel materials (uranium and thorium), radium, etc.	Practice	Subject	The BSS exemption level is basically applied.	10uSv/y
8	Radon	Radon generated from radium sources under regulation	Practice	Subject	The BSS exemption level is basically applied.	_
		Occupational radon in mines for nuclear raw material	Practice	Under the Mine Safety Law	_	_
		Radon in houses and general occupational environment, except radon in the above	Intervention	Not Subject.	Measures level	Future review

*1: Cases that should be examined in the table represent some substances provided through literature survey and an actual condition survey on substances considered to contain relatively great amount of NORM. For reference, contents of NORM vary with production areas, class and quantity of substances and minerals, so it is required to identify substances whose concentration could exceed a certain level and also to properly control substances that should be under radiation protection.

*2: Substances are basically subject to "Practice," but may subject to both "Practice" and "Intervention". Exposure in an initial process where these raw materials are treated becomes subject to "Intervention" in a sense.

*3: The Basic Committee did not consider Categories 7 and 8 as exemption in this document.

ICRP Publ.82 [7] proposes about 1 mSv of annual individual dose for exemption criteria on "Intervention" for commodities. An individual dose of 1mSv is suggested also as a dose constraint can be considered appropriate to be 1mSv/y for exemption of this "Intervention", because these substances become subject to both "Practice" and "Intervention".against "Practice". Therefore, a dose criteria for exemption of target substances in Categories 4 and 5

NORM containing substances in Categories 4 and 5 are generally handled in large quantity. In addition, their activity concentrations are not the same or vary with veins and shafts in producing countries and production areas. For these reasons, it is actually difficult to measure their concentrations and determine them or a huge cost might be needed to measure. It is not appropriate to define an exemption level for these substances. The Groupe considers it suitable to preliminarily identify substances whose average activity concentration could exceed a certain level, and evaluate exposure doses for actual workers and the public involving in the handling of those substances. If the exposure doses exceed 1 mSv/y, then it is appropriate to require proper control for radiation protection. In this case, the exemption levels given in the BSS [3] and RP-122 [8] should be referred to establish a certain level for determining substances to be regulated. The use of consumer goods in Category 6 is basically equivalent to "Practice", so it can be considered that they are treated in the same manner as artificial radioactive substances. However, they have widely-varying activity concentrations, are sometimes not used for radiation purposes and widely distributed due to the fact that they have been not regulated so far. For these reasons, it is important not to apply the BSS exemption level to all consumer goods but to conduct reasonable and proper regulation. Hence, in case of consumer goods whose activity concentration and activity exceed the BSS [3] exemption level, it is appropriate to confirm that user's exposure from each consumer good is below 1mSv/y (ICRP Pub.82 [7], a maximum value of a dose constraint for the public, and to conduct rationalized regulation such as indication of inclusion of NORM and NORM information disclosure to users; those are equivalent to authorization based on their design which adopted in regulation of artificial radiation sources in various foreign countries.

4.2. NORM Guideline

According to the regulatory policy mentioned above and the IAEA documents RS-G-1.7 [4] published after the General Administrative Group's report mentioned in previous section, a guideline of voluntary regulation of NORM was published in June 2009 [2]. The guideline requires with the combination of radioactivity (concentration and quantity) and radiation exposure based on that actual exposure to the workers should be important criteria considered to be 1 mSv/y as an exemption.

The guideline requires self regulation for two target industries; one is for manufacturing industry shown in Fig.1, another is for manufacturers and importers of consumer goods shown in Fig.2. As for consumer goods, as there is almost no possibility of radiation exposure of more than 1 mSv/y, except for the case where such goods are used in contact with or close to human bodies, only those consumer goods that are used in contact with or close to human bodies are made subject to the guidelines.

As the quantity of external exposure to natural occurring uranium and thorium is much more than that of pure refined one from the view point of radioactive equilibrium, the specified raw materials are divided two categories, one is ores and mineral sand such as monazite, bastnaesite, zircon, tantalite, phosphate ore, uranium ore, thorium ore, titanium ore (rutile, ilmenite, etc.) and coal ash, another is metals, glass and others added with refined uranium and thorium. Exemption concentration criteria of the natural occurring one were defined to be 1 Bq/g according to RS-G-1.7 [4]. As for the refined one, the exemption criteria was defined 10 Bq/g referring natural uranium in secular equilibrium shown in BSS [3]. The exemption criteria of radioactive quantity were also defined for consumer goods in order to reduce the contained radioactivity. Assuming the consumer goods are used in contact with or close to human bodies, the exemption values equivalent to 1 mSv/y are derived 8,000 Bq for natural raw material and 80,000 Bq for refined one using the similar calculation methods shown in RP65 [9].

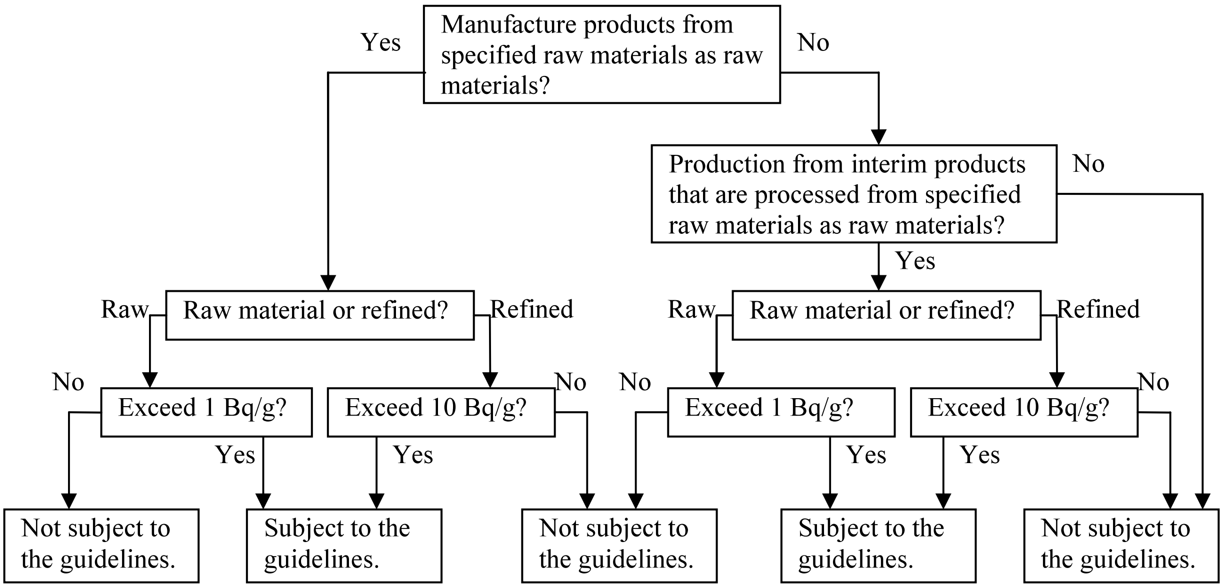

Fig.1. Flow chart to identify targeted manufacturers engaged in the manufacturing industry [2]

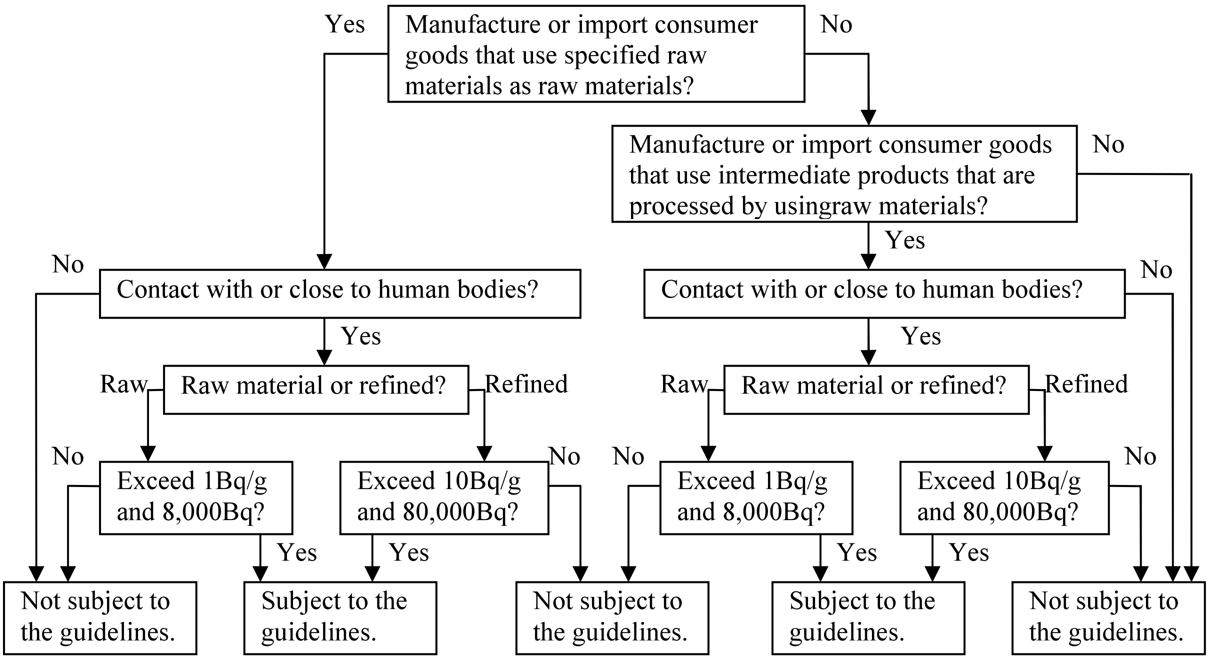

Fig.2. Flow chart to identify targeted manufacturers and importers of consumer goods [2]

The NORM guideline indicates following requirements. Identification of target manufacturers and importers shown Fig.1 and 2. For the target manufacturers and importers, measurements of radiation exposure rate in the working places and in the ambient environment of the manufactory by survey-meter and evaluate annual dose with normal working conditions. If the evaluation of exposure dose excesses 1 mSv/y, measures to reduce radiation exposure are to be requested. On shipment, necessary information to reduce the exposure to workers at destinations or consumers is to be provided. Records of measurement and evaluation are to be saved for certain periods. Education program to reduce the exposure of workers are to be conducted.

5. CONCLUSION

The current status of industrial use of NORM in Japan was surveyed and the guideline for NORM was issued as a voluntary regulation last year for ensuring safety. By the appropriate application of the guideline in the industry, the decrease of unnecessary exposures is expected. The authors wish to acknowledge Ministry of Education, Culture, Sports, Science and Technology (MEXT) who afforded an opportunity to make this report.

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DATABASE OF ACTIVITY CONCENTRATIONS IN NORM USED AS INDUSTRIAL RAW MATERIAL IN JAPAN

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Abstract

Natural radioactive nuclides, such as Uranium-238 (^{238}U), Thorium-232 (^{232}Th), and Radium-226 (^{226}Ra), are widely distributed in the environment. Zirconium (Zr) ore, titanium (Ti) ore, and phosphate (P) ores which are generally used as industrial raw materials, contain radioactive nuclides in a relatively high concentration. The International Commission on Radiological Protection (ICRP) 1990 Recommendations recommended that an occupational exposure to some NORM should be controlled. However, the current extent of the industrial use of NORM is not clearly perceived, because the activity concentrations in NORM have a wide distribution from low to high level, and NORM is used for a variety of purposes. Because Japan has poor natural resources, most ores used as industrial raw materials are imported significantly. There can be a case that workers handling imported raw materials would be exposed to high levels of radiation without being aware of it. The activity concentrations in the materials should be investigated to evaluate the radiation exposure of workers. In this study, we collected imported industrial raw materials, and measured the activity concentrations in these resources by using ICP-MS (inductively-coupled plasma mass spectrometry) and gamma ray spectrometry. Furthermore, we developed a database of activity concentrations of NORM by referring to the measured results as well as referring to literatures, and published a database on the web. The purpose of the database is to relieve anxieties among the general public and to provide extensive data regarding NORM for researchers and regulators. The database is providing more than 1000 pieces of activity concentrations in NORM at no fee.
(NORM database; http://www.nirs.go.jp/db/anzendb/NORMDB/ENG/index.php).

1. INTRODUCTION

Natural radioactive nuclides are widely distributed in the environment. The International Commission on Radiological Protection (ICRP) 1990 Recommendations recommended that NORM should be identified by a regulatory agency and an exposure to them should be controlled as an occupational exposure. In Japan, a guideline for safety control of natural materials containing uranium and thorium was published in June, 2009 by Ministry of Education Culture, Sports, Science and Technology (MEXT) which is a regulatory agency for nuclear materials.

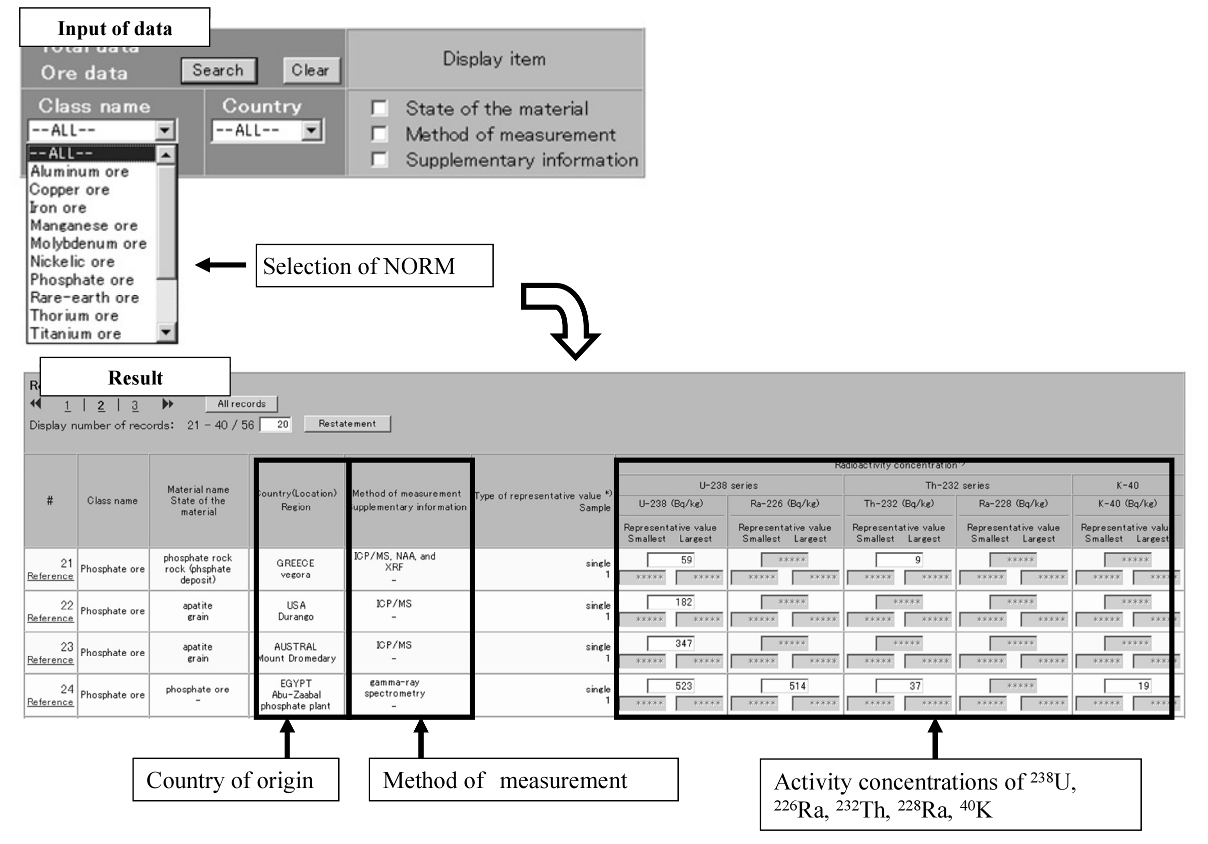
Many types of NORM are imported and used as industrial raw materials since Japan is poor in natural resources. However, activity concentrations of NORM have not yet been well identified because the activity concentrations in NORM vary over a wide range, starting at very low levels. Therefore, the activity concentrations in NORM should be investigated to evaluate the radiation exposure of workers. In this study, imported raw materials from foreign countries in Japan were collected, and measured the activity concentrations in the materials using ICP-MS (inductively-coupled plasma mass spectrometry) and gamma ray spectrometry. Furthermore, we developed a database of activity concentrations in NORM by reflecting the measured records as well as referring to literatures, and published a database on the web. The purposes of the database are to relieve anxieties among the general public and to provide extensive data regarding NORM for researchers and regulators. This paper presents an overview of the database.

2. SYSTEM OF NORM DATABASE

The database can be freely access on the internet (NORM database; http://www.nirs.go.jp /db/anzendb/NORMDB/ENG/index.php). The database mainly consists of two parts, which are “activity concentration” and “dose assessment”.

2.1 Activity concentration

In the part of the “activity concentration”, the users can see more than 1000 pieces of data of activity concentrations of ^{238}U series, ^{232}Th series and ^{40}K in materials such as rocks and ores etc. (Fig. 1) using a search system. The classification of these materials was defined by referring to the harmonized system (HS) code defined by the World Customs Organization (WCO). The outline of this search system is shown in Fig. 1. The users can easily find out the needed data by selecting the name of materials and the countries of their origin (local origin).



Display number of records: 21 – 40 / 56 20

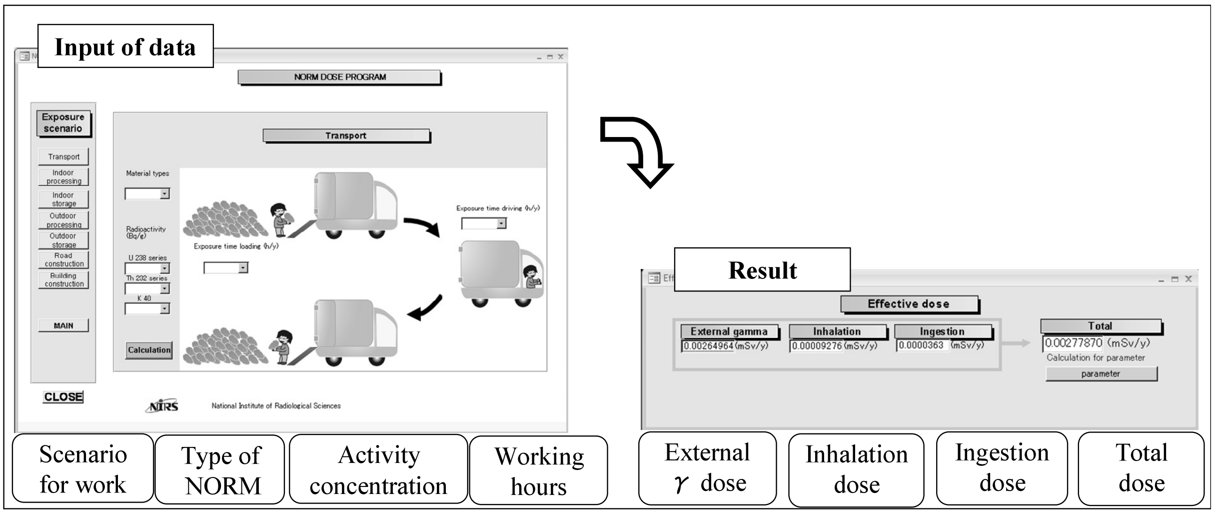
#	Class name	Material name State of the material	ountry(Location) Region	Method of measurement upplementary information	Type of representative value *) Sample	Radioactivity concentration *)														
						U-238 series						Th-232 series						K-40		
						U-238 (Bq/kg)			Ra-226 (Bq/kg)			Th-232 (Bq/kg)			Ra-228 (Bq/kg)			K-40 (Bq/kg)		
						Representative value	Smallest	Largest	Representative value	Smallest	Largest	Representative value	Smallest	Largest	Representative value	Smallest	Largest	Representative value	Smallest	Largest
21 Reference	Phosphate ore	phosphate rock rock (phsphate deposit)	GREECE vegora	ICP/MS, NAA, and XRF -	single 1	59	*****	*****	*****	*****	*****	9	*****	*****	*****	*****	*****	*****	*****	*****
22 Reference	Phosphate ore	apatite grain	USA Durango	ICP/MS -	single 1	182	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
23 Reference	Phosphate ore	apatite grain	AUSTRAL Mount Dromedary	ICP/MS -	single 1	347	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
24 Reference	Phosphate ore	phosphate ore -	EGYPT Abu-Zaabal phosphate plant	gamma-ray spectrometry -	single 1	523	*****	*****	514	*****	*****	37	*****	*****	*****	*****	*****	19	*****	*****

FIG. 1. Outline of search system for activity concentration

2.2 Dose assessment

In the part of the “dose assessment”, the users can use a program for calculating effective dose to workers handling NORM (Fig. 2). Models for dose assessments described in Radiation Protection 122 publications of the European Commission [1] are used for the program. At this time (January 2010), user can only use the program of Japanese version. The program of English version will be available in the near future.

The outline of this program is shown in Fig. 2. The users can easily calculate the effective dose by inputting only four items (“Scenario for work”, “Type of NORM”, “Working hours”, and “Activity concentration of NORM”). In the “Scenario for work”, the users can choose the scenario for work from variations such as “transport”, “indoor storage”, “outdoor storage”, “road construction”, and “building construction”. In the “Type of NORM”, the users can choose the type of NORM from variations such as “rock”, “sand”, “ash”, “slag”, and “sludge”. In the “Working hours”, the users can input the working time. In the “Activity concentration of NORM”, the users can input the values of activity concentration of NORM by referring to the database.



External gamma 0.00264964 (mSv/y)
Inhalation 0.00009276 (mSv/y)
Ingestion 0.0000363 (mSv/y)
Total 0.00277870 (mSv/y)

FIG. 2. Outline of program for dose assessment

3. SOME DATA OF NORM DATABASE

3.1 Ore and rock, etc.

Some data for ores and rocks, etc. in the database are shown in Table I. These data regarding activity concentrations are the mean values of activity concentrations calculated by referring to the data of the database in January 2010.

3.2 Consumer products

Some data of Japanese consumer products aimed at promoting health in the database are shown in Table II.

3.3 Radon spa

Some data of Japanese radon spa in the database are shown in Table III. These data regarding activity concentrations are the mean values of radon concentrations of water. These data will be updated to the database in the near future.

TABLE I. ACTIVITY CONCENTRATION OF ORE AND ROCK ETC. [2]

Materials	^{238}U series		^{232}Th series		^{40}K	
	Number[a]	Activity[b] (Bq/kg)	Number[a]	Activity[b] (Bq/kg)	Number[a]	Activity[b] (Bq/kg)
Ore						
Al ore	9	8.7E+01	5	1.3E+02	2	2.8E+01
Cr ore	1	<1	1	<1	1	2.8E+01
Zr ore	17	4.9E+03	20	3.5E+03	10	1.2E+02
Ti ore	27	1.5E+02	27	1.5E+02	10	5.5E+01
Th ore	7	3.2E+04	9	2.6E+05	3	9.5E+03
Mn ore	2	5.0E+00	2	4.0E+00	1	<1
Mo ore	6	3.0E+01	6	4.7E+00	3	3.4E+01
P ore	53	1.6E+03	36	2.0E+02	23	8.9E+01
Zn ore	2	1.2E+01	2	5.0E+00	1	6.3E+01
Co ore	9	2.8E+02	1	3.4E+01	1	2.6E+02
Rock						
Peridotite	5	2.6E+00	5	2.2E+00	5	3.4E+01
Granite	184	5.8E+01	179	1.0E+02	177	1.2E+03
Tuff	6	2.3E+02	6	1.8E+02	6	1.7E+03
Basalt	8	6.7E+01	4	1.9E+02	4	9.3E+02
Limestone	3	2.8E+01	3	7.9E+00	3	1.4E+02
Marble	32	2.3E+01	30	8.5E+00	30	9.1E+01
Mudstone	10	3.1E+01	8	3.1E+01	8	5.5E+02
Gabbro	9	5.3E+00	8	7.2E+00	8	1.2E+02
Schist	10	5.7E+01	7	3.5E+01	7	6.2E+02
Gneiss	8	5.6E+01	5	6.3E+01	5	7.9E+02
Other						
Cement	19	4.7E+01	15	3.3E+01	15	3.1E+02
phosphoric acid	18	1.1E+03	17	2.4E+02	5	9.2E+01
phosphate fertilizer	25	3.3E+02	22	1.9E+02	13	1.4E+02
lignite	13	2.1E+02	9	2.2E+01	9	1.1E+02
gypsum	26	7.2E+02	18	8.8E+01	13	1.4E+02
coal ash (fly ash, etc.)	41	4.1E+02	28	6.2E+01	25	2.5E+02
peat	4	9.8E+00	3	3.8E+00	2	1.7E+01

[a] Number: the numbers of data in the database.

[b] Activity: the mean values of activity concentrations calculated by referring to the database in January 2010.

TABLE II. ACTIVITY CONCENTRATIONS OF JAPANESE CONSUMER PRODUCTS [3]

Materials	^{238}U (Bq/kg)	^{232}Th (Bq/kg)
Bed clothing	2.6E+02	2.6E+02
Wristband	8.8E+03	8.8E+03
Undershirt	1.0E+03	1.0E+03
Household machine for artificial radon spa A	3.4E+04	3.4E+04
Household machine for artificial radon spa B	1.0E+04	1.0E+04
Negative ion sticker	6.7E+02	6.7E+02
Belly band	9.4E+02	9.4E+02

TABLE III. ^{222}Rn ACTIVITY CONCENTRATIONS OF JAPANESE RADON SPA [4]

Spa name (Place)	Number of samples	^{222}Rn (Bq/L)
Ikeda	5	22812
Masutomi	80	2680
Tarumizu	2	2442
Ena takayama	25	1151
Ena kasagi	4	791
Raihokyo	3	782
Misasa	277	742
Ena tsuruma	1	636
Ena hirukawa	15	631
Arima	25	624

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THE EVIRONET – NETWORK ON ENVIRONMENTAL MANAGEMENT AND REMEDIATION

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The successful implementation of environmental remediation (ER) projects depends on the appropriate combination of different factors that include technical and non-technical issues. Some countries have achieved more successful outcomes in the implementation of their ER-projects than others. As a result, they are holders of experience on how to deal with some of the issues mentioned above. It is true that many solutions for the problems we face are not universally applicable, i.e. a technology that proved to be effective at one site may not be the most appropriate one to be applied at another. Interaction with stakeholders is another example in which the "no-one-solution fits all" principle applies.

Taking all these elements into account, the IAEA has been working to provide its Member States with relevant support, while promoting technologies that can aid in the implementation of environmental remediation projects. This will have the consequent benefit of improving the environmental conditions in areas submitted to radioactive contamination in the past including areas affected by NORM industries.

The IAEA tries to fulfil this very important mission by: i) publishing technical documents, safety standards, safety guides and technical report series, ii) organizing training courses, workshops and seminars, while providing for the implementation of scientific visits and experts missions under the activities of its Technical Cooperation Department, iii) organizing international conferences and iv) providing and supporting peer-review missions.

It has been observed, however, that there is still plenty of room to improve the type of assistance that the IAEA provides to its Member States. One of the initiatives being implemented by the IAEA at this end is the operation of networks. Specifically, in the field of waste management, decommissioning and environmental remediation, four of these networks are in operation: the first one to be created was the URF Network (Underground Research Facility Network concerned with geological disposal). It was followed by the IDN (International Decommissioning Network) and the DISPONET (International Low-Level Waste Disposal Network). The ENVIRONET deals with legacy issues at existing contaminated sites, as well as life-cycle approaches that are required in order to minimize the need for future remediation measures resulting from the operations of Nuclear Facilities and NORM industries.

Ultimately, ENVIRONET is intended to aid Member States solve the problems created in the past while avoiding the generation of new contaminated sites.

Topics to be covered by the ENVIRONET will include:

i) Life-cycle planning of both facility operations and environmental remediation;
ii) Project planning (quality control & assurance);
iii) Data management,
iv) Integration and communication;
v) Site characterization;
vi) Modelling (fate and transport, engineering design and economic);
vii) Risk assessment;
viii) Remediation technology development and selection;
ix) Monitoring;
x) Stakeholder involvement and communication;
xi) Regulation and policy development;
xii) Risk communication;
xiii) Funding.

More information and further contact with Waste Technology networks can be obtained at:
http://www.iaea.org/OurWork/ST/NE/NEFW/wts_NETWORKS_homepage.html

ESTIMATES OF EFFECTIVE DOSES AMONG CZECH URANIUM MINERS

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Czech uranium mining started on industrial base in the 1890s. It is estimated that total production has been 110 000 t of uranium and the uranium industry employed nearly 100 000 underground workers. Radiation doses in uranium mines include contribution form inhalation of uranium dust (long lived radionuclides), inhalation of radon and doses from external gamma radiation.

The presentation is based on recent observations in Czech uranium mines. The Czech uranium mines belong to very few ones operated in Europe. The presentation is aimed at the estimation of radiation doses from long lived radionuclides, which is based on measurements of physical and chemical characteristics conducted recently in the Czech uranium mines. The main studied parameters were: size, chemical solubility in lung fluid, and amount of Rn gas emanating from uranium particles.

The mean size of particles for different radionuclides in terms of AMAD was in the range 5.2-7.8 µm. Study of kinetics of dissolution of uranium collected on filters from personal dosemeters ALGADE resulted in estimated rapidly dissolved fraction (solubility class F) of 0.142 and 0.177 for U-238 and U-234, respectively. Fraction of Rn gas escaping from uranium particles was estimated by measuring the ratio of activities of radon progeny and Ra-226. These fractions, which determine how the gross long lived alpha activity is divided into separate radionuclides of the uranium series, were in the range 23% - 56% with the mean of 40%.

Based on these parameters, committed effective doses from long lived radionuclides in uranium dust were calculated using conversion tables given in ICRP Publications 68 and 72 (Table 1).

TABLE 1: CALCULATION OF EFFECTIVE DOSES FROM LONG LIVED RADIONUCLIDES

		Dose F*	[mSv/kBq] S*	Fraction of F	Dose according to fractions F and S	Proportion from gross activity of long lived radionuclides	Effective dose $H_E(50)$
U-238	α	0.55	5.7	0.22	4.57	0.16	0.73
U-234	α	0.61	6.8	0.22	5.44	0.16	0.87
Th-230	α	110	8.4	0.14	22.62	0.16	3.62
Ra-226	α	0.45	7.9	0.11	7.08	0.16	1.13
Rn-222	α					0.09	
Po-218	α					0.09	
Po-214	α					0.09	
Pb-210	β	1.1	4.8	0.26	3.84	(0.09)	0.35
Po-210	α	0.75	3.2	0.18	2.76	0.09	0.25
Total						1	6.95

*Committed effective dose per 1 kBq at solubility F and S

Data on effective doses form all three radiation components (long lived alpha, radon, and external gamma radiation) and their correlations are given in the following tables.

TABLE 2: DISTRIBUTION OF EFFECTIVE DOSES (ADJUSTED FOR ANNUAL DURATION OF 1700 HOURS)

Effective dose (mSv)	Alpha	Rn	Gamma	Total dose
0-5	79.2%	79.2%	70.2%	10.1%
5-10	15.9%	19.3%	24.2%	43.2%
10-15	4.1%	1.5%	4.4%	21.3%
15-20	0.5%		0.8%	13.2%
20-25	0.1%		0.2%	5.7%
25-30			0.1%	3.9%
30-35				1.7%
35-40				0.7%
40-45				0.2%
mean	3.2	3.5	4.6	11.3
SD	3.4	2.2	3.0	6.6

TABLE 3: CORRELATIONS OF EFFECTIVE DOSES (ADJUSTED FOR DURATION OF EXPOSURE)

	Alpha	Rn	Gamma
Alpha	1.00	0.39	0.57
Rn	0.39	1.00	0.46
Gamma	0.57	0.46	1.00

In conclusion, the results demonstrate that in present uranium mines, the annual effective doses from all three radiation components are approximately equal and separately well below 20mSv. The total annual effective dose adjusted for annual duration of 1700 hours in most workers (88%) is below 20mSv. Annual doses experienced by workers exceed the 20 mSv limit for only 3% and their mean is 8.3mSv.

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NATURAL RADIONUCLIDES INTAKE INTO SOYA, CORN AND LETTUCE GROWN ON SOIL AMENDED WITH PHOSPHOGYPSUM

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Abstract

Phosphogypsum is a by-product of the phosphate fertilizers industry and is produced by precipitation during wet process of phosphate rocks, thus posing serious problems with its utilization and safe disposal. In Brazil, three main industries are responsible for the production and storage of about 5.5×10^6 tons per year. PG may contain radionuclides of U and Th series. The main objective of this study is to evaluate the environmental impact of the use of phosphogypsum as soil amendment by evaluating the radionuclides transfer in the soil/plant system. To accomplish this task an experiment was carried out in green house, where two major crop groups (soya and corn) and leafy vegetable (lettuce) were grown in two types of soil (clay and sandy) amended with phosphogypsum. The radionuclides ^{226}Ra, ^{228}Ra and ^{210}Pb were determined by a radiochemical procedure and by gamma spectrometry. ^{210}Po was spontaneously plated on a silver disc and measured by alpha spectrometry. Activity concentrations of ^{238}U and ^{232}Th in soil, phosphogypsum, crops and lettuce were determined by using instrumental neutron activation analysis (INAA). The transfer-factors were evaluated for all the radionuclides analyzed.

1. INTRODUCTION

It is recognized that several non-nuclear industries have a potential threat to cause environmental and occupational radiological impacts. The main problem associated with these industries is the generation of effluents, residues and by-products containing not just natural radionuclides, but also other toxic elements, such as heavy metals and anions.

Phosphogypsum (PG) is a TENORM (Technologically Enhanced Naturally Occurring Radioactive Material) by-product of the phosphate fertilizer industry. In Brazil, three main industries (Copebras, Ultrafertil and Fosfertil) are responsible for the production and storage of about 5.5×10^6 tons per year. It may contain high quantities of P_2O_5, trace metals and radionuclides of U and Th series.

Depending upon the level of radioactivity the TENORM industries are subjected to the recommendations given by *Comissão Nacional de Energia Nuclear* (CNEN), which include compliance with the radiological protection regulations [1, 2].

Several publications are available in the literature related with the radiological characterization of Brazilian phosphogypsum [3-7] however few publications discuss about the metals characterization in phosphogypsum.

In the Brazilian factories, the method used for the production of phosphoric acid is based on drastic treatment of the primary rock with sulphuric acid. This process forms a precipitate of calcium sulphate, called phosphogypsum, as a by-product, which is stockpiled and is considered waste due to its elevated levels of impurities (Eq. (1)). Phosphogypsum produced during the process is filtered off and pumped as slurry to nearby ponds, where it stays for a period sufficient to allow complete deposition. This waste is then moved to nearby storage areas, the so-called “gyp-stacks”. The production of phosphoric acid can be described by the following reaction:

$$Ca_{10}F_2(PO_4)_6 + 10H_2SO_4 + 10nH_2O \rightarrow 10CaSO_4nH_2O + 6H_3PO_4 + 2HF \quad (1)$$

All the countries that produce phosphate fertilizer by acid wet process are facing the same problem of finding solutions for the safe application of phosphogypsum, in order to minimize the impact caused by the disposal of large amounts of this by-product. Phosphogypsum can be used in agriculture as a soil amendment, however, for its safe application the mobility and intake of natural radionuclides from soil to food crops should be known. Another point that should be taken into account is the long term accumulation of these elements after several applications, with possible contamination of soil and ground waters. It is, therefore, necessary to evaluate the bioavailability of these elements and their absorption by plants.

The main objective of this study is to evaluate the environmental impact of the use of phosphogypsum as soil amendment and to understand the mechanism of radionuclides transfer in the soil/plant system (Eq.(2)). The soil-to-plant transfer factor (TF) is defined as the ratio of the concentration of radionuclides in plant (Bq kg^{-1} dry mass) to that in soil (Bq kg^{-1} dry mass).

$$FT = \frac{Cp}{Cs} \quad (2)$$

To accomplish this task an experiment was carried out in green house in the Soil Department of the Universidade Federal de Viçosa – Minas Gerais State. Two major crop groups (soya and corn) and leafy vegetable (lettuce) were grown in two types of soil (clay and sandy) amended with phosphogypsum. The planting of the three cultures was carried out in two vases: one without the addition of phosphogypsum, and the other with the double of the recommended phosphogypsum dosage, that is, 1.0 g dm^{-3} for the clayish soil and 0.4 g dm^{-3} for the sandy soil, according to the EMBRAPA recommendation [8]. The PG used comes from Ultrafertil facility, located in Cubatão, São Paulo state. The phosphate rock used in this installation is an igneous rock constituted by apatite, magnetite and olivine, which presents in its composition concentrations of natural radionuclides of the U series (^{238}U, ^{226}Ra, ^{210}Pb and ^{210}Po) up to 1480 Bq kg^{-1} and for the Th series (^{232}Th and ^{228}Ra) up to 393 Bq kg^{-1} [3, 4]. The radionuclides ^{226}Ra, ^{228}Ra and ^{210}Pb present in crops and lettuce were determined by radiochemical separation followed by gross alpha and beta counting using a gas flow proportional counter. The same radionuclides in soil and PG samples were determined by gamma spectrometry. ^{210}Po was spontaneously plated on a silver disc and measured by alpha spectrometry. Activity concentrations of ^{238}U and ^{232}Th in soil, phosphogypsum, crops and lettuce were determined by using instrumental neutron activation analysis (INAA).

The two soils used in the experiment come from the city of Três Marias – Minas Gerais State and were never treated with any kind of fertilizer. The first one, classified as red-yellow dystrophic latosol, is composed mainly of caulinita (>30%) fine-grained argilaceous silty clay (particles diameter around 250 μm); the second one, classified as yellow dystrophic latosol, is composed mainly of quartz (> 30%) with particles diameter varying in the range of 105 to 250 μm. The chemical analysis of both soils revealed acid characteristics and low fertility, with low concentration of nutrients such as Ca, Mg, K and P. The argilaceous soil presented slightly better fertility, with higher concentrations of Ca and organic matter. Both soils present higher levels of Al and acid characteristics, which are typical of Cerrado soils, with more than 30% of Al saturation.

2. EXPERIMENTAL

Samples of phosphogypsum, soil, phosphogypsum added soil and corn, soya and lettuce grown in soil and in phosphogypsum added soil were analyzed for the determination of radionuclides. All the samples, excluding lettuce, were dried at about 60°C to remove moisture and crushed to fine powder (30 to 60 mesh). The lettuce samples were dried in a ventilated oven, at 60°C for 48 hours, ground and sieved.

2.1. Activity concentrations of ^{226}Ra, ^{228}Ra and ^{210}Pb in soil and phosphogypsum samples using gamma spectrometry

Activity concentrations of ^{226}Ra, ^{228}Ra and ^{210}Pb were measured in soil and phosphogypsum samples by gamma spectrometry with a hyper-pure germanium detector, GEM–15200, from EG&G Ortec. Samples were packed in 100 cm^3 cans and sealed for about four weeks prior to the measurement in order to ensure that equilibrium has been reached between ^{226}Ra and its decay products of short half-life. The ^{226}Ra activities were determined by taking the mean activity of three separate photo peaks of its daughter ^{214}Pb at 295 keV and 352 keV, and ^{214}Bi at 609 keV. The ^{228}Ra content of the samples was determined by measuring the intensities of the 911 keV and 968.9 keV gamma-ray peaks from ^{228}Ac. For the determination of ^{210}Pb, the photopeak of 46.5 keV was used. This peak, due to its low energy, needed auto-absorption correction, which was carried out according to the procedure proposed by Cutshall [9]. Minimum detectable activity concentrations for gamma spectrometry were obtained by measuring deionized water in the same geometry as the samples, and the results were 10 Bq kg^{-1} for ^{226}Ra and 20 Bq kg^{-1} for ^{210}Pb, for a counting time of 150,000 seconds.

2.2. Activity concentrations of ^{226}Ra, ^{228}Ra and ^{210}Pb using alpha and beta gross counting and ^{210}Po using alpha spectrometry in soya, corn and lettuce samples

For the determination of ^{226}Ra, ^{228}Ra and ^{210}Pb in soya, corn and lettuce samples 500 mg from were dissolved in mineral acids in a microwave digestor and submitted a radiochemical procedure. Radium was co-precipitated as Ba(Ra)SO$_4$ by adding H$_2$SO$_4$. The mixed sulphates were dissolved with NTA (nitrilotriacetic acid). Barium (radium) sulphate was re-precipitated by adding acetic acid (pH 4.5–5.0) whereas lead remained in the aqueous phase. The aqueous and solid phases were separated and the Ba(Ra)SO$_4$ was purified by dissolution in an EDTA solution at pH 10. Then the sulphate mixture was again precipitated by acetic acid (pH 4.5–5.0) and filtrated. After the procedure, the ^{226}Ra and ^{228}Ra concentration were determined by gross alpha and beta counting of the Ba(Ra)SO$_4$ precipitate and the ^{210}Pb concentration through its decay product, ^{210}Bi, by measuring the gross beta activity of the PbCrO$_4$

precipitate. Both radionuclides were determined in a low background gas flow proportional detector.

For ^{210}Po determination, a modified methodology of Matthews was used [10]. The solution obtained after the chemical attack was evaporated to dryness in the presence of exact aliquots of ^{209}Po used as tracers. The residue was dissolved in 6.25M HCl, filtered in Millipore 0.1µ and 20% hydroxylamine hydrochloride, sodium citrate and stable Bi^{+3} was added. After the pH was adjusted to 1.5, polonium contents was spontaneously plated on the silver disc at 90°C for 4 hours, with agitation of the solution. The alpha measurements were performed on a surface barrier detector, EG&G Ortec.

2.3. Activity concentrations of ^{238}U, ^{232}Th in soil, phosphogypsum and vegetal samples using instrumental neutron activation analysis (INAA)

The ^{238}U and ^{232}Th characterization was performed by instrumental neutron activation analysis (INAA). The elements determination was made by irradiation of approximately 150 mg of each sample, during 16 hours at a neutron flux of 10^{12} n.cm^{-2}s^{-1}, at Instituto de Pesquisas Energéticas e Nucleares (IPEN) research reactor IEA-R1. The induced radioactivity was measured with a Ge-hyperpure detector, Intertechnique, with 2.1 keV resolution for the 1332 keV ^{60}Co photo peak. The concentration of the analyzed elements was determined by comparing activities obtained in the samples with standard materials Buffalo River Sediment (NIST-2704) and Soil-7 (IAEA).

3. RESULTS AND DISCUSSION

The results obtained for the radionuclides concentrations (^{238}U, ^{226}Ra, ^{210}Pb, ^{210}Po, ^{232}Th and ^{228}Ra) in soil, PG, soil + PG and crop samples are presented in Table 1. The two kinds of soil presented radionuclides concentrations for the U and Th series in the same range observed for natural soils in UNSCEAR report (35 Bq kg^{-1} for U and Ra, and 30 Bq kg^{-1} for Th) [11]; although in clay soil higher concentrations were observed, specially for ^{238}U (average concentration of 137 Bq kg^{-1}). The PG used in this study comes from Ultrafertil facility, located in Cubatão, and presents activity concentrations for all the radionuclides similar to the phosphate rock used as raw material, except for ^{238}U [5]. The average concentrations observed were 323±13 for ^{226}Ra, 440±27 for ^{210}Pb, 319±6 for ^{210}Po, 125±8 for ^{232}Th and 210±10 for ^{228}Ra. The addition of PG to the soils did not alter significantly the levels of radioactivity for all the radionuclides; consequently the soil-to-plant transfer factors for U, Th, Ra, Pb and Po did not present significant variations due to the addition of PG (Table 2). The results obtained in this study for the TF of radionuclides will be compared with the review made by Vandenhove et al. [12], who compiled data, based on an extensive literature survey, concerning soil-to-plant transfer factors for U, Th, Ra, Pb and Po.

The TF for U was observed only for the corn grown in sandy soil, with a value of 3.1 x10^{-2} kg kg^{-1}. This result is in good agreement with the geometric mean observed by Vandenhove et al. [12], of 2.27 x10^{-2} kg kg^{-1} for a total of 781 observations of more than 57 references.

Th is a very immobile element. The generic geometric mean for TF-Th evaluated by Vandenhove et al. [12] is 3.5 x10^{-3} kg kg^{-1}; in the present study, the TF-Th observed for corn, lettuce and soya were on the average 4.9 x10^{-3} kg kg^{-1}, of the same order of magnitude.

Radium is the last member of the alkaline earth elements, a group of metals whose lighter members (Ca and Mg) play a very important role in plant growth and nutrition. The Ra transfer factor depends on soil characteristics, plant type, the plant part concerned, climate conditions, and the physico-chemical form of radium. Radium has also a high affinity for the regular exchange sites of the soil. The TF-Ra obtained in this study for lettuce, corn and soya varied from 1.7 x10^{-1} to 6.1 x10^{-1} for ^{226}Ra and from 4.1 x10^{-2} to 7.4 x10^{-1} for ^{228}Ra, independent upon the addition of PG to the two types of soil. The TF reported for clay soil were similar for both radionuclides, for the sandy soil, the ^{228}Ra seemed to be 2-fold more available than ^{226}Ra. In the database presented by Vandenhove et al. [12], considering those studies where both ^{226}Ra and ^{228}Ra were measured, an overall 2.5-fold higher TF was found for ^{228}Ra than for ^{226}Ra. The same authors observed that clay and organic soils showed the lowest TF-Ra and sand and loam soil the highest, with difference of only 4-fold, the derived generic TF-Ra geometric mean was 2 10^{-2} kg kg^{-1}, with a range in observed values of 7 orders of magnitude. The results obtained in this study for lettuce, corn and soya TF ^{228}Ra also presented difference of 4-fold, for sandy and clay soils.

The main source of ^{210}Pb and ^{210}Po in the environment is from the decay of ^{222}Rn gas emanated from the soil into the atmosphere. These radionuclides deposit on the ground in association with aerosols via washout and sedimentation. Other sources of theses radionuclides can include burning of fossil fuels and TENORM industries. The uptake of ^{210}Pb in plants can occur through the root system and via direct deposition from atmosphere. The TF-Po obtained in this study for lettuce, corn and soya was on the average 4.5 x10^{-2} for clay soil and 1.1 x10^{-1} for sandy soil, with difference of only 4-fold, independent upon the addition of PG to the two types of soil. The generic value obtained by Vandenhove et al. [12] for TF-Po was 5.6 x10^{-3} kg kg^{-1}, with a range in observed values of 5 orders of magnitude. The TF for Pb were obtained only for the clay soil, with an average value of 2.4 x10^{-1}. The overall geometric mean for the TF-Pb obtained by Vandenhove [12] was 2.0x10^{-2} kg kg^{-1} and the range covered 5 orders of magnitude; the results obtained in this study for corn and soya bean (1.6 x10^{-1} on the average) is within this range and for lettuce was 20 fold higher than the geometric mean.

4. CONCLUSION

The addition of PG to the two soils studied, in the dosage of 1.0 g dm^{-3} for the clayish soil and 0.4 g dm^{-3} for the sandy soil, did not alter significantly the levels of radioactivity in the final mixture and consequently the TFs obtained for lettuce, soya and corn. The TFs values were generally lower for the clay soil than for the sandy soil. Overall, highest TF derivations were obtained for the leafy vegetable while lowest TF estimates were obtained for grains. The TF estimates reported in this study may be valuable for screening assessment, but more sites specific values may be recommended for predicting generic long-term effective impact.

TABLE 1. ACTIVITY CONCENTRATION OF ^{238}U, ^{226}Ra, ^{210}Pb, ^{210}Po, ^{232}Th AND ^{228}Ra IN PG, CLAY AND SANDY SOIL, SOIL + PG AND CROP SAMPLES IN Bq kg^{-1}.

	U-238	Ra-226	Pb-210	Po-210	Th-232	Ra-228
PG (5)	<0.9	(3.2±0.1) E+2	(4.4±0.3)E+2	(3.2±0.1)E+2	(1.3±0.1)E+2	(2.1±0.1)E+2
Clay soil (3)	(1.4±0.2)E+2	(5.8±0.2)E+1	(5.2±0.7)E+1	(5.1±0.3)E+1	(1.0±0.2)E+2	(9.6±0.3)E+1
Lettuce (3)	<0.9	9.6±0.9	(2.2±0.2)E+1	2.7±0.1	(2.1±0.1)E-1	(1.5±0.1)E+1
Corn (3)	<0.9	<2.2	8.3±0.8	1.41±0.04	<0.1	3.9±0.4
Soya bean (3)	<0.9	<2.2	7.6±0.8	3.3±0.1	<0.1	8.5±0.8
Clay soil + PG (3)	(1.3±0.2)E+2	(5.8±0.2)E+1	(5.6±0.7)E+1	(5.5±0.5)E+1	(1.0±0.3)E+2	(10±0.5)E+1
Lettuce (3)	<0.9	(1.1±0.1)E+1	(2.3±0.2)E+1	2.2±0.1	(3.5±0.2)E-1	(1.9±0.2)E+1
Corn (3)	<0.9	<2.2	(1.1±0.1)E+1	3.3±0.2	<0.1	4.7±0.5
Soya bean (3)	<0.9	<2.2	8.7±0.8	1.74±0.05	<0.1	(1.4±0.1)E+1
Sandy soil (3)	(3.9±0.6)E+1	(1.5±0.1)E+1	<20	(1.7±0.3)E+1	(3.2±0.2)E+1	(2.9±0.3)E+1
Lettuce (3)	<0.9	7.3±0.7	(2.3±0.3)E+1	2.0±0.1	(2.4±0.1)E-1	(2.2±0.2)E+1
Corn (3)	1.2±0.1	<2.2	(1.1±0.1)E+1	1.7±0.1	(2.1±0.1)E-1	4.7±0.5
Soya bean (3)	<0.9	4.4±0.4	8.3±0.8	2.1±0.1	(2.3±0.2)E-1	(1.4±0.1)E+1
Sandy soil + PG (3)	(4.5±0.7)E+1	(1.5±0.1)E+1	<20	(1.8±0.1)E+1	(3.1±0.1)E+1	(3.0±0.4)E+1
Lettuce (3)	<0.9	9.1±0.9	(2.0±0.2)E+1	2.0±0.1	(2.4±0.1)E-1	(1.9±0.2)E+1
Corn (3)	<0.9	<2.2	6.6±0.6	1.53±0.05	<0.1	4.4±0.4
Soya bean (3)	<0.9	5.2±0.5	6.9±0.7	2.3±0.1	<0.1	(1.6±0.2)E+1

(n) Number of samples analyzed.
(Mean value ± standard deviation)

TABLE 2. RADIONUCLIDE TRANSFER FACTOR FROM SOIL TO PLANT IN kg/kg

	U-238	Ra-226	Pb-210	Po-210	Th-232	Ra-228
Lettuce						
Clay soil	-	1.7E-01	4.2E-1	5.3E-2	2.1E-3	1.6E-1
Clay soil + PG	-	1.8E-01	4.1E-1	3.9E-2	3.5E-3	1.9E-1
Sandy soil	-	4.9E-01	-	1.2 E-1	7.5E-3	7.4E-1
Sandy soil + PG	-	6.1E-01	-	1.1E-1	7.7E-3	6.4E-1
Corn						
Clay soil	-	-	1.6E-1	2.8E-2	-	4.1E-2
Clay soil + PG	-	-	1.9E-1	6.0E-2	-	4.7E-2
Sandy soil	3.1E-2	-	-	1.0E-1	6.6E-3	1.6E-1
Sandy soil + PG	-	-	-	8.5E-2	-	1.5E-1
Soya bean						
Clay soil	-	-	1.5E-1	6.5E-2	-	8.9E-2
Clay soil + PG	-	-	1.6E-1	3.2E-2	-	1.4E-1
Sandy soil	-	2.9E-1	-	1.2E-1	2.2E-3	5.0E-1
Sandy soil + PG	-	3.5E-1	-	1.3E-1	-	5.4E-1

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RADIONUCLIDES AND TRACE ELEMENTS RELATED TO MORPHOLOGY OF PARTICLES IN PHOSPHATE ROCK AND PHOSPHOGYPSUM

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Abstract

In this work, a morphological characterization was performed in phosphate rock (PR) and phosphogypsum (PG) samples, in order to improve the knowledge on the behavior of radioactive and toxic elements. Scanning electron microscope analysis (SEM) was applied to both PR and PG samples. Morphology was established by SEM in secondary electron imaging mode (SEI). Most of PR particles exhibit angular shapes with estimated sizes between 3 µm to 80 µm, while PG crystals exhibited shapes like tables, acicular, tubular shapes, small crystals clusters and rhombic types. High contents of Ca and P as well as impurities such as Fe, Al, Mg, Na and S were observed in PR. The composition of PG crystals is mainly Ca and S. Homogeneity or heterogeneity distribution of trace elements, in both PR and PG samples, were determined by SEM in backscattered electron imaging mode (BEI). These particles tend to form thin layers or to be imbedded in the PR grains; while these particles are insolated in PG. Finally, a semiquantitative analysis by scanning electron microscope/energy dispersive using X-ray analysis (SEM-EDX) was applied to the particles observed in the BEI mode. In this way, some trace elements, such as Fe, Pb, Ba and rare earth elements (REE) were observed associated to small particles. From results obtained by this technique demonstrated that toxic elements are not distributed homogeneously into phosphogypsum and that most of these elements are concentrated in particles <20 µm of high porosity, which could be easily mobilized by leaching and/or erosion.

1. INTRODUCTION

Some factories related to phosphoric acid and fertilizer manufacture are located in the estuary of the Tinto and Odiel rivers (Huelva, SW Spain). It is well established that these industries of phosphoric acid and fertilizers use, as raw material, phosphate rock (of marine sedimentary origin) mainly from Morocco and Senegal [1]. The phosphate rock is, due to its origin, affected by high concentrations of naturally-occurring radionuclides and other so-called trace elements [2, 3]. The industrial processes, applied to the phosphate rock in these factories, therefore also lead to high concentrations of toxic elements in both products and wastes. Hence, the presence of trace elements and natural radionuclide concentrations, at higher than natural levels, would be considered environmental contamination. In Huelva, these industries use the "di-hydrated" process to obtain phosphoric acid, whereby the phosphate rock is treated chemically with sulfuric acid[3]. Other products obtained in the reaction are hydrogen fluoride and phosphogypsum (PG). PG is calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$), with trace concentrations of toxic elements (impurities, heavy metals and radioactive elements). The concentration of these elements into PG may vary mainly depending on the origin of the phosphate rock and, to a lesser extent, on factors such as plant operation and PG age [4]. In previous studies, the fluxes and contents of U in the phosphoric acid production process have been determined. The results show that the U, present in the PR, is distributed in different proportions into the products: a greater proportion in phosphoric acid (approximately >80 %), and the rest in phosphogypsum [1, 5-7]. However, if the whole U content in phosphogypsum is considered, then 23 % is bounded to the bioavailable fraction [8].

In our study, the phosphogypsum was collected in open-air piles near to the factories. It is estimated that annually 2.5 million tons of phosphogypsum are deposited in these piles. Since the 1980's, elemental, chemical and radiochemical analyses have been applied in order to monitor the possible radioactive impact to the estuary [6]. However, further information is required on the distribution of particles in stockpiled phosphogypsum, which can help towards a better understanding of the possible environmental contamination. Improvements in the data, such as sample heterogeneity, are necessary to fully evaluate the environmental impact and risks [9].

Several preliminary studies on alternative applications of PG have been developed. The first consequence of the use of PG elsewhere would be the decrease of the wastes of the factories and, therefore, a minor environmental impact. Thus, the most common uses of phosphogypsum are: in agriculture [10, 11], as a substitute of gypsum in building, in the production of cement [12], and as a conditioner of soil for road construction [13]. In addition, it can be used in landfills related with urban solid wastes [14]. However, the main restrictions for the applications of phosphogypsum are related to its high content of both toxic elements and radioactivity, and hence it is necessary to obtain a deeper understanding of physical-chemical characteristics of this by-product.

The main objective of this work is to observe the morphology of the phosphate rock and phosphogypsum, particularly the existence of particles and the elemental composition of such particles.

2. MATERIALS AND METHODS

Phosphate rock (PR) samples were collected in the Fertiberia factory of Huelva. Phosphogypsum samples (PG) were taken from a stack belonging to a phosphoric acid industry, located next to the Tinto river (37° 15.3'N, 6 ° 54'W). This PG stack has been inactive since the beginning of the 1990's. Sampling was carried out in 2005, following the procedure described by Abril (2009) [10]. Samples were ground and sieved to 100 μm diameter and, these were then dried at 50 ºC for 48 h.

Morphology and particle composition of samples were performed using a JEOL 6460LV Scanning Electron Microscope (SEM) with acquisition of digital images in both secondary (SEI) and backscattered (BEI) electron imaging modes (maximum resolution 3.5 nm). This device was coupled to an EDX microprobe and fitted with an ATW2 beryllium window (resolution 137 eV at 5.9 keV). The semi-quantitative analysis was performed using the Oxford INCA software.

3. SEM-EDX CHARACTERIZATION

3.1 Phosphate rock

By using SEM in SEI and BEI mode, the morphology of PR particles was determined, see Figures 1 and 2. Most of the particles exhibit angular shapes with estimated sizes between 3 μm and 80 μm. The semi-quantitative composition of phosphate rock particles was determined by

SEM-EDX, which showed high contents of Ca and P and impurities such as Fe, Al, Mg, Na, and S.

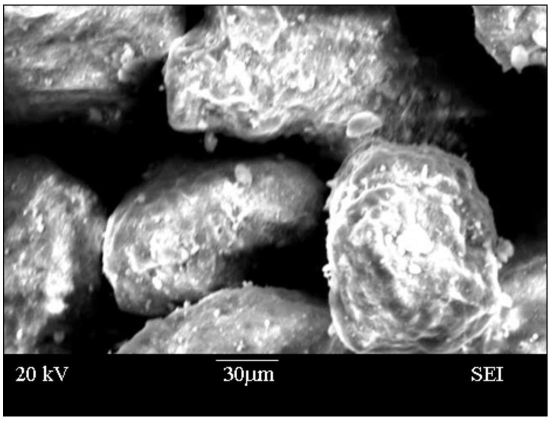

Figure 1 Morphology of PR grains, determined by SEM-SEI.

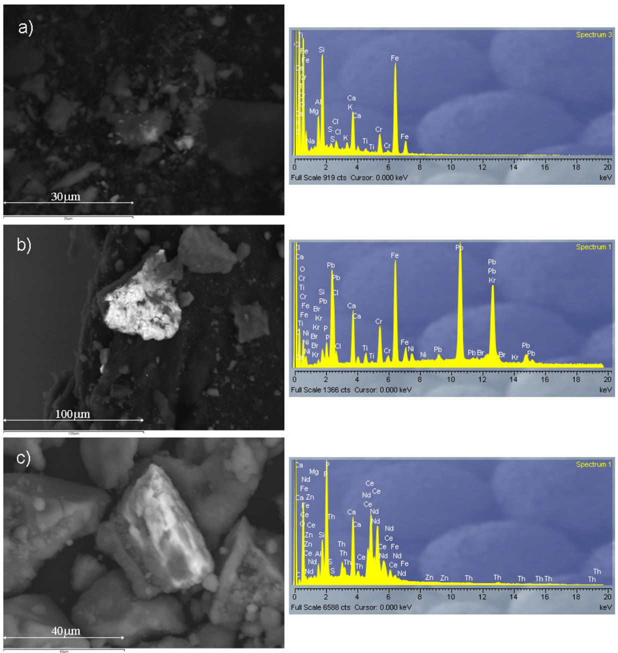

Figure 2 Morphology of PR grains, determined by SEM-BEI, where the distribution of trace elements is observed. If SEM-EDX analyses is applied to the particles, the trace elements are identified. In these three cases, the major trace element associated to each particle were: a) iron (bar 30 µm), b) lead (bar 100 µm) and c) cerium-lanthanum-neodymium (bar 40 µm).

In the samples analyzed in BEI mode, slightly bright white particles were observed. Based on SEM-EDX, those particles were found to have a different composition, mainly of iron, and some trace elements, such as lead, barium and REE. As it is shown in figure 2, these particles tend to form thin layers or to be embedded in the phosphate rock grains. In addition, it is important to note that certain trace elements appear in association with the composition of these particles.

3.2 Phosphogypsum

The morphology of the PG particles was also determined using SEM in SEI mode (see Figure 3). The PG crystals exhibited shapes in the form of tables, in acicular form, in tubular form, as small crystal clusters and rhombic forms. The size of particles was varied. Large crystals were of a size between 110 and 160 µm in length, from 50 to 60 µm in width, and of a thickness from 5 to 10 µm; acicular crystals showed dimensions from 40 to 60 µm in length and fine crystals showed a diameter <15 µm. The elemental composition of such crystals is determined by SEM-EDX, mainly Ca and S (Figure 4), as expected.

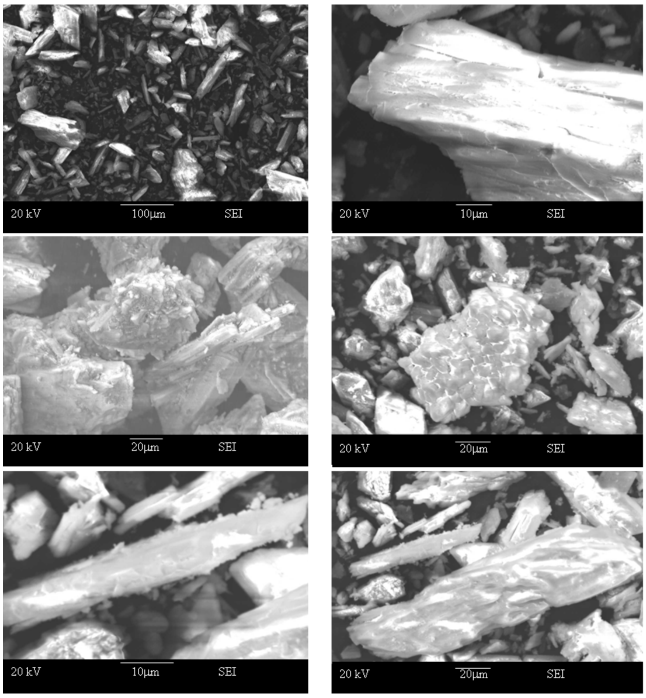

Figure 3 Morphology of PG, determined by SEM-SEI: a) bulk phosphogypsum crystals (bar 100 bar µm), b) shape like tables (bar 10 µm), c) small crystals clusters (bar 20 µm), d) agglomerates (bar 20 µm), e) acicular shape (bar 10 µm), and e) cylindrical shape (bar 20 µm).

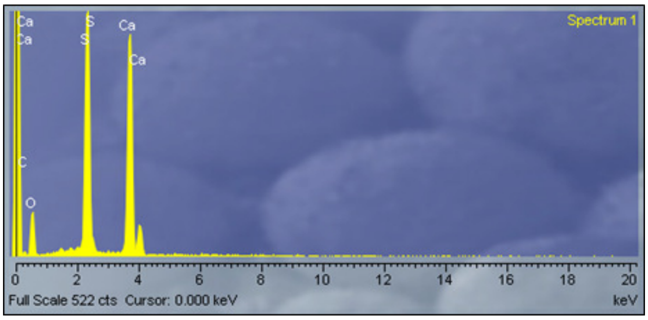

Figure 4 SEM-EDX analyses of PG crystals. In this case, S and Ca were the main components of those crystals according to the expected CaSO4·2H2O.

However, other trace elements are heterogeneously distributed in small particles in the PG. These particles appear as agglomerates and display a high degree of porosity, and a large surface area. The elemental composition, determined using SEM-EDX, showed that each particle is composed of different elements. Some elements, such as iron and lead, was also observed in PR, but other elements, such as Ba and Ag as well as lanthanides such as Ce, La, and Nd, were not observed in PR (see Figure 5).

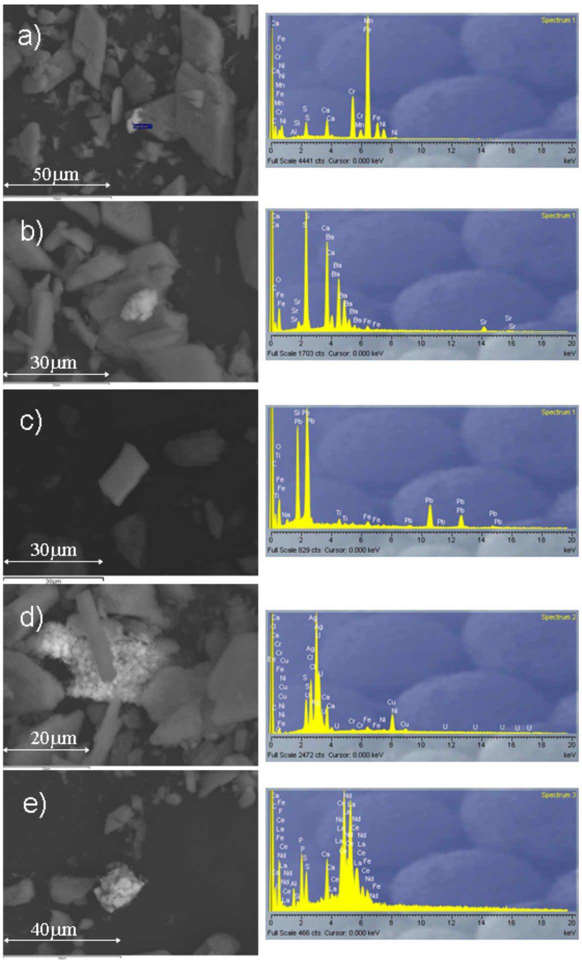

Figure 5 Morphology of PG, determined by SEM-BEI, where the distribution of trace elements is observed. Results of SEM-EDX, where the particles, analyzed by a spot, are composed by different elements, a) iron (bar 50 µm), b) barium (bar 30 µm), c) lead (bar 30 µm), d) silver (bar 20 µm) and g) cerium-lanthanum-neodymium (bar 40 µm).

All particles exhibited low concentrations of some trace elements. For instance, in iron particles, other elements such as Mn, Cu, Cr and Ni were found with lower concentrations. Lead and barium particles showed smaller contents of Ti and Sr, respectively. In articles where REE elements, Ce, Nd and La, are the major trace elements, the presence of P, Ca and S was also observed. Minor elements associated to silver particles were Si, Ca and U in lower concentrations. However, we believe that U could be adsorved into pores of PG cristals, but unfortunately, SEM-EDX only gives us information on the surface composition of the particle.

It should be borne in mind that these particles are small in size, with the majority <20 µm. Moreover, these particles presented contents of Si, Al and K, which are the main elements of clays, thereby corroborating both the presence of impurities determined through XRF and the fact that trace elements are adsorbed onto mainly iron oxide surfaces.

4. CONCLUSIONS

Using SEM-EDX, the PR and PG particles are found to be composed of mainly apatite and gypsum, respectively, and of low quantities of some impurities. The U was only found in association with silver. In both matrices, most of the trace elements tend to appear concentrated in particles <20 μm, and are always associated to some impurity element or other trace element (as base element).

From an environmental point of view, a clear risk of environmental impact is present due to the enhancement and weak bond of toxic elements in phosphogypsum. Indeed, these elements would be concentrated within small particles with a high surface area, which implies easy mobilization by leaching and/or erosion.

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IS TIN TAILING SAND THE SOURCE OF A HIGH NATURAL GAMMA BACKGROUND IN NA MOM DISTRICTS, SONGKHLA PROVINCE, SOUTHERN THAILAND?

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Abstract

This study aims at quantitatively analysis of the activity concentration of the naturally occurring radionuclides in samples collected from the abandoned tin mining areas in Na Mom district of Songkhla province of Southern Thailand. The main objective is to assess whether the tin tailing sand from abandoned tin mines used for house construction in the district could affect the gamma dose rate exposed to public in the area or not. In this study the gamma-ray ground survey was performed using a portable NaI(Tl) Gamma spectrometer to determine the absorbed dose rate in the study area. The 22 sand samples were collected from house construction sites and tin tailing sites in Na Mom district and from clean sand quarries in Hatyai districts, Songkhla province. Totally 34 soil samples were also collected from Na Mom district. All collected samples were analyzed using a high resolution HPGe gamma-ray spectrometer. Results show the external gamma dose rate in Na Mom district ranged 39 - 235 nGy/h and is averaged at 103 nGy/h. Results clearly showed that the specific activities of the Naturally Occurring Radionuclides in tin tailing sand samples collected from Na Mom district are 2 - 6 times higher than those collected from the clean sand quarries in Hat Yai district. However, radium equivalent activities and the radiation hazard indices of the measured samples used to assess the radiation hazards arising due to the use of these tin tailing sands in constructing of dwelling were within the safety limits recommended by the UNSCEAR.

1. INTRODUCTION

Cancer unit, faculty of medicine, Prince of Songkla University, reported abnormal cancer incidence rate in Na Mom district of Songkhla province, Southern Thailand. The first highest esophagus cancer and oral cancer incidences were found here with the age-standardized incidence rate (ASR) of 24.8 and 16.8, respectively (Tongsuksai, *et al.*, 1997). These figures were very high when comparing with the second highest ASR (11.9 and 13.1, respectively) found in Kuan Nieng, the district nearby. Wutthisasna *et al.* (2005) reported the Ra-226 concentration in well water in Na Mom district ranging from 3.51 to 292.1 mBq/l, with a geometric mean 50.7 mBq/l. However, about 30% of the collected water samples have had the Ra-226 concentration exceeded 111 mBq/l.

The Na Mom district of Songkhla province, Southern Thailand, locates between the grids 664000E-681000E and 760000N-777000N on the topographic map sheet 5122 IV, scale 1:50000. Geologic map (Figure 2) shows the unconsolidated sediments deposited in the central part of the district. The country rocks exposed in the study area consist of the sedimentary rocks, i.e., interbedded sandstone, siltstone, mudstone, and shale (Figure 2). The intrusive igneous rocks in the study area comprise of biotite granite, leucogranite, aplite dikes and quartz veins. Tin ores, mainly cassiterite were mined from the disseminations in the leucogranite and in quartz veins. A radioactive mineral, torbernite occurred along the fractures of the granite, quartz veins and quartzite, often found in altered leucogranite (Pungrassami, 1984).

This work aims to investigate the sources of the high background radiation in Na Mom district by conducting a ground radiometric survey in the district with portable gamma ray spectrometer, and analyzing the radionuclide concentration in soil, construction sand and rock samples collected in the district with a low background gamma spectrometer,

2. MATERIAL AND METHODS

A ground radiometric survey was performed using a portable NaI(Tl) Gamma spectrometer (Geofyzika, GS-512, Czech Republic) to determine the U-Th-K concentrations and the estimated absorbed dose rate in the study area. The 22 sand samples were collected from house construction sites and tin tailing sites in the area and from clean sand quarries in Hat Yai, the district nearby. Totally 34 soil samples, 33 shallow well-bottom sediment samples and 25 rock samples were collected from Na Mom district. All prepared samples were analyzed using a high resolution low background HPGe gamma-ray spectrometer (Canberra, Inspector2000; IAEA reference material; Genie2k software; Model 747 lead shield). Radium equivalent concentration (R_{eq}) and absorbed dose rate in air at 1 m above ground surface (D) were estimated by the following equations.

$$Ra_{eq}(Bq/kg) = 370\left(\frac{A_U}{370} + \frac{A_{Th}}{259} + \frac{A_K}{4810}\right)$$

$$D(nGy/h) = 0.462A_U + 0.604A_{Th} + 0.0417A_K$$

where A_U, A_{Th} and A_K are the activity concentration (Bq/kg) of U-238 (or Ra-226 in equilibrium), Th-232 and K-40, respectively.

3. RESULTS AND DISCUSSIONS

Figure 1 shows the airborne radiometric map of equivalent uranium (ppm eU) in southern Thailand that indicates large areas where the uranium contents are high between 4 - 8 ppm eU (DMR, 1989). Results from ground radiometric survey data analysis are present as the color-shaded radionuclides concentration maps which show the area where the uranium, thorium and potassium concentrations are consistently high (Figures 3-5). The high radiation area is found to be coincident with the area exposed by granitic rock and fault zone where the granite has been decomposed by hydrothermal activities. Table 1 shows the results of radiometric analysis including ground radiometric survey, radionuclide concentrations in soil samples, well-bottom sediment samples, rock samples and construction sand samples.

4. CONCLUSION

1) Ground radiometric survey shows the high gamma dose rate over the area where the decomposed granitic rocks exposed to ground surface and in the fault zone. Gamma spectrometric analysis of rock samples confirms a high content of uranium and thorium in them.
2) The concentration of the radionuclides in tin tailing sand samples collected from Na Mom district are 2 - 6 times higher than those collected from the clean sand quarries in Hat Yai district.
3) Higher radionuclide concentrations in shallow well-bottom sediment samples indicate that well water has a high radium content which was adsorbed by clay particles in well bottom.
4) Mining activities in Na Mom district probably enhance and accelerate the dispersion of radionuclides to the environment in Na Mom district and its vicinity.

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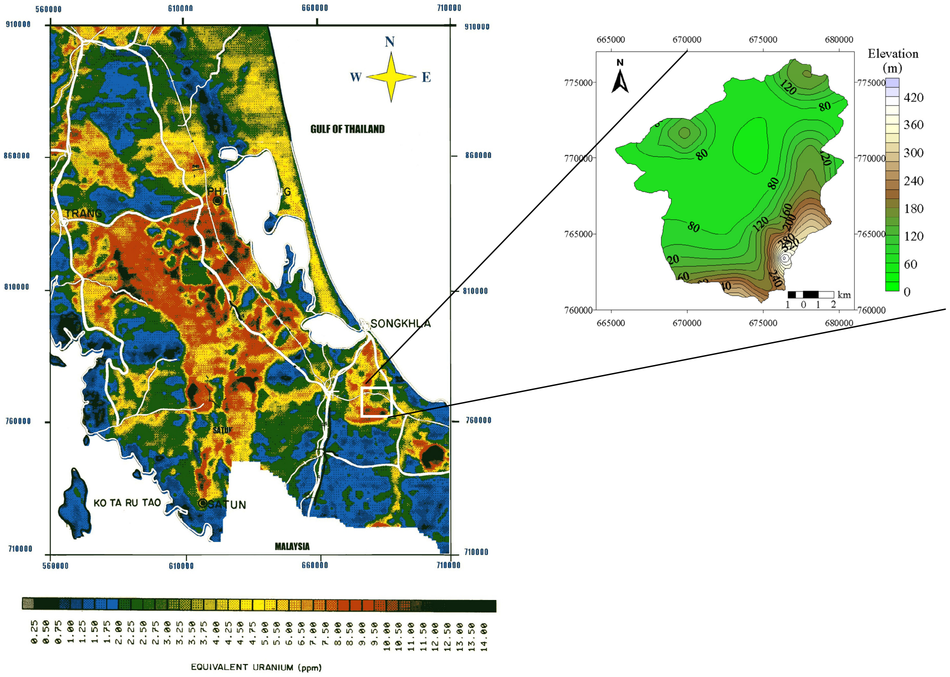

Figure 1 Airborne radiometric map (equivalent uranium) of southern Thailand and the study area in Na Mom District of Songkhla province. (DMR, 1989)

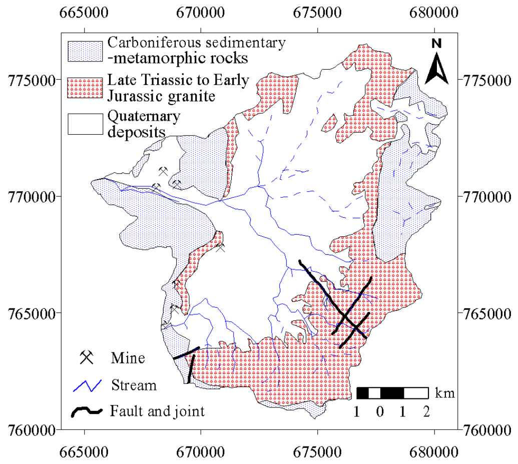

Figure 2 Geology map of Na Mom district, Songkhla province, Southern Thailand.

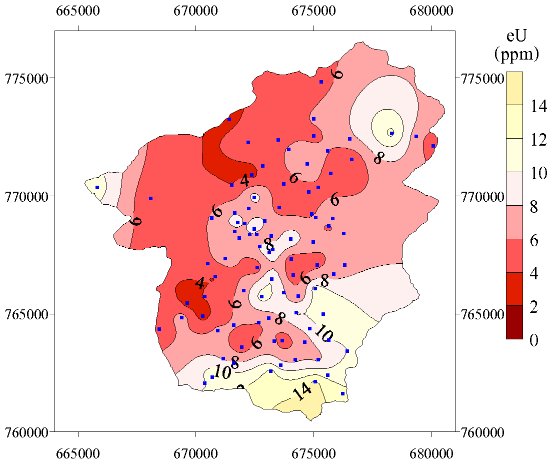

Figure 3 eU concentration at ground surface at Na Mom district, Songkhla province, Southern Thailand.

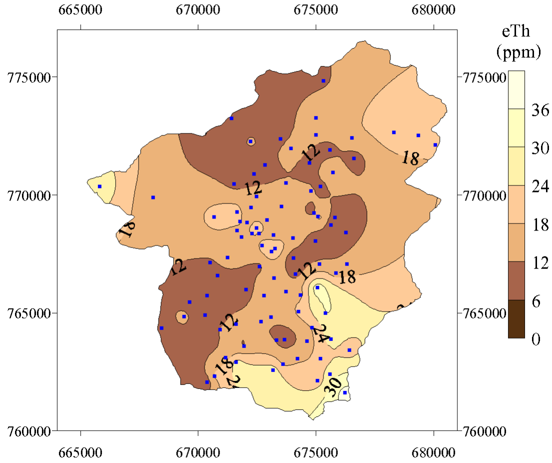

Figure 4 eTh concentration at ground surface at Na Mom district, Songkhla province, Southern Thailand.

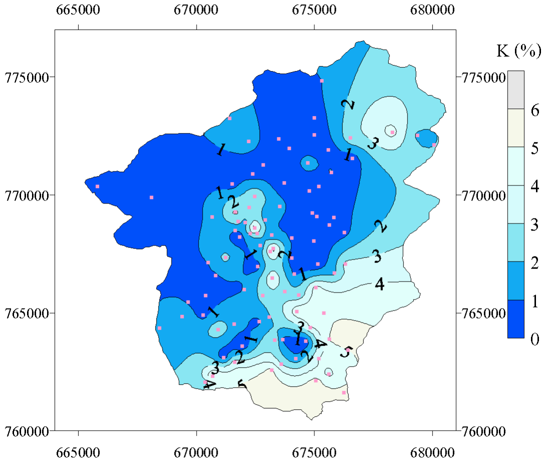

Figure 5 K concentration at ground surface at Na Mom district, Songkhla province, Southern Thailand.

TABLE 1 RADIONUCLIDE CONCENTRATION, ABSORBED DOSE RATE AND RADIUM EQUIVALENT IN NA MOM DISTRICT.

Sample type	**Sub-district (No. points)**	**Average radionuclide concentration ± standard deviation**			**Absorbed dose rate (nGy/h)**	**Radium equivalent (Bq/kg)**
		eU (ppm)	**eTh (ppm)**	**K (%)**		
Ground gamma spectrometric survey	Klongrang (31)	8.3 ± 2.4	18 ± 7.8	2.5 ± 1.9	124 ± 53	267 ± 111
	Na Mom (12)	6.5 ± 2.2	15.9 ± 5.6	1.3 ± 1.0	93 ± 32	204 ± 68
	Pijit (16)	5.7 ± 2.2	12.8 ± 4.7	1.1 ± 1.1	79 ± 36	172 ± 75
	Tungkamin (32)	7 ± 2.5	14 ± 5.5	1.9 ± 1.4	99 ± 42	214 ± 88
	Over all (133)	**7.1 ± 2.5**	**15.5 ± 6.5**	**1.9 ± 1.6**	**103 ± 46**	**223 ± 97**
Soil samples	Klongrang (10)	7.23 ± 3.94	15.5 ± 8.95	2.22 ± 1.97	108 ± 66	232 ± 140
	Na Mom (8)	4.23 ± 1.59	10.43 ± 4.66	1.07 ± 1.18	64 ± 33	138 ± 69
	Pijit (7)	5.26 ± 2.83	11.14 ± 6.6	0.85 ± 1.07	68 ± 44	150 ± 93
	Tungkamin (9)	4.59 ± 2.46	9.84 ± 6.39	0.90 ± 1.45	62 ± 47	135 ± 99
	Over all (34)	**5.42 ± 3.03**	**11.91 ± 7.07**	**1.32 ± 1.56**	**77 ± 52**	**167 ± 110**
Shallow well-bottom sediment	Klongrang (8)	21.23 ± 14.13	48.13 ± 25.81	1.52 ± 0.74	259 ± 137	577 ± 308
	Na Mom (9)	11.17 ± 7.38	24.68 ± 8.71	1.17 ± 0.62	139 ± 56	309 ± 124
	Pijit (6)	13.11 ± 5.67	28.88 ± 14.62	1.5 ± 0.89	165 ± 73	365 ± 163
	Tungkamin (10)	13.27 ± 7.1	30.31 ± 15.64	2.19 ± 1.72	178 ± 81	409 ± 219
	Over all (33)	**14.6 ± 9.58**	**32.83 ± 18.68**	**1.63 ± 1.15**	**185 ± 98**	**409 ± 219**
Rock	Granite (12)	20.77 ± 8.15	28.63 ± 8.27	3.96 ± 0.5	240 ± 53	517 ± 118
	Sedimentary rk. (10)	1.28 ± 0.79	9.93 ± 10.31	0.93 ± 1.24	44 ± 45	96 ± 97
	Metamorphic rk. (3)	2.1 ± 1.6	7.54 ± 3.89	0.92 ± 0.89	42 ± 18	92 ± 38
Construction Sand	Inside Na Mom district (16)	4.5 ± 1.4	11.5 ± 6.6	3.3 ± 1.1	-	204 ± 68
	Outside Na Mom district (6)	1.4 ± 0.2	3.9 ± 0.5	0.6 ± 0.1	-	53 ± 4
	Median values of world soil (UNSCEAR2000)	**2.8 (35 Bq/kg)**	**7.4 (30 Bq/kg)**	**1.3 (400 Bq/kg)**	-	-

NATURAL RADIOACTIVITY IN A RAISED PEAT BOG

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Peatlands generally accumulate C because the rate of biomass production is greater than the rate of decomposition. The apparent long-term rate of carbon accumulation for boreal and subarctic regions is estimated to 15-30 g C m^{-2} $year^{-1}$. Peatlands are archives of past diversity, climate, and other environmental conditions. The recently formed surface layers of peat land are an archive for recent environmental information and offer an opportunity to understand how environmental conditions have been recorded in peat profiles by relating the signals in the peat to recent historical records. Since they have not undergone the same decay and compression, the temporal resolution of surface peat can be considerably higher than deeper layers.

Peatland has accumulated huge amounts of pollutants including radioactivity. The activity can be released by using peat as fuel for electricity and heat production or by the global warming causing higher decomposition. The activity can then either be released to the atmosphere or concentrated in ashes or be released to the water sheds. Of special interest are raised bogs since they receive pollutants only from the atmosphere.

Natural radioactivity such as ^{210}Po, ^{210}Pb and Uranium isotopes have been studied in peat. Also anthropogenic radionuclides such as ^{137}Cs and $^{239+240}$Pu were studied in the same samples.

Peat cores, about 20 cm in length, were sampled from Axmar raised peat bog (61^o0^l N, 17^o2^l E), Sweden with a cylindrical steel corer (Ø = 8 cm). The cores were sliced in 1 cm sections and dried (60^o C). ^{210}Po was deposited spontaneously on Ag or Ni discs after mineral acid digestion. ^{210}Pb was determined by ingrown ^{210}Po and repeated deposition. Uranium isotopes and Plutonium were sequentially separated by anion exchange. As radiochemical yield determinants ^{209}Po, ^{232}U and ^{242}Pu were used. The samples were measured by alpha spectrometry using ion implanted silicon detectors. ^{137}Cs was measured by a HpGe well type detector.

The results are shown in Fig. 1 (a)-(f). The activity concentrations of ^{210}Po and ^{210}Pb agree very well by the method used. This is also expected since analysis was carried out 1 year after sampling. Otherwise sometimes equilibrium has not been reached in the top-layer. The dating of the peat bog using unsupported ^{210}Pb works very well and shows a growth rate of 1.5 mm per year corresponding to a net mass increase of 170 g m^{-2} per year.

Uranium concentrations are increasing with depth from 4 to 25 Bq kg^{-1} (1-17 cm). Most of the uranium must have other origin than atmospheric deposition for example migrating from deeper layers. The ^{234}U/^{238}U activity ratio is generally smaller than one which is unusual for water and biological material. It is known that ^{234}U has a higher solubility from mineral surfaces due to the alpha particle recoil.

As can be seen there is a peak at 8 cm depth for ^{137}Cs which then corresponds very well to the major nuclear tests 1962-1963 especially considering some overlapping from earlier tests 1957-1958. The peak from the Chernobyl accident, 1986, should be at about 3 cm depth but we have also observed that a large fraction of radiocaesium is found in the top layers where there is growing plant material.

Plutonium has also a maximum at 8 cm depth but not as distinct as for ^{137}Cs in this profile. The contribution of $^{239+240}$Pu from the Chernobyl accident was relatively much smaller than that for ^{137}Cs.

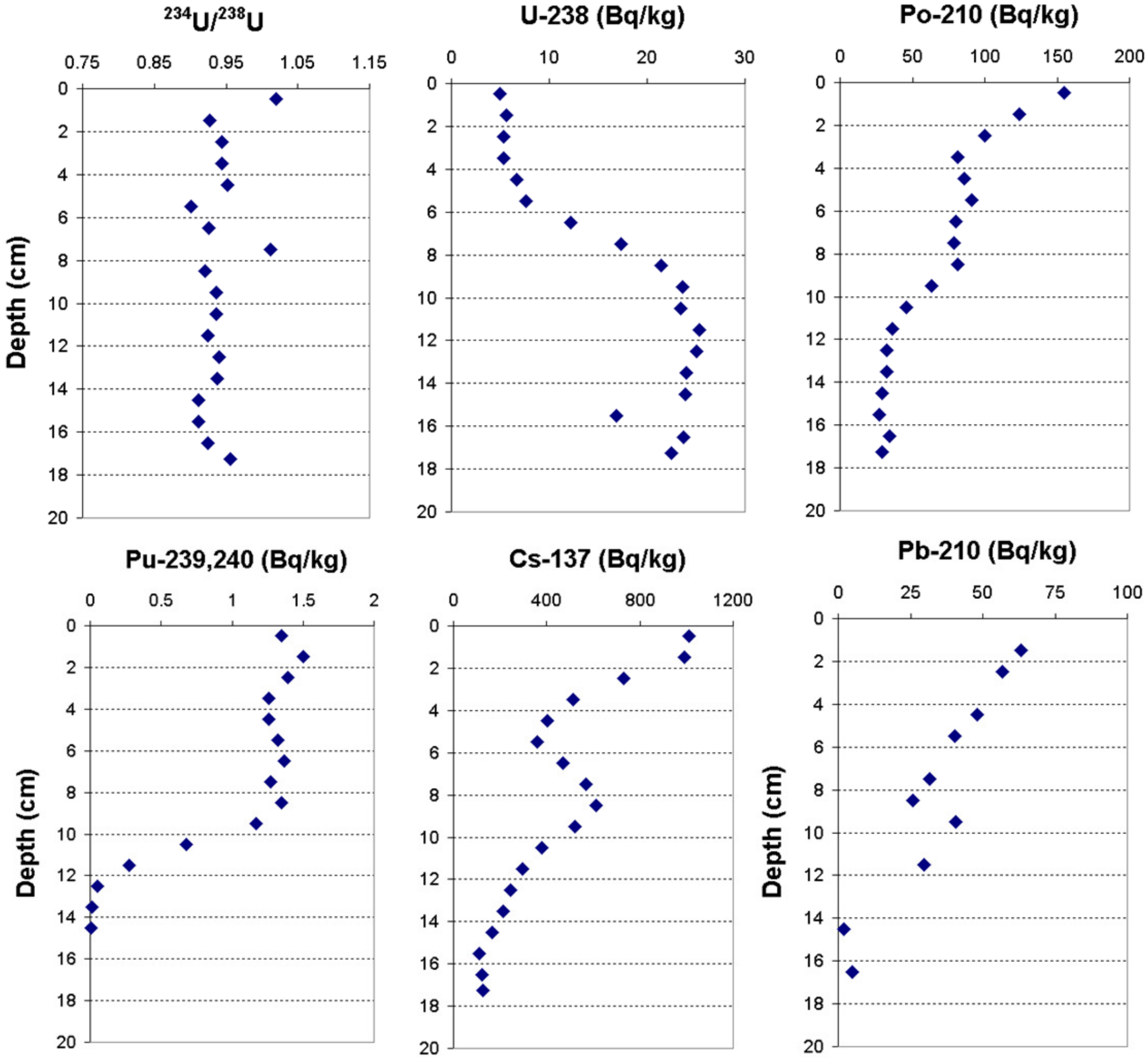

Fig. 1, a,b,c,d,e,f. Activity ratio ^{234}U/^{238}U and activity concentrations of ^{210}Po, ^{238}U, $^{239+240}$Pu, ^{137}Cs and ^{210}Pb as function of depth in a peat profile.

USE OF Pb AND Po AS RADIOTRACERS FOR METEOROLOGICAL PURPOSES

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Abstract

The paper describes the use of ^{218}Po for evaluation of height of a mixing layer and ^{210}Pb for monitoring of air pollution sources. In the first part a new method of evaluation of the mixing layer height was presented. The novelty of this method consists in the measurement of ^{218}Po concentration in the air. The concentration of ^{218}Po was measured in the surface layer by means of an alpha spectrometer. The remote sensing method (sodar) was chosen as a reference method. The obtained results show that the variation of ^{218}Po concentration in response to the daily changes of the mixing layer of the lower troposphere may become a good tracer to estimate the atmosphere dynamics and transport of pollution by turbulent mixing of the atmospheric air. A statistically significant correlation between the mixing layer height and ^{218}Po concentration in the air was observed and, as a result, a statistical model was developed to determine the mixing layer height. The second part describes the use of ^{210}Pb to determine the air pollution sources. Changes of ^{210}Pb concentrations in the atmosphere were analysed. During the analyses the annual series of 24-hour measurements of the content of ^{210}Pb in particulate matter (PM) and its air concentration were carried out in a specially built air monitoring station in Tarnowskie Góry. The analysis of 24-hour concentrations allowed to assess the average 24-hour background of ^{210}Pb at the level of about 0.4 mBq/m^3. Using a stochastic neural network, 24-hour concentrations of ^{210}Pb and 1-hour data on a wind vector a 1-hour concentration of ^{210}Pb were determined. This enabled the assessment of conditional distributions of ^{210}Pb versus 10-degree inflow sectors.

1. ESTIMATION OF MIXING LAYER HEIGHT BASED ON ^{218}Po CONCENTRATION MEASUREMENTS

There is a feedback between meteorological conditions and the quality of the ambient air. Weather conditions determine the transport of substances in the air, while the presence of pollutants influences the climate and the weather. From the point of view of environmental protection against gaseous and dusty air pollutants (including anthropogenic pollutants) or artificial radioactivity the most important are operational abilities to measure atmospheric characteristics responsible for their dispersion. Thermodynamic instability of the air flow is characteristic for the lower troposphere. The mixing layer height (MLH) is one of the basic characteristics of ventilation of the atmospheric boundary layer (ABL), especially in urban meteorology [1]. There is a series of methods, both experimental and theoretical, allowing to identify this parameter with various accuracy [2]. In this paper a new experimental indicative method to assess the mixing layer properties was presented. It is based on the assumption that measurements of the air concentration of the direct product of ^{222}Rn decay, namely polonium ^{218}Po, allows to estimate the MLH. The essence of our work was to elaborate an algorithm of an isotope method for estimating the MLH.

1.2. Research characteristics

Quite noticeable variability of the MLH can be observed under conditions of insolative irradiative conditions, with large negative vertical daytime temperature gradients and temperature inversion at night, small velocity of lower wind, low general cloudiness and lack of rainfall. Due to the fact that pronounced dynamics of the mixing layer can be best observed at warm seasons of the year, polonium concentrations in the ground atmospheric layer were measured from May to October, although there were also several measuring campaigns during the cold season with the presence of a snow cover.

1.2.1. Study areas

The method used in this paper is based on natural radioactivity, the volume of which depends on the complex of geological and geographical factors [3]. Therefore, the field studies were performed in three geologically diverse areas in geographical sub-provinces of Silesian-Cracovian Highland (measuring points: Katowice and Cracow) and Northern Subcarpatian (measuring point: Ostrava).

The choice of location for measurements of radon concentrations in the soil air and polonium in the atmospheric air was dictated by the availability of the reference method for mixing layer assessment (sodar) as well as by the availability of the observational base for meteorological conditions. Hence, the field studies were performed in the National Weather Service (NWS) stations, whose location, equipment and measuring system complied with standards of the World Meteorological Organisation (WMO). Thus a uniform series of spatially representative and comparable data was acquired.

1.2.2. Methods of measurements

Measurements of radon concentration in soil air

Measurements of ^{222}Rn concentration in the soil air were performed with the BARASOL type probe produced by the French company Algade. The probe was placed 1 m under the ground level, because at that depth radon concentration is not disturbed by exhalation into the atmosphere. Soil air concentrations of radon were registered as 15 minute averages.

Measurements of polonium concentrations in atmospheric air

The alpha spectrometry was used to measure the concentrations of ^{218}Po in the surface layer of the air at equal time intervals. This approach was adopted for several reasons. Firstly, because this isotope is a direct product of radon decay. Secondly, the half-decay time of ^{218}Po is short ($T_{1/2}$ = 3.05 min) and an equilibrium with ^{222}Rn ($T_{1/2}$ = 3.8 day) sets in, hence concentrations of these isotopes are well correlated. Finally, because under normal conditions polonium is a metal not a gas like radon. Therefore, it binds to aerosols in the air and can be easily filtered out, which facilitates its detection.

Measurements of short-lived radon progeny in the air were performed by measuring the activity of the filter on which products of radon decay were collected (including ^{218}Po). The air was aspired with the pomp of a nominal flow of 170 dm^3/min under the basic load. The air flow intensity through the filter was 60 dm^3/min and the low limit detection LLD was 0.05 Bq/m^3 at 0.05 significance level. The air reached the filter through a slit, 2 mm high and 20 mm wide. The device for measuring polonium concentration in the atmospheric air was placed 50 cm above the ground level. Daily ^{218}Po measurements were performed with 1-hour intervals.

Mixing layer measurements

The mixing layer height was determined by an active acoustic ground-based remote sensing method using the sodar. SODAR (SOund Detection And Ranging) is a device for probing atmosphere by scattering sound waves on air density fluctuation and Doppler motion [4]. Information on the structure of the boundary layer was acquired in the operational mode in real time. In order to get uniform temporal data concerning the atmosphere with those on polonium, sodar probing was averaged to 1 hour interval.

1.2.3. Methods of data analysis

An assumption of slightly variable ^{222}Rn concentration in the soil air is a prerequisite for using the measurements of natural radioactivity in the ground atmospheric layer to assess the ventilation properties of the ABL [5,6].

It is because radon concentration in the soil air determines its concentration in the air as well as concentrations of its decay products. As it is well known, the soil air radon concentration depends on the complex of geological and geophysical factors as well as on meteorological conditions in the ground ABL. Consequently, the temporal variability of ^{222}Rn in the soil air and its dependence on various factors were investigated. In order to determine the daily and seasonal variability of radon concentrations in the soil air a time series of historical data starting with 1999 in the areas of later polonium measurements as well as continuous record of measurements at study locations during the period 2001-2006 were analysed. The following methods were used:

- Frequency analysis - DFT discrete Fourier transform and wavelet analysis - amplitude of wavelet transform,
- Rescaled range analysis - Hurst exponent.

Relationship between ^{218}Po and ^{222}Rn concentrations and meteorological conditions was investigated using techniques of linear and multiple regression. Regression coefficients in the models were tested at the significance level of 0.05.

1.3. Results and discussion

1.3.1. Radon concentration in soil air

Based on mathematical methods used for analysing the relationship between ^{222}Rn in the soil air and meteorological and hydrological conditions the following conclusions can be drawn:

- mechanism of emanation and exhalation of ^{222}Rn from the lithosphere to the atmosphere as well as concentration of its products in the ground atmospheric layer are similar in the areas of extensive coal mining (Katowice) and areas not transformed by this activity (Cracow);

- comparison of daily averaged ^{222}Rn concentrations in the soil air between Katowice and Cracow showed that ^{222}Rn concentrations observed in Cracow were about 6-7 times higher than in Katowice, average measured radon concentrations were of the order of several thousands (Bq/m^3) in Katowice and several dozen thousand (Bq/m^3) in Cracow, respectively;
- frequency domain analysis (Fourier and wavelet) and fractal analysis (Hurst exponent) showed that there was no cyclic long-term variability of ^{222}Rn in the soil air at the depth of 1 m, radon concentration level was constant; there were some positive or negative trends in sufficiently long time intervals, thus not influencing the measurements of its short-lived decay products including ^{218}Po in the atmosphere;
- no variations of ^{222}Rn concentration in the soil air were observed which might be attributed to daily patterns of meteorological factors, which means that short term changes in meteorological factors do not have an impact on ^{222}Rn concentrations;
- in the study areas there was no direct relationship between the groundwater level and the soil air radon concentration at 1 m depth, and the statistical relationship between radon concentration and climatic water balance was insignificant;
- cumulative values of the complex of meteorological factors (air temperature, wind speed, precipitation) characterising soil conditions have an impact on the level of radon concentration in the soil air in time scales of dozens to several tens of days,
- in particular, it was proven that temporal variability of radon concentration in the soil air did not depend on weather conditions but was a secondary effect due to long-time joint interaction of the complex of these conditions.

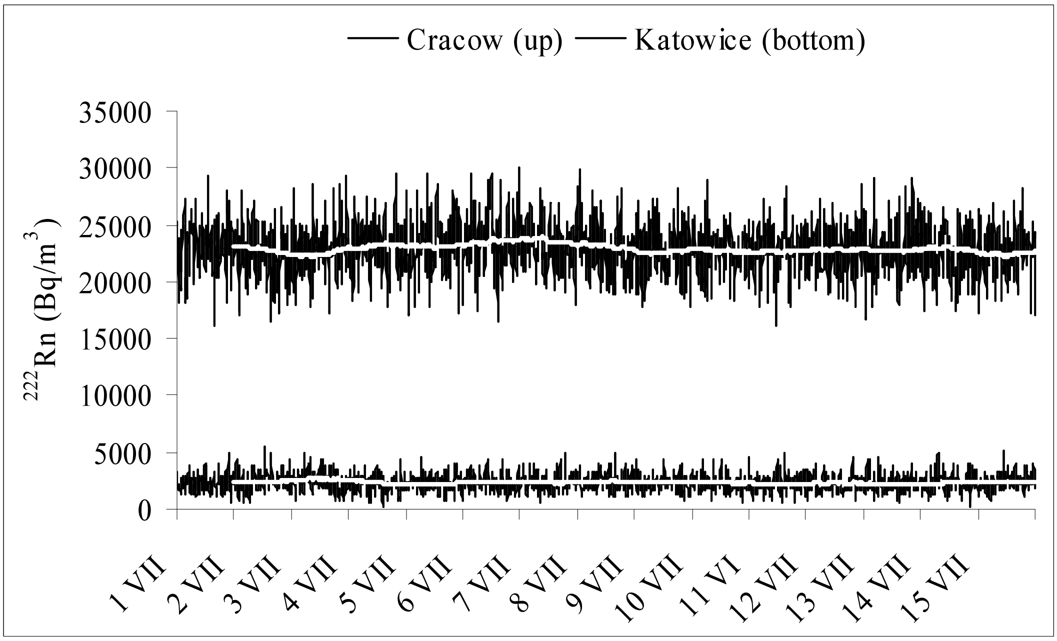

Fig. 1. Average daily radon concentration in soil air vs. momentary concentration, 1-15 July 2001

The assumption about slight variability of ^{222}Rn concentration in the soil air in short time scales (order of 1 hour) was positively verified and consequently taken as true in further investigations (Figure 1).

1.3.2. Polonium concentration in atmospheric air

Our research indicates that the relationship between ^{218}Po concentration and vertical thermo-dynamical stratification of the atmosphere manifests as an increase of its concentration during stable equilibrium and lowering its concentration with atmosphere instability. Accordingly, irrespective of the study area, a characteristic daily pattern of ^{218}Po concentration in the atmospheric air can be observed, with a maximum in early morning hours and minimum at noon when the range of the mixing layer is maximal. Hence, the ^{218}Po concentration shows that the daily pattern is inversely proportional to the pattern of the mixing layer height. On average, the measured values of ^{218}Po concentrations were generally of the order of several Bq/m^3 in Katowice and several tens of Bq/m^3 in Cracow.

Figure 2 shows the daily pattern of polonium concentration in the atmospheric air. The relationship between the daily averaged ^{218}Po concentration $\overline{C_{^{218}Po}}$ and the daily averaged ^{222}Rn concentration $\overline{C_{^{222}Rn}}$ can be approximated by the following formula:

$$\overline{C_{^{218}Po}} \approx \sqrt[3]{\overline{C_{^{222}Rn}}}\ .$$

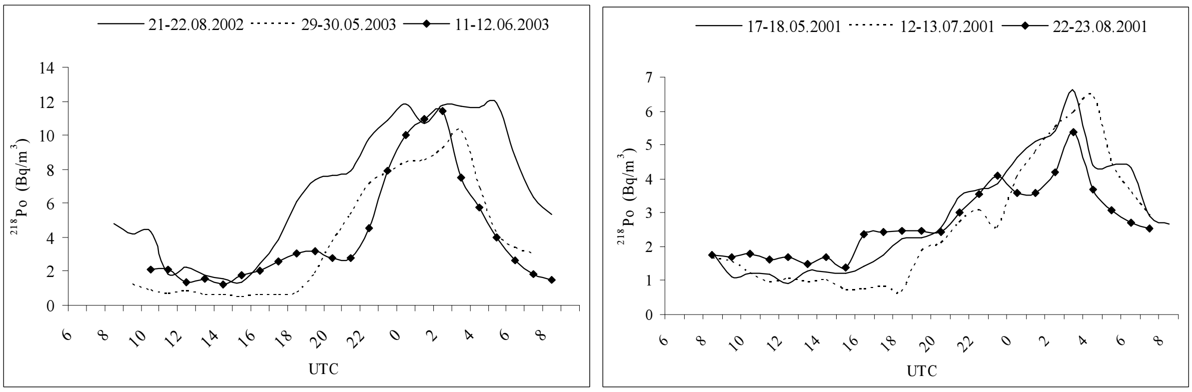

Fig. 2. Daily variation of polonium concentration in atmospheric air for Cracow (left) and Katowice (right).

1.3.3. Polonium concentration and mixing layer

The comparative analysis of ^{218}Po concentration and the mixing layer height estimated from sodar (MLHs) revealed negative correlation coefficients within the range of 0.443-0.830 for Katowice and 0.416-0.733 for Cracow. Differences in correlations could be attributed to different meteorological conditions during field experiments. Figure 3 shows the daily pattern of ^{218}Po concentration in the ground ABL together with the MLHs. The average correlation coefficient between the MLHs determined by acoustic remote sensing technique and ^{218}Po concentration in the ground atmospheric layer is equal to -0.596.

The analysis of the relationship between ^{218}Po concentrations in the atmospheric air and MLH leads to the following conclusions:

- both the MLHs and ^{218}Po concentration in the atmospheric air are higher in Cracow than in Katowice,
- differences in MLHs in these two places are caused by local topographic and climatic conditions,
- higher ^{218}Po concentration in Cracow, as compared with Katowice, is probably due to higher radon potential in Cracow measuring point.

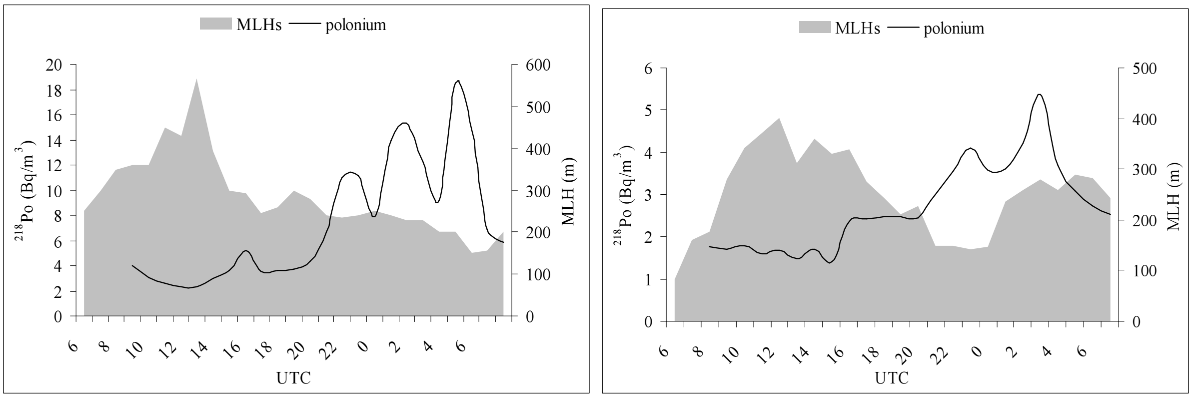

Fig. 3. Daily variation of polonium concentration in atmospheric air and mixing layer height MLHs for Cracow, 3-4 October 2001 (left) and Katowice, 22-23 August 2001 (right).

1.4. Isotopic method for mixing layer assessment

1.4.1. Polonium concentration in atmospheric air as mixing layer indicator

The mathematical model for the assessment of the mixing layer height was developed on the basis of data collected for Katowice and Cracow in the period of 2001-2003. As a result of numerous experiments different approaches to the construction of a formula describing the MLH as a function of ^{218}Po concentration in the ground ABL were proposed [7,8,9,10].

The analysis of measurements shows a direct relationship between the measured values, i.e. concentration of ^{218}Po, MLHs, a logarithm and a square root of these values as well as their hourly increments. A statistically significant relationship between ^{218}Po concentration ($\overline{C_{^{218}Po}}$) (Bq/m^3) in the ground atmospheric layer and the height of the mixing layer (MLHeq) (m) was determined (at the significance level 0.05). This relationship can be expressed by the equation:

$$MLHeq = [c_1 \cdot \ln\left(C_{^{218}Po}\right) + c_2]^4$$

where: c_1 - constant coefficient equal ~ -0,5,

c_2 - variable coefficient dependent on local physico-geographical and physico-geological conditions laying in the range ~ (4-6).

For Katowice $c_2 = 4.3$, while for Cracow $c_2 = 5.1$, and for Ostrava $c_2 = 5.5$.

The developed statistical model for the assessment of the mixing layer height calculated MLHeq using ^{218}Po concentrations and provides relatively good fits of calculated values to those determined with sodar MLHs. The average value of the correlation coefficient between the MLHs and MLHeq varies from 0.648 for Katowice to 0.662 for Cracow.

For daily patterns of the mixing layer height coefficients of correlation between MLHeq and MLHs range from 0.465 to 0.876 for Katowice and from 0.394 to 0.899 for Cracow.

Applicability of the developed model for estimating the mixing layer height from ^{218}Po concentrations in the form of an experimental formula is restricted to warm seasons of the year, i.e. from May to October (no snow cover). Accuracy of the mathematical formula in this season is satisfactory. The agreement between the model and reality depends mainly on meteorological conditions. It is especially sensitive to the wind speed in the mixing layer. It shows the tendency for underestimation of mixing conditions in situations with the wind speed $u > 3$ m/s. It is due to a relatively high correlation between anemological conditions and polonium concentration in the air. Elaboration of an universal equation for the whole year is not possible at this stage of research as the number of measurements in the winter season (especially during the snow cover) in comparison to the summer one is too small. This is, however, the problem which needs further investigation.

1.4.2. Testing of isotopic method

Testing of the developed statistical model was performed in different geographic and meteorological conditions during warm season in Ostrava and Cracow in the years 2004-2006.

The results obtained in Cracow were satisfactory – linear regression confirmed statistical significance of the relationship between the mixing layer height determined by sodar and by the isotopic method, and, hence, confirmed the utility of the developed model in this region (Figure 4). In the second case, studies performed in the independent industrial-urban region of Ostrava were less advantageous. However, the linear relationship obtained was statistically significant.

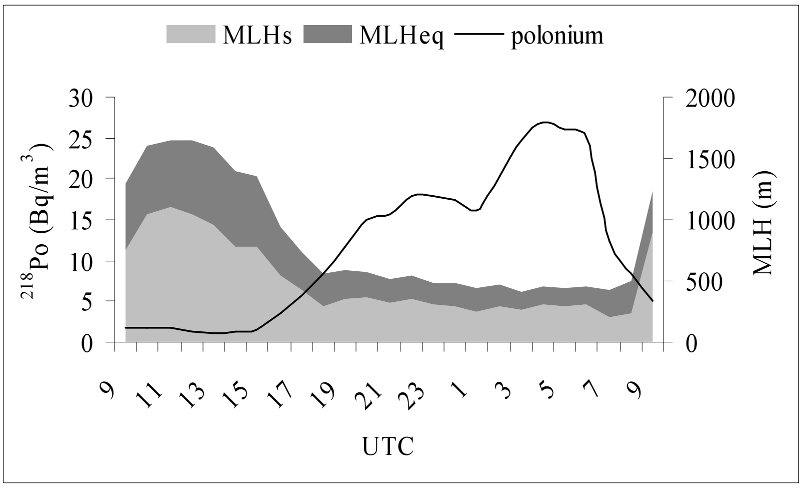

Fig. 4. Daily variation of polonium concentration in atmospheric air and mixing layer height, measured MLHs and calculated MLHeq for Cracow, 21-22 September 2006.

1.5. Conclusions

The isotopic method of estimating the height of the mixing layer is an alternative to methods used so far in environmental engineering, particularly in environmental monitoring and environmental protection. Mobility, low cost and experimental simplicity of the indicator makes it useful for the assessment of mixing conditions of the atmospheric boundary layer. In its present form inaccuracy during the winter period and the need of its calibration to different conditions of radon emanation are the main drawbacks of this method.

2. APPLICATION OF ^{210}Pb FOR ASSESSING CONTRIBUTION OF DUST FROM DIFFERENT COAL COMBUSTION PROCESSES

Results obtained from radioactive air contamination monitoring stations ASS-500 show that the average concentration of ^{210}Pb in the near-ground layer of the air in Poland is 0.44 mBq/m^3 [11]. In Katowice the average quarterly concentration is slightly higher - 0.47 mBq/m^3. The differences among measurement points in Poland vary from 20 to almost 100% of the average value.

Fig. 5 shows average weekly concentrations of ^{210}Pb in the near-ground layer of the atmospheric air in Katowice. The maximum concentration in this period was almost 2.0 mBq/m^3, whereas the minimum one was 0.124 mBq/m^3. The range of the observed variability is greater than the variability resulting from radon concentration changes. Apart from short-term changes some seasonal changes can also be observed due to the increased industrial emission or the so called „low emission".

The main source of ^{210}Pb in the air is a parent isotope ^{222}Rn. It must be noted here, however, that due to significant delays in the production of ^{210}Pb the daily changes in radon concentrations will not have a remarkable impact on its changes in the air. On the other hand, the behaviour of short-life products of radon decay, which form in the air the, so called, "radioactive aerosols", is – to a large extent – responsible for much lower concentration of ^{210}Pb than could be expected based on the radioactive decay and concentration of ^{222}Rn. It is estimated that the retention time of radioactive aerosols in the air is 6 days [12]. It must be stressed here, that ^{210}Pb is a product of radon decay with a significant time shift of up to several days. Therefore, the impact of all meteorological factors determining the exhalation of radon is averaged and Pb concentration changes will only indicate long-term trends in the changes of radon concentrations.

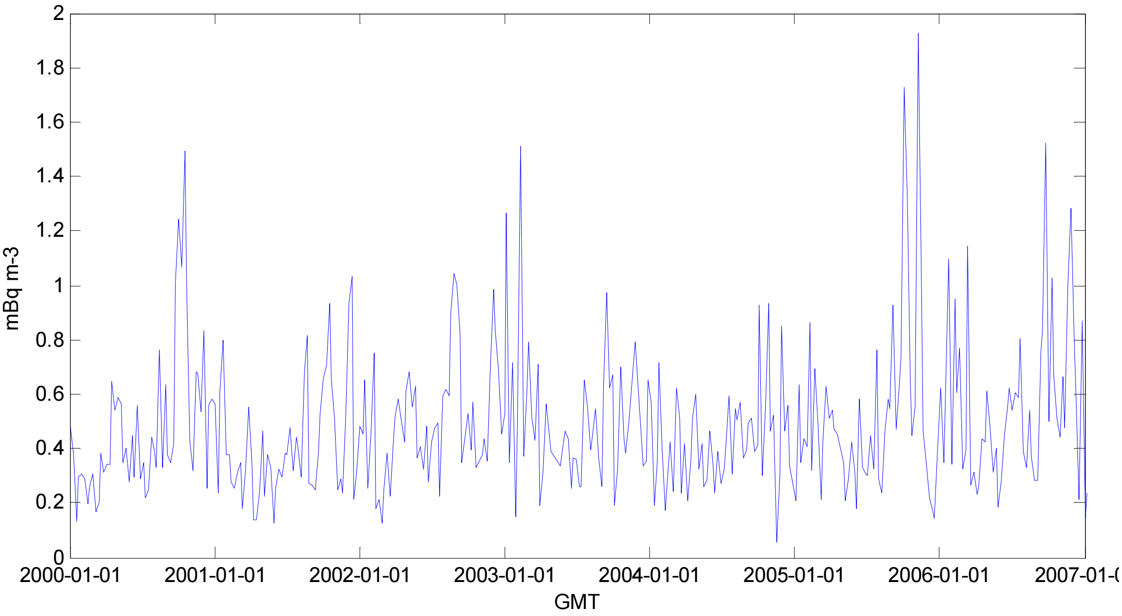

Fig. 5. Weekly ^{210}Pb concentrations in years 2000-2006 in ASS-500 station in Katowice

Another natural factor which may have an impact on the air concentration of ^{210}Pb is the occurrence of ^{226}Ra in suspended particular matter. The carried out measurements show that the average concentration of ^{226}Ra over the territory of Poland is about 5 μBq/m^3, which means that the expected concentration of ^{210}Pb cannot exceed this value.

The third factor determining the occurrence of ^{210}Pb is anthropogenic emission. In combustion of fossil fuels, ore enrichment and metal smelting most of ^{210}Pb contained in raw materials may be released into the atmosphere. Assuming that as a result of combustion of 1 kg of coal 10 m^3 of flue gases are obtained and that the entire Pb contained in coal, i.e. about 20 Bq/kg [13], goes to flue gases, we will obtain a local emission source of ^{210}Pb, which will be even three orders of magnitude higher than natural sources.

The contribution of industrial emission to the total air concentration of ^{210}Pb is determined locally and depends on many factors, both meteorological and those connected with a particular combustion process. The anthropogenic emission, in comparison to slow changes in concentration of ^{210}Pb caused by natural emissions, is very dynamic. These emissions contribute to relatively high concentrations of the ^{210}Pb isotope in the air in the area affected by the emission source. Therefore, all local rapid changes in the concentrations of ^{210}Pb should be of anthropogenic origin.

The aim of this paper was to demonstrate that based on average daily measurements of ^{210}Pb concentrations and hourly measurements of the wind directions conducted during measurements of ^{210}Pb concentrations we can identify:

- location of pollutant sources and influx of pollutants
- contribution of natural and anthropogenic sources to measured concentration.

In this case anthropogenic sources include industrial energy sources based on hard coal (power plants, heating plants) and household energy appliances (domestic boilers and furnaces).

2.1. Emission of ^{210}Pb from coal combustion process

The main sources of dust from hard coal combustion processes are big industrial sources and a large number of small boiler-houses and furnaces in residential and municipal buildings. Based on the data on emission sources for the System for Identification of Air Pollution Inflow [14], which has been operating in the Institute for Ecology of Industrial Areas, a characteristics of dust emission sources in the vicinity of the Tarnowskie Góry monitoring station was developed. Locations of residential buildings and point emitters in 22.5° sectors near the monitoring station in Tarnowskie Góry are presented in Fig. 6.

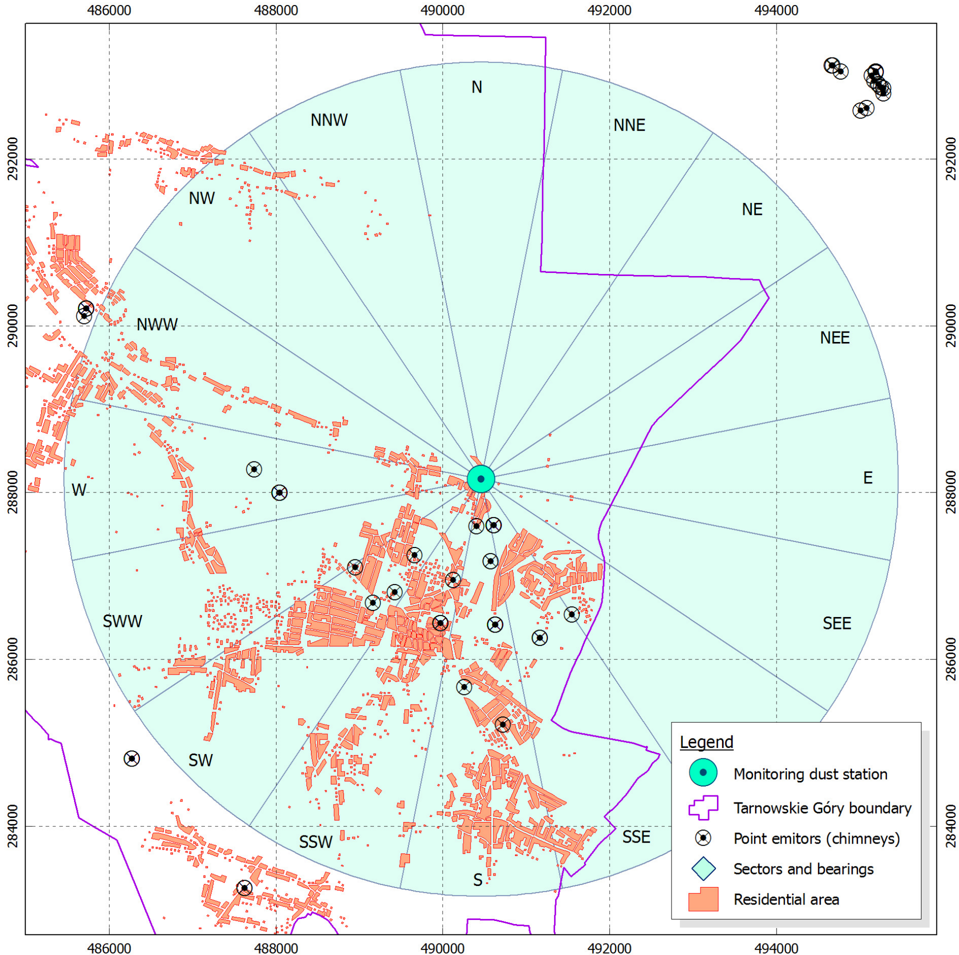

Fig. 6. Industrial and residential sources of ^{210}Pb

TABLE 1. CHARACTERISTICS OF ^{210}Pb EMISSION FROM INDUSTRIAL INSTALLATIONS, DOMESTIC FURNACES AND BOILER-HOUSES, AND GROUND

Type of emission source	Variability range from [Bq/kg]	Variability range up to [Bq/kg]	Average value [Bq/kg]	Standard deviation [Bq/kg]
Industrial installations	100	350	189.3	91.9
Domestic furnaces and boiler-houses	750	1400	1096.3	444.1
Ground	20	50	48.6	22.6

TABLE 2. NUMBER OF INDIVIDUAL FURNACES AND BOILERS IN RESIDENTIAL BUILDINGS AND NUMBER OF INDUSTRIAL SOURCES IN SECTORS

Sector	Number of individual hard coal combustion installations in the sector: Boiler-houses	Furnaces	Total	Number of industrial emitters in the sector[a]
N	0	0	0	0
NNE	28	19	47	0
NE	27	19	46	(8)
NEE	0	0	0	0
E	16	11	27	0
SEE	43	31	74	0
SE	122	85	207	1
SSE	190	134	224	2
S	925	661	1586	5
SSW	2530	1804	4334	2
SW	1410	1006	2416	4(1)
SWW	994	706	1700	0
W	251	179	430	2
NWW	256	181	437	(2)
NW	45	31	76	0
NNW	20	13	33	0

[a] in parentheses is the number of emitters outside of the indicated radius

2.2. Concentrations of ^{210}Pb in the air

The content of ^{210}Pb in air dust and concentration of ^{210}Pb in the atmospheric air were determined based on an annual cycle of daily measurements at the IETU monitoring station in Tarnowskie Góry (see Fig. 7).

24-hour dust (particulate matter) samples were collected using a Staplex sampler. As a filter the FPP-15 fabric was used. The same kind of fabric is used in ASS-500 stations.

Samples were collected in three measurements cycles:

- winter cycle: 8 February - 26 March 2006 – 16 samples
- summer cycle: 30 June - 6 August 2006 – 12 samples
- autumn-winter cycle: 27 October 2006 - 22 January 2007 - 44 samples.

Measurement of ^{210}Pb contained in the particulate matter collected on the filter was carried out using the LSC method (liquid scintillation counting). The method enables detection of α and β radiation emitted by radioactive isotopes contained in the analysed material with high, almost 100% efficiency. The method is also used for differentiation of radiation energy, which enables the identification of isotopes which are the source of measured radiation. The prerequisite for applying the method of scintillation spectrometry is conversion of the analysed material into a solution. The solution, mixed with a liquid scintillator, constitutes a sample which is then measured using a QUANTULUS low background scintillation counter.

Based on the flow or mass of the particulate matter accumulated on the filter the specific activity of ^{210}Pb in particulate matter can be calculated as well as its radioactive concentration in the air.

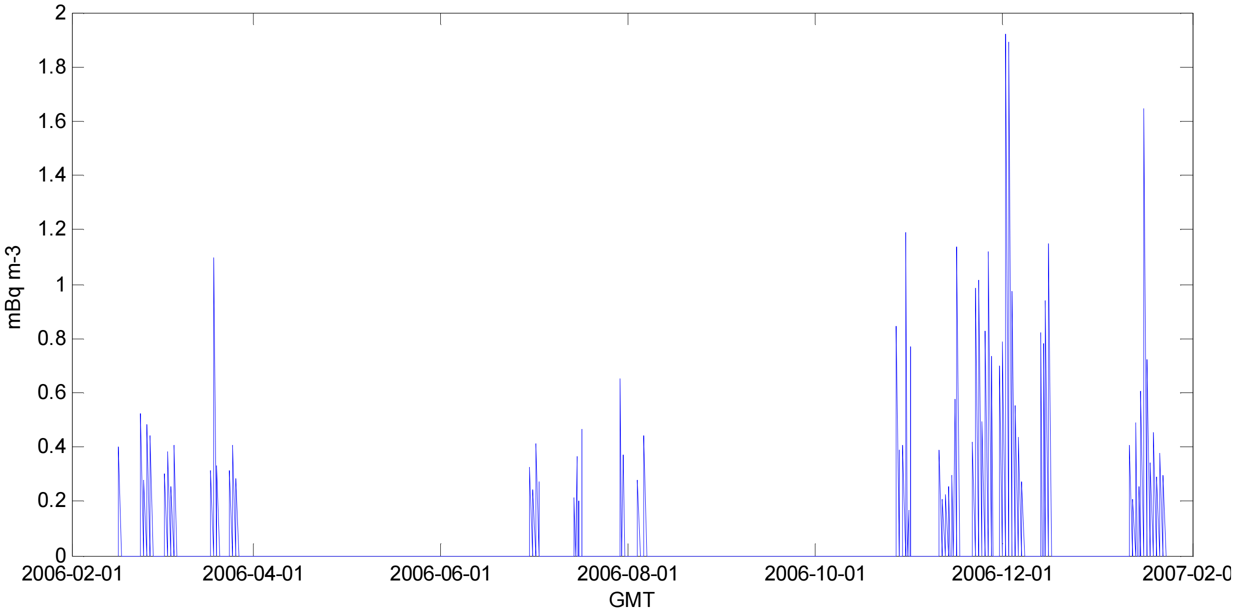

Fig. 7. Daily ^{210}Pb concentrations in Tarnowskie Góry monitoring station

2.2.1. Daily concentrations of ^{210}Pb

Concentrations of ^{210}Pb in the atmosphere are a sum of two independent random variables:

A – concentrations caused by anthropogenic emission sources
B – concentrations caused by natural sources (background concentrations).

The carried out measurements showed that the average daily concentrations of ^{210}Pb varied from 0.16 to 1.62 mBq/m^3, the average value was 0.67 mBq/m^3 and standard deviation - 0.42 mBq/m^3. The cumulative distribution function of the daily ^{210}Pb concentrations - $\boldsymbol{F_{A+B}}$ is presented in Fig. 8.

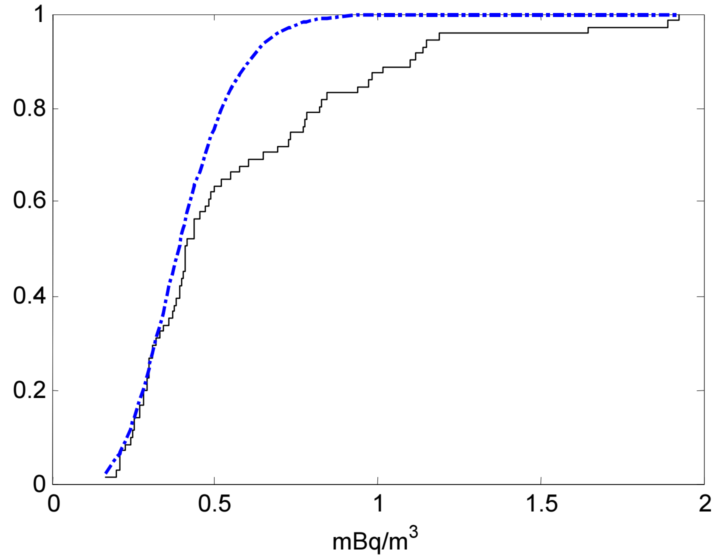

Fig. 8. Empirical cumulative distribution function of the daily ^{210}Pb air concentrations in Tarnowskie Góry monitoring station (solid line) and cumulative distribution function of daily concentrations of ^{210}Pb background

It can be assumed that the cumulative distribution function of daily concentrations of ^{210}Pb caused by natural sources is similar to the cumulative distribution function of daily concentrations of other air pollutants from a uniform emission field. Distribution of these concentrations is similar to gamma distribution. Based on this assumption and taking into consideration the fact that percentiles P of a lower order than 50% satisfy the inequality:

$$P(y, \boldsymbol{B}) < P(y, \boldsymbol{A} + \boldsymbol{B}) \text{ for } y<50$$

it can be concluded that the average value of ^{210}Pb background concentration $E(\boldsymbol{B})$ does not exceed the value of 0.41mBq/m^3 at a standard deviation $D(\boldsymbol{B})$ =0.15 mBq/m^3. Graph of the cumulative distribution function of the daily ^{210}Pb concentrations and background concentrations is presented in Fig.4. Analysing both graphs in Fig.4 it can be noticed that anthropogenic concentrations of ^{210}Pb occur relatively rarely and do not exceed the background concentrations.

2.2.2. ^{210}Pb concentration changes due to different spatial distribution of emission sources

Table 1 shows that industrial and domestic dust emission sources, including hard coal combustion installations in the vicinity of Tarnowskie Góry monitoring station are unevenly distributed. This is the main reason for differences in ^{210}Pb concentrations at various inflow directions. Concentrations of ^{210}Pb accompanying the wind from particular sectors around the monitoring station can be described using random variables. Let $X(s)$, s=1,...,16, be a sequence of random variables of 1-hour ^{210}Pb concentrations observed in the monitoring station. If air masses in this period flowed from sector s, i.e. the average wind direction d in a given 1-hour period fulfilled the condition: $s \cdot 22.5^{\circ}\mathrm{N} - 11.25^{\circ} \leq d < s \cdot 22.5^{\circ}\mathrm{N} + 11.25^{\circ}$.

2.2.3. ^{210}Pb concentration changes due to daily changes of pollutant dispersion conditions

As mentioned earlier, an important source of ^{210}Pb in the air are natural changes of radon. Its concentrations in the near-ground layer over the mainland, due to exhalation process, remain at almost fixed level of several Bq/m^3. This value depends – first and foremost - on properties of a given site, for example – geological structure or land use pattern. Therefore, it can be assumed that hourly background concentrations of ^{210}Pb will undergo daily fluctuations of a similar characteristics to radon concentrations. As a consequence, daily fluctuations will be also observed in total ^{210}Pb concentrations as the ^{210}Pb background constitutes its crucial part. Let's assume that the daily ^{210}Pb concentration pattern is in the form of a sequence ($r_1,\ldots,r_{24}$) with the average of 1, which imitates the daily variability of radon concentration.

2.3. Solution to the problem

To solve the challenging *problem* outlined in the introduction a neural network modelling hourly ^{210}Pb concentrations in particular sectors around the monitoring station was applied.

For a description of hourly concentrations of ^{210}Pb in the monitoring station a table of discrete random variables $X(h, s)$, h=1,..,24, s=1,...,16, containing ^{210}Pb concentrations in an hour h, at the air inflow from sector s was used. Each random variable $X(h, s)$ is a set of numbers:

$$X(h, s)=\{x_{h\,s\,i}: i=1,\ldots,n\}$$

each of which represents ^{210}Pb concentration from sector s, in an hour h within 24 hours.

To estimate the function $X(h, s)$ a stochastic neural network ***N*** was created. The stochastic neural network [15] is a generalisation of a classical neural network [16], due to the introduction of random variables into the structure of the neural network.

The stochastic neural network ***N*** used to solve the *problem* consists of three layers:

- L_1 - input layer $l(h)$, h=1,...,24 consisting of 24 nodes; node $l(h)$ contains the number of an air inflow sector within an hour h;
- L_2 – layer of random variables $X(h, s)$
- L_3 – output layer containing average daily ^{210}Pb concentrations c during measurement.

There are two activation functions between the network layers: activation function w from L_1 to L_2 and activation function W from L_2 to the output layer L_3.

The ***N*** network training was carried out based on the obtained measurements [17]. Table 3 includes characteristics of ^{210}Pb concentrations $X(s)$ obtained from ***N*** network training. In Column 2 the 50th percentiles were presented which help identify the most frequent concentrations in a given sector. The 95th percentile shows ^{210}Pb concentration values in the sector. In Column 4 and 5 average values and standard deviations of hourly ^{210}Pb concentrations in each of the 16 inflow sectors were presented.

It was assumed that the lowest average ^{210}Pb concentration in sectors (346 µBq/m^3 in sector NNW) is comparable with the average background concentration. The obtained background concentration is lower than the background concentration estimated on the basis of the daily concentration analysis (410 µBq/m^3). At such assessed background concentrations level, the average concentration from anthropogenic sources in sectors was determined. It was estimated that the highest concentration of ^{210}Pb isotope was observed in sector SSW, in which the biggest number of hard coal-fired domestic installations (over 4300) and 2 industrial emitters are located.

TABLE 3. 50th AND 95th PERCENTILES, AVERAGE VALUE, STANDARD DEVIATION OF ^{210}Pb RADIOACTIVE CONCENTRATIONS X_s AND AVERAGE ANTHROPOGENIC CONCENTRATION A_s IN SECTORS.

Sector	$P(50, X_s)$	$P(95, X_s)$	$E(X_s)$	$D(X_s)$	$E(A_s)$
N	437.6	948.3	486.8	305.6	140.8
NNE	322.0	492.4	349.0	118.0	3.0
NE	301.1	683.1	385.6	197.8	39.6
NEE	317.8	524.1	393.9	180.4	47.9
E	408.4	842.1	442.1	198.7	96.1
SEE	402.1	1123.0	514.3	272.7	168.3
SE	489.9	1146.1	628.1	302.5	282.1
SSE	695.9	1159.1	711.1	336.9	365.1
S	427.2	1152.5	615.5	360.3	269.5
SSW	541.1	1825.7	737.8	510.0	391.8
SW	405.6	1439.8	614.1	420.1	268.1
SWW	376.2	1046.1	484.7	308.5	138.7
W	395.9	1007.8	466.6	247.2	120.6
NWW	406.5	1021.0	512.5	261.3	166.5
NW	320.2	641.4	384.0	154.0	38.0
NNW	336.4	536.2	346.6	163.5	0.6

2.4. Conclusions

The aim of this study was to investigate the possibilities of applying ^{210}Pb as a marker of dust from hard coal combustion processes in the air. ^{210}Pb is a natural component of hard coal and occurs in the atmosphere as a result of coal combustion. The main sources of dust from hard coal combustion processes are big industrial sources (mainly energy sources) and a large number of small boilers and furnaces in residential and municipal buildings.

It was shown that based on daily measurements of ^{210}Pb concentrations and hourly data on wind direction the location of sources emitting dust from hard coal combustion processes and their contribution in the concentration of this isotope can be identified.

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ENVIRONMENTAL ASPECTS, RISKS AND SAFETY CONSIDERATIONS AT A URANIUM MINING, PROCESSING AND TAILING MANAGEMENT FACILITY IN ROMANIA

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Abstract

Mining of very low radioactive mining ore (NORM) is mined and processed by the URANIUM NATIONAL COMPANY (CNU) of ROMANIA. Naturally Radioactive Occurring Material-NORM (mining ore, tailings, uranium waste) is a subject of investigation for a safe disposal and environmental monitoring, operation for which Romanian Nuclear Regulatory Body–CNCAN is responsible, as well as CNU. The specific problems related to a safe and security in transport of mining process waste and uranium ore are also to be taken into consideration. In view of the appropriate treatment of the tailings and the effluents, regular monitoring and regularly review of the radionuclides in the environments a comprehensive surveillance is maintained around the mines, mill and tailings pond in order to evaluate the effectiveness of control measures, assess the environmental impacts and ensure the regulatory compliance. The paper gives a brief account of the environmental aspects, possible risks and radiological consequences due to uranium mining, ore processing, transport and waste management operations.

1. INTRODUCTION

This paper is a part of the research activities carried out by the main author to assess environmental aspects, radiological consequences, risk and safety of NORM materials disposal and transportation in Romania and is a result of the work within the IAEA CRP (Co-coordinated Research Programme) on NORM entitled**:** *The appropriate level of regulatory control for the safe transport of naturally radioactive material (NORM)* where the main author, is Chief Scientific Investigator for the Romanian Scientific Research Contract concluded with the IAEA Vienna [1]. Safety and security during mining operation of very low radioactive material (NORM) such as uranium ore, tailings and uranium waste, transport are matters of international importance [1-3].

*The objective***:** is to protect persons, property and the environment from the effects of radiation during these operations of radioactive material [3].

The Management of Radioactive Material (RAM) including NORM-Naturally Occurring Radioactive Material is an essential activity and, consequently, the IAEA will continue to preserve an important role in the international approach for a safe management of these materials;

Safety and Security in the transport of NORM is a national responsibility while international standards and approaches to safety promote consistency, help to provide assurance that nuclear materials and radiation related technologies are used safely and facilitate international technical cooperation and trade [1-3];

In Romania, the Uranium National Company (CNU) is responsible, for [2]:

- exploitation of the uranium ore;
- transport and processing of the uranium ore;
- concentrates processing and delivering of the final products, e.g. U_3O_8 and UO_2.
- Safety disposal and transportation of the processing waste.

The company has several subsidiaries in Romania, among them are: Bihor (Baita), Suceava (Crucea), Banat (Oravita) and Feldioara (Brasov).

In Figure 1 are presented the routes of NORM (uranium ore and uranium concentrate) Transportation in Romania.

FIG. 1. Routes of NORM transportation in Romania (uranium ore and uranium concentrate)

2. TRANSPORT OF URANIUM ORE

As indicated on the map, the uranium ore is transported from Bihor (Baita), Suceava (Crucea), Banat (Oravita) subsidiaries, by railway, to the CNU Feldioara for processing. Every special wagon used for transport has approximately 50 t of uranium ore.

From uranium ore mine, Crucea to the Vatra Dornei railway station (Suceava subsidiary), approx. 42 km, and the ore is transported by road, by means of the special licensed trucks.

Every truck is loaded with 13 tones of uranium ore. From uranium ore mine Baita to the Stei railway station (Bihor subsidiary), approx 26 km, the ore is transported by road, by means of special licensed trucks also [1-2].

The uranium dioxide concentrate, processed at CNU Feldioara (Brasov) is transported, by road, to the Nuclear Fuel Plant, Pitesti.

3. DISPOSAL OF THE URANIUM MILL TAILINGS AT CNU FELDIOARA BRASOV AND DISPOSAL OF THE STERILE URANIUM ORE AT CNU SUBSIDIARIES URANIUM MINES AND ITS MANAGEMENT

3.1. Disposal of the uranium mill tailings at CNU Feldioara Brasov

The disposal option in mud-setting ponds sites was chosen for very low-level waste resulting from handling or the transformation of Naturally Occurring Radioactive Material (uranium ore). Whatever the waste level of activity to be considered, the intrinsic safety of the selected option is assessed through an approach without exemption or clearance levels, which is only based on radiological impact studies demonstrating the special care and respect for human beings of the limit of exposure of the public of 1 mSv.person. y^{-1}.

The mill tailings present a low to very low activity which decreases very slowly. They owe their radiological characteristics to the natural radioactive elements initially present in the ore (mainly radium 226). Approximately the total sum of the daughters of uranium are present in mill tailing and the specific activity accounted is about 10^5Bq/kg. The mail tailings are disposed (at Feldioara CNU Subsidiary) near the place of production, in natural basins (mud-setting pond), valley closed by dam. These entire disposal are managed by CNU Bucharest. The disposal site was subjected to remediation

On arrival, at CNU Feldioara processing facility, the uranium ore is processed in order to obtain uranium concentrate (yellow cake). After processing within Feldioara nuclear facilities, the resulted uranium mill tailings, is transported by means of an Ø 219 mm pipe, approx. 2 km, to a mud-setting pond. In this sludge bed pond take place the gravity settling decantation. The solid uranium mill tailings fall at the bottom of the pond and the liquid part is transferred, through a pumping system in the Mittelzop sludge bed. The uranium waste has an uranium content of about 6mg/l and the activity of about 152.1 Bq. Again, from this liquid part, the uranium is recovered, through a special procedure, and the remained liquid is transferred to the OLT River. The maximum uranium content of the waste transferred into the waters of OLT River will not exceed 0.6 mg/l. The restriction (pass criteria) for uranium content of the waters of OLT River is less than 0.021 mg U/l.

The CNU have written a detailed procedure related to ***the remediation of the disposal site***, among them are the followings:

- disposal in conventional landfill sites is the best solution of the efficient management of the mill tailings;
- Radiological impact is of prime importance but should not be neglected other concerns including the potential damages of the dam (earthquake, erosion, rupture of dam, etc.);
- the change of the use of underground waters may be checked by means of constraints;
- radiological consequences within the long term must be assessed through the study of standard scenarios corresponding to possible hazards situations;
- the procedure have to be done taking into consideration the concern of ensuring the diversity of the expertise and the correct and prompt information of the public;
- Protection of the health of population against the danger of ionizing radiations in accordance with the Euratom Directive no. 96/29. The dose limits applicable to the population have to be estimated in the most realistic way.

3.2. Disposal of the sterile uranium ore at CNU subsidiaries uranium mines and its management

The uranium ore extracted from the uranium mine CRUCEA, BAITA and Oravita is radiometric sorted and if the quantity of the ore has less than 0.004% uranium content this is considered sterile and is deposited on a special conventional landfill sites.

These places are strictly delimitated as “controlled zone” which is checked regularly by the Nuclear Regulatory Body from Romania–CNCAN (National Commission for Nuclear Activities Control).

The ore, with more than 0,02% uranium content is transferred in special tanks and from here the uranium ore is transferred into the trucks and transported to the respectively railway stations.

In the followings figures 2, 3 and 4 these activities are shown:

FIG. 2 Disposal of uranium sterile

A specific study has to be performed for each types of waste of each producer e.g. all CNU’s subsidiaries. The results have to be addressed to the administration of disposal sites along with the request for elimination as a basis for the definition of the source term to consider the impact study and to assess the acceptability of the wastes.

When the dose is higher than 1mSv, the producer has to search an appropriate way to dispose of its waste taking into consideration the providing of the radiation protection programme.

FIG. 3 Truck loading with uranium ore

FIG. 4 Preparing the uranium sterile landfill

4. ENVIRONMENTAL ASPECTS

Potential release of radionuclides from NORM–uranium ore-as air dispersion or to water pathway have been assessed taking into account site-specific geological and hydro-geological conditions and based on to normal scenario.

This scenario describes expected evolution of the disposal system including natural degradation of engineered barriers in long term perspective such as: minimal intrusion time through the repository 150 years, advection flow through repository for 250 years is 0.1x Inf (Inf = natural infiltration rate of 0.015m/y), for 250-650 years is 0.5 x Inf, for 650 Years - 1x Inf.

Based on the results obtained, the maximum activity concentration of radionuclides in the water through environment, in the last 5 years is, for Baita uranium mine location, presented in the next two figures, 5 and 6, as follows:

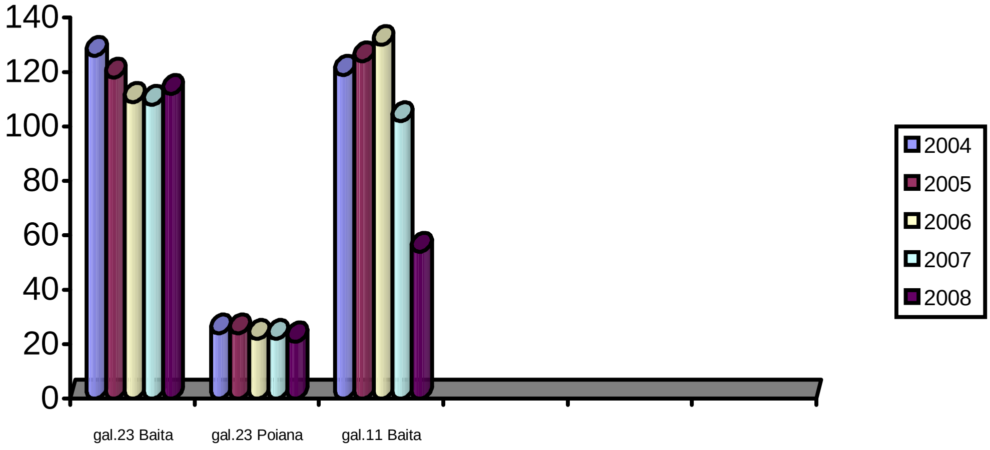

FIG.5 The contents (Bq/g) evolution of U nat from the mine gallery water evacuated through the environment

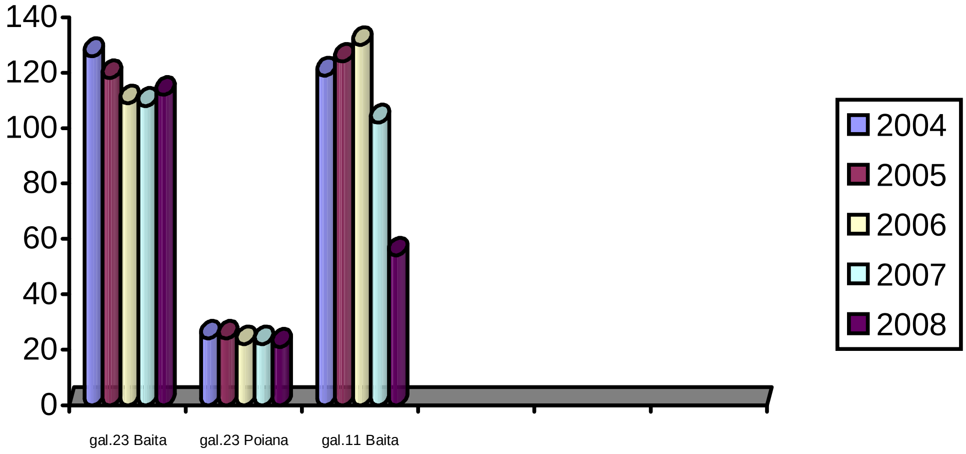

FIG. 6 The contents (Bq/g) evolution of the Ra-226 from the mine gallery water evacuated through the environment

It is to be considered that the activity concentration of other radionuclides in groundwater is considerably lower. If we referring to the Uranium mine Baita also [1], it was determined that the effective dose for workers to be no more than 20 mSv/y; The equivalent dose for the population around the mine (about 3km radius) it was determined to be 0.3 mSv/y; The collective dose determined was to be 0.2 mSv/y within the same area [1]. These doses were estimated using the IAEA's computer code INTERTRAN II and the SANDIA's RADTRAN 5 computer code.

5. THE DISPERSION FACTORS

Around mining area (about 1km), where the mining rocks formation taken place in a zone with the higher background, the problem of the correct interpretation of data as there were estimated by computer codes is a sensitive target [1].

The following results were obtained:

- External irradiation: (0.5 ÷ 5 µSv/h);

Average contents of U nat and Ra 226, in soil:

- U nat = (8.72 ± 0.97) g / t
- Ra 226 = (40.14 ± 2.07) g / kg

Average contents of U nat and Ra 226, in vegetal area:

- U nat = (7.72 ± 0.65) g / t
- Ra 226 = (110,0 ± 12.0) g / kg

With referring to the Radon 222, it is to be noted that the values of concentration are smaller than the sensitive limit of 1589 Bq/m3. The Radon Concentration (RC) was determined [1] by using a specific formula in two zones: *the witness and the impact* zones.

In the Witness zone we determined:

- Total effective dose (mSv) = 5.88

And in the *Impact* zone we determined:

- Total effective dose (mSv) =15.50

In case of the normal evolution scenario the annual effective dose for all radionuclides transferred to the environment it was estimated not to exceed 1.4 x 10xE-6 Sv/y;
The estimated annual effective dose is lower than dose constraint of 0.2 mSv/y

6. IDENTIFICATION AND THE EVALUATION OF THE POTENTIAL RISKS DUE TO THE TRANSPORT AND DISPOSAL OF THE VERY LOW LEVEL RADIOACTIVE WASTE

6.1. Transport by road

As shown in Figure 1 the routes for transport of the uranium ore and uranium concentrate are both by road and by rail modes. In order to evaluate the dose resulting from possible road accidents involving these radioactive shipments [4-6], based on the frequency of occurrence of accidents of specified severities the IAEA computer code INTERTRAN II has been used. On the other hand for rail transport a probabilistic risk assessment method (PRA) has been adopted for this work aimed at quantifying the potential radiological consequences and the expected probability of occurrence of such accident sequences [7]. Data to be used as input data to the computer code INTERTRAN II has been provided by postulate possible accidents scenarios [2-6] such as: transport hazards (fixed impact hazard, mobile impact hazard), accident frequencies by road. Based on these there were calculated road accident probabilities such as

- probability of impact only: 0.421×10^{-5} per journey;
- probability of impact and fire: 1.50×10^{-10} per journey;

It is also assumed that, following an impact, the content may become available for dispersion. The collective dose assessed areas follows:

- dose to public along route: 0.25×10^{-5} person.Sv.y^{-1};
- dose to public during stops: 0.37×10^{-8} person.Sv.y^{-1} ;
- dose to truck crew: 0.47×10^{-5} person.Sv.y^{-1}

The total annual collective dose is: 0.72037×10^{-5} person.Sv.y^{-1}. The associated latent cancer fatality risk is estimated at 0.77×10^{-10} y^{-1}.

6.2. Transport by rail

There are different kinds of operation contributing to the overall risk, such as: rail transport, rail road transfer activities (from Crucea to Vatra Dornei and from Baita to Stei), handling and misoperation activities, etc. Transport and handling possible accidents may occur and pose a potential risk for the public and the environment [1-2]. Because the occurrence of such accidents is statistical in nature, the probability risk assessment (PRA) has been adopted in order to quantify the potential radiological consequences and the expected probability of occurrence of such accidental sequences.

The potential radiological consequences have been calculated by using INTERTRAN II computer code. The calculated radiological risks include [1-6]:

- radwaste exposure of the public and transport personnel from routine (incident free) transport of the very low level radioactive material (uranium ore);
- transport accident resulting in radiation exposure of the population and contamination of the environment

The accidental sequences include steps such as:

- characterization and the type and quantity of shipment;
- determination, selection and description of the type, severity and probability of occurrence of transport and handling accidents;
- assessment of potential radiological consequences for the spectrum of wealth condition encountered along the rail route;

The IAEA computer code INTERTRAN II has been used to determine the collective dose to population and transport personnel and the preliminary risk assessment results are [2, 4, 5]:

- crew: 1.34×10^{-5} person.Sv/y;
- members of the public: 1.78×10^{-5} person Sv/y;

TOTAL: 3.12×10^{-5} person Sv/y

Radioactivity releases are not expected to occur in close proximity to a possible accident site at a probability level as low as 10^{-7}, i.e. a chance of 1 in 10 million for the total volume of the uranium ore to be transported.

7. CONCLUSIONS

The disposal of the mining processing waste (uranium ore) as well as the disposal of sterile in Romania is a very complex problem taking into consideration the importance and the need of the safety for such activities.

The Romanian Nuclear Regulatory Body-CNCAN set up strictly regulation and procedures according to the Recommendation of the IAEA Vienna and other international organizations. The National Uranium Company (CNU) has adopted and implemented the adequate regulation and procedures in order to keep the environmental impacts and the radiological consequences at the lower possible. The levels of the estimated doses for transport and disposal are within the acceptable limits provided by national and international regulations and recommendations.

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NATURALLY OCCURRING RADIONUCLIDES AND RARE EARTH ELEMENTS PATTERN IN WEATHERED JAPANESE SOIL SAMPLES

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Abstract

From the viewpoint of radiation protection, determination of natural radionuclides e.g. thorium and uranium in soil samples are important. Accurate methods for determination of Th and U is gaining importance. The geochemical behavior of Th, U and rare earth elements (REEs) are relatively close to one another while compared to other elements in geological environment. Radioactive elements like ^{232}Th and ^{238}U along with their decay products (e.g. ^{226}Ra) are present in most of the environmental matrices and can be transferred to living bodies by different pathways that can lead to sources of exposure of man. Therefore, it is necessary to monitor these natural radionuclides in weathered soil samples to assess the possible hazards. The activity concentrations of ^{226}Ra, ^{228}Th, and ^{40}K in soils have been measured using a γ-ray spectroscopy system with high purity germanium detector. The thorium, uranium and REEs were determined from the same sample using inductively coupled plasma mass spectrometry (ICP-MS). Granitic rocks contain higher amounts of Th, U and light REEs compared to other igneous rocks such as basalt and andesites. Therefore, it is necessary to understand the interaction between REEs and nature of soils, as soils are complex heterogeneous mixture of organic and inorganic solids, water and gases. In this paper, we have discussed about distribution pattern of ^{226}Ra, ^{232}Th and ^{238}U along with REEs in soil samples of weathered acid rock (granite and ryolite) collected from two prefectures in Japan: (1) Gifu and (2) Okinawa.

1. INTRODUCTION

The REEs (La to Lu) have proved to be powerful tools in geochemical investigations and their distribution in rocks and minerals has received much attention in recent years due to the development and steady introduction of analytical methods suitable for their quantification [1]. From the viewpoint of radiation protection, accurate determination of natural radionuclides e.g. Th and U in soil samples are also important. It has been observed that granitic rocks contain higher amounts of Th, U and light rare earth elements (REEs) compared to other igneous rocks such as basalt and andesites [2, 3]. Historically, it has been believed that the REEs are immobile during weathering and alteration processes. Indeed, this assumption has led to the common use of these elements and their isotopes in weathered and metamorphosed rocks for petrogenetic modeling purposes and provenance studies. REE appear as natural trace metals in the whole geosphere and have become important geochemical tracers during last few decades [4, 5]. The REEs have also been used as analogues for the actinide elements in studies related to radioactive waste disposal in order demonstrate their general immobility in the weathering environment [6]. Therefore, determination of REEs in soil samples has become important to obtain REE profiles in order to foretell any possible environmental effects.

The aim of the present study is to characterize the background levels of Th, U and REEs in weathered soil samples from two prefectures of Japan i.e. Gifu and Okinawa. The specific activities of ^{232}Th and ^{238}U in soil samples were measured using a high-purity germanium detector (HP Ge) and compared with inductively coupled plasma mass spectrometry (ICP-MS).

2. EXPERIMENTAL PROCEDURE

2.1. Sample collections

The study areas (Fig. 1) were selected based on weathered rock areas referring the geological map of Japan. The bedrock of each sampling point in Gifu prefecture (GI) corresponds to 1. Ueno-basalt, 2. Naegi-granite, 3. Nohi-rhyolite, 4. Mino-region sedimentary rock and 5. Mizunami-region sandstone/mudstone. The soils distributed in Okinawa prefecture (OK) are generally classified into dark red soils, residual regosols and red and yellow soils. The islands in Okinawa prefecture are bordered with recent coral reef. The main geology of the islands is the Pleistocene limestone of coral reef origin. The limestone is generally covered with red soils which is a typical case in Japan.

We have collected surface soil samples (0-10cm) from these locations where radon/thoron exhalation rates were simultaneously measured. In this study, we have selected two areas of different climates. Okinawa is relatively warmer (subtropical) than Gifu. We have collected from five locations in Gifu prefecture and from eight locations in Okinawa prefecture. Location of soil samples, gamma dose rate, water content, dry bulk density and its porosity have been summarized in Table 1. The mean, minimum and maximum gamma radiation dose in air is estimated to be 61, 24, 106 nGy h^{-1}, respectively. Radon/thoron exhalation rates were obtained from the same locations on seasonal basis whereas we have carried out chemical analyses of Th, U and REEs once from the soil samples.

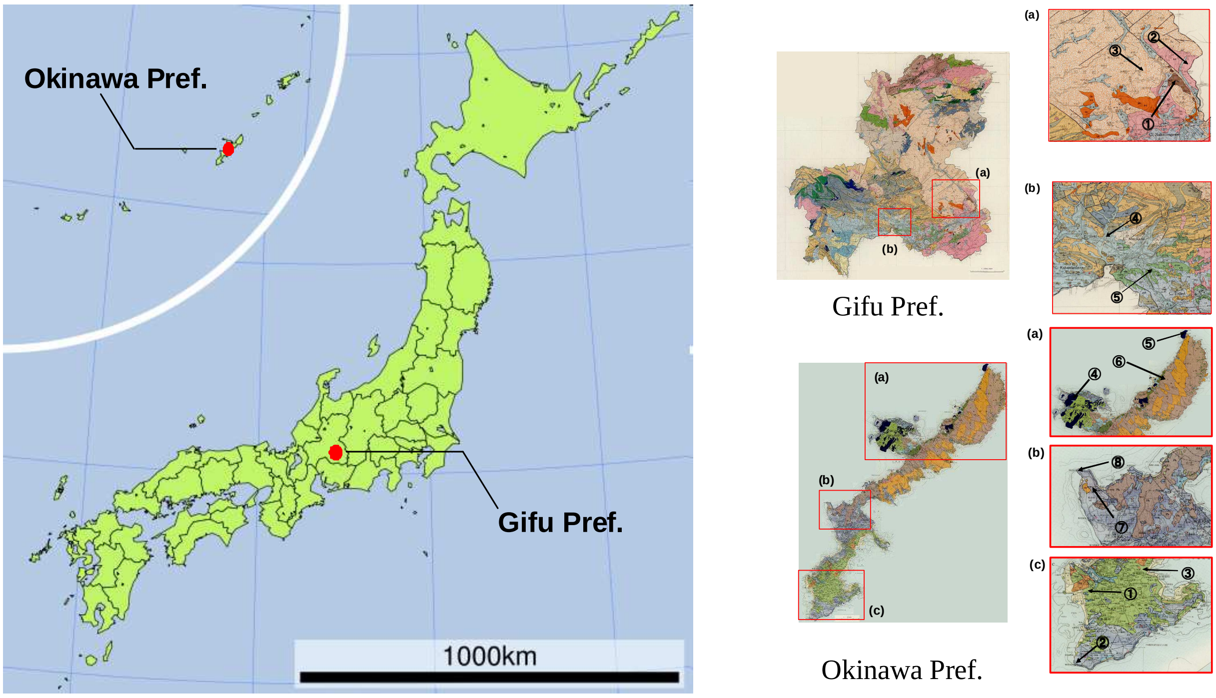

Fig.1 Map showing sampling stations in Japan (Geological map of Gifu prefecture right side upper one and Okinawa prefecture lower one)

TABLE 1 SAMPLE LOCATION AND GENERAL CHARACTERISTIC OF SOIL

Sample Station	Location		γ-ray dose rate (nGy h^{-1})	Water content (m^3 m^{-3})	Dry bulk Density (g cm^{-3})	Porosity
	Longitude	Latitude				
①GI	N 35°35′20.2″	E 137°29′58.4″	28±5	0.455±0.039	1.19	0.54
②GI	N 35°32′36.3″	E 137°28′38.4″	106±5	0.171±0.029	1.41	0.46
③GI	N 35°33′29.0″	E 137°21′46.2″	76±3	0.137±0.045	1.50	0.43
④GI	N 35°29′35.2″	E 136°57′07.7″	40±2	0.277±0.055	1.55	0.41
⑤GI	N 35°22′32.5″	E 137°07′00.8″	36±3	0.152±0.064	1.28	0.51
①OK	N 26°10′51.8″	E 127°39′20.9″	24±5	0.299±0.036	1.33	0.50
②OK	N 26°04′45.2″	E 127°40′10.7″	67±8	0.113±0.015	1.10	0.57
③OK	N 26°12′12.6″	E 127°45′07.6″	42±6	0.167±0.026	1.43	0.47
④OK	N 26°41′29.9″	E 127°55′45.0″	30±6	0.145±0.024	1.18	0.56
⑤OK	N 26°51′57.2″	E 127°14′56.0″	45±7	0.163±0.019	1.08	0.60
⑥OK	N 26°43′50.9″	E 127°11′25.9″	64±8	0.210±0.024	1.23	0.56
⑦OK	N 26°25′15.3″	E 127°43′50.0″	49±7	0.176±0.018	1.08	0.59
⑧OK	N 26°26′24.2″	E 127°42′54.9″	58±8	0.262±0.024	1.03	0.61

2.2. Sample preparation for measurement by γ-spectrometry

All samples were dried in a temperature controlled furnace (oven) at 110 °C for about 24 hours to ensure that moisture is completely removed. After moisture removal, the sample is cooled down in a desiccator. All dried samples (about 100 g) were crushed to a fine powder. The dried samples were used for the determination of specific activity of ^{232}Th and ^{238}U. Later samples were placed in U8 standard cylindrical containers (diameter = 48 mm; h = 58 mm). They were sealed using adhesive in order to avoid any possibility secular equilibrium with its gamma emitting decay products. The sealed samples were kept for about 30 days (equivalent to 7 half-lives of ^{222}Rn) in order that ^{226}Ra and ^{222}Rn (t1/2 = 3.8 d) and its short-lived gamma emitting decay products, ^{214}Bi and ^{214}Pb attained secular equilibrium in sealed containers. Since radium (^{226}Ra) and its progeny produce 98.5% of the radiological effects of uranium series, the contribution of ^{238}U and the precursors of ^{226}Ra are normally ignored. Therefore, the reference of this series radionuclide is often ^{226}Ra instead of ^{238}U. ^{228}Ra and ^{228}Th will also have attained secular equilibrium with its gamma emitting decay products.

The specific activity of ^{226}Ra, ^{228}Th were measured using a high purity germanium detector (ORTEC GEM-100210) γ-spectroscopy coupled with a 16k multi-channel analyser (ORTEC, 7700-010) with a range 0-4000 keV and computer software Gamma Studio (Seiko EG & G, 2000) for gamma-ray spectral analysis. The detector efficiency was determined using a 100 g multi-nuclide standard source supplied by Japan Radioisotope Association with quoted gamma energies ranging from 60 to 1333 keV an overall uncertainty of less than 5%. The results were compared with a natural soil standard IAEA-375 to check the reproducibility of the method. The counting time was pre-set at 80 000 s. The gamma emitting decay products, ^{214}Pb (295.2 keV), ^{214}Pb (351.9 keV) and ^{214}Bi (609.3.keV) in secular equilibrium in about 30 days with ^{226}Ra, ^{228}Ac (911.2 keV) with ^{228}Ra, ^{212}Pb (238.6 keV) and ^{212}Bi [mean of ^{208}Tl (583.2 keV), and ^{208}Tl (2614.53 keV) divided by branching ratio of 0.36] with ^{228}Th, and ^{40}K gamma (1461 keV), were counted simultaneously. The data for radionuclide gamma energy and branching ratio were taken from the Table of Isotopes (Firestone 1996) [7].

2.3. Sample preparation for measurement by ICP-MS analysis

Inductively coupled plasma mass spectroscopy (ICP-MS) is one of the most powerful technique for the analysis and quantification of trace elements in both solid and liquid samples. Concentrations of thorium and uranium were measured using an ICP- MS instrument Agilent 7500 (Agilent Technologies, Tokyo, Japan). Prior to ICP-MS analyses, standard solutions were prepared from SPEX multi-element plasma standard (Spex CertiPrep, NJ, USA) at 0, 50, 100, 500 and 2500 ppt to derive a calibration curve. To check the accuracy of the calibration, two standard samples, namely JLK and JB-1 supplied by Geological Survey of Japan, were used. The soil samples were dried at 110°C in the oven to constant weight and then grounded to a powder. The samples were then digested in TeflonTM PFA pressure decomposition vessels in a microwave unit (MLS 1200 mega, Milestones, Italy) using an acid mixture of HNO_3, $HClO_4$ and HF (Tamapure chemical industries, Kawasaki, Japan), and high purity water (Milli-Q water purification system). After the samples were completely digested, they were transferred into Teflon beakers and evaporated to dryness on a hot plate. Later, the residues were dissolved in 3% HNO_3 to yield the sample solution for measurement [8, 9]. REE data obtained by certified and measured values obtained for standard reference materials. The precision by ICP-MS achieved is better than 5% RSD with a comparable accuracy.

3. RESULTS AND DISCUSSIONS

3.1. A comparison between two measurement methods (HPGe and ICP-MS)

The specific activity of ^{238}U (HPGe) is assumed to be the same as that of ^{226}Ra. Analytical results obtained using (ICP-MS) for U and Th in soil samples were compared with γ-ray counting (HPGe). The measurement of ^{238}U with the HPGe detector and ICP-MS shows a good agreement with a coefficient of determination $R^2 = 0.77$, as shown in Fig. 2. Similarly, ^{232}Th showed a good agreement between both methods with a correlation coefficient, $R^2 = 0.84$, as shown in Fig.3. ICP-MS method is rapid, precise and can detect at ultra-trace amount. Therefore, both analytical techniques are suitable to measure trace amount of radioactive elements in environment samples. The specific activity of ^{226}Ra and ^{228}Th in the samples are follows: (1) ^{226}Ra : 14.3 ± 0.7 Bq kg^{-1} to 87 ± 0.9 Bq kg^{-1} with a mean of 48 ± 1 Bq kg^{-1} and (2) ^{228}Th: 29.7 ± 1.2 Bq kg^{-1} to 135.4 ± 1.7 Bq kg^{-1} with a mean of 63 ± 1 Bq kg^{-1}. Most of these soil samples have specific activities less than world averages values, as reported in UNSCEAR [10]. The specific activity of ^{226}Ra in Okinawa-2 was highest among all of the samples whereas Gifu-2 has high ^{228}Th content. There is a heterogenous distribution of uranium in both areas [9, 11].

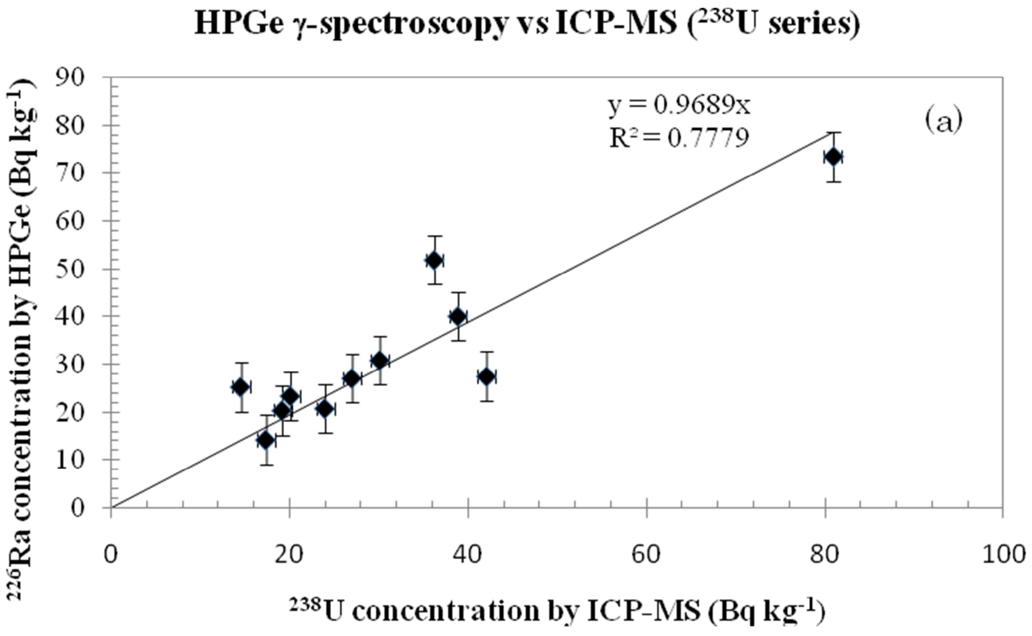

Fig. 2 Correlation between the measurement of ^{238}U using ICP-MS and γ-spectroscopy

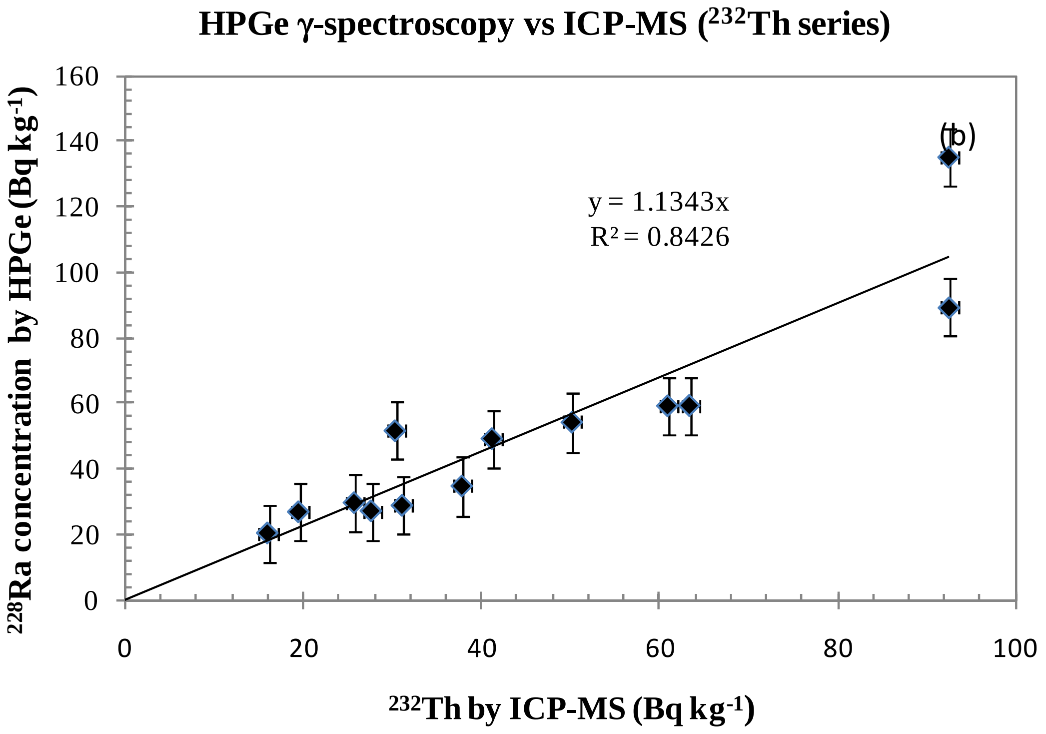

Fig.3 Correlation between the measurement of ^{232}Th using ICP-MS and γ-spectroscopy

3.2. Uranium and thorium distribution

The concentration of Th and U determined by ICP-MS are summarized in Table 2. The U/Th ratio between 0.2 to 0.3 is present in continental crust [12]. However, OK3 and 4 both sample show execess of uranium in comparison to thorium. In case of Gifu samples, ratio varies from 0.14 to 0.21 showing excess of thorium.

TABLE 2. CONCENTRATION (μg g^{-1}) OF Th AND U IN SOIL SAMPLES MEASURED BY ICP-MS

Location	Th	U
① GI	6.34	1.39
②GI	22.76	3.12
③GI	12.36	1.62
④GI	10.15	2.17
⑤GI	7.93	1.17
①OK	6.81	1.54
②OK	22.77	4.09
③OK	2.34	1.93
④OK	1.48	0.33
⑤OK	7.67	6.50
⑥OK	14.65	2.42
⑦OK	15.60	3.38
⑧OK	9.91	2.91

3.3. REEs in soil samples

The determination of REEs in geological samples is extremely important in earth science studies because their chemical behaviour is governed by the systematic contraction of trivalent ionic radii with atomic number as the shielded electrons are added to the inner 4f shell and some of the elements, especially Ce and Eu occur in oxidation states other than +3, the main oxidation state of the group. We have measured REEs from the soil samples using ICP-MS.

Sample preparation can be a major problem with REE analysis as the bulk of these elements and particularly the heavier REEs (Dy-Lu), commonly resides in refractory accessory minerals such as zircon, sphene and garnet phases. In this study, microwave digestion was successfully used for complete dissolution of sample. We have selected two samples from Gifu and Okinawa prefectures to check the REE pattern of soil samples.

Chondritic meteorites are chosen for normalization as they are thought to be relatively unfractionated samples of the solar system dating from the original nucleosynthesis. Leedy chondrite normalized patterns are shown in Fig. 4 which allows a better insight into geological processes [13]. The REEs exhibit light REE-enriched patterns when normalized to chondrite which indicates that the REEs are taken up in proportion to their relative concentration in the source rocks or heavy REEs are preferentially mobilised. There are no significant variation in the concentration of REEs, U and Th related to general location within the study area which may be reflective of one type of source in the concentration of these elements in the reservoir rocks at depth.

Negative Eu anomaly was noticed in soil samples and chiefly controlled by feldspars, particularly in felsic magmas, Eu (+2 oxidation state) is compatible in plagioclase and potassium feldspars, in contrast to the trivalent REE which are incompatible. Thus the removal of feldspar from a felsic melt by crystal fractionation or the partial melting of a rock in which feldspar is retained in the source will give rise to a negative Eu anomaly in the melt. Ce negative anomaly is more predominant for Okinawa samples in comparison with Gifu samples. This could be explained by the redox behaviour of Ce in contrast with other REEs, which occur in both trivalent and tetravalent state. Ce appears at the surface as Ce (IV) in CeO2. This oxide is less soluble than the other REE oxides and consequently, Ce will be depleted with respect to other REE in deeper part of soil. This can be attributed to the fact that

REEs in soil come mainly from minerals inherent in soil and are not influenced by environmental conditions.

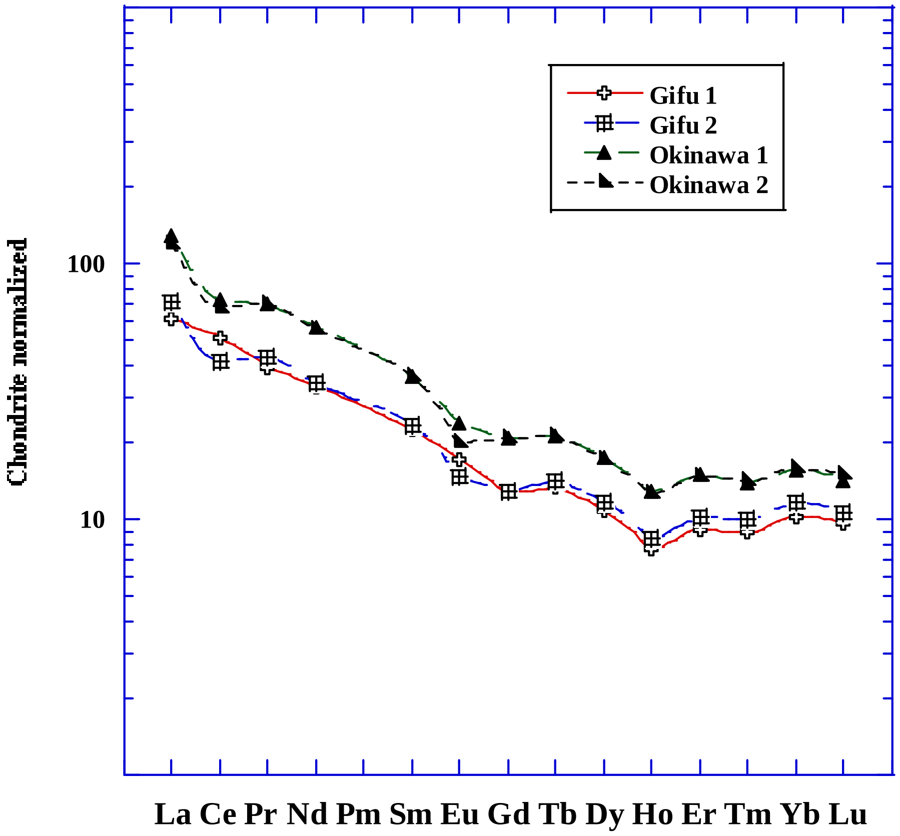

Fig.4 Leedy chondrite normalized REE pattern of soils

4. CONCLUSION

ICP-MS is currently playing a leading role in the analysis of Th, U and REEs and has proven to be a powerful technique for handling routine analytical problems involving both elemental and isotopic analysis. Soil samples analyzed in both prefecture, appear to be of same geological origin but enrichment in elements differ.

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TENORM IN AN INSULATION FACTORY

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Abstract

Our investigation was connected to measurements of activity concentrations of natural radionuclides in raw materials, ash, dust and brickets. Results of the measurements of activity concentrations in dust together with working hours spent on five selected working places were used for dose assessment for workers. The highest activity concentrations of ^{238}U, ^{226}Ra, ^{210}Pb and ^{232}Th of raw materials were measured in bauxite, 482 ± 52 Bq/kg, 354 ± 9 Bq/kg, 110 ± 64 Bq/kg and 442 ±12 Bq/kg, respectively. Activity concentration of ^{210}Pb, measured in ash was 24500 ± 1555 Bq/kg. Effective doses because of inhalation of natural radionuclides in dust estimated for workers on different working places ranged between 1.1 and 17.3 μSv per year.

1. INTRODUCTION

Regarding our Ionizing Radiation Protection and Nuclear Safety Act [1], the ministry competent for health shall order the employer or operator of the facility in question implementing of measures for reducing the exposure of workers and members of the public, if on the basis of the systematic surveillance it is established that the exposure of individuals due to natural radiation sources exceeds dose limits for members of the public.

In the factory for production of insulation material they are using natural raw materials like black coal (koks), bauxite, basalt and cement. These materials can contain enhanced activity concentrations of natural radionuclides of uranium and thorium decay series. By transporting, crumbling and burning of raw materials dust and ash (as TENORM) are producing. As a by product they are producing brickets for covering courtyards or small roads.

Workers working on the production line inhale dust with possible enhanced activity concentrations of natural radionuclides. Ash uses for production of brickets for covering courts, yards or parking places. A part of ash deposits on the municipal dumps.

2. SAMPLING METHODOLOGY

Natural raw materials like black coal (koks), bauxite, basalt and cement used in production line were sampled for gamma spectrometry. Samples were dried, weighted and put in plastic canisters. On different places in the production line also air samples were taken. Air filters were prepared and measured on detector for gamma spectrometry. Sampling, sample preparation and measurements on high purity germanium detectors was performed regarding standard ISO 17025.

Natural radionuclides ^{238}U, ^{226}Ra, ^{210}Pb, ^{232}Th and ^{40}K were determined. For ^{238}U determination energy lines 63.4 keV and 92.6 keV of ^{234}Th were used. For ^{226}Ra determination energy lines 352.0 keV, 609.3 keV and 1120.3 keV of radionuclides ^{214}Pb and ^{214}Bi were used. For ^{210}Pb determination line 46.5 keV was used. For ^{40}K determination energy line 1460.8 keV was used. For ^{232}Th determination radionuclides ^{228}Ra and ^{228}Th were used. Selected energies were 911.2 keV and 968.9 keV for ^{228}Ra and 583.2 keV for ^{228}Th.

3. RESULTS

3.1. Activity concentrations in raw materials

Table 1 shows activity concentrations of natural radionuclides in samples of black coal, cement, bauxite and basalt. Specific activities of natural radionuclides in black coal and basalt are not high; activity concentrations in cement are much higher but in sample of bauxite activity concentrations of natural radionuclides are very high.

TABLE 1. ACTIVITY CONCENTRATIONS OF NATURAL RADIONUCLIDES IN RAW MATERIALS

Sample code	RV970506	RV940506	RV910506	RV960506
Sample	black coal	bauxite	cement	basalt
Sampling date	22.5.2006	22.5.2006	22.5.2006	22.5.2006
Date of measur.	29.5.2006	25.5.2006	25.5.2006	26.5.2006
Radionuclide	Activity concentration (Bq / kg)			
U - 238	46,1 ± 7,7	481,9 ± 54,2	109,6 ± 13,1	25,3 ± 3,5
Ra - 226	45,4 ± 1,7	353,9 ± 8,8	91,3 ± 2,5	26,2 ± 0,8
Pb- 210	48,5 ± 10,0	109,8 ± 64,3	13,1 ± 5,0	19,2 ± 3,8
Th - 232	16,3 ± 1,9	441,5 ± 12,2	153,9 ± 4,5	28,3 ± 1,4
K - 40	43,1 ± 11,4	169,2 ± 17,9	47,6 ± 6,8	570,0 ± 22,7

3.2. Activity concentrations in by products

Activity concentrations of natural radionuclides in by products – brickets – are presented in table 2.

TABLE 2. ACTIVITY CONCENTRATIONS OF NATURAL RADIONUCLIDES IN BY PRODUCTS

Sample code	RV900506
Sample	bricket
Sampling date	22.5.2006
Date of measur.	27.5.2006
Radionuclide	(Bq / kg)
U - 238	98,2 ± 9,1
Ra - 226	99,5 ± 8,5
Pb- 210	89,2 ± 8,9
Th - 232	95,3 ± 8,8
K - 40	155,5 ± 13,4

Regarding our regulation [2], valid for building materials, activity concentration index was determined:

$$C_T/200 + C_R/300 + C_K/3000 \leq 1, \qquad (1)$$

where C_T, C_R in C_K are the radium, thorium and potassium activity concentrations (Bq/kg) in the building material. Activity concentration index for brickets has value I = 0.85.

3.3. Activity concentrations on air filters

Activity concentrations of natural radionuclides ^{238}U, ^{232}Th and ^{226}Ra on filters are lower than 1 mBq/m^3. Activity concentrations for ^{210}Pb are lower than 2 mBq/m^3 (Table 2). Measured values for all radionuclides are lower than derived activities (Table 3), [2].

TABLE 3. ACTIVITY CONCENTRATIONS OF NATURAL RADIONUCLIDES ON AIR FILTERS

Sample code	RV1000506	RV990506	RV1030506	
Sampling date	22.5.2006	22.5.2006	22.5.2006	
Date of measur.	29.5.2006	25.5.2006	31.05.06	Derived activity
Sample vol. (m^3)	129,6	129,6	129,6	
Radionuclide	Activity concentration (Bq / m^3)			Bq/m^3
U - 238	9E-4 ± 8E-4	1E-3 ± 5E-4	< 5E-3	0,0180
Ra - 226	7E-4 ± 1E-4	4E-4 ± 8E-5	< 5E-5	0,0150
Pb- 210	1E-3 ± 7E-4	2E-3 ± 6E-4	2E-3 ± 8E-4	0,0160
Th - 232	< 3E-4	3E-4 ± 1E-4	7E-4 ± 3E-4	0,0013
K - 40	< 2E-3	< 5E-3	< 7E-3	

4. DOSE ASSESSMENT

Workers working on different locations in the production line wear respirators for protection. Their working time ranges from 1 hour up to 5 hours per day, no more than 200 days per year. For dose assessment we have used data presented above and data for committed effective dose per unit intake via inhalation, presented in [2]. Estimated effective doses for workers ranged between 1.1 µSv/year and to 17.3 µSv/year.

5. CONCLUSIONS

Activity concentration index for brickets has value I = 0.85 and brickets can be used for covering covering courtyards or small roads.

Effective doses for workers are lower than 1 mSv/year and regarding our regulations [3] no further restrictions (more measurements, regular monitoring or short working time) are needed.

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[2] Decree on dose limits, radioactive contamination and intervention levels, Official Gazette of the Republic of Slovenia, No. 49/2004.

[3] Rules on the requirements and methodology of dose assessment for the radiation protection of the population and exposed workers, Official Gazette of the Republic of Slovenia, No. 115/2003.

REMOVAL OF ^{226}Ra AND ^{228}Ra FROM GROUNDWATER RESOURCES IN USE FOR DRINKING WATER SUPPLY PURPOSES (CZECH REPUBLIC)

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Abstract

Water for drinking water supply purposes in the Czech Republic is abstracted from both surface water and groundwater resources and groundwater represents 40% of the total drinking water supply. Natural concentrations of naturally produced radionuclides in surface waters are generally small, amounting normally to 10 mBq/l of radium radioisotopes and less then 0.002 mg/l of uranium. In groundwaters, dependably on hydrogeological conditions, ^{222}Rn concentrations can reach 200 – 4000 Bq/l. ^{226}Ra and ^{228}Ra concentrations do not exceed 0.3 Bq/l and uranium concentrations are below 0.2 mg/l. Increased concentrations of ^{226}Ra, ^{228}Ra and uranium that have been detected for some water resources are not normally correlated with ^{222}Rn concentrations. Water treatment technologies normally include water aeration, sand filtering and health treatment. These technologies were originally designed to remove carbon dioxide, iron and manganese. It was shown in the following period that the aeration process, initially implemented by aeration in a horizontal arrangement, reduced the ^{222}Rn concentration by about 80%. Currently, the proposed aeration towers achieve effective reduction of ^{222}Rn by more than 95%. Depending on local conditions, sand filters with natural cover by iron oxides and manganese are able to capture 30 to 70% of radium radioisotopes. These water treatment processes do not reduce concentrations of uranium. For reduction of radium isotopes, these processes can be intensified by dissolving the layer of iron and manganese by acids and its recovering by dosing of potassium permanganate in shorter intervals. Waste from the water treatment originates mainly from backwash sludge. The washing water is returned after sedimentation as raw water and the sludge is discharged into municipal wastewater treatment plants or landfills. Concentrations of ^{226}Ra and ^{228}Ra in the filter cartridges are in the range from 0.5 to 5 kBq/kg. Experience has shown that the duration of their use does not affect the removal efficiency of radioisotopes of radium. Filter layers can be used for a long time. Concentrations of radioactive substances in waters that have been treated by applying the above technologies meet the requirements for their content in drinking water according to Decree of State Office for Nuclear Safety no. 307/2002 Coll. on Radiation Protection, as amended.

1. INTRODUCTION

In producing water for drinking water supply purposes in the Czech Republic, both surface water and groundwater resources are used. Groundwater represents 40% of the total drinking water supply. Background concentrations of natural radionuclides in surface waters are generally small, amounting normally to 10 mBq/l of radium radioisotopes and less then 0.002 mg/l of uranium. In groundwater, dependably on hydrogeological conditions, ^{222}Rn concentrations can reach 200 – 4000 Bq/l. ^{226}Ra and ^{228}Ra concentrations do not exceed 0.3 Bq/l and uranium concentrations are below 0.2 mg/l. Increased concentrations of ^{226}Ra, ^{228}Ra and uranium that have been detected for some water resources are not normally correlated with ^{222}Rn concentrations.

Water treatment technologies normally include water aeration, sand filtering and health treatment. These technologies were originally designed to remove carbon dioxide, iron and manganese.

It was shown in the following period that these technologies reduced also ^{226}Ra and ^{228}Ra concentrations.

2. RADIOANALYTICAL METHODS

2.1. Determination of ^{226}Ra activity

Water Quality Standard ČSN 75 7622 - the determination of radium 226 activity by the emanometry without pre-concentration After its proper modification, the water sample is placed in an emanometric container. Then the residual ^{222}Rn is removed by use of aeration. In the second step, ^{222}Rn gas is developed in the emanometric container by the radioactive decay of ^{226}Ra contained in the water sample. After the specified time lapse, this ^{222}Rn is squeezed out into a circulation circle with the scintillation detecting element. The number of radioactive impulses of ^{222}Rn and its alpha particles emitting short-term by-way products is transferred to the appropriate ^{226}Ra activity.

The detection limit of ^{226}Ra for 1L sample and a counting time of 1000 s was 0.017 Bq/l at the level of significance of 0.05.

2.2. Gammaspectrometric determination of ^{40}K, ^{226,228}Ra and ^{228}Th activity

The activities of ^{40}K, ^{226,228}Ra and ^{228}Th in large samples of water and water treatment sludge and filter media were measured using gamma-spectrometry according to ČSN ISO 10703 Water Quality Standard.

Large samples of water (20L) were evaporated, burned-off (350 °C) and closed hermetically. The filter media and sludge were dried (105 °C) and closed hermetically as well. The samples were measured using a CANBERRA-PACARD instrument with semiconductor germanium detector.

The detection limits of ^{40}K, ^{226}Ra, ^{228}Ra and ^{228}Th in water for a counting time of 2 days were 0.040 Bq/l, 0.005 Bq/l, 0.008 Bq/l and 0.003 Bq/l respectively at the level of significance of 0.05.

The detection limits of ^{40}K, ^{226}Ra, ^{228}Ra and ^{228}Th in filter media and sludge for a counting time of 4 hours were 20 Bq/kg, 40 Bq/kg, 40 Bq/kg and 20 Bq/kg respectively at the level of significance of 0.05.

2.3. Dose assessment

Reduction of doses consequently to the decrease in concentrations of ^{226}Ra a ^{228}Ra was calculated by using conversion factors for adults (Sv/Bq), water consumption of 700 l/yr and the decrease in concentrations of ^{226}Ra and ^{228}Ra by 0.030 Bq/l.

3. RESULTS AND DISCUSSION

The method mostly used for reduction of ^{226}Ra and ^{228}Ra in raw water is to catch these radioisotopes together with ions of iron and manganese on MnO_2 coated sand. Iron and manganese hydroxides have a considerable sorption capacity for the divalent metal ions. The basic mechanism of the sorption process is following [1-3]:

$$M^{+} + x(=MeOH) \Leftrightarrow M(=MeO)x^{(n-x)^{+}} + xH^{+}$$

where
M is adsorbed metal ion,
(=MeOH), (=MeO) are hydroxides and oxides.

At present, opened and pressurized filters are used to catch radium radioisotopes on MnO_2 coated sand during filtration.

Figure 1 shows an example of the open filtration used for reduction of ^{226}Ra in water. Filter sand is naturally coated by iron and manganese oxides that are contained in the raw water. Filtration cycle lasts for 72 hours with backwashing lasting 1 hour.

Fig. 1. Water treatment plant for reduction of ^{226}Ra concentration by using open filters

The results of long-term observation of the effectiveness of ^{226}Ra removal are shown in Figure 2. During the observation period of 12 years, the mean ^{226}Ra activity in raw water was 0.188 Bq/l, while in the purified water it was 0.057 Bq/l (the mean values were calculated from the results of the emanometric and gammaspectrometric analyses, the detection limit was used for the values below it). Mean effectiveness of the ^{226}Ra removal was 69.7%.

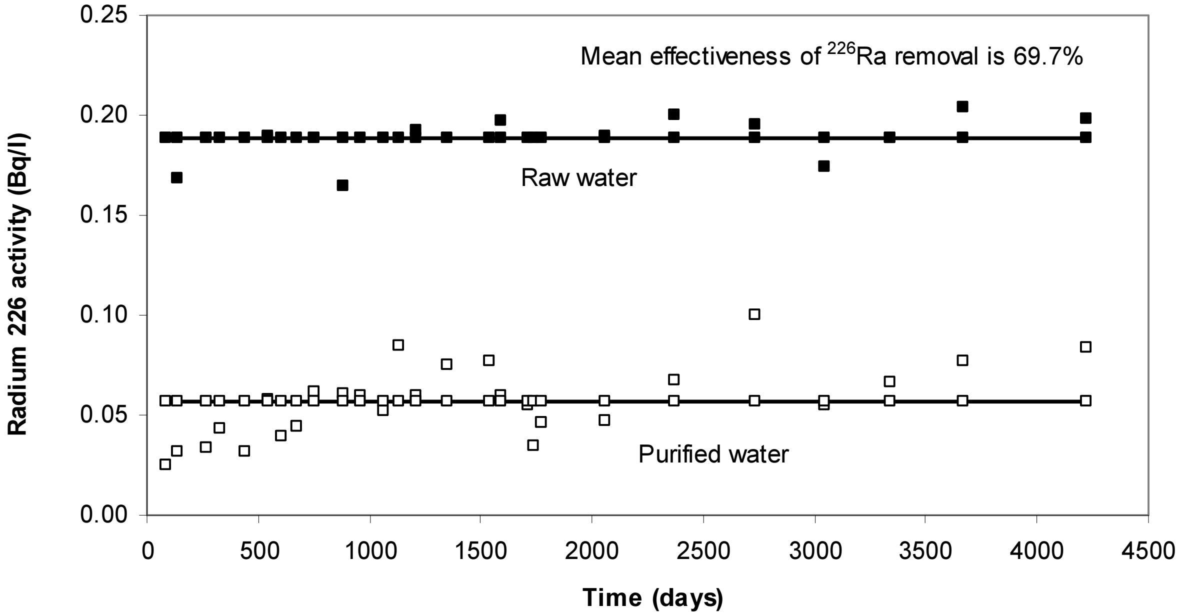

Fig. 2. ^{226}Ra activity in raw water and water purified in open filters in the period 1998–2009

The results of the analysis of an average quantity of radioactive substances in filter cartridges and backwash sludge (counted for dry mass at 105 °C) are summarized in Table 1.

TABLE 1. ^{226}Ra, ^{228}Ra, ^{228}Th AND ^{40}K ACTIVITY IN FILTER CARTRIDGES AND SLUDGE FROM FILTER BACKWASHING (OPEN FILTERS), 2009

Radionuclide	^{26}Ra	^{228}Ra	^{228}Th	^{40}K
	Bq/kg in dry matter			
Filtration sand	2744	2911	2476	< 273
Sludge	3862	6752	790	583

An example of the use of pressurized filters for reduction of the concentrations of ^{226}Ra and ^{228}Ra is given in Figure 3. The total duration of the cycle was 36 hours, of which 24 hours was used for filtration and 12 hours for regeneration of the filters. Filter filling, sand and anthracite, was MnO_2 coated.

Figure 4 shows ^{226}Ra activities in raw and purified water. The mean ^{226}Ra activity is 0.063 Bq/l in raw water and 0.024 Bq/l in purified water (the mean values were calculated from the results of the emanometric and gammaspectrometric analyses). The mean effectiveness of ^{226}Ra removal was 61.9%.

Fig. 3. Installation for filtration by using pressurized filters and MnO_2-coated filtration media

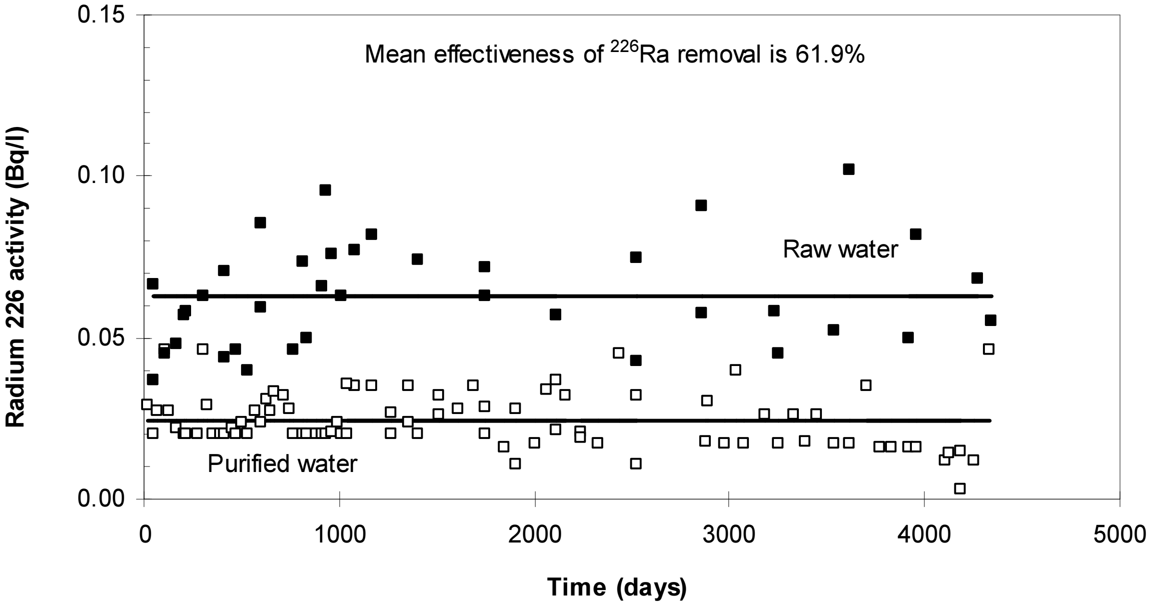

Fig. 4. ^{226}Ra activity in raw water and water purified in pressurized filters in the period 1998–2009

Figure 5 shows ^{228}Ra activities in raw and purified water. The mean ^{228}Ra activity is 0.054 Bq/l in raw water and 0.013 Bq/l in purified water (the mean values were calculated from the results of the emanometric and gammaspectrometric analyses). The mean effectiveness of ^{228}Ra removal was 75.9%.

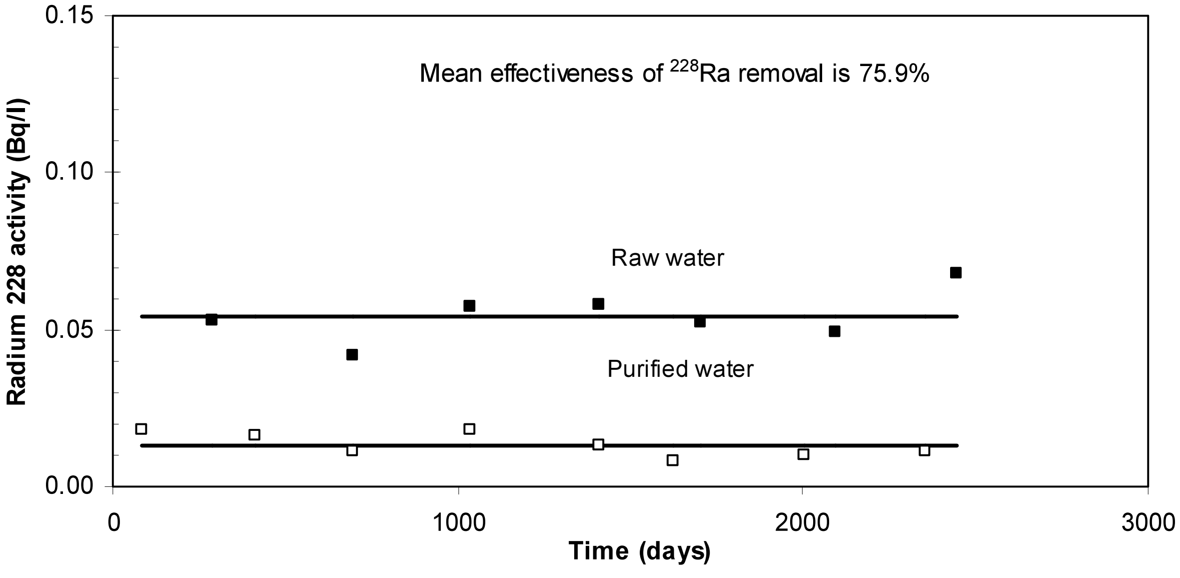

Fig. 5. ^{228}Ra activity in raw water and water purified in pressurized filters in the period 2003–2009

The results of the analysis of an average quantity of radioactive substances in filter cartridges and backwash sludge (counted for dry mass at 105 °C) are summarized in Table 2.

TABLE 2. ^{226}Ra, ^{228}Ra, ^{228}Th AND ^{40}K ACTIVITY IN FILTER CARTRIDGES, SAND AND ANTHRACITE, AND IN SLUDGE FROM FILTER BACKWASHING (PRESSURIZED FILTERS), 2009

Radionuclide	^{226}Ra	^{228}Ra	^{228}Th	^{40}K
	Bq/kg in dry matter			
Filtration sand	1845	1512	712	< 146
Anthracite	2256	1767	816	< 163
Sludge	3872	4111	738	< 280

4. CONCLUSION

Depending on local conditions, sand filters with natural cover of iron and manganese oxides are able to capture 30% – 70% of radium radioisotopes. The experience has shown that the duration of their use in case of slow filtration through open filters does not affect the removal efficiency of radioisotopes of radium. Filter layers can be used for a long time. For reduction of radium isotopes, these processes can be intensified by dissolving the layer of iron and manganese oxides by acids and their recovering by dosing of potassium permanganate in shorter intervals. Waste from the water treatment originates mainly from backwash sludge. The washing water is returned after the sedimentation as raw water and the sludge is discharged into a municipal wastewater treatment plants or landfills. Concentrations of ^{226}Ra and ^{228}Ra in the filter cartridges are in the range from 0.5 to 5 kBq/kg. Concentrations of radioactive substances in waters that have been treated by applying the technologies mentioned above meet the requirements for their content in drinking water according to Decree of State Office for Nuclear Safety No. 307/2002 Coll. on Radiation Protection, as amended.

The calculated reduction in the ^{226}Ra and ^{228}Ra concentrations during the water treatment by 0.030 Bq/l would be reflected in the reduction of their dose from drinking of water by 0.021 mSv/yr.

ACKNOWLEDGEMENT

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THE INTERNATIONAL PHOSPHOGYPSUM WORKING GROUP (PGWG)

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1. PHOSPHOGYPSUM

Phosphogypsum (PG) — calcium sulphate — is produced together with phosphoric acid (P_2O_5) by the "wet process" method of digesting phosphate rock:

$$Ca_5(PO_4)_3F + 5\ H_2SO_4 + 10\ H_2O \rightarrow 3\ H_3PO_4 + 5\ CaSO_4 \cdot 2\ H_2O + HF.$$

Some 5-6 t of PG are produced for every tonne of phosphoric acid. It is estimated that some 3 billion t of PG are currently stored in stacks worldwide. There are stacks in more than 50 countries, some active, some closed, some lost or abandoned.

2. PHOSPHATES: A NORM INDUSTRY

Phosphorus is a non-substitutable, non-renewable resource, derived on a large scale from rocks containing various forms of calcium phosphate. These deposits contain the naturally occurring radionuclides ^{238}U and ^{232}Th and their decay products. In some source rock, the uranium content is high enough for commercial recovery. The presence of these radionuclides creates a potential need to control exposures of workers and members of the public. Control is in accordance with the Fundamental Safety Principles [1] and the requirements of the International Basic Safety Standards for Protection against Ionizing Radiation and for the Safety of Radiation Sources (the BSS) [2]. In particular:

- The activity concentrations of the ^{238}U decay series radionuclides mean that the phosphate industry is one of 11 listed by the IAEA as being likely to require some form of regulatory consideration [3].
- The P industry is also the subject of an IAEA Safety Report on radiation protection and NORM residue management in the phosphate industry, now in an advanced state of preparation.
- World-wide, regulations regarding the radionuclide content of phosphogypsum in particular, but also phosphate fertilizers in general, are very diverse — even conflicted.

3. THE STACK FREE PROJECT

Since 2005, Aleff Group has partnered with the Florida Institute of Phosphate Research (FIPR) in the project **Stack Free by '53**. This partnership is led by Dr. Brian Birky and Professor Julian Hilton as Co- Principal Investigators. (www.stackfree.com). The Stack Free team (Phase 1, Reserach and Development), based on a new methodology developed for assessing risks and benefits of sustainable, safe and beneficial PG use, has assembled and analysed a very large repository of knowledge and experience in PG use, accessible on line. It is now turning that knowledge (Phase 2, Implementation) into use via Manuals, training, consultancy and advocacy, in close collaboration with the PGWG. The focus is on agriculture, construction, landfill management, road building and "value add" uses, such as in coastal and marine settings.

4. STACK FREE: RESULTS MARCH 2005–MARCH 2010

- Completed Research and Development Phase and Knowledge Gap Analysis (Phase 1)
- Initiation of Implementation Phase (Phase 2) with associated International Action Plan (proposed), with IAEA
- Creation of PG Safety framework (including radionuclides and heavy metals)
- Establishment of a dedicated competency centre with associated training programme and materials
- Ongoing expert working group (PGWG)
- Establishment of PG Guide Principles for Good Phosphogypsum Management Practices (GPGMP)
- Taxonomic list of stacks and estimated stored tonnages
- Searchable database of 2,000+ publications on PG use and related topics
- Case studies
- Comparative regulations
- Reports, publications and presentations
- Manuals
    - Agriculture
        - Crop response (50+ crops)
    - Road Building
    - Construction

5. THE INTERNATIONAL PHOSPHGYPSUM WORKING GROUP (PGWG)

The international Phosphogypsum Working Group (PGWG) has its origins in joint meetings of the Stack Free project and the IAEA. (2006). These led to formal joint meetings of the IAEA and FIPR (2006, 2007) and to a number of collaborative activities. Out of these activities came two IAEA sponsored meetings on PG, in 2008 and 2009. Another is planned for 2010.

The PGWG has adopted the following vision and mission statements

- **Vision:** PG is a resource not a waste
- **Mission**: Find the point of equilibrium between PG production and consumption based on safe, sustainable use.

6. SAFE, BENEFICIAL USES OF PHOSPHOGYPSUM — A CONTRIBUTION TO RESOURCE CONSERVATION AND SUSTAINABILITY

(a) In the context of the policy of sustainability, PG has a well-demonstrated role to play in the conservation and optimisation of resources. In the context of definitions of waste, PG has both foreseen and foreseeable uses and is thus not a *de facto* waste.

(b) Three categories of PG use may be regarded as safe and sustainable, with a significant body of supporting scientific evidence:

  (i) Agriculture,
  (ii) Construction,
  (iii) Road building.

(c) A further two categories are very promising and are now under active review:

  (iv) Landfill
  (v) Coastal and marine.

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