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NATURAL RADIOACTIVITY AND ^{222}Rn EXHALATION RATE FROM BRAZILIAN PHOSPHOGYPSUM BUILDING MATERIALS

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Abstract

Phosphogypsum is classified as a NORM residue and one of the main environmental concerns of its use is the radon exhalation from this material. The aim of this study is to determine the activity concentration of natural radionuclides, radium equivalent activities, external and internal hazard index and the radon exhalation rate from bricks and plates made of phosphogypsum. The activity concentration and radon exhalation rate were in accordance with literature values. The results of radium equivalent, external and internal hazard index showed that plates and bricks from Ultrafertil and Fosfertil presented values above the recommended limits; indicating the necessity of using more realistic models for the safe application of phosphogypsum as building materials. The results of this study can contribute for the establishment of guidelines by the Brazilian regulatory agency, for the safe use of phosphogypsum as building material

1. INTRODUCTION

Radon is a natural radioactive noble gas that can be found in soil, water, outdoor and indoor air. Exposure to radon accounts for more than half of the annual effective dose from natural radioactivity [1].

Building materials are one of the main radon sources in houses, since they can contain small amounts of natural radioactivity such as ^{226}Ra, ^{232}Th and ^{40}K [2]. The content is usually low, but some materials, like phosphogypsum, may contain higher concentrations depending on the origin of the raw material used [3].

Phosphogypsum is classified as a NORM (Naturally Occurring Radioactive Material) residue and one of the main environmental concerns of its use is the radon exhalation from this material. Phosphogypsum is a residue from the wet-acid process of phosphoric acid production. The Brazilian phosphate industry is responsible for the production of 5.5 million ton per year of phosphogypsum [4].

The radioactivity present in the phosphogypsum, among other impurities, prevents its reuse for a variety of purposes. In Brazil, industries dealing with NORM residues are subjected to the recommendations given by Comissão Nacional de Energia Nuclear (CNEN), which include compliance with the radiological protection regulations [5]. CNEN has also established, recently, the exemption levels of 1000 Bq kg^{-1} of ^{226}Ra and ^{228}Ra for the use of phosphogypsum in agriculture and cement industry [6]. However, there is not yet a specific regulation for the use of PG as a building material.

One possible application of phosphogypsum is in the manufacture of building materials. In this case, one of the major radiological concerns is the radon exhalation from this material. The exhalation rate is defined as the amount of activity released per unit surface area per unit time from the material. It depends on the ^{226}Ra content of the material, emanation factor, gas diffusion coefficient in the material, porosity and density of the material [7-9].

Several studies were undertaken in Brazil concerning the radiological impact of using the phosphogypsum as building material [10-15]. An early publication of Mazzilli and Saueia [10] presented the activity concentration of ^{226}Ra, ^{232}Th and ^{40}K in Brazilian phosphogypsum samples and discussed the radiological implications of using it as building materials. In this paper a conservative model was applied to evaluate the external and internal exposure for

people living in a hypothetical house made with this material. In order to apply a more realistic model an experimental house was constructed with walls and roof made of phosphogypsum plates from different origins. In this study a comprehensive radiological evaluation was performed, including measurement of the external gamma exposure and radon concentrations. The results showed that the annual increment in the effective dose to an inhabitant of the house was below the 1mSv limit for every reasonable scenario [11-14].

Nisti et al. [15] evaluated the radon exhalation rate from phosphogypsum piles from different phosphate fertilizer industries, by using by the activated charcoal collector method and theoretical model suggested by UNSCEAR [1].

As a complementary study, this paper aims to determine the activity concentration of natural radionuclides, radium equivalent concentration, external and internal hazard indices and the radon exhalation rate from bricks and plates made of phosphogypsum from three Brazilian phosphate fertilizer industries: Ultrafertil, Fosfertil and Bunge. Samples of phosphogypsum bricks and plates were analyzed by gamma spectrometry for their radionuclide content. The radium equivalent activity, external and internal hazard indices and radon exhalation rate were determined using theoretical models. The Figure 1 presents bricks and plates made of phosphogypsum.

FIG. 1. Bricks and Plates made of phosphogypsum.

2. MATERIALS AND METHODS

Samples of phophogypsum were dried for 24 h in an air circulation oven at 60^{o}C, packed in a polyethylene bottle of 100 ml and sealed for about four weeks prior to measure in order to ensure that radioactive equilibrium had been reached between ^{226}Ra and its progeny. After this time phosphogypsum samples were measured by gamma-ray spectrometry with a hyper-pure germanium detector Canberra model GX2518, 25% relative efficiency, effective resolution of 1.8 keV on the 1332 keV ^{60}Co with associated electronics and coupled to a microcomputer.

The activity concentration of ^{40}K was determined directly by its own gamma-ray peak at 1460.8 keV, while concentrations of ^{226}Ra and ^{232}Th were calculated based on the weighted mean value of their respective decay products in equilibrium. The activity concentration of ^{226}Ra was determined using the 295.2 and 351.9 keV gamma rays from ^{214}Pb and the 609.3 keV from ^{214}Bi. The activity concentration of ^{232}Th was determined using the 338.4, 911.1 and 968.9 keV photopeaks from ^{228}Ac, the 238.6 and 727.3 keV photopeaks from ^{212}Pb and ^{212}Bi, assuming ^{232}Th – ^{228}Ra equilibrium.

All spectra were analyzed with the Interwinner 6.0 from Eurisys Measurements Incorporation [16] software for personal computer analysis of gamma-ray spectra from HPGe detectors. The background radiation was obtained by measuring water in the same sample geometry used for samples. The counting time was determined from the model proposed by

Nisti et al. [17]. The determination of the minimum detectable activity (MDA) followed the model proposed by Currie [18], each sample was collected and analyzed in triplicate.

The ^{226}Ra, ^{232}Th and ^{40}K activity concentrations of Brazilian phosphogypsum building materials were used for the calculation of radium equivalent activity and external and internal hazard indices [19].

The radium equivalent activity was obtained by the equation (1):

$$C_{Ra,eq} = C_{Ra} + 1.43C_{Th} + 0.077C_K \quad (1)$$

where
$C_{Ra,eq}$ is the radium equivalent activities (Bq kg^{-1}),
C_{Ra} is the activity concentrations of ^{226}Ra (Bq kg^{-1}),
C_{Th} is the activity concentrations of ^{232}Th (Bq kg^{-1})
C_K is the activity concentrations of ^{40}K (Bq kg^{-1})

1.43 and 0.077 index values were defined on hypothesis that 370 Bq kg^{-1}, 259 Bq kg^{-1} and 4810 Bq kg^{-1} for ^{226}Ra, ^{232}Th and ^{40}K produce the same gamma ray exposure.

External and internal hazard indices were calculated using the following equation (2) and (3), respectively:

$$\frac{C_{Ra}}{370} + \frac{C_{Th}}{259} + \frac{C_K}{4810} \leq 1 \quad \text{for external exposure} \quad (2)$$

$$\frac{C_{Ra}}{185} + \frac{C_{Th}}{259} + \frac{C_K}{4810} \leq 1 \quad \text{for internal exposure} \quad (3)$$

where
C_{Ra} is the activity concentrations of ^{226}Ra (Bq kg^{-1}),
C_{Th} is the activity concentrations of ^{232}Th (Bq kg^{-1}),
C_K is the activity concentrations of ^{40}K (Bq kg^{-1}),
370, 259 and 4810 are the indices for external exposure,
185, 259 and 4810 are the indices for internal exposure.

The radon exhalation rate of 222Rn was determined using a theoretical model proposed by UNSCEAR [1], through the 226Ra concentration. The determination radon exhalation rate used the equation (4).

$$J_D = C_{Ra}\lambda_{Rn} f\rho L \tanh(d/L) \quad (4)$$

where
J_D is the radon exhalation rate of ^{222}Rn (Bq m^{-2} h^{-1}),
C_{Ra} is the activity concentration of ^{226}Ra (Bq kg^{-1}),
λ_{Rn} is the decay constant of ^{222}Rn (h^{-1}),
f is the emanation fraction,
ρ is the density (kg m^{-3}),
d is half-thickness (m),
L is the diffusion length (m^2).

3. RESULTS AND DISCUSSION

The activity concentration obtained in the phophogypsum samples are presented in the Table 1 and 2. Samples were analyzed in triplicate.

TABLE 1. AVERAGE CONCENTRATIONS OF ^{226}Ra, ^{232}Th AND ^{40}K (Bq kg^{-1}) FROM PHOSPHOGYPSUM BRICKS.

	Concentrations(Bq kg^{-1})		
Samples	^{226}Ra	^{232}Th	^{40}K
Ultrafertil	388 ± 4	273 ± 5	< 22
Fosfertil	307 ± 2	175 ± 4	< 22
Bunge	30 ± 6	37 ± 5	< 22

TABLE 1. AVERAGE CONCENTRATIONS OF ^{226}Ra, ^{232}Th AND ^{40}K (Bq kg^{-1}) FROM PHOSPHOGYPSUM PLATES.

	Concentrations(Bq kg^{-1})		
Samples	^{226}Ra	^{232}Th	^{40}K
Ultrafertil	392 ± 10	253 ± 3	< 81
Fosfertil	294 ± 3	151 ± 6	< 56
Bunge	16 ± 1	26 ± 3	< 39

The concentrations obtained in this work are in good agreement with values reported in literature for Brazilian phosphogypsum [3]. Ultrafertil and Fosfertil industries presented higher values for the activity concentration; the results obtained for phosphogypsum from Bunge industry are lower and of the same order of magnitude of the total average radionuclides concentration in soil from UNSCEAR [1].

Table 3 presents results of radium equivalent activities and external and internal hazard indices.

TABLE 3. RADIUM EQUIVALENT ACTIVITIES ($C_{Ra,eq}$) AND EXTERNAL AND INTERNAL HAZARD INDEX.

Samples	$C_{Ra,eq}$	Hazard indices	
(bricks/plates)	(Bq kg^{-1})	ext.	int.
bricks (Ultrafertil)	780	2.1	3.2
bricks (Fosfertil)	559	1.5	2.3
bricks (Bunge)	84	0.2	0.3
plates (Ultrafertil)	755	2.0	3.1
plates (Fosfertil)	512	1.4	2.2
plates (Bunge)	55	0.2	0.2

The results of radium equivalent, external and internal hazard indices showed that plates and bricks from Ultrafertil and Fosfertil present values above the recommended limits, suggesting the application of a more realistic model for the evaluation of the exposure in dwelling. Maduar et al. [14], using an experimental house with walls and roof made with phosphogypsum of different origins evaluated the dose conversion factors for the external exposure. The results obtained in this paper showed that the annual increment in the effective dose to an inhabitant of the house is below the 1 mSv limit for this specific scenario.

Table 4 presents the results of radon exhalation rate from bricks and plates made of phosphogypsum, these results are in accordance with literature values for phosphogypsum blocks [20], and are of the same order of magnitude of ordinary building materials, such as

sand and concrete [21-22]. The radon exhalation rate was also measured in the Brazilian phosphogypsum stacks from Fosfertil and Ultrafertil giving results varying from 341 to 562 Bq m^{-2} h^{-1}, respectively [15]. The results obtained in the phosphogypsum stacks were two orders of magnitude higher than those from plates and bricks, giving evidence that the porosity, density and gas diffusion coefficient in the material play an important role in the radon exhalation.

TABLE 4. RADON EXHALATION RATE FROM BRICKS AND PLATES MADE OF PHOSPHOGYPSUM (Bq m^{-2} h^{-1}).

Samples	Bricks (Bq m^{-2} h^{-1})	Plates (Bq m^{-2} h^{-1})
Ultrafertil	5.67	4.30
Fosfertil	3.78	3.21
Bunge	0.41	0.16

4. CONCLUSION

The results of radium equivalent, external and internal hazard indices for phosphogypsum form Ultrafertil and Fosfertil were above the recommended levels. Therefore, further studies using more realistic models are necessary for the safe application of phosphogypsum as building material.

The ^{222}Rn exhalation rates from phosphogypsum plates and bricks are of the same order of magnitude of ordinary building materials, such as sand and concrete, therefore its use will note imply in any additional risk for dwellings due to radon inhalation.

The results obtained in this study will contribute for the establishment of guidelines by the Brazilian regulatory agency for the safe use of phosphogypsum as building material.

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LEACHABILITY OF NATURAL RADIONUCLIDES AND RARE EARTH ELEMENTS IN BRAZILIAN PHOSPHATE FERTILIZERS AND PHOSPHOGYPSUM

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Abstract

The Brazilian phosphate fertilizers are obtained by wet reaction of the igneous phosphate rock with concentrated sulphuric acid, giving as final product phosphoric acid and dehydrated calcium sulphate (phosphogypsum - PG) as by-product. The level of impurities (metals and radionuclides, among others) present in the phosphate rock used as raw material is distributed among products and by-products. In Brazil, PG has been used for many years in agriculture as a soil amendment. The characterization of natural radionuclides elements in Brazilian PG and the most used phosphate fertilizers, single super phosphate (SSP), triple super phosphate (TSP), monoammonium phosphate (MAP) and diammonium phosphate (DAP) has been already published by the same authors. However, for a long-term safe application of these fertilizers and PG it is important to study the availability of these elements to the environment. For this purpose, the evaluation of radionuclides and rare earth elements concentration in the labile fraction is more suitable than the total concentration, since this fraction is more available for the absorption by plants and water contamination. In order to evaluate the available fraction of these elements to the environment, PG and phosphate fertilizers samples were leached with water and EDTA solution. The total and leached concentrations of radionuclides (^{226}Ra, ^{228}Ra and ^{210}Pb) were determined by using high-resolution gamma spectrometry and by measuring the gross alpha and beta counting after a radiochemical separation of the elements of interest, respectively. The concentration of rare earth elements - REEs (Ce, Eu, La, Lu, Sm, Tb and Yb), U and Th were determined by instrumental neutron activation analysis. The results obtained using the methodology with mild leaching with EDTA and with water showed that the radionuclides and REEs although present in the PG are not available to the environment.

1. INTRODUCTION

The presence of natural radionuclides and metals in mineral ores and their redistribution in industrial products and wastes is well known. Brazilian fertilizer industries produce phosphoric acid by reacting phosphate rocks with sulphuric acid giving as by-product phosphogypsum (PG). Phosphoric acid is the starting material for the most utilized Brazilian fertilizers: triple superphosphate (TSP), single superphosphate (SSP), mono ammonium phosphate (MAP) and diammonium phosphate (DAP).

In Brazil, the main producers of phosphate fertilizers are responsible for the production of approximately 5.4×10^6 tons of phosphogypsum per year. This PG has been used for many years in agriculture as a soil amendment. For its safe long term application, it is necessary to characterize the impurities present in PG. This study is important since such impurities can migrate to agricultural products and food chain. Several papers were published concerning the characterization of radionuclides and heavy metals in PG and phosphate fertilizers [1, 2, 3].

Although there is little information about rare earth elements toxicity and mobility in the environment, the characterization of these elements in the phosphate industry is important because these elements are present in the phosphate rock used as raw material [4].

The main objective of this paper is to determine the radionuclides (^{238}U, ^{226}Ra, ^{228}Ra, ^{210}Pb and ^{232}Th) and REEs (Ce, Eu, La, Lu, Sm, Tb and Yb) in Brazilian PG and the most used phosphate fertilizers, single super phosphate (SSP), triple super phosphate (TSP), monoammonium phosphate (MAP) and diammonium phosphate (DAP). In order to evaluate the availability of these elements to the soil and plants, the PG samples were extracted with water and a solution of EDTA- NH_4 0.05 mol L^{-1} at pH 7.

2. MATERIAL AND METHODS

The samples analyzed in this study come from the three main fertilizers facilities, Copebras and Ultrafertil, located in Cubatão - São Paulo and Fosfertil, located in Uberaba - Minas Gerais.

The radionuclides ^{226}Ra, ^{228}Ra and ^{210}Pb were measured in PG and phosphate fertilizers samples using high-resolution gamma spectrometry, with a hyper-pure germanium detector, EGNC 150-190 R, from Eurisys Measures, with resolution of 1.8 keV for the 1332 keV ^{60}Co photopeak and 15% efficiency. The detector was calibrated using natural soil, rock and water spiked with radionuclides certified by Amersham. The ^{226}Ra activities were determined by taking the mean activity of its daughter nuclides: ^{214}Pb at 295 keV and 352 keV, and ^{214}Bi at 609 keV. The ^{228}Ra was determined by measuring the 911 keV and 968 keV gamma-ray peaks from ^{228}Ac. The concentration of ^{210}Pb was determined by measuring the intensity of the 46.5 keV peak. Self-absorption correction was applied to ^{210}Pb since the attenuation for low energy gamma rays is highly dependent upon sample composition. The approach used was suggested by Cutshall [5].

The total concentration of the radionuclides ^{226}Ra, ^{228}Ra and ^{210}Pb in the leaching solution was determined by the measurement of the gross alpha and beta counting after a radiochemical separation of the elements of interest. 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. The accuracy and precision was performed by measuring the reference materials IAEA 326 - Radionuclides in soil, and IAEA 300 - Baltic Sea Sediment, and ranged from 2.7 to 7.9% and from 2.2 to 7.6%, respectively.

The REEs, U and Th were determined by instrumental neutron activation analysis (INAA). The determination was carried out by irradiation of approximately 150mg of each sample and 150 mg of reference materials, during 8 hours at a neutron flux of 1012 $n.cm^{-2}s^{-1}$, at Instituto de Pesquisas Energéticas e Nucleares (IPEN) research reactor IEA-R1. The first count was made after 5 to 10 days of decay and allows identifying La, Sm and U. The second count was made after 15 days of decay and allows identifying Ce, Eu, Lu Tb, Yb and Th. Gamma spectrometry was measured with a Ge-hyperpure detector, Intertechnique, with 2.1 keV resolution for the 1332 keV ^{60}Co photo peak. The accuracy and precision was performed by measuring the reference materials Buffalo River Sediment (NIST-8704) and Soil-7 (IAEA). The accuracy ranged from 0.4% to 8.8% and the precision from 1.3% to 8.3%.

The extraction with water was obtained by dissolving 2.4 g of PG in 1L of water. This extraction was made in order to check the amount of radionuclides that are dissolved when the solubility product constant of PG (0.24 g/100mL at 20°C) is achieved. The mild extraction was obtained by stirring 5g of PG in 50 mL of EDTA-NH4 solution 0.05 mol L^{-1} at pH 7, procedure established by [6] Certification of the contents (mass fraction) of Cd, Cr, Cu, Ni, Pb and Zn in an organic-rich soil following harmonized EDTA and acetic acid extraction procedures BCR 700- Information Reference Materials.

3. RESULTS AND DISCUSSION

Concentrations of ^{238}U, ^{226}Ra, ^{228}Ra, ^{210}Pb and ^{232}Th in the PG and phosphate fertilizers and in the leachate are presents in Table 1 and Table 2, respectively. The results obtained for the total concentration of ^{226}Ra, ^{228}Ra, ^{210}Pb and ^{232}Th show that these radionuclides are

present in higher concentrations only in the PG and fertilizers SSP and TSP. The production of phosphoric acid can be described by the following reaction:

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

Since Ra isotopes and Pb form insoluble compounds with sulphates, they will concentrate in the final product of the reaction: calcium sulphate (PG).

During the chemical attack of the phosphate rock, different compounds can be formed, depending upon the experimental conditions and the stoichiometry of the reaction. Single superphosphate (SSP) is formed by reacting sulphuric acid with phosphate rock, according to the reaction:

$$Ca_{10}(PO_4)6F_2 + 7H_2SO_4 + 6.5\ H_2O \rightarrow 3\ Ca(H_2PO_4)_2.H_2O + 7\ CaSO4.\ ½H_2O + 2\ HF$$

In the production of triple superphosphate (TSP), phosphoric acid reacts with apatite, according to the reaction:

$$Ca_{10}(PO_4)6F_2 + 14\ H_3PO_4 + 10\ H_2O \rightarrow 10\ Ca(H_2PO_4)_2.H_2O + 2\ HF$$

In both cases, most of Ra and Pb will be present in the SSP and TSP. The concentration of ^{226}Ra, ^{228}Ra and ^{210}Pb found in the labile fractions, on the other hand, are less than 10% of the total available content of these radionuclides in PG, in spite of the high dissolution of PG in water (more than 90%). A possible explanation for such behavior is that the radium and Pb in the PG precipitate with barium sulphate instead of calcium sulphate in the chemical reaction, forming insoluble compounds. Similar behaviour was observed by Santos [7], who performed a sequential extraction of Brazilian PG and found that most of the radium and lead are located in water insoluble (non-$CaSO_4$) fraction. In the case of the fertilizers SSP and TSP, the concentration found for the radionuclides in the labile fraction presented slightly higher values, indicating that in these samples the radionuclides are more available to the environment. The concentration of ^{226}Ra, ^{228}Ra and ^{210}Pb found in the labile fraction of the fertilizers MAP and DAP is negligible.

TABLE 1. RADIONUCLIDE CONCENTRATION IN PHOSPHOGYPSUM (Bq kg^{-1}) AND IN THE LABILE FRACTION (Bq L^{-1})

		U-238	Ra-226	Pb-210	Th-232	Ra-228	Solubility (%)
PG Copebras	Total conc	<2	744±138	1061±132	232±35	242±23	
	Leached H_2O	<2	105±6	35±4	ND	3.5±0.2	96
	Leached EDTA	ND	16±0.7	26±1	<3	45±4	10
PG Fosfertil	Total conc	<2	186±46	182±46	90±20	151±27	
	Leached H_2O	ND	17±1	8.1±0.6	ND	10±1	93
	Leached EDTA	<2	1.5±0.2	12±1	<3	22±4	9
PG Ultrafertil	Total conc	<2	344±65	347±44	212±41	219±40	
	Leached H_2O	<2	15±1	6.1±0.4	ND	3.1±0.3	90
	Leached EDTA	ND	4.2±0.2	17±1	<3	16±2	15

TABLE 2. RADIONUCLIDE CONCENTRATION IN PHOSPHATE FERTILIZERS (Bq kg^{-1}) AND IN THE LABILE FRACTION (Bq L^{-1})

			Ra-226	Pb-210	Ra-228	Solubility (%)
Copebras	SSP	Total conc	720±96	1084±106	196±33	43
		Leached EDTA	11.0±0.4	75±2	9.2±0.1	
	TSP	Total conc	546±10	904±60	157±24	76
		Leached EDTA	100±3	316±4	72±6	
Fosfértil	MAP	Total conc	10±4	<19	293±74	86
		Leached EDTA	1.0±0.2	2.0±1	25±4	
	TSP	Total conc	105±28	175±54	189±28	65
		Leached EDTA	2.6±0.2	29±1	24±3	
Ultrafértil	MAP	Total conc	9±1	40±2	126±11	85
		Leached H_2O	2.7±0.2	5±1	20±2	
	DAP	Total conc	5±1	<19	48±5	81
		Leached EDTA	3.7±0.2	7±1	17±1	

Concentrations of REEs in the PG and in the leachate are presented in Table 3. It can be seen that the REEs concentrate preferentially in PG. Although there are no limits available for the concentration of REEs in phosphate fertilizers and PG, such characterization is relevant since they complete a database for the safe application of PG. Elevated concentrations of REEs, like most heavy metals in solution, above those which plants are accustomed to, may cause toxic reactions and negative effects on plants. Tyler [8] reported that the transfer of REEs from soil to plants is generally low and that the uptakes are correlated with the soil acidity and the solubility of the REEs, therefore only a small part of the total concentration is available to the environment. The results of the extraction with the EDTA solution showed that only 10% of the PG mass was dissolved in the solution and that less than 1% of the REEs were extracted. The results of the extraction with water showed that, although the high dissolution of PG (~90%), only a small amount of REEs was extracted. It can be concluded that the relatively high concentration of REEs present in the PG is not available to the environment.

4. CONCLUSION

In general, the total concentration obtained for the radionuclides and REEs were higher in the PG samples. The results obtained using the methodology with mild leaching of PG with EDTA and total dissolution in water showed that these elements are not available to the environment, giving evidence that the application of PG and phosphate fertilizers in agriculture is safe as far as contamination by such elements.

TABLE 3. CONCENTRATION OF REE IN PHOSPHOGYPSUM (Bq kg^{-1}) AND IN THE LABILE FRACTION (Bq L^{-1}) (mg kg^{-1})

		La	Ce	Sm	Eu	Tb	Yb	Lu	Solubility (%)
PG Copebras	Total conc	1178 ± 18	2480 ± 102	139 ± 5	33 ±2	6.4 ± 0,6	7.2 ± 0.9	0.16 ± 0.05	
	Leached H_2O	<0.9	<2.5	<0.05	<0.06	ND	ND	ND	96
	Leached EDTA	0.94 ±0.02	2.7 ±0.2	0.42 ±0.02	0.07 ±0.01	<0.26	<0.36	ND	10
PG Fosfertil	Total conc	1017 ± 16	956 ± 55	123 ± 4	26.3 ± 2.0	7.3 ± 0.7	10 ± 2	0.4 ± 0.1	
	Leached H_2O	<0.9	<2.5	<0.05	ND	ND	ND	ND	88
	Leached EDTA	5.4 ±0.1	11 ±1	1.32 ±0.04	0.22 ±0.03	<0.26	<0.36	ND	9
PG Ultrafertil	Total conc	1349 ± 17	2977 ± 123	154 ± 4	34 ± 2	6.9 ± 0.6	7.2 ± 0.9	ND	
	Leached H_2O	<0.9	<2.5	<0.05	<0.06	ND	ND	ND	90
	Leached EDTA	5.3 ±0.1	12 ±1	1.23 ±0.04	0.18 ±0.03	<0.26	<0.36	ND	15

ACKNOWLEDGMENTS

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DETERMINATION OF SOIL SCREENING LEVELS FOR U AND Th IN MINAS GERAIS STATE, BRAZIL

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Abstract

Soil screening levels express the levels of contaminant concentration in the soil, which guide the actions to be taken following investigation to confirm contamination. The list of toxic substances or elements under Brazilian legislation includes organics, volatile organics and metals but does not consider radioactive elements. Radioactive elements are all potentially carcinogenic and therefore need to be subject to legal control. The National Nuclear Energy Commission, the federal agency currently responsible for legislation regarding the control of Naturally-Occurring Radioactive Material (NORM) facilities does not establish guiding values for intervention in terms of soil activity concentration in the case of contamination with radioactive elements. In mining, the processing and treating of ores such as cassiterite, uranium, phosphate, niobium, and rare earths contribute to the generation of large amounts of NORM residues. Obviously, the improper disposal of these materials may lead to situations that result in soil and groundwater contamination and unnecessary exposure of the population in general. In order to establish guiding values for soil quality for natural radionuclides in the state of Minas Gerais, the study area included the entire state, which has unique characteristics related to the lithology, genesis, and morphology of the soils. These characteristics have tremendous influence on the petrogeochemistry of elements and radionuclides. A total of 110 soil samples were collected and analyzed in order to determine the activity concentration of U_{nat} and Th. In general, it was possible to verify that the activity concentrations of U_{nat} are higher than those of Th. This fact can be explained by the intense weathering that most of the state's soil has undergone and the chemical and geochemical characteristics of the two elements. The values obtained up to the present are higher than the reference values for soil quality adopted in other parts of Brazil and the world.

1. INTRODUCTION

The Earth's crust contains radionuclides that are a major source of Naturally-Occurring Radioactive Materials (NORM) in the environment. The majority of these radionuclides belong to the decay chains that begin with U-235, U-238, and Th-232.

When the radioactive nuclides associated with natural material come about after industrial processes, the material is called TENORM, Technologically Enhanced Naturally-Occurring Radioactive Material. Mining and processing of ore for metal production generates large amounts of solid waste, around 1.5 billion tons per year, 100 million tons of which are metallurgical slag (Pontedeiro, 2006). The immense volume of NORM waste generated each year has drawn the attention of domestic and international environmental agencies as well as other regulatory agencies.

Inadequate disposal of this NORM/TENORM waste in the soil can cause problems such as damage to human health, degradation of the quality of water resources, restrictions to soil usage, damage to public and private property, and reduction of property values, as well as environmental damage. The contamination of the soil with radionuclides of natural series has become an even more serious problem since they have a long half-life and most are carcinogenic elements (Peres, 2007).

Management of contaminated areas seeks to minimize risks to which the population and environment are exposed by means of a set of measurements that ensure the areas and their impacts are known. They provide the instruments needed to make decisions about the most appropriate form of intervention.

In order to facilitate the decision making process for management of contaminated areas, establish priorities and reduce costs, environmental agencies from Brazil and several other countries have opted to establish soil value guidelines to be used in the first step of the decision making process. These are in turn defined as concentrations of a specific substance in the soil or groundwater that identify a soil as clean (CETESB, 2001).

Minas Gerais is an important historical reference in Brazilian cassiterite production, also standing out as a precursor of the metallurgical production of tin in the town of São João Del Rey in the 1940s. Cassiterite deposits have a genetic affinity with the Eastern Pegmatite Province of Minas Gerais, associated with columbite-tantalite and djalmite. It has been the target of intensive prospecting since the beginning of the 1940s.

For this reason, studies that contribute to establishing criteria and value guidelines for prevention and control of potentially toxic chemicals in the soil and groundwater are extremely important to the management of contaminated areas in the state of Minas Gerais.

2. PROCEDURES

2.1. Definition of the study area

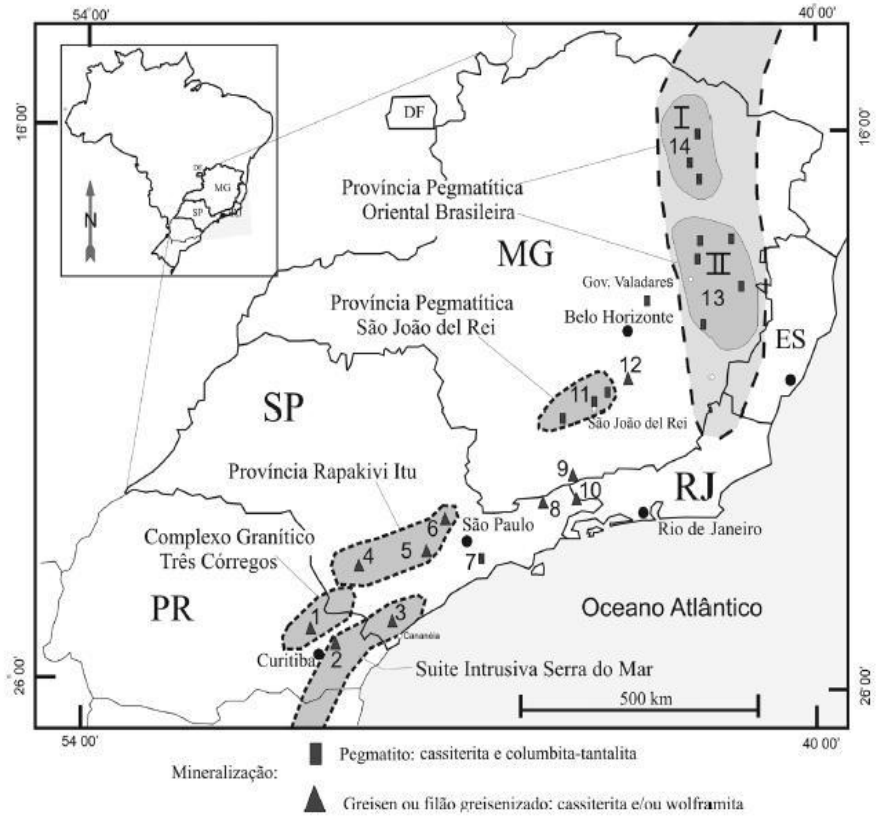
This study encompasses the whole state of Minas Gerais, which is located in south-eastern Brazil. It is the country's fourth-largest state, with an area of 588,384 km^2, equivalent to 7% of the nation's territory. The state has the third-largest economy in the country.

The history and traditions of the state of Minas Gerais are closely tied to mining activities and its enormous mineral reserves. The state extracts more than 160 million tons of iron ore, 29% of the country's mineral production, 53% of metallic mineral production, and around 50% of the country's gold production.

Uranium and thorium can occur in many types of rock. Three have the largest distribution: 1) bands of pre-Cambrian rocks; 2) areas with permeable sediment; and 3) areas with detrital sand accumulation.

In Minas Gerais, deposits can be considered large that have peculiar characteristics related to lithology, genesis, and morphology of soil that has significant influence on the pedogeochemistry of trace elements, metals, and radionuclides.

Figures 1 and 2 show the locations of large ore occurrences in the state of Minas Gerais.



Eastern Pegmatite Province; São João Del Rei Pegmatite Province; Rapakivi Itu Province; Três Córregos Granite Complex; Serra do Mar Intrusive Suite; Atlantic Ocean
Deposit: Pegmatite: cassiterite and columbite-tantalite; Greisen of greisenized vein: cassiterite and/or wolframite

FIG. 1. Map of some pegmatite occurrences in the state of Minas Gerais (adapted from PPeGeo, the electronic Geosciences periodical portal).

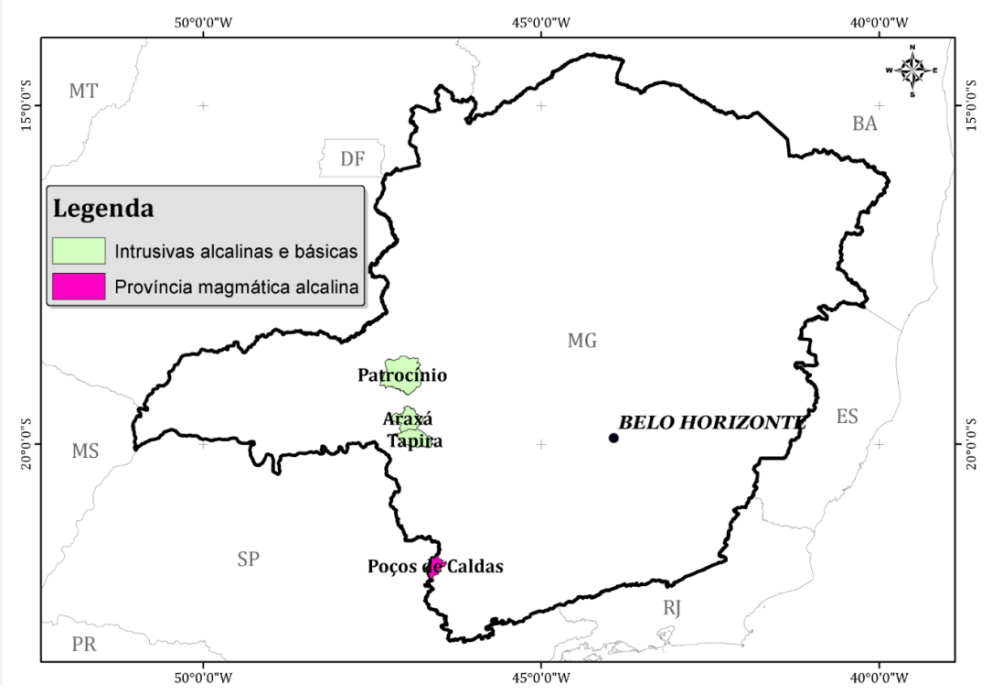


FIG. 2. Map of some occurrences of intrusive alkaline and basic rocks in the state of Minas Gerais.

2.2. Sampling and analytical method

Samples were randomly collected within the map unit, observing the predomination of preserved or minimally impacted vegetation such as natural pastures. Other criteria were utilized to confirm the mapping unit, such as observation of soil profiles in highway excavations, erosions, and gullies, as well as interpretation of vegetation and geomorphology. The soil samples were taken from a depth of 0 to 20 cm, which is equivalent to horizon A for most soil.

For U_{nat} and Thorium analysis, 110 samples were chosen from the 500 that are in the Soil Database by superimposing existing information about soil classes and the geology of each region and trying to obtain greater reach and make them more representative within the analytical limitations. 12 of the samples taken were tripled in order to make sure that the U_{nat} and Th analysis and preparation method could be reproduced.

The points chosen for U_{nat} and Th analysis are well distributed throughout Minas Gerais as can be seen in Figure 3.

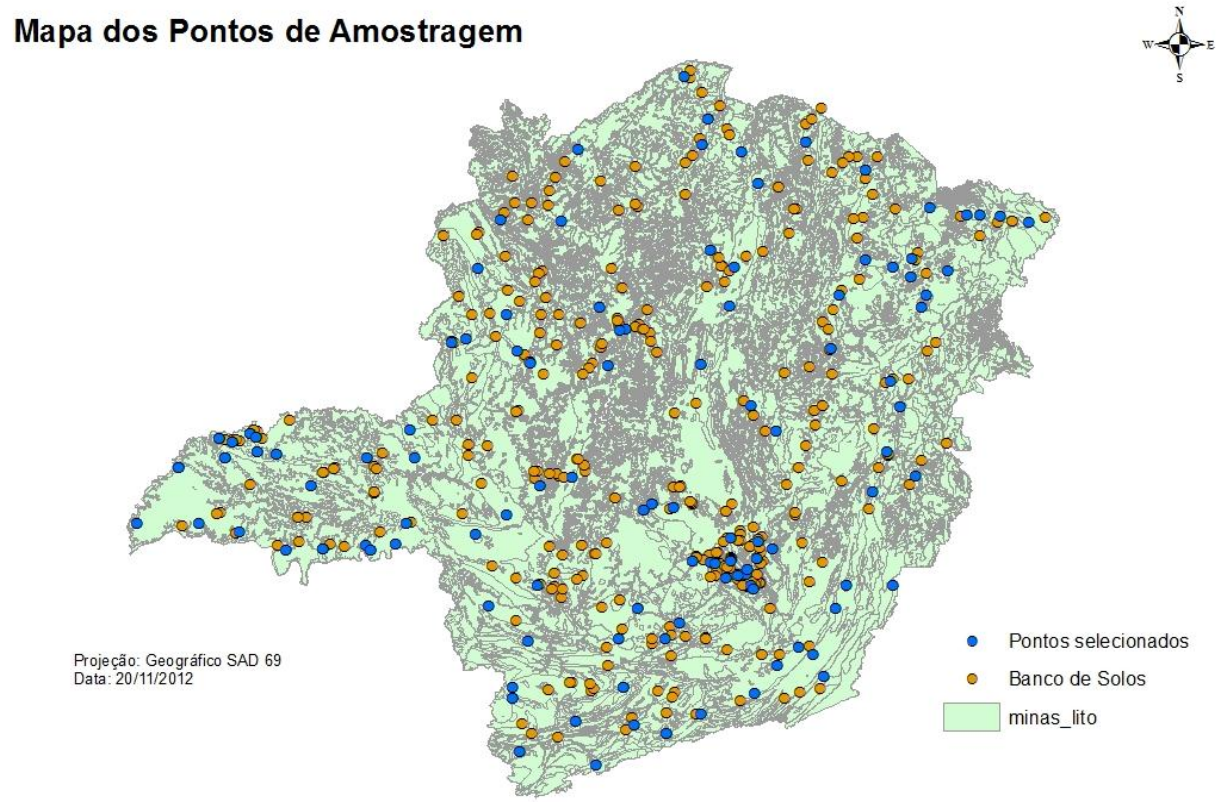


FIG. 3. Location of the samples chosen from the state of Minas Gerais Soil Database to determine soil quality reference values for Unat and Th.

The UV-VIS molecular absorption spectrometry method (Savvin, 1961) was used to determine uranium and thorium concentration in the soil samples. This method was chosen because it is simple, accessible and inexpensive when compared to other uranium-determination methods. Pre-concentration and extraction steps were employed to increase the detection limit and analytical sensitivity.

The method was validated by means of IAEA reference 327, *Radionuclides in Soil*. Table 1 shows the methods' Minimum Detection Limits for U_{nat} and Th.

TABLE 1. MINIMUM DETECTION LIMITS OF THE METHODS

Radionuclide	LD (mg/L)
U_{nat}	0.021
Th	0.065

3. RESULTS AND DISCUSSION

3.1. U_{nat} and Th concentration results

Figure 4 shows the results for U_{nat} concentration distributed by yield class on the petrologic map; Figure 5 shows the results for Th.

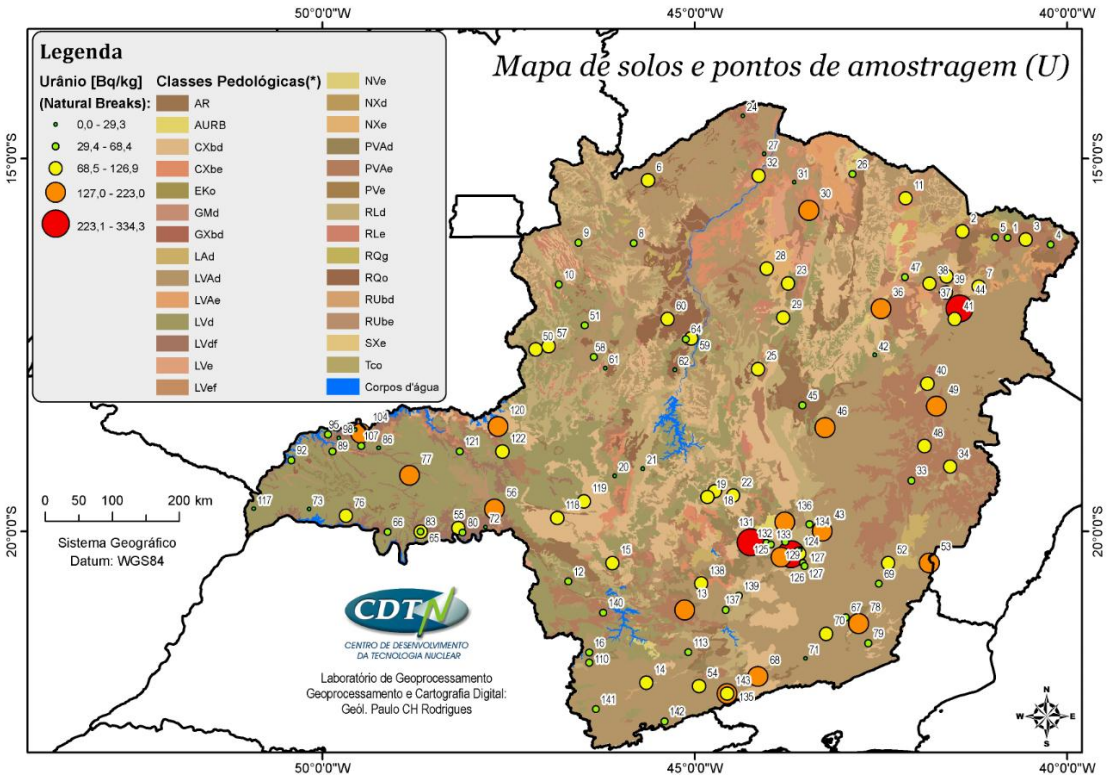
The Natural Breaks method was used to cluster numerical data into U_{nat} and Th concentration yield classes (Jenks, 1967). This method identifies the limits of each class. The Natural Breaks method is a data classification method that determines the best arrangements of values in different classes and seeks to reduce variance within classes and maximize variance between classes.

The concentration level variation obtained can be visualized from its spatial distribution on the map.

As can be seen in Figures 4 and 5, there is a large variation in U_{nat} and Th concentrations. From spatial observation, there seems to be no clear correlation between concentration levels for the two elements.

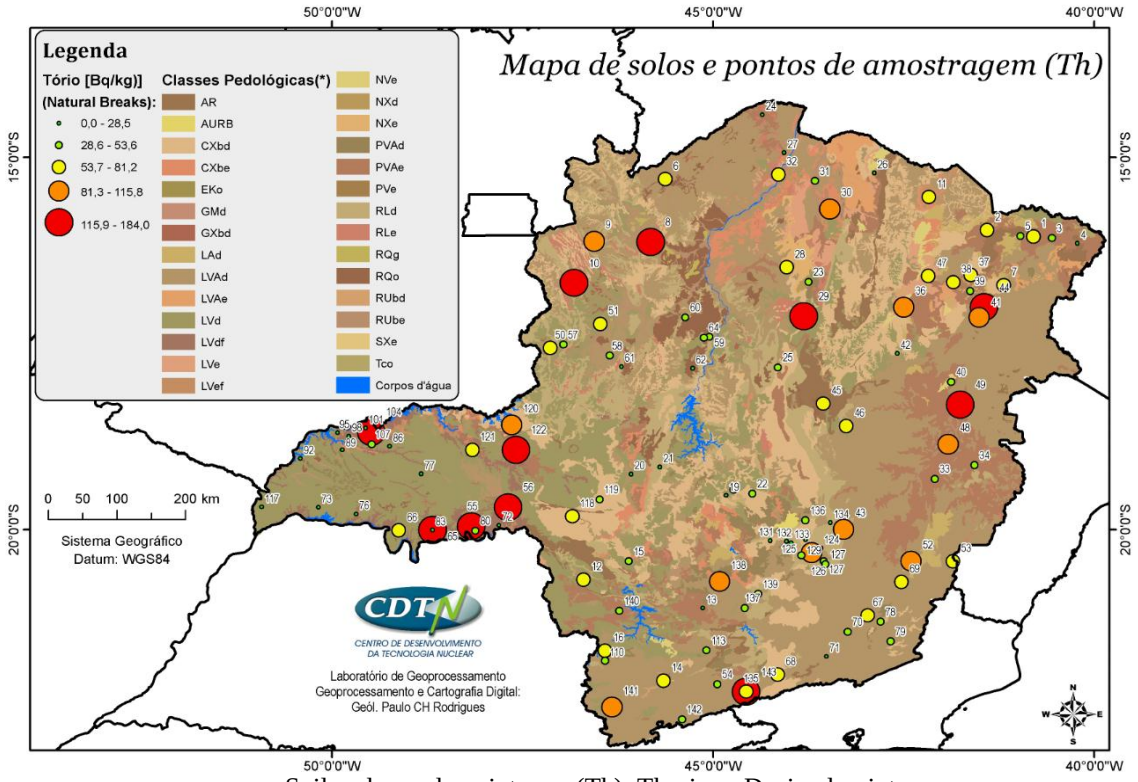
High U_{nat} and Th concentration values were found in regions where the elements are common, for example: the pegmatite provinces in the northeast of the state; the alkaline magmatic provinces of Poços de Caldas; the basic and alkaline intrusive in Tapira, Araxá and Salitre; the migmatite bands in the São João Del Rei and Itabirito regions; as well as the detrital sand accumulation at Rio das Mortes in São João Del Rei.

In order to isolate the most relevant and stable structures and standards identified by the set of object data, a descriptive analysis of the U_{nat} and Th concentration data set was carried out. The results are shown in Figures 6 and 7.



Soil and sample point map (U); Legend; Uranium; Petrologic class; Bodies of water; Geographical system; Geoprocessing laboratory; Geoprocessing and digital cartography; Decimal points in table, eg, 0.0 – 29.3

FIG. 4. Unat concentration distributed by Unat concentration level classes (Bq.kg^{-1}).



Soil and sample point map (Th); Thorium; Decimal points

FIG. 5. Th concentration distributed by Th concentration level classes (Bq.kg^{-1}).

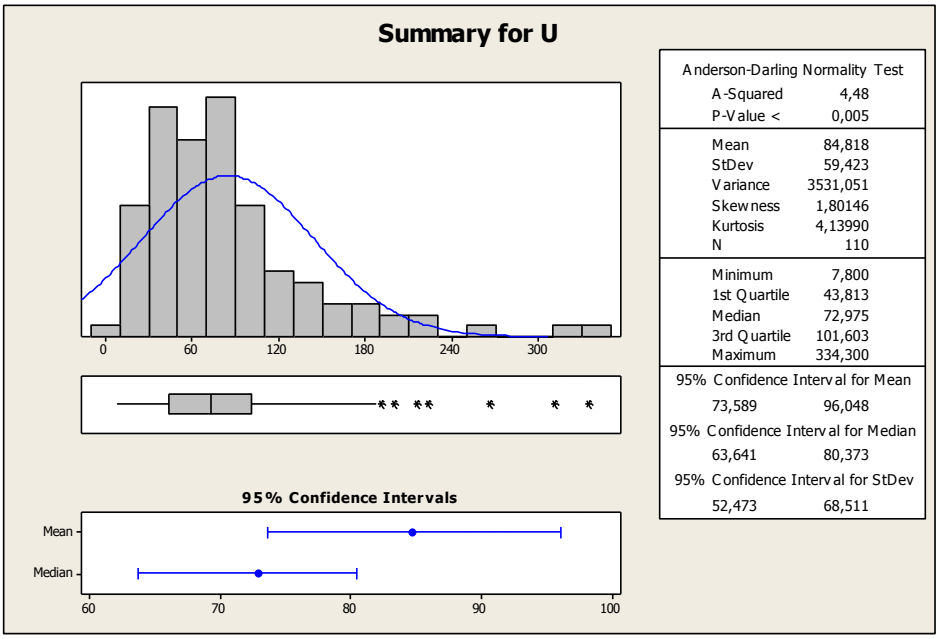


FIG. 6. Descriptive analysis of Unat results.

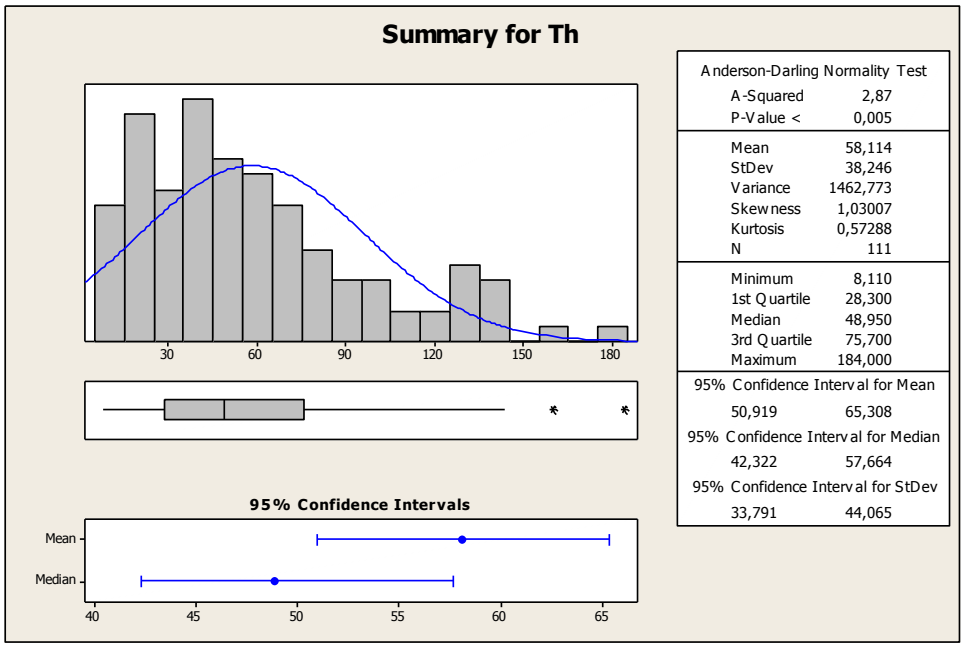


FIG. 7. Descriptive analysis of Th results.

3.2. Soil quality reference values

Soil quality reference values (QRV) for U-238 and Th-232 in soils in the state of Minas Gerais were based on statistical processing of the data applied in the two sets of concentration results (Table 2).

TABLE 2. QUALITY REFERENCE VALUES (QRV) FOR U_{nat} AND Th IN SOILS IN THE STATE OF MINAS GERAIS.

Radionuclide	Quality Reference Value ($Bq.kg^{-1}$)
U_{nat}	101.6
Th	75.7

4. CONCLUSIONS

QRVs were determined based on statistical processing of concentration results. Proposed values were 101.6 $Bq.kg^{-1}$ for U_{nat} and 75.7 $Bq.kg^{-1}$ for Th. These values are higher than both those found in the state of São Paulo (Peres, 2007) and world average concentration values of Th (26 $Bq.kg^{-1}$) and U-238 (35 $Bq.kg^{-1}$) found in soil (UNSCEAR, 2000), indicating the importance of the geological characteristics of each region.

Note that the highest concentration values for both U_{nat} and Th were seen in regions of Minas Gerais in which there are radioactive anomalies, such as: the pegmatite provinces in the northeast of the state; the alkaline magmatic provinces of Poços de Caldas; the basic and alkaline intrusive in Tapira, Araxá and Salitre; the migmatite bands in the São João Del Rei and Itabirito regions; as well as the detrital sand accumulation at Rio das Mortes in São João Del Rei.

Generally speaking, U_{nat} concentrations in the soil were higher than Th concentrations. This can be explained by the weathering process that most of the soils in the state of Minas Gerais have undergone as well as the chemical and geochemical characteristics of the two elements. In oxidizing surface environments, in general Th^{+4} remains unaltered and immobile, remaining nearer the rock of origin, while U^{+4} oxidizes to U^{+6}, forming uranyl ion $(UO_2)^{2+}$, which gives it great geochemical mobility.

In addition, it was verified that the greatest U_{nat} concentrations are located in the pegmatite deposits in Minas Gerais. The peak Th concentration values were found across the state. Note that U and Th behave differently. They are elements contained in accessory minerals that in part behave as resistates during weathering, that is, they can remain intact for great distances during transport. As a rule, U can even be mobilized because it appears in more soluble forms (uranyl ion in oxidizing conditions) and therefore can be leached, a situation that doesn't exist for Th (Ulbrich *et al*, 2009).

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CONTINUOUS MEASUREMENT OF THE RADON EXHALATION RATE OF SOIL IN BEIJING

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Abstract

The continuous measurement of the radon exhalation rate of soil is quite important for local radon level estimation. A continuous measurement system was developed and was applied to the measurement of the radon exhalation rate of soil in Beijing. The measurement results show that the average value of soil radon exhalation rate is 42.5 $mBq \cdot m^{-2} \cdot s^{-1}$ in spring with a variation of 13.1~110 $mBq \cdot m^{-2} \cdot s^{-1}$ and 20.8 $mBq \cdot m^{-2} \cdot s^{-1}$ in summer with a variation of 1.1~112 $mBq \cdot m^{-2} \cdot s^{-1}$, which is quite constant with former survey. The precipitation has a important influence on the radon exhalation rate, normally the radon exhalation rate increases after a small rainfall, but it decreases to nearly zero shortly after a huge rainfall(with a precipitation rate of 238.5$mm \cdot h^{-1}$). In May, the radon exhalation rate of soil in Beijing shows a clear periodic variation, which higher at noon and lower at midnight.

1. INTRODUCTION

Radon (^{222}Rn) and its short-lived decay products in the atmosphere are the most important contributors to human exposure from natural sources [1]. It is a gaseous radioactive product of the decay of the radium isotopes ^{226}Ra, which is present in all terrestrial materials. It could emanate from soil and building materials and enter the atmosphere, where it decays into a series of short-lived product, then inhaled into human lung and form inner exposure. For outdoors and most indoor environment, radon mainly comes from soil. So the measurement of radon exhalation rate of soil is quite important for estimating local radon level.

In the last decade, many measurement methods for soil radon exhalation rate have been designed. Charcoal methods, solid state nuclear track detectors as well as electrostatic method are used in radon exhalation rate measurement [2-4]. Those methods are wildly used in soil radon exhalation rate survey [5-6]. Due to its time-consuming of in-situ survey, only limited results were gotten. In China, Guo Qiuju et al first performed survey of radon exhalation rate from soil in several cities in China [7]. Wang Nanping et al also finished some survey of radon exhalation rate from soil in some sedimentary and granite areas in China [8].

All those results are mainly gotten by grasp method in a short time or passive method at one point for a long time, which could only be taken as an instantaneous value or average value for a long time. However, the physical process of radon exhalation is affected by many environmental factors such as temperature, humidity as well as water content and so on, which change with time [9]. The radon exhalation rate of soil could hardly be constant and it fluctuates with time in a large range. So sometimes we also need continuous measurement to point out its relationship with many environmental factors in more details.

In this paper, a continuous measurement system of radon exhalation rate was built after the work of Hosoda [10]. This measurement system was applied to continuous measurement of the radon exhalation rate of soil in Beijing in the last year. Some quite interesting results were found.

2. MATERIAL AND METHODS

2.1. Continuous measurement system of radon exhalation rate

The continuous measurement system of radon exhalation rate is shown in Figure 1. Lift is a picture of our system. Right is the sketch map of this system.

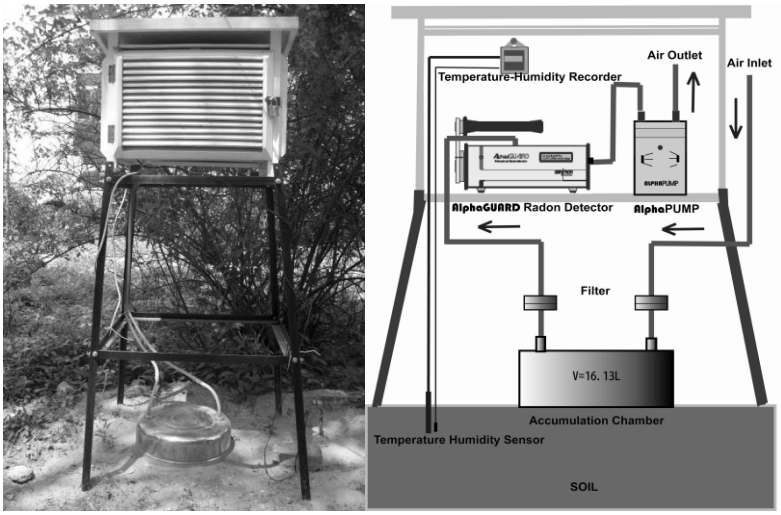

FIG.1. The continuous measurement system of radon exhalation rate.

This system is mainly constituted with an accumulation chamber with a volume of 16.13L, a sampling pump, a radon monitor and a temperature and humidity detector for soil. AlphaPUMP and AlphaGUARD PQ2000Pro which produced by Genitron Instruments GmbH company Germany is used as the pump and radon monitor in this system. Air nearly without radon which inhaled at 1.5m high at a flow rate of 0.3L/min takes turns passing through the accumulation chamber, the radon monitor and the pump. The soil temperature and humidity are recorded every 10min by M267221 detector (Midwest LTD Co. Beijing) with a relativity error of ±0.5℃ and ±3% RH respectively. The accumulation chamber is built by stainless material with an open face of 0.1075m2. The radon concentration in accumulation is recorded by AlphaGUARD PQ2000Pro at 10min intervals.

2.2. Theory of continuous measurement of radon exhalation rate

Some basic assumption should be made before the calculation of radon exhalation rate. First, soil seems to be uniform porous media and radon concentration distribution is thought to be even in the accumulation chamber. Second, due to the continuous sampling progress, we can easily assume that the radon exhalation and the ventilation are in quasi-equilibrium. Then the radon concentration in the chamber could be expressed as:

$$\frac{dA_{Rn}}{dt} = \frac{JS}{V} - \lambda_{Rn} A_{Rn} - \frac{v}{V} A_{Rn} \qquad (1)$$

where, J is radon exhalation rate (mBq·m^{-2}·s^{-1}), A_{Rn} is the radon concentration in the chamber (Bq·m^{-3}), λ_{Rn} is the radon decay constant, v is the sampling rate (L/min), V and S is the volume and surface area of the chamber (m^3 and m^2). Consider the quasi-equilibrium assumption, the left side is zero. Then the relationship between the radon exhalation rate and the radon concentration in the chamber could be expressed as follow:

$$J = \frac{(\lambda_{Rn} + v/V)VA_{Rn}}{S\left[1 - e^{-(\lambda_{Rn}+v/V)t}\right]} \qquad (2)$$

Because v/V is much larger than λ_{Rn} and for continuous measurement $e^{-(\lambda_{Rn}+v/V)t} \approx 0$, then the upper equation could be sampled as follow:

$$J = \frac{vA_{Rn}}{S} \qquad (3)$$

So we could figure out the radon exhalation rate of soil through continuous measurement of radon concentration in the accumulation chamber.

Due to AlphaGUARD's sensitivity and the lower level detection limit are 1 cpm at 20 Bq/m^3 and 2 Bq/m^3 respectively, the sensitivity of radon exhalation rate measurement system is 0.047 mBq·m^{-2}·s^{-1}/(Bq·m^{-3}) and the low level detection limit is 0.093 mBq·m^{-2}·s^{-1} considering 95% confidence limits.

3. RESULTS AND DISCUSSION

To measure the variety of radon exhalation rate of soil in Beijing, two seasons were chosen to do this field measurement. The continuous measurement was conducted during April 17 ~ May 23 and Jun 20 ~ Aug 1, 2012 in a small garden in Peking University. Those results are shown in the following figures.

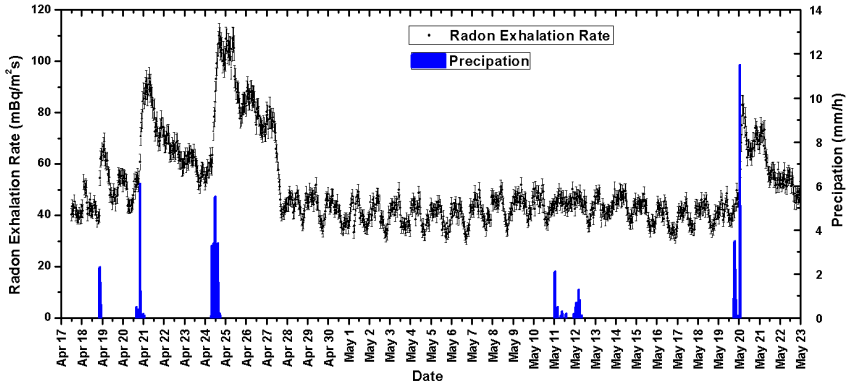

FIG. 2. Continuous measurement of radon exhalation rate in field from April 17 to May 23 (spring)

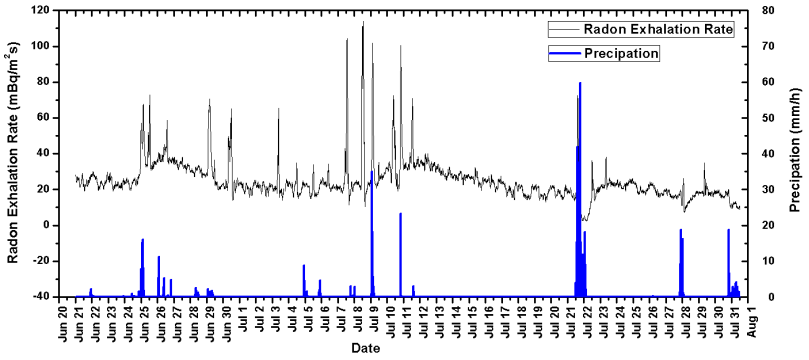

FIG. 3. Continuous measurement of radon exhalation rate in field from Jun 20 to Aug 1 (summer)

The dark point is radon exhalation rate of each hour, the blue histogram illustrate the rainfalls with different precipitation. According to continuous measurement, quite interesting results were found.

The radon exhalation rate change with the rainfall. Radon exhalation rate go up shortly after rain. This increasing seems have a positive relationship with the precipitation. The larger is the precipitation, the higher goes the radon exhalation rate. But a exception was in July 21, the radon exhalation rate fall nearly to zero after a high rain with a precipitation rate of 238.5mm·h^{-1}, which is the biggest rain in the last 60years in Beijing! Those phenomena could be expressed by the increasing of the soil humidity. In certain range, the exhalation rate goes up with the humidity. But after a huge rainfall, the pore space between soil gains is block totally by the water, then radon exhalation progress become quite harder.

The average radon exhalation rate seems larger in spring than the average value in the summer, the average value of soil radon exhalation rate is 42.5 mBq·m^{-2}·s^{-1} in spring with a variation of 13.1~110 mBq·m^{-2}·s^{-1} and 20.8 mBq·m^{-2}·s^{-1} in summer with a variation of 1.1~112 mBq·m^{-2}·s^{-1}. This difference might be due to the difference of soil temperature and soil humidity. The temperature in summer is higher than in spring which leads a decreasing of soil humidity in surface soil, then the radon emanation might be lower and exhalation rate might be smaller. Comparing the lasting time of radon exhalation rate increasing after a rainfall, we could also get a similar result. In summer, the high temperature leads the soil vaporizing much quicker than in the spring, then the soil humidity decreasing much quicker, which finally results in a quicker decreasing of radon exhalation rate after a rainfall.

Take out the measurement result between April 29 and May 19 for analysis, we could find another interesting phenomenon. This result is shown in figure 4 with soil temperature and humidity marking on it.

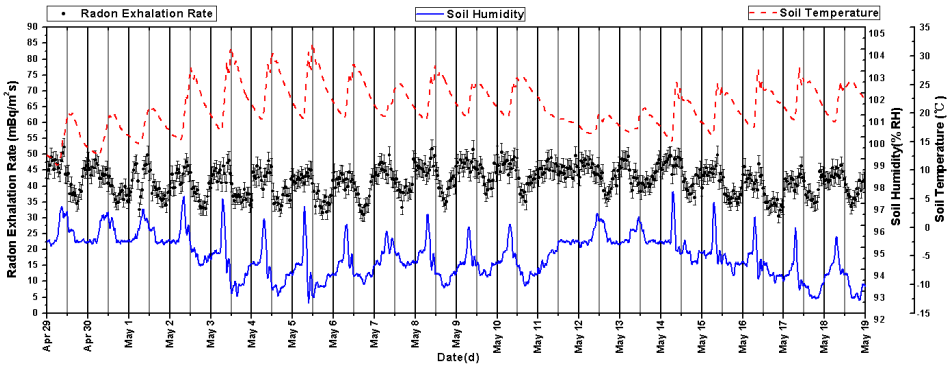

Fig.4. Measurement results of radon exhalation rate as well as soil temperature and humidity during April 29 ~ May 19

During April 29 to May 19, the radon exhalation rate presents periodic variation with higher value in the daylight and lower in the night. This might be relevant to the periodic soil temperature and soil humidity. In those days, the temperature in Beijing exist a periodic change and the sunshine lead a periodic change of soil humidity. Those finally lead the radon exhalation rate exist a periodic change with highest at 11:00 and lowest at nearly 18:00. Unfortunate, similar result was not found in summer, which might because the soil humidity did not change so large, so the radon exhalation rate only changed a litter and it's hard for detection.

4. CONCLUSION

A continuous measurement system was developed and was applied to the measurement of the radon exhalation rate of soil in Beijing during April 17 ~ May 23 and Jun 20 ~ Aug 1,

2012. The average value of soil radon exhalation rate in Beijing is 42.5 $mBq \cdot m^{-2} \cdot s^{-1}$ in spring with a variation of 13.1~110 $mBq \cdot m^{-2} \cdot s^{-1}$ and 20.8 $mBq \cdot m^{-2} \cdot s^{-1}$ in summer with a variation of 1.1~112 $mBq \cdot m^{-2} \cdot s^{-1}$, which is constant with Wang's survey [8].

The precipitation has a important influence on the radon exhalation rate, normally the radon exhalation rate increases after a small rainfall, but it decreases to nearly zero shortly after a huge rainfall(with a precipitation rate of 238.5$mm \cdot h^{-1}$). The radon exhalation rate of soil in Beijing shows a clearly periodic variation during April 29 to May 19, which higher at noon and lower at midnight.

The radon exhalation rate of soil shows a large variety after a small rainfall, which could increase shortly from 41.3±2.5 $mBq \cdot m^{-2} \cdot s^{-1}$ to nearly 94.5±4.3 $mBq \cdot m^{-2} \cdot s^{-1}$. 2~3 times increasing occurred in only 4hours! This phenomenon need be paid attention especially at uranium tailings where the radon exhalation rate might be quite high. And how the quick increasing of radon exhalation rate of soil might impact on the change of natural blackguard also need study.

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NATURAL RADIOACTIVITY IN SOME COMMERCIAL BOTTLED WATERS IN CAMEROON

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Abstract

The aim of this work was to check and determine the activity concentration of ^{40}K, ^{226}Ra and ^{228}Ra in some commercial bottled water used as drinking water in Cameroon by means of using High-Purity Germanium based gamma spectrometry techniques. The water samples were firstly chemically treated by adding nitric acid and then pre-concentrated further by evaporating them up to a certain level. The water residues were transferred to small cylindrical containers and were kept sealed in order to ensure secular equilibrium between U-238, Th-232 and their daughter products. The calculated activity concentration for ^{226}Ra (U-series) and ^{228}Ra (Th-series) were used to estimate the annual effective doses for different age groups infants (age 1-2 years), children (age 7-12 years) and adults (age ≥17years) by taking into account the ingested dose conversion factors obtained from the International Commission on Radiological Protection (ICRP) as well as their yearly average bottled water consumption. The evaluated annual effective dose due to life-long consumption of water for different group ages where below the recommended values by WHO, IAEA and UNSCEAR. The paper presents the overview of the technique used and the summary of findings from this survey.

1. INTRODUCTION

The mineral water industry in Cameroon is growing and the production of mineral bottled water in the country has also increased over years. In additional to health benefits of drinking mineral water due to the presence of several nutrients the presence of dissolved mineral radioactivity derived from mineralized rocks is also concerned [Nguyen Dinh Chau and Barbara Michalec; 2009]**.** The geological sources of natural mineral water are known as aquifers, which may be of different types and they vary greatly in terms of depth, compositions and their permeability [Elena Botezatu et al.; 2001]. The occurrence of these natural radionuclides in drinking water may pose a problem of internal health hazard when the uptake occurs during the ingestion process. Depending on the origin of groundwater, it might have high amount of the primordial radionuclide or radioactive elements such as uranium, thorium, potassium, and their radioactive decay products [UNSCEAR; 1988, Amrani; 2002]. Measurement of natural radioactivity levels in drinking water is relevant in assessing the contribution to environmental radiation health hazard due to water consumption [Amrani; 2002, Hess; 1985].

The natural radioactivity of bottled mineral waters has been a subject of numerous studies but some of them dealt with a part of natural radionuclide activity concentrations. For instance, the measurements of radium isotopes (^{228}Ra, ^{226}Ra), ^{222}Rn and ^{40}K concentrations in the bottled water for Northeastern Romania, Algeria, Austria and Poland were presented by Elena Botezatu et al.(2001), Amrami (2002), Wallner et al.(2007) and Nguyen et al.(2009). In Cameroon, studies related to natural radioactivity monitoring in bottled mineral water have

not been carried out so far. The aim of this work was to present a first overview of the radiological situation of all bottled mineral water produced and mostly consumed in Cameroon. This was achieved by first measuring the activity concentration of ^{226}Ra (from U-238 series), ^{228}Ra (from Th-232 series) and ^{40}K in several samples of bottled mineral waters by means of using high-purity germanium based gamma spectrometry techniques. The annual effective dose for different age groups resulting from consumption of these waters due to their natural radionuclides contents (^{226}Ra, ^{228}Ra and ^{40}K) were estimated since it represents an accurate evaluation of radiation dose received by the population due to intake process.

2. EXPERIMENTAL PROCEDURE

2.1. Sampling and sample preparation

In order to measure the natural radioactivity in minerals bottled water produced in Cameroon, a number of six (06) different mineral bottled waters were purchased from different markets in the Central Region of Cameroon. The collected mineral bottled waters are mostly distributed and consumed by the population living in the majority cities of Cameroon.

The method adopted for the determination of environmental natural radioactivity level required relatively large volume of water up to 20 L in total per each mineral bottled water type. Concentration has been carried out by gradual evaporation of each water sample in an oven at a temperature of 70^0 C and ending up with a volume of 125 ml residue out of 20L of initial mineral water. To prevent adherence of the radionuclides on container walls drops of nitric acid (HNO_3) were added into the sample. After being evaporated, the residues were then transferred into a thoroughly washed and dried 120 mL cylindrical container and hermetically sealed with a plastic tape to ensure air tightness and kept for 30 days to establish secular equilibrium between ^{238}U, ^{232}Th and their daughter products [Alam et al. 1999].

2.2. Experimental setup

After the in-growth period, each water sample was subjected to a low background gamma-ray spectrometer consisting of Broad Energy Germanium Detector (BE6530) manufactured by Canberra Industries. As reported by the manufacture it has a resolution of 0.5 keV at 5.9 keV of ^{55}Fe, 0.75 keV at 122 keV of ^{57}Co and 2.2 keV at 1332 keV of ^{60}Co, respectively. To prevent high background counts due to external radioactive sources, with the intention to reduce the counting time and improve the detection limit, the detector is placed in a low-level Canberra Model 747 lead shield having a thickness of 10 cm. Furthermore, a Multiport II Multichannel Analyzer (MCA) was used to generate energy distributions of the radioactive samples. In order to obtain a statistically good computational net peak area, each sample was measured for 86400 s. The background has been evaluated before running the samples and it was measured for 172800 s.

The efficiency calibration files have been generated by means of using Canberra designed LabSOCS (Laboratory Sourceless Object Counting System) mathematical calibration software that incorporates the characterization information of a BEGe6530 high-pure germanium detector. When generating the efficiency calibration file, the LabSOCS calibration software is taking into account all parameters related to these measurements including dimensions of the counting geometries, physical and chemical compositions as well as the distance source-to-detector end-cap. To validate the accuracy of the LabSOCS mathematical efficiency calibration, some test have been conducted comparing the LabSOCS generated efficiency results with the empirical peak efficiency for a ^{60}Co point source positioned at a distance of 25cm from the detector end-cap. The calculated results were in good agreement showing that differences between mathematical and empirical peak

efficiencies are within 3-5%. To avoid error due to extrapolating the curve, the calibration curve is plotted in dual mode with cross-over energy at 165.85 keV (^{139}Ce). A fourth order polynomial equation was the best fit for the lower and higher energy curve and the fitting equations are the following:

For the energy less than 165.85 keV the best fit is:

$$- \ln(Eff) = -1.193E02 + 1.025E02 * \ln(E) - 3.399E01 * \ln(E)^2 + 5.046E00 * \ln(E)^3 - 2.831E-01 * \ln(E)^4 \quad (1)$$

For the energy greater than 165.85 keV the best fit is:

$$- \ln(Eff) = -4.851E01 + 3.057E02 * \ln(E) - 7.331E00 * \ln(E)^2 + 7.550E-01 * \ln(E)^3 - 2.893E-02 * \ln(E)^4 \quad (2)$$

Genie 2000, Gamma Acquisition V.3.2.1 and Gamma Analysis Software, V.3.2.3 was used for data acquisition and analysis [Genie^{TM} 2000 Spectroscopy Software]. Following the sample analysis, the specific activity concentration for each identified radionuclide has been reported in unit of Becquerel per liter (Bq/L). Furthermore the software is taking care to automatically check and perform the interference correction and calculate also the weighted mean for those radionuclide that emit more than one gamma ray. In addition, CANBERRA's patented Cascade Summing Correction algorithms allows us to correct the nuclide activities for losses or gains due to the presence of cascade summing effect related to these close counting geometries. Assuming secular equilibrium between ^{228}Ra (^{232}Th-series), ^{226}Ra (^{238}U-series) and their decay products the activity of the radionuclides under study has been determined as following:

- ^{226}Ra concentration is calculated based on the gamma ray transitions of ^{214}Pb
- ^{228}Ra concentration is calculated based on the gamma ray transitions of ^{208}Tl and ^{228}Ac
- ^{40}K was directly determined using 1460.83 keV (10.7%) gamma-ray transition.

3. ANNUAL EFFECTIVE DOSE

The annual effective dose (mSv/y) from ingestion of radionuclide in water samples was estimated on the basis of the mean activity concentrations of the radionuclides. This was done for different age categories. Assumptions on the rate of ingestion of bottled mineral water were made. In this paper, the intake rates based on a US national survey [Ershow et al., 1989] are used; 0.6 L/day and 0.8 L/day for infants (age 1-2 year) and children (age 7-12 years) respectively, and 1.3 L/day for adults (age < 17 years). The recent dose conversion factors for ^{226}Ra and ^{228}Ra ingestion reported by the International Commission on Radiological Protection [ICRP, 1996] for three age categories: 1-2 year, 7-12 years and < 17 years were used for calculations. The annual effective dose of the water ($H_{ing}(W)$) was computed by the following formula (ICRP, 1996):

$$H_{Ing}(w) = \sum_{i=1}^{2} DCF_{Ing}(i) \times A_{Spi} \times I \quad (3)$$

where: $DCF_{ing}(i)$ - Dose conversion coefficients of a particular radionuclide *i-th* in Sv/Bq for a particular age categorie; Asp_i - Specific activity concentrations of radionuclide i-th in the water samples in Bq/L and I - Radionuclide intake in litres per year for each age category.

4. RESULTS AND DISCUSSIONS

The activity concentration of ^{40}K, ^{226}Ra and ^{228}Ra in bottled mineral waters used as drinking water in Cameroon as well as the annual effective dose for different age categories are presented below on Table 1.

TABLE 1. ACTIVITY CONCENTRATION (mBq/L) OF ^{40}K, ^{226}Ra AND ^{228}Ra IN WATER SAMPLES AND THE ANNUAL EFFECTIVE DOSE (mSv/y) FOR DIFFERENT AGE CATEGORIES.

Sample		Activity concentration (mBq/L)			Annual eff. dose (mSv/y)		
ID	Sample name	^{40}K	^{226}Ra	^{228}Ra	Infants	Children	Adults
BW1	SUPERMONT	67.90±14.7	10.40±2.70	23.5±4.81	0.032	0.029	0.009
BW2	SEMME	153±67.10	29.3±4.63	10.2±9.07	0.019	0.018	0.007
BW3	MADIBA	156±67.30	38.2±6.01	121±8.99	0.159	0.147	0.045
BW4	LE FEBE	87.7±26.20	10.40±6.91	5.12±1.53	0.009	0.008	0.003
BW5	PURA	6.69±1.67	6.98±1.72	9.92±1.94	0.014	0.013	0.004
BW6	TANGUI	123±66.70	38.2±5.71	28.1±7.28	0.043	0.041	0.014
Average		**107.30**	**22.25**	**35.96**	**0.050**	**0.046**	**0.015**

As seen, the activity value of ^{40}K concentration varied from 6.69±1.67 to156±67.30 mBq/L with an average value of 107.1 mBq/L. The specific activity concentration of ^{226}Ra ranged from 6.98±1.72 to 38.2±5.71 mBq/L with an average value of 22.25 mBq/L. The activity concentration of ^{228}Ra varied between 5.12±1.53 and 28.10±7.28 mBq/L with an average value of 35.96 mBq/L. This variation in activity concentration of ^{40}K, ^{226}Ra and ^{228}Ra observed in these samples indicate that the origins of these waters are not the same and that they come from different depths and pass through different geological layers. Likewise, this irregular distribution of activity concentrations of the selected nuclides in these minerals water may depend on their contents in rocks or solid aquifers in the areas where the water is located and the residence time of waters/rocks-soils in contact as well. On the other hand, these variations in activity concentration of the selected radionuclides strongly depend on the physical and chemical properties of each water sample.

For comparison purposes, the results for ^{40}K, ^{226}Ra and ^{228}Ra in the present work and the reported values for other countries obtained from the literature of natural radioactivity in water are shown below on Table 2. When comparing these data, the activity concentration of ^{40}K, ^{226}Ra and ^{228}Ra in water samples reported by many authors varies from one country to another and some differences are clearly seen. For instance, the average activities concentrations of ^{226}Ra are found to occur over a wide range from 0.026 to 7.15±6.95 Bq/L. This wide range of ^{226}Ra concentration is in relation to the geological structure and to the characteristics of the areas.

The average value of ^{40}K (0.107 Bq/L) in the present study is comparatively higher than the average value obtained in Italy (Milano) (0.054 Bq/L) by Roscuni (2003). In the same way the average concentration of ^{228}Ra (0.036 Bq/L) is comparatively lower than those published values selected from the literature. The values obtained in this study were thus compared favourably with the reported average values published by other authors selected from the worldwide investigation of natural radioactivity in different water types.

The activity concentrations of ^{40}K, ^{226}Ra and ^{228}Ra obtained in the present study were also compared with the guideline activity concentration values of the selected radionuclides in drinking water recommended by the WHO and other data obtained from IAEA. This comparison showed that our results were found to be below the guidelines values of the selected radionuclides.

TABLE 2. COMPARISON OF MEAN CONCENTRATIONS OF NATURAL RADIONUCLIDES IN MINERAL WATER WITH PREVIOUS MEASUREMENTS PERFORMED IN DIFFERENT COUNTRIES

Radionuclides	Country	Number of sample	Mean concentration (Bq/L)	Reference
^{40}K	Nigeria(Akure)	20	13.54±10.18[a]	[Ajayi et al.(2007)]
	Nigeria	15	19.09[c]	[Ajayi et al.(2009)]
	Algeria	08	1.0	[Amrani(2002)]
	Bangladesh	30	4.16[c]	[Alam(1999)]
	Italy(Milano)	—	0.052[b]	[Rusconi et al.(2003)]
	Cameroon	06	0.107	[Present study]
^{226}Ra	Nigeria(Akure)	20	7.15±6.95[a]	[Ajayi et al.(2007)]
	Nigeria	15	7.75[c]	[Ajayi et al.(2009)]
	Algeria	08	0.026	[Amrani(2002)]
	Argentina	25	4.4	[Bomben(1996)]
	Cameroon	06	0.022	[Present study]
^{228}Ra	Nigeria(Akure)	20	9.86±12.89[a]	[Ajayi et al.(2007)]
	Nigeria	15	2.03[c]	[Ajayi et al.(2009)]
	Cameroon	06	0.036	Present study

[a]well water, [b]tap water, [c]drinking sachet water

The annual effective dose due to ingestion of the monitored bottled water was estimated for different age groups including infants, children and adults; considering only the ingestion of ^{226}Ra and ^{228}Ra as shown in Table 1. Potassium (^{40}K) values were not considered during the calculation of the radiation dose because the absorption of the essential potassium element is under homeostatic control and takes place mainly from ingested food. Thus, the potassium contribution to the dose from ingestion in water, with its relatively low dose conversion factor (5×10^{-9}Sv/Bq) will be much less than of many other radionuclides. The calculated radiation dose for different age groups were ranged from 0.009 to 0.159 mSv/year for infants, between 0.008 and 0.147mSv/year for children, and varied from 0.003 to 0.045 mSv/year for adults with average values of 0.050, 0.046 and 0.015mSv/year, respectively. It can be seen that radiation dose received by infants are relatively higher than that received for children and adults.

Following the WHO, IAEA and UNSCEAR [WHO, 2004; IAEA, 2002; UNSCEAR, 2000] recommendations, the recommended reference levels of the effective dose for infants, children and adults corresponding to one year consumption of drinking water are 0.26, 0.2 and 0.1mSv/year, respectively. The doses obtained in the present study are low than the recommended reference level and from radiation protection point of view, life-long consumption of these investigated bottled mineral waters may not cause any significant radiological health risk.

5. CONCLUSIONS

This work presents the first detailed radioactivity monitoring campaign in some bottled mineral waters produced and available at local markets in Cameroon. The natural

radioactivity level of ^{40}K, ^{226}Ra and ^{228}Ra have been measured in several bottled mineral water produced in Cameroon by using high-pure germanium based gamma spectroscopy techniques. The activity profiles of the radionuclides have clearly showed low activity concentrations across the monitored bottled mineral waters. This may explain the low level of natural radioactivity in bedrocks system in the areas where the water in coming from. Based on the results obtained from this survey, we can conclude that Cameroon bottled mineral waters that were subject of this study are suitable for human consumption and do not present any significant radiological risk related to its life-long consumption. Furthermore, the research findings showed an important role in helping us to gain additional knowledge related to both radioecology and environmental radioactivity monitoring issues.

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MEASUREMENT OF THE CONCENTRATIONS OF ^{222}Rn IN SOIL AND AIR OF THE BUILDING OF THE NATIONAL INSURANCE COMPANY OF BAGHDAD PROVINCE AND THE SURROUNDING AREAS AND ESTIMATE THE HEALTH DANGERS

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Abstract

Research includes finding concentrations of radon (^{222}Rn) and its decay results inside and outside the National Insurance Company building and the surrounding sites , the door of the east - the city of Baghdad for a month, using nuclear track detectors CR-39. The company consists of eight floors, some busy and some deserted. Through the results obtained the value of radon concentrations in the air of all sites of the building at variable rates and was the highest concentration in the ground floor - the basement of the building and was (266.999 Bq/m^3) and the result is high compared with the limit. There are two reasons for this result first to the lack of ventilation completely in the basement and secondly increasing concentrations of radon gas in low places and the old and less concentration found on the seventh floor - the secretarial (27.293 Bq/m^3). The concentrations of radon (^{222}Rn) in soil was within this limit except the dust that was collected from the dust accumulated on the fourth floor - and the thrusters (171.461 Bq/m^3) and where the place is deserted, and with virtually no ventilation. This increase in concentration back to the walls of the building is the main source for the generation of radon inside, it was found that construction materials have played an important role in increasing concentrations of radon inside buildings as well as the old age of the building.

1. INTRODUCTION

Conducted extensive studies in the field of nuclear physics and radiation spectra of background study, as it is gaining an important aspect of studies to protect the environment from pollution and natural radioactivity monitoring and exploring the possibility of the presence of radioactive materials. Where is the study background radiation character important to distinguish between isotopes found in nature and quantity of outputs nuclear tests [1].

All living beings are exposed to certain amount of natural radiation in the form of particles and radiation, including cosmic rays coming from space and from background natural radiation, especially natural uranium, half-life (4.49x109 yr) which containing isotopes (uranium-238) (% 99.29) and (uranium-235) (% 0.71), these elements decay through a series of the decays which emits alpha particles and beta particles and gamma rays to reach to the stable element lead[2]. The commonly used building materials (rocks based) contain small amount of isotope of natural uranium and thorium series and cause emanation of isotopes radon (Rn-222) half-life (3.82 d) and thoron (Rn-220) half-life (56 sec) [3]. Accordingly, the various buildings and places such as mines existing underground tunnels containing these natural isotopes that give small amounts of external exposure to gamma rays and alpha particles. The greatest risk comes from radon exposure and thoron through inhalation of these isotopes that cause lung cancer [4].

There exists several technique to determine concentrations of uranium and its daughters in environmental matrices. Solid State Nuclear Track Detectors (SSNTDs) [6], being simple and not needing complex devices and high efficiency to detect low concentrations uranium and progeny are commonly used [5].

In most types of rocks the concentrations are scarce, however, higher levels are found in igneous rocks and volcanic Alkranayat, black shales and phosphate rock and other metamorphic rocks derived from these rock types [7].

Techniques used to calculate the concentrations of radioactive materials within the residential buildings are Solid State Nuclear Track Detectors (SSNTD), as the use of this technique has a way distinctive being simple and easy to use and high-sensitivity detection of alpha particles[8]. Detectors effects are electrically insulating solids, resistivity ranges between (1020-106 ohm.cm), Upon passage of radiation (charged particles such as protons, alpha particles and fission fragments) through these detectors where narrow paths are generated in the form of the effects of thin, called the latent effects (Latent Tracks) [9].

National Insurance Company and its location: The Company building is in the eastern door - the center of the capital Baghdad and consists of:

1. Eight floors – several of them are mostly busy, others empty, as noted by the Working Group of the this company whose halls and corridors are very wide and outdated and poor air exchange/ventilation and some of the floors are full of dust.
2. There are sites for storage and other pushes, generators and a basement and there is no ventilation.
3. The fourth floor of the building subjected to bombings and arson.
4. Water tanks on the eighth floor - a surface old, rusted and need maintenance and renewal.
5. All rooms occupied by employees are large halls and staff sits like classroom and there are no breakers and unventilated.

National Insurance Company is working on the provision of the insurance, which is defined as a way to compensate the individual for financial loss which resolved as a result of the occurrence of a particular risk by distributing this loss on a wide range of individuals have all exposed to this risk under the prior agreement.

2. METHODOLOGY

Team began its work on 8/8/2010 in the National Insurance Company, located in the eastern door, where meetings are held with some of the workers in the company.

2.1. First track - (work site):

The work was divided into two groups, as follows:

(a) The first group had identified sites at the company and its surrounding sites and then the deployment of nuclear track detectors type CR-39, both inside and outside these sites and left for a period of one month in order to identify and measure the levels of radon in the air.
(b) The second group has collected samples from the surface of the soil from the same sites of the company and its surroundings and put them inside plastic cans especially installed in down its cover the nuclear track detectors type CR-39 and ceded for a period of one month in order to identify and measure the levels of radon in the soil

The Working Group collected these detectors after a period of one month from the date of posting in selected sites for inspection that have been selected according to the available means and information on the air exchange rates as well as from busy location for the purpose of comparison.

2.2. Second track - (work of laboratory):

The nuclear track detectors were collected from the sites identified for the study after a month, and processed using the chemical etching by sodium hydroxide solution (NaOH) with 6.25N at temperature 60°C for six hours, followed by calculation of the effects density ρ_x of unknown samples by optical microscopy.

As for the calibration, detector CR-39 has been put inside a standard can (radon monitor) and suspended inside a room size (21m ³) by irradiating with the radon from standard radium (^{226}Ra) source having the activity of 5μCi. The exposed films were processed in a similar manner for different periods of time. Calibration graphs were prepared by drawing relationship between the average time of exposure to radon (Ex) units ((Bq / m³/d) and density effects ρ_x for unknown samples units (Track / mm²) and the linear relationship as in Figure 1.

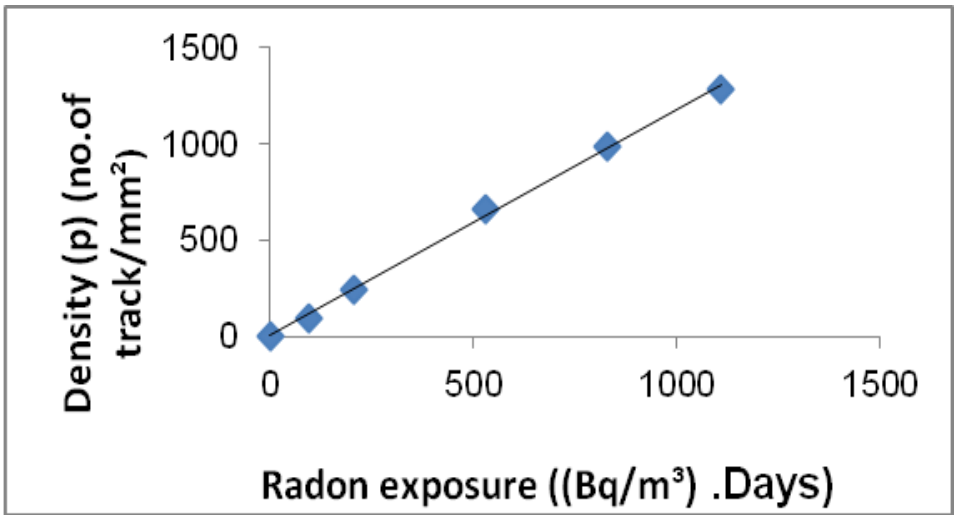

FIG. 1. Calibration graph.

The radon exposure at unknown samples E_X was calculated by the following equation:

$$E_x/\rho_x = E_s/\rho_s \quad (1)$$

$$E_x = \rho_x / \text{slope} \quad (2)$$

and the concentration at unknown samples C_x was estimated by the following equation [10]:

$$C_x = E_x / te \quad (3)$$

Where, te total time of exposure of the film to radon gas (days).

The dose (D_o) is estimated by using the following equation [11-12]:

$$D_o = C_x * df * te \quad (4)$$

Where

D_o the dose (Sv),
C_x the main concentrations (Bq/m^3),
df the conversion factor, ^{226}Ra and ^{222}Rn (4.55×10^{-8} $Sv.m^2/Bq.y$) [13-14],
te the exposure time 30 days= 0.08 y,

3. RESULTS AND DISCUSSION

The concentration of the radon gas and the resulting dose to all of the samples of air and soil at various chosen locations in the National Insurance Company building and its surrounding sites have been estimated using a special computer program and the results are shown in Table 1 and Table 2.

The calculated concentration and the exposure showed linear relationship as shown in Figure 1. All the results were within the national allowed limit and the highest concentration was observed in the ground floor basement of the building (267 Bq/L) with the resulting dose of 100.93 x 10^{-8} Sv. The lower concentration was found on the seventh floor - the secretarial office (27 Bq/L) with the dose of 10.32 x 10^{-8} Sv as in Figure 2.

Table 1 also shows concentration and exposure in the air to radon gas. The measuring results of the concentration and exposure in the soil to the radon gas is provided in Table 2.

The concentrations of radon (^{222}Rn) in soil was lower except on the fourth floor and the thrusters (172 Bq/m^3) with the exposure of 65 x 10^{-8} Sv. Lower concentrations were found in the intermediate alley nearly 100 Bq/m^3 with the exposure of 387 x 10^{-8} Sv as shown in Figure 3.

TABLE 1 RADON CONCENTRATION IN AIR

No	Floor	Location	Density effects (No. of tracks /mm^2) x 10^{+4}	Concentration (Bq/L)	Dose estimate x 10^{-8} (Sv)
1	Ground floor	Basement-machines	32.040	266.999	100.927
2	First	Albedala	9.398	78.320	29.605
3	Second	Hall of reading	5.269	43.907	16.597
		Library	7.832	65.266	24.671
4	Third	Nursery school	5.696	47.467	17.943
		The drawer	8.544	71.200	26.914
		Store of buildup	9.826	81.880	30.951
5	Fourth	Branch of sea	4.842	40.347	15.251
		Iraq box	7.974	66.453	25.119
		Baghdad branch	6.693	55.773	21.082
6	Fifth	Branch of arson	6.978	58.146	21.979
		Branch of assuring iraqi	5.697	47.467	17.943
7	Sixth	Slings	8.687	72.387	27.362
		Computers area	3.987	33.227	12.560
8	Seventh	Intermediate alley	7.405	61.706	23.325
		Room of managing	3.987	33.227	12.560
		Secretarial	3.275	27.293	10.317
		The archive dept.	6.408	53.400	20.185
9	Eight	Cafeteria	4.557	37.973	14.374

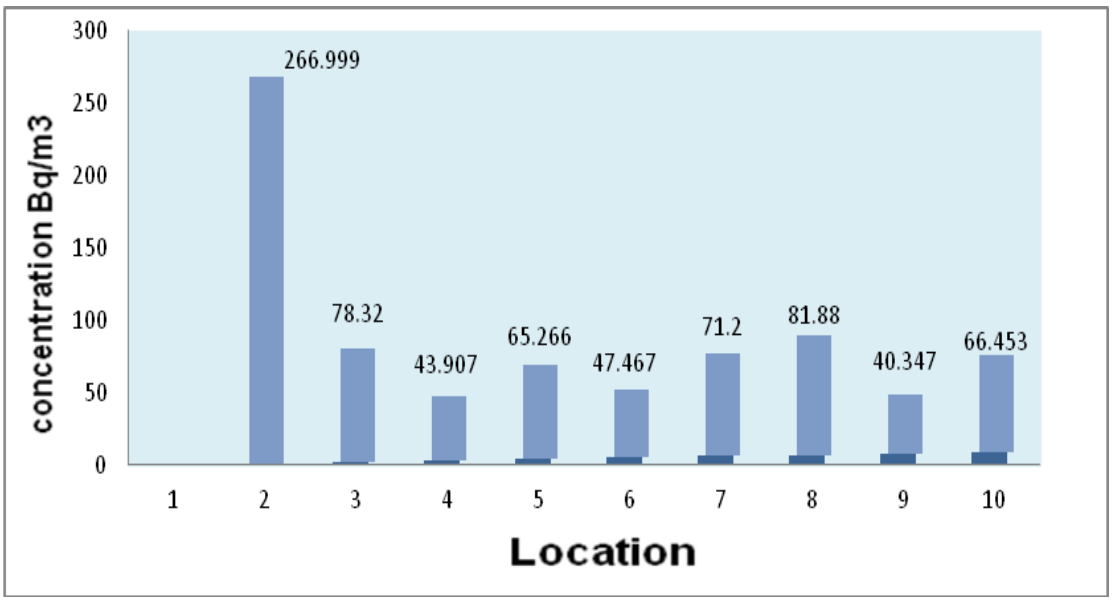

FIG.2 Concentration of radon gas in the air

TABLE 2 RADON CONCENTRATIONS IN SOIL GAS

No.	Location	Density effects (No. of tracks /mm^2)	Radon concentration (Bq/m^3)	Dose 10^{-8} (Sv)
1	common street	39.909	125.722	46.523
2	Fourth floor	54.422	171.461	64.813
3	Al-grach	40.980	127.315	48.331
4	Hind side - Out of building	47.794	133.030	51.491
5	Intermediate alley	31.746	100.019	37.807

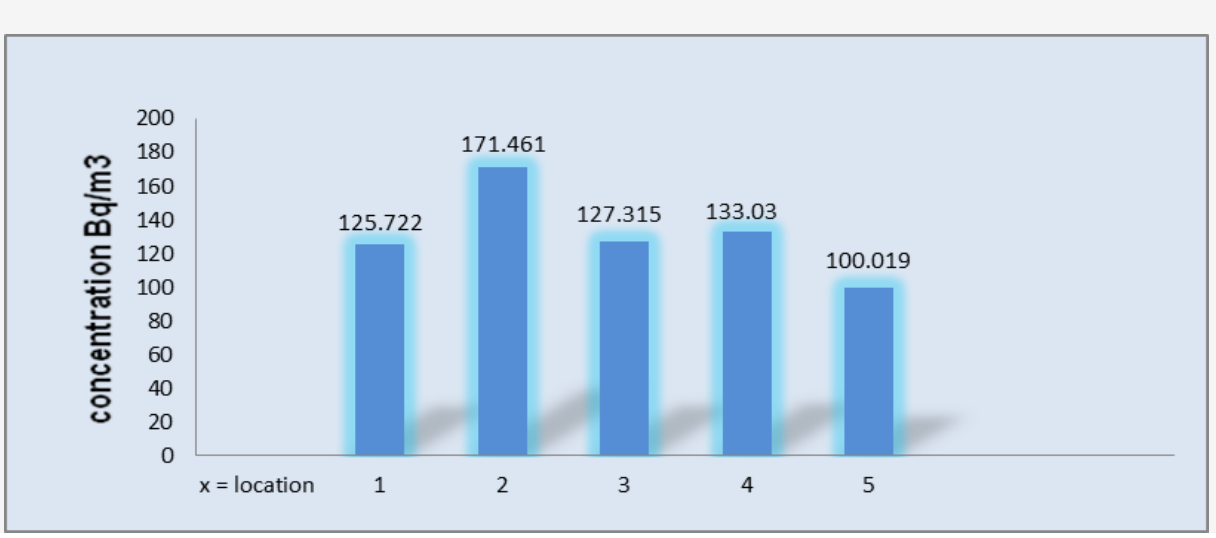

FIG. 3 Concentrations of radon gas in the soil.

4. CONCLUSIONS

From the results obtained the value of radon concentrations in the air of all sites of the building are at varying rates and the highest concentration was observed in the ground floor - the basement of the building. The result is high compared with the limit and there are two reasons for this, first to the lack of ventilation completely in the basement increasing the concentrations build-up and secondly increasing concentrations of radon gas in low places and the old building parts. Lowest concentration was found on the seventh floor - the secretarial (28 Bq/m^3). The concentrations of radon (^{222}Rn) in soil was all results within the limit except the dust that was collected from the dust accumulated on the fourth floor - and the thrusters (172 Bq/m^3) and where the place is deserted, and with virtually no ventilation. This increase in concentration back to the walls of the building is the main source for the generation of radon inside. It was also found that construction materials have played an important role in increasing concentrations of radon inside buildings as well as the old age of the building.

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NORM MEASUREMENTS IN SOIL FROM DUKHAN OIL FIELD AND SLUDGE SAMPLES FROM OFFSHORE AT QATAR STATE USING HIGH-RESOLUTION GAMMA-RAY SPECTROMETRY

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Abstract

The main aim of this work is to measure the activity concentrations of Naturally Occurring radioactive Materials (NORM) produced in the extraction and processes of oil industry. The analyses of NORM waste give available information for guidelines concerning radiation protection. Recently NORM is subjected to restricted regulation issued by the high legal authority of Qatar state. Twenty five samples of soil from Dukhan onshore oil field and 10 sludge samples collected from 2 offshore fields in the Qatar state. The activity concentrations of 226Ra, ^{232}Th and ^{40}K have been measured by gamma-ray spectroscopy. Radiation hazard index (H_{ex}), Radium equivalent activity (Ra_{eq}), and the absorbed dose (D) were calculated to assess the radiological risk for each samples. 22 of soil samples indicate that the soil sample are normal and represent the natural background. Three of soil samples have high activity concentration of Ra-226 which is likely to be result of contamination by NORM. The Ra-226 concentrations of sludge samples, was greater than 1100Bq/kg the exempted values set by the Quatrain regulation. The (H_{ex}), (Ra_{eq}), and (D) values for these samples are higer than the published maximum permissible.

1. INTRODUCTION

Various industrial processes of oil and gas extracting and processing operations lead to enhanced natural radioactivity. Since Ra-226 is slightly soluble, it mobilizes from subsurface formation in the liquid phases and transported to the surface in the produced water. As the produced water is brought to the surface, some of the dissolved radium precipitates out in solid. The primary radionuclides of concern in oil and gas stream are Ra-226, Th-232, and K-40 which are responsible for most of the external exposure in such facilities [1].

Radium solubility and mobility depend on the salinity of the formation water; higher salinity is aligned with greater solubility [2].

2. MATERIAL AND EXPERIMENTAL ARRANGEMENTS

2.1. Samples locations

Twenty five samples of soil from Dukhan at north west of coast which is a big onshore oil field in the state of Qatar. It comprise three reservoirs, the oldest one was AL- Khatiyah which started the oil production at 1947 till now. The other two sectors are Fahahil starting producing oil at 1954 followed by Jaleha in 1955.

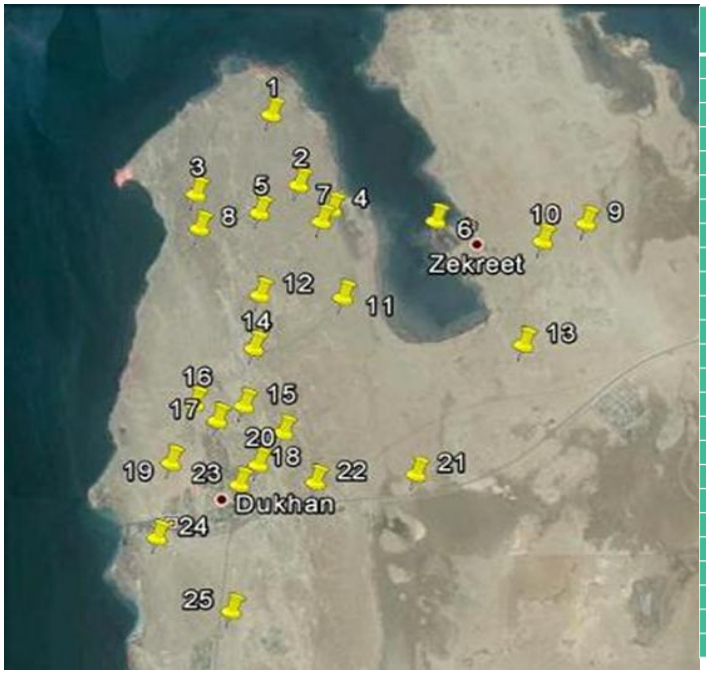
The most important production of oil in the state of Qatar are the offshore oil fields which are operated by Qatar Petroleum (QP), sharing with other international oil companies according to the exploration and development sharing agreements (DPSA).

Ten samples of sludge were collected from separation tanks from two offshore fields, the first one the field PS and the second location were from Al Shaheen field.

2.2. Samples preparation

Twenty five samples of soil from Dukhan field were collected from random points located near the oil well head. *FIG.1* shows the values using Back-Back detector. Each

sample 1-2 kg was then transferred to a 2 mm sieve and kept into sealed labeled polyethylene bags.



Samp ID	X- coordinate	y- coordinate
1	25,513939	50,794430
2	25496432	50801298
3	25494108	50775719
4	25490234	50809536
5	25489459	50791512
6	25487445	50835457
7	25487290	50806961
8	25485585	50776615
9	25486825	50872879
10	25482331	50862064
11	25468384	50812283
12	25469004	50791683
13	25456605	50857258
14	25455675	50790138
15	25441414	50787649
16	25441879	50775375
17	25437694	50781040
18	25434749	50797434
19	25427230	50769453
20	25426765	50791254
21	25424362	50830479
22	25422346	50805416
23	25421804	50786576
24	25408547	50766018
25	25390249	50784473

FIG. 1. Samples location on Qatar map.

The samples were dried to get rid of any significant moisture content using an oven set at 353 K for 12 hours. Each soil sample was packed and sealed in an airtight PVC Marinelli beaker. The beakers were stored for 30 days before counting in order to reach secular equilibrium between the daughter products of radon (^{222}Ra), (^{220}Ra) and their short lived decay products.

2.3. Gamma ray system calibration

Measurements were conducted by gamma ray spectroscopy system equipped with Canberra n-type detector of high-purity germanium (HPGe).

The detector has a resolution of 2.5 keV and relative efficiency of 30% for 1.332 MeV gamma energy of ^{60}Co. The output of the detector is connected to PC. The spectral data is analyzed using the "Genie 2000 Gamma Analysis Software package."

The absolute photo-peak efficiency calibration of the system were carried out using standard source of ^{152}Eu in Marinelli beaker because of its suitable half-life and the wide range of gamma ray energies produced during its decay process .

The specific radioactivities of 226Ra under the peak energy of 186.21 keV are the sum of ^{235}U under the peak energy of 185.7 keV and peak energy of ^{226}Ra alone. Thus the radioactivity of ^{226}Ra alone calculated by subtracting the specific radioactivity of ^{235}U which is calculated from the peak energy of 143.76 keV from the total specific radioactivity calculated for ^{226}Ra. can be measured from the weighted mean of the activity concentration of Pb-214 and Bi-214.

3. THEORY

The main objective $\mathbf{H_{ex}}$ is to limit the radiation dose to the admissible annual dose equivalent limit of 1 mSv/y [3]. Beretka et.al.[4] derived the following equation;

$$H_{ex} = \{ (C_{Ra}/370) + (C_{Th}/259) + (C_K/4810) \} \leq 1$$

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 values of this index must be less than one in order to keep the radiation hazard without posing any significant radiological threat to public.

The (Ra_{eq}) in Bq/ kg are used to assess the radiological hazards associated with materials that contain ^{226}Ra, ^{232}Th and ^{40}K in Bq/kg [5] . Yu et al. [6] used the following equation to calculate Ra_{eq}.

$$Ra_{eq} = C_{Ra} + (1.43C_{Th}) + (0.07C_K)$$

The total external terrestrial Gamma radiation absorbed dose rate (D) in air due to gamma rays emitted by the ^{238}U, ^{232}Th decay chain and ^{40}K at 1m above the ground level. The published maximum dose rate is 51 nGy/h.

Rohit Mehra et al [7] used the following equation to calculate the absorbed dose rate (D) in air: These equations have been used in this study for estimating the indices.

$$D(\text{ nGy/h}) = 0.461\, C_{Ra} + 0.623C_{Th} + 0.0414C_K$$

4. RESULTS AND DISCUSSION

The activity concentrations of natural radionuclides Ra-226,Th-232,and K-40 of the 25 samples from Dukhan oil field and the corresponding values of (H_{ex}), (Ra_{eq}), and (D) were calculated for each samples and are summarized in Table 1. 22 of the investigated soil samples have normal activity of Ra-226, and shows that the average activity concentration of Ra-226,Th-232,and K-40 ,were 20.05 , 16.43, and 216.69 Bq/kg respectively, which is below the world wide averaged value of Ra-226,Th-232,and K-40 in normal soil which are 33, 45, and 420 Bq/kg respectively cited by UNSCEAR[5].

The average H_{ex} for the 22 samples was less than unity. The average value of (D) for 22 investigated soil samples was found to be 26.04 nGy/h which is less than the published maximal permissible. The average value (Ra_{eq}) was 53.29 which is less than the published maximal permissible value 370 Bq/kg [5].

All data for the 22 samples indicate that the soil samples represent normal level of natural background radiation of soil at that area.

Three soil samples (No. 5, 8, and 12) have high activity concentration of Ra-226 which is more than 185 Bq/kg the exempted level for NORM in the Quatrain regulation recently issued. It is likely that the high radioactivity of Ra-226 for this samples are as a result of contamination of soil by NORM since these area have many abandoned oil well. The Ra-226 concentration reported more than 185 Bq/kg in this study agrees with a previous study from the same area by Al-Sulaiti et al [8]. The (H_{ex}) was less than unity, the (Raeq) was less than 370 Bq/kg ,and the (D) values were also less than the published maximal permissible value 51 nGy/h .

Table 2 shows the activity concentrations of natural radionuclides Ra-226,Th-232,and K-40 of the 10 sludge samples from offshore oil fields.

The Ra-226 activity concentrations of these samples were greater than 1100 Bq/kg the exempted values set by Quatrain regulation. The (H_{ex}) values were more than unity, (Ra_{eq}) and D were more than the published maximal permissible value by many factors, which means that the human exposure to such material impose risk, thus the sludges must be stored in safe storage for final disposal.

TABLE 1 RADIONUCLIDE CONCENTRATION IN SOIL SAMPLES OF DUKHAN OIL FIELDS

Sample No.	40 K Bq/Kg	232 Th Bq/Kg	226 Ra Bq/Kg	Hex	D nGy/h	Raeq
1	284.20	24.80	21. 3	0.21	25.82	48.04
2	190.80	46.60	15.70	0.18	44.17	95.69
3	167.05	17.69	35.90	0.20	34.49	72.48
4	261.59	24.49	25.49	0.22	37.83	78.82
6	234.86	22.65	20.85	0.19	33.40	69.68
7	252.95	18.53	45.64	0.25	43.05	89.84
9	206.02	10.67	26.40	0.16	27.34	55.68
10	198.79	6.78	23.69	0.13	23.37	47.30
11	174.39	10.69	12.32	0.11	19.56	39.81
13	249.63	10.82	16.44	0.14	24.65	49.39
14	218.21	17.14	16.59	0.16	27.36	56.37
15	211.89	20.61	30.94	0.29	35.87	75.24
16	229.58	12.54	26.12	0.17	29.36	60.12
17	135.56	7.77	12.79	0.09	19.48	33.39
18	127.74	13.35	12.34	0.11	19.29	40.37
19	192.39	9.83	12.09	0.11	19.66	39.61
20	255.19	19.14	17.26	0.17	30.44	62.49
21	179.52	11.09	10.87	0.11	19.35	39.29
22	222.16	12.48	14.68	0.13	23.74	48.08
23	254.19	10.69	21.05	0.15	26.89	54.13
24	272.70	19.35	19.25	0.18	32.22	66.00
25	247.90	13.80	16.29	0.15	26.37	53.37
Average	216.69	16.43	20.05	0.16	26.04	53.29
5	**112.50**	**8.80**	**226.70**	**0.67**	**114.65**	**247.16**
8	**109.90**	**6.70**	**289.50**	**0.83**	**142.18**	**306.77**
12	**120.80**	**9.80**	**198.30**	**0.599**	**102.52**	**220.70**

TABLE 2 RADIONUCLIDE CONCENTRATION IN SLUDGE SAMPLES FROM OFFSHORE STORAGE

Sample No.	40 K Bq/Kg	232 Th Bq/Kg	226 Ra Bq/Kg	Hex	D nGy/h	Raeq
1	394.49	74.57	62.8	1.37	230.92	505.52
2	1189.3	30.6	110.6	3.36	571.91	1240.8
3	1253.98	46.75	107.34	5.21	611.65	1328.34
4	27884.9	94.07	98.6	75.74	12917.63	28026.32
5	13983.4	53.99	102.7	38.02	6484.23	14067.79
6	16080.3	79.8	106.8	47.8	7467.16	16201.89
7	20827.5	64.43	97.9	56.55	9645.67	20926.49
8	25805.84	85.48	86.5	70.1	11953.32	25934.13
9	18289.9	54.6	99.8	49.66	8469.79	18374.96
10	20065.7	67.2	100.5	54.51	9296.31	20168.83

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FUNDAMENTAL STUDY ON OPTIMIZED OPERATION OF RADIATION PORTAL MONITOR (RPM) AT HARBOURS IN KOREA

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Abstract

Radiation portal monitor (RPM) is an installed device to monitor illicit radioactive materials possibly embedded in loads at harbors. In Korea, RPMs have been installed at harbors in accordance with the Act on Protective Action Guidelines against Radiation in the Natural Environment which have enforced since July 26, 2012. Nuclear Safety and Security Commission (NSSC), the regulatory body of Korea, has accomplished to install 10 RPMs in harbors, and have planned to increase a number of RPMs gradationally. However, according to the results from the investigations about suspicious materials (the loads which make radiation alarms from RPMs), most of them showed background radiation dose rate and the activity concentration under the exemption level pursuant to the Act, so it is necessary to reconsider the radiation alarm level. Moreover, some problems revealed to operate of RPMs and to take the actions for alarm-occurring cargos, so RPMs have difficulty fulfill their purpose what prevent the distribution of suspicious materials effectively. Therefore, the purpose of this research is to consider the points for operation optimization of RPMs by figuring out problems of current operation of RPMs in Korea.

1. INTRODUCTION

Radiation portal monitor (RPM) is a stationary mounted device to monitor illicit radioactive materials possibly embedded in loads at harbors. RPMs have been installed at harbors in accordance with the Act on Protective Action Guidelines against Radiation in the Natural Environment (hereinafter referred to "the Act") which have enforced since July 26, 2012 [1]. RPMs have installed the place that RPMs monitor imported cargos efficiently at harbors, so most of all imported cargos are monitored currently. Nuclear Safety and Security Commission (NSSC) has accomplished that 10 RPMs install in harbors, and have planned to increase a number of RPMs gradationally.

When radioactive material passes through the RPMs, if enough or more radiations are detected than set alarm level, a radiation alarm happened [2]. If a radiation alarm happens when a cargo passes through the RPMs, the cargo could be suspicious material. Suspicious material means detected matter whose radioactive concentration exceeds or is suspected to exceed limits determined and published by the NSSC. It should be defined by the Act when suspicious material find, its specific information (detection time and location, owner, radiation level, and the kinds of radioactive materials) should be figured out [1]. Therefore, professional organization, which is designated by NSSC for performing investigations on safety management of radiation in the natural environment, figures out the specific information and the owner, and does field survey for the cargo when a radiation alarm happens [1].

However, lots of problems happen during the process to find out the specific information and the owner of the cargo which makes radiation alarm. First of all, there are many companies to be involved in the freight of cargos, from the loading dock of the port to their destinations. Each company has its own business and all related companies are connected each other, systemically and sequentially. For example, when a cargo is imported, container terminal operation company unloads it from the ship, and another transportation company brings it to a bonded warehouse. After this, another transport company delivers it to

its owner. Also, licensed customs agents consider the tax about it. However, lots of companies which are involved the freight of cargos have limited or wrong information about its cargo, so too much time and effort are spent to find the specific information and the owner of the cargo.

Moreover, after the field survey, it is revealed that the optimization of radiation alarm level should be necessary. Some alarm-occurring cargos were measured background radiation level in dose rate on the field survey. These results mean that complete investigations on the every alarm-occurring cargo could be unnecessary and caused waste of time, cost and human resources in current situations. Also, due to the field survey is done for just alarm-occurring cargos, so if suspicious material is imported without alarm, no more additional investigation like field survey is done. The alarm level is not fixed value and radiation count rate of RPMs is not affected by only radioactive material in the cargo, but other factors (carriage statement of the cargo, detecting situation, whether, car speed, etc.) [3]. Therefore, the optimization of alarm level should be necessary to improve efficiency of suspicious material monitoring.

The last problem to deal with the alarm-occurring cargos is that there are systematic and technical difficulties on immediate action at harbor. According to the Act, RPM operators should deal with alarm-occurring cargos at each harbor [1]. They should figure out specific information about the cargo and report the results to the professional organization and NSSC. However, RPM operators cannot deal with alarm-occurring cargos because they don't have enough specialized knowledge of radiation and detecting equipment to figure out whether the alarm-occurring cargo contains suspicious materials. Therefore, they have summited just an alarm-occurring report to the professional organization when an alarm occurred. Also, the professional organization deals with the alarm-occurring cargo after receiving the report. In this situation, it is hard to hold the suspicious material until the relevant measurement is done in the site where the one is detected.

2. OBJECTIVE

The summary of the problems with the operation of RPMs in Korea is following three sentences.

- The difficulty to find out specific information of alarm-occurring cargo
- RPM's alarm level which is non-optimized yet
- The absence of immediate action of the alarm-occurring cargo at harbor

To solve these problems, the purpose of this research is to consider the points for operation optimization of RPMs by figuring out problems of current operation of RPMs in Korea. To accomplishing this purpose, we arranged the alarm-occurring cargos and each action, analyzed radiation count rates of the cargos, and established the method of optimized RPM operation.

3. METHODOLOGY

3.1. Arrangement of the alarm-occurring cargos and each action

Above all, the number of radiation alarm was arranged. To optimize the operation of RPMs, the current state of RPMs should be checked. The number of radiation alarms was classified into occurring location and the type of cargos. The RPMs has installed and operated in different harbor, so radiation alarms were arranged by harbors. Also, 3 big groups are set up to classify the type of cargos because cargos had lots of kinds. The three groups are following;

- ‘Material’ means the type of cargos which is as raw material to make some product. This type of cargos goes to the factory or any other working place and is experienced processes to make new products.

- ‘Product’ means the type of cargos which is already processed product so that no additional process happens to make new products.

- ‘LCL(Less than Container Load)’ means the type of cargoes which has at least 2 different kinds of loads and owners.

Each big group consisted of specific groups except LCL. Even though the cargos at harbors had many diverse kinds and states, it was possible to classify more specific groups except LCL. ‘Material’ group consisted of 6 specific groups; Potassium Chloride (KCl), Ceramic, Slag&Cement, Abrasive material, Crushed rock and etc. ‘Product’ groups consisted of another 6 specific groups; Block, Processed stone, Tile, Ceramic product, Abrasive product, and etc. ‘LCL’ group consisted of each diverse cargo so that LCL had no specific group.

After that, the actions for alarm-occurring cargoes were arranged. When the alarm happened from RPMs, the RPM operator sent the alarm-occurring report to the professional organization [1]. Based on these reports, the professional organization looked for specific information and owner of the cargo. If the alarm-occurring cargo was LCL, the sea consolidated cargo manifest was used to find the type of loads and each owner. After finding the specific information and the owner, the field survey was carried out if the situation on the cargo met the following conditions;

- New type of alarm-occurring cargos

- Loads in LCL cargo that were considered to make radiation alarm

- The type of alarm-occurring cargos that were impossible to figure out specific information or owners.

If the alarm-occurring cargo showed high radiation count rate or had a concern that the cargo might be registered by the Act during the field survey, the investigator took samples about the cargo. The samples have been analyzing now, but some cargos already got the information radioactive materials and activity concentration.

3.2. Analysis radiation count rates of the alarm-occurring cargos

To figure out all types of suspicious materials in the cargos, the radiation count rate of alarm-occurring cargos were analyzed. According to the IAEA technical document, the standard deviation of background radiation count rate was used to set up radiation alarm level for RPMs [4]. The reason why the standard deviation was used to set alarm level was that the background radiation was not fixed values, it showed distribution of radiation count rate, and it was different by installed locations. These diverse could increase false alarm rate, which was the alarm rate when the cargo without suspicious materials passed through RPMs, or suspicious material could pass the RPMs without radiation alarm. Therefore, the diverse of background radiation could overcome using the standard deviation of background count rate as alarm level. The RPMs in Korea have implemented the standard deviation, too.

However, there were 2 problems by a period of RPM operation and the field survey. Even though false alarm rate from background were reduced, it was not sure whether alarm level was appropriate set to reduce false alarm rate and the rate of suspicious material without alarm. Many factors, for example activity concentration, the states of cargos, transport

vehicle, detecting situation, whether, etc., affected radiation count rate. Therefore, more studies were necessary to define the connection radiation count rates and other factors.

For the first part of these studies, activity concentration was compared with radiation count rate. 4 kinds of cargos to compare; Potassium Chloride (KCl), refractory block, artificial sand, and the cargos without radiation alarm. Even though the radiation count rate was affected by many factors, if the count rate difference by activity concentration was the strongest, the difference from other factor could be compensated by activity concentration. Due to background radiation was very diverse and different by situation and location, the ratio of cargo-induced count rate per background count rate was utilized for this comparison.

3.3. Establishment of optimized RPM operation

In this part, the 3 ways to optimize RPM operation and to take the actions efficiently were considered. First, RPM operators could not take the immediate action due to low of ability, lack of equipment. So, the ways were looked for how to improve abilities of RPM operators and equipment. Second, the secondary ways was found to figure out the information and owners of the alarm-occurring cargos. Lastly, analysis radiation count rates of the alarm-occurring cargos were used for optimization of RPM operation.

4. RESULT AND DISCUSSION

4.1. Arrangement of the alarm-occurring cargos and each action

Figure 1 showed the percentage of radiation alarm-occurring cargos by harbors. There were 4 harbors that had installed RPMs, and it made alarms when the cargos with suspicious material passed through the RPMs. Among the Harbors, harbor A and B had 99% of alarm-occurring cargos and harbor C had 1%, and harbour D had no occupation. The reason that the distribution of alarm by harbours was that the types of cargos at harbor A and B were very diverse. Therefore, that many types of cargos which contained natural radionuclides passed through the RPMs. On the other hand, steel materials or steel products were mainly imported at harbour C and D, so few or no alarms happened at harbor C and D.

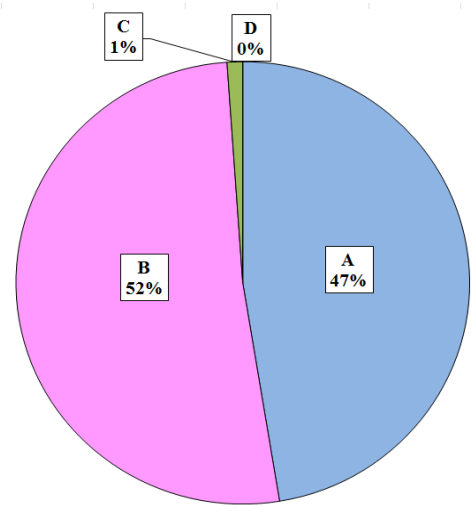

FIG. 1. The percentage of radiation alarm-occurring cargos by harbours

Table 1 showed the percentage of radiation alarm-occurring cargos by harbors. There were three big group by cargo types, and the big group of ‘Material’ and ‘Product’ consisted of 6 specific groups (specific types) and LCL had no specific groups. The ‘Material’ groups

had 23.7% of total alarm-occurring cargos, and the ‘Product groups’ had 72.2%. ‘LCL’ had 4.1%. In ‘Material’ group, Ceramic showed the largest occupation, the percentage was 7.8%. The second occupied type of cargos was Potassium chloride, the percentage was 6.7%. The other groups, Slag&Cement, Abrasive material, Crushed rock, and Etc., showed less that 3%. In the ‘Product group, Block showed the largest occupation, the percentage was 35.6%. The second occupied type of cargos was Processed stone, the percentage was 21.5%. The other groups, Tile, Ceramic product, Abrasive product, and Etc., showed less than 6%. The reason why the percentages of alarm-occurring about ‘Block’ and ‘Processed stone’ were a lot was that the warehouse of these cargos located in inside of harbors and brought in them to outside of the harbor frequently.

TABLE 1. THE PERCENTAGE OF RADIATION ALARM-OCCURRING CARGOS BY THE TYPE OF CARGOS

Type	Specific type	Alarm fraction (%)
Material	Potassium Chloride (KCl)	6.7%
	Ceramic	7.8%
	Slag&Cement	3.0%
	Abrasive material	1.5%
	Crushed rock	2.6%
	Etc.	2.2%
Product	Block	35.6%
	Processed stone	21.5%
	Tile	5.6%
	Ceramic product	5.6%
	Abrasive product	1.9%
	Etc.	2.2%
LCL		4.1%

The field surveys were done for alarm-occurring cargos. The types of cargos with field surveys were Ceramic, Potassium Chloride, Cement, Refractory block, Processed stone, vermiculite, anion-occurring bedding, and bauxite. Most cargos were treated as suspicious materials, so most field survey involved the sampling of the cargos. The samples from field surveys have been being analyzed to figure out those cargos are suspicious materials. However, some cargos showed background radiation count rate and no artificial radioactive isotope found, so no sampling was done. That meant that unnecessary field survey was done, so that time and human resources wasted.

4.2. Analysis radiation count rates of the alarm-occurring cargos

The alarm trigger level was set the standard deviation of background radiation. According to IAEA report, 1.2 times of background radiation count rate was recommended [4]. The alarm level under 1.2 times of background radiation count rate made false alarms even no vehicle passed through the RPMs. Therefore, 1.2 times of background radiation count that was the same value from IAEA report was accepted.

About 200,000 cargos were monitored per month by the installed RPMs in harbors in Korea, and 0.08% of cargos made alarms. According to the document presented by Joint Research Center (JRC) in Europe, there were 1~2% of innocent alarms happened in the total of monitored cargos by RPMs [5]. Innocent alarm means the alarm that happened by NORMs

(Natural Occurring Radiation Materials), medical isotopes, or legal shipment of radioactive sources. Comparing to the alarm-occurring ratio from Europe and Korea, Korea showed 10% of alarm-occurring ratio than Europe. Therefore, the setting of alarm level in Korea was well to find suspicious materials with controlling false alarm.

Figure 2 showed the results activity concentration was compared with radiation count rate over background. The graph showed count rates for 4 kinds of cargos over background raidtion count rates; Potassium Chloride (KCl), refractory block, artificial sand, and the cargos without radiation alarm. Also, these count rate results arranged by passage time. No alarm cargo showed shadow shielding effect, which occurred when cargo passed through the RPMs, the cargo shielded RPMs from background ration, so the count rate decreased. Potassium chloride cargo showed the largest count rate per background, the maximum value was 2.7 times upper than background. Due to K-40 was a major substance of the Potassium chloride cargo, and it is a suspicious material, so that the largest values were shown. Refractory block and artificial sand showed 1.3 times and 1.7 times radiation count rates more than background.

However, it was revealed that radiation count rate affected by other factor (activity concentration, the states of cargos, transport vehicle, detecting situation, whether, etc.) could not be compensated by activity concentration. The activity concentration of refractory block was higher than artificial sand, but the radiation count rate of artificial sand was upper than refractory block. At result, radiation count rate was connected with activity concentration, but more studies were necessary to reveal the amount of effect to radiation count rate by other factors.

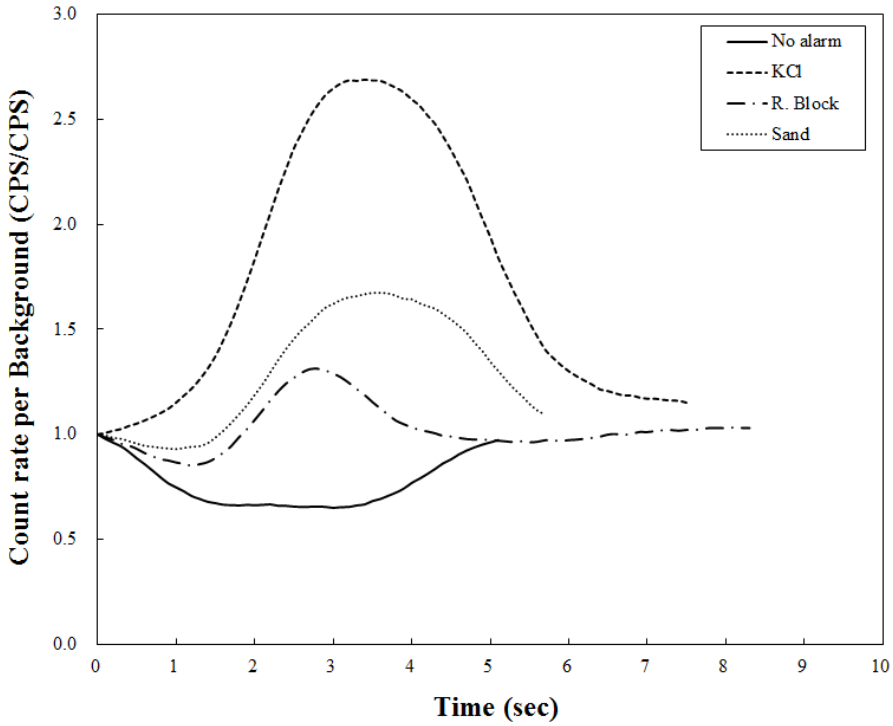

FIG. 2. Radiation count rate over background per vehicle passage time. Zero second means the start time that vehicle passes through RPMs. (No alarm: the cargo without alarm, KCl: Potassium chloride, R. Block: refractory block, Sand: artificial sand)

4.3. Establishment of optimized RPM operation

Due to RPM operators were unusually familiar with radiation and radiation safety, it was limited for them to take the immediate action to the alarms. No operators were from radiation or radiation-related majors, so that they did not understand about the importance of radiation safety and RPM operation perfectly. So, several training were held for the operator, the situation was better than before the training, but it was expected that it would be necessary lots of time to operate RPMs and to take the actions for radiation alarm perfectly.

Moreover, the actions after radiation alarm were done without accurate information about cargo, so that it made immediate action impossible. To figure out whether suspicious materials were embedded at cargos, the specific information and owner of the cargos were necessary above all things. However, the transportation process at harbors was very complex and related at least several companies, and each company had limited information about the cargos and its owner. Therefore, it took a lot of time to take the actions, and that was the reason why the immediate actions were impossible.

Consequently, making the consultative group was planned. The consultative group is the cooperation which is connected with related government organizations of trade and radiation safety, such as Korea Custom Service, the Regional Maritime Affairs & Post offices of each harbor, NSSC, and the professional organization. Korea Custom Service is in charge to import duties, so that they have all information about cargos at harbors. The Regional Maritime Affairs & Post offices of each harbor are the actual operators of the RPMs. NSSC has the authorities on radiation and radiation safety. At last, the professional organization does the actual actions about alarm-occurring cargos and figures out whether suspicious materials embed in the cargos.

The consultative group will implement the tasks which are for the optimized operation and actions of RPMs. The consultative group gives regular programs to RPM operators. Also, the consultative group shares the role models of RPM operation and actions for the radiation alarm. The problems and solutions of RPMs operation and response actions are discussed, too. Due to the consultative group is the cooperation of RPMs, it is possible to take the cooperated actions to look for the specific information of cargos and its owners. Therefore the necessity of the consultative group is increasing now.

In addition, to set up the on-line radiation monitoring system was planned. The professional organization is in charge to take the action of alarm-occurring cargos. Current way of actions is based on the off-lines system (receiving alarm-occurring report and responding), so it takes long time and some reports could be omitted by human-error or etc. Therefore, the on-line radiation monitoring system will be built, and the system will connect to the RPM devices at harbors to a terminal which is installed the professional organization in case of detecting an illicit radiation isotope or undeclared material which should be registered by the Act.

For optimization of RPM operation and responding actions, it was necessary to reconsider the alarm level. The result from analysis radiation count rates of the alarm-occurring cargos, the cargos without any suspicious material could make alarms, Even though the RPMs run with false alarm restriction. Therefore, it is decided to make two alarm levels to implement discriminated actions by each alarm level. These two alarm levels are Screening Level and Investigation Level. Screening Level is the same level with the current alarm-occurring level. The other level, Investigation Level is an emergency level to take immediate actions when it occurs.

These two levels decide whether additional actions like field surveys do. If Screening Level happens, the professional organization performs the actions which figure out the specific information of cargos and its owners and completes this work. Some cases with Screening Level go with field survey. The cases are following;

- New type of alarm-occurring cargos
- Already known cargos which show double radiation count rate compared to previous cargos
- Artificial radioactive isotopes

If Investigation Level happens, this cargo will be isolated immediately, and the professional organization will take the actions. Therefore, such graded approach with two steps of radiation alarms makes discriminated actions possible, and reduces the wastes of time, human resource, and cost.

5. CONCLUSION

In this study, the methods were looked for to optimize the RPM operation and the actions for the alarm-occurring cargos. For this optimization, the current problems about RPMs were defined. To solve these problems, current state of the RPMs and performed actions were arranged, and radiation count rates were analyzed to figure out how the RPMs were operated. Then, the setting of the consultative group, on-line radiation monitoring system, and two steps of radiation alarm levels are planned to the optimization.

The RPMs in Korea has implemented since July 26, 2012 by the Act. So, little information and experiences are possessed to RPM operators, other related government branches, and the professional organization. Current state of RPM operation is just first step. Therefore, more studies and polices have planned to localize and to optimize for Korea situations.

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USE OF ^{7}BE TO ASSESS SOIL EROSION AND TO STUDY THE EFFECTIVENESS OF SOIL CONSERVATION METHODS IN THE SEHOUL REGION

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Abstract

Accelerated erosion and soil degradation currently cause serious problems to the Sehoul region, Morocco, located between the highway from Rabat to Fes in the north and the Grou River in the south. Furthermore, there is still only limited information on rates of soil loss for optimising strategies for soil conservation. In this study we have used the ^{7}Be technique to assess the soil erosion rates on an agricultural land in Sehoul area, Morocco. Three representatives agricultural fields; under same natural conditions; were selected for to years 2009 and 2010 to investigate the soil degradation required by soil managers in this region; first field is planted with rotation cereal / cereal (barley / wheat), the second one with monoculture (vine) and the last one is neglected for 15 years and in 2009 the site owner tried bean culture. The transect approach was applied for sampling to identify the spatial redistribution of ^{7}Be. The results obtained from this study show erosion rates of about 6.7 t ha^{-1}, 0.9 t ha^{-1} and 5.8 t ha^{-1} in 2009 and 13.9 t ha^{-1}, 3.3 t ha^{-1} and 1.7 t ha^{-1} in 2010 for agricultural sites; wheat / barley rotation, vine monoculture and bean in a field neglected for 15 years; respectively for tow years.

1. INTRODUCTION

Water erosion is one of the most serious forms of agricultural land degradation plaguing the world. Moroccan soils like the rest of the world are threatened by the risk of this phenomenon that contributes to the deterioration of soil structure, reducing soil productivity is affected and also a major source of water pollution area in agriculture and the siltation of reservoirs. Indeed, the agricultural sector in Morocco occupies an important place in economic activity. In 22 watersheds covering an area of 15 million hectares, about 11 million hectares are highly threatened by water erosion. The annual loss of soil is estimated at 100 million tonnes and reduced the storage capacity of dams is about 50 million m^{3} per year.

The Sehoul area is selected because despite its location in the more favourable lands of Morocco in terms of climatic conditions, it consists of marginal land with a high poverty and important indicators of degradation. Desertification is both related to natural factors (vulnerability) and to human factors (poverty, mismanagement). It is exacerbated by events of drought which create new factors of vulnerability. In this context, using the technique of ^{7}Be is a recent tool in the investigation of soil erosion.

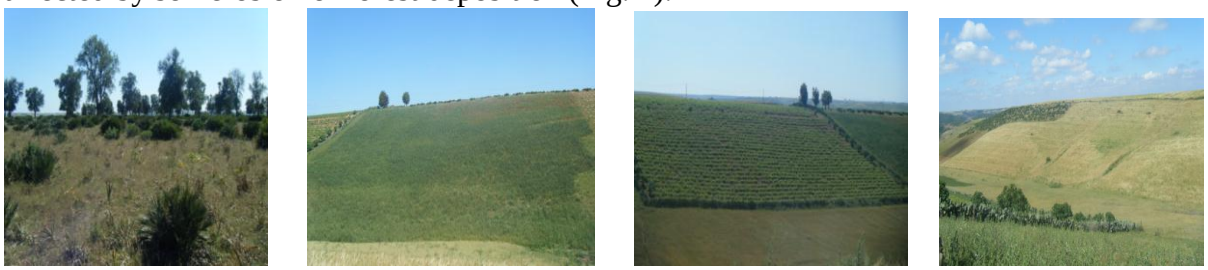
This paper deals the a research project; DESIRE (Desert Remediation); funded by the UNESCO-GN in collaboration with the CNESTEN of Morocco, was conducted to estimate the short-term soil loss caused by water erosion in this region; sehoul; and to check the validity of soil conservation technique used.

2. STUDY SITES

The Sehoul area, 40 Km from Rabat, is located in the north west of Morocco between the Mamora forest in the north and the Grou river in the south West. Its surface is about 35100 ha. The climate of the region is classified as Mediterranean, characterised by mean annual rainfall of about 664 and 929 mm respectively for the study period 2009 and 2010. The soils on the plateau surface are very fragile. The present human pressure on the land and forest leads to the removal of the superficial sand layer and the formation of new dunes. The organic layer is rapidly destroyed during the dry years and the re-stabilization is very difficult to obtain.

The investigations reported in this paper focused on one reference site and three agricultural fields. First filed is vine monoculture, its surface is about 0.33 ha and a slope of 10%. The second one with a surface of about 0.12 ha and a slope of 11%, it is a site neglected for 15 years and in 2009 the site owner tried bean culture, in 2010 the site is neglected. The last one is cultivated with barley in 2009 and with wheat in 2010, its surface is about 0.81 and a slope of 10% (Fig. 1).

The choice of a suitable reference site is important. The reference site should have received the same annual precipitation and have the same geomorphological parameters as the studied field. There were no uncultivated native grassland sites in the general area and it was difficult to find sites that had clearly been undisturbed since 1950. Thus, an undisturbed reference site was selected in the forest with a flat topography for this study. It was not affected by soil erosion or forest deposition (Fig. 1).



Reference site Bean field Vine field Wheat/ Barley field

FIG.1. Different agricultural fields and reference site

3. METHODOLOGY

The sampling procedure is based on the transect approach; this consists of a sequence of samples collected along the axis of the greatest slope from the upslope to downslope boundary. A cylindrical tube (ca. diameter: 15 cm and length: 5cm) was inserted to a depth of 5cm to ensure that all ^{7}Be is retained. For the three agricultural fields sampling was carried out as follows:

Bean field: A grid framework was established consisting two parallel transect across the field. A long each transect, five soil cores were collected and the distance between two adjacent sampling points was 30 m this in 2009. In 2010, seven soil cores were collected and 20 m between two adjacent sampling points.

Vine field: A grid framework was established consisting two parallel transect across the field. A long each transect, five soil cores were collected and the distance between two adjacent sampling points was 30 m. In 2010, six soil cores were collected and 20 m between two adjacent sampling points.

Wheat field: A grid framework was established consisting two parallel transect across the field. A long each transect, five soil cores were collected and the distance between two adjacent sampling points was 30 m.

Barley field: A grid framework was established consisting one transect across the field, seven soil cores were collected and 20 m between two adjacent sampling points.

Eight reference samples were collected inside two circles of 20 m and 40 m in diameter in the undisturbed site. To obtain information concerning the depth distribution of ^{7}Be concentration, the soil core was divided into 5 mm and 3 mm incremental samples.

These cores obtained are placed in plastic bags and transported to the laboratory for processing.

4. ^{7}Be TECHNIQUE

Beryllium-7 ($E\gamma$ = 477.6 KeV and $T_{1/2}$ = 53 days) is a natural fallout radionuclide generated in the stratosphere and upper troposphere through the cosmic ray spallation of nitrogen and oxygen nuclei. The principle of using the ^{7}Be technique is simple, is a comparison between the rates of ^{7}Be activities found in the study sites and the reference site. The reference sites are localized areas near the study site, considered spared erosion and deposition from the initial impact of radio-beryllium in the environment (forest or old fields uncultivated since the 60 years). The erosion surfaces are identified by a negative deviation relative to the local reference and the deposition by a positive deviation. Quantitative estimates of erosion and deposition are based on models of conversion.

5. RESULTS AND DISCUSSIONS

5.1. Reference site

The ^{7}Be activity concentration profile for the identified reference site shows a sharp decrease of ^{7}Be activity concentration with increasing mass depth (Fig. 2), which can be fitted by an exponential function $C(x)=C(0)e^{(-x/h_0)}$. This distribution is typical of an undisturbed site. Most of the ^{7}Be is contained within the upper few millimetres of the soil (<10 Kg m^{-2}). This provides further confirmation of the validity of using data from this site to establish the reference inventory of the field studies.

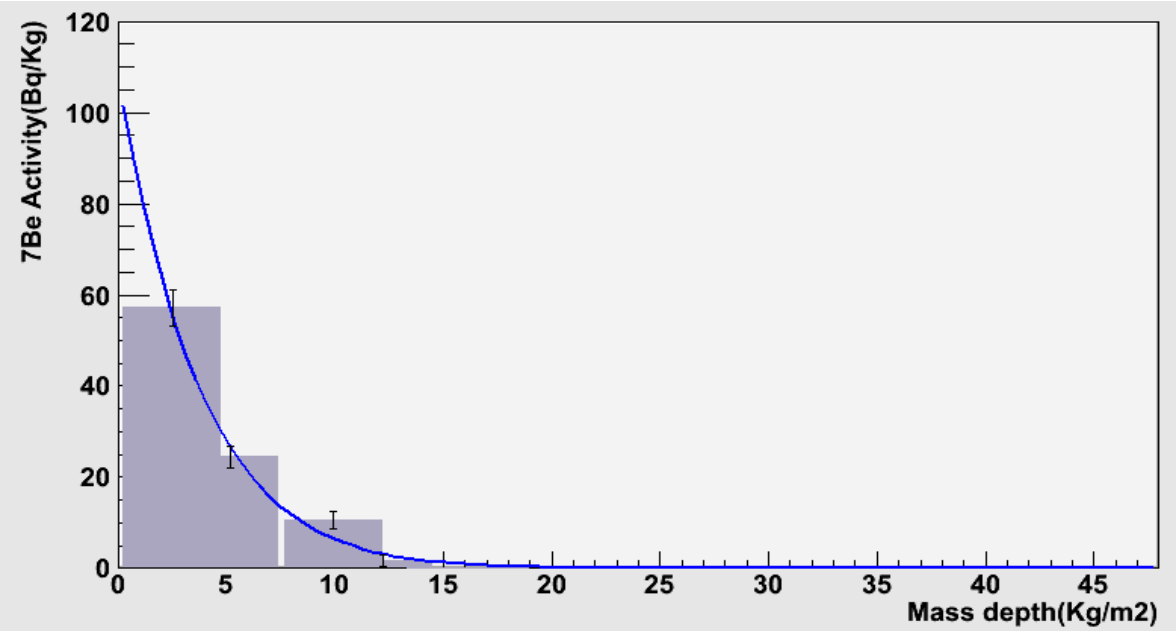


FIG. 2. The depth distribution of ^{7}Be for the local reference site.

The mean ^{7}Be activity obtained for the reference site is about 315.43 Bq m^{-2} with a relative standard deviation of 18%

5.2. Studied fields

Concerning the three studied fields in this work (vine monoculture, wheat/barley, bean/fallow), the ^{7}Be inventories established from the sampling points collected at each transect lead to a negative sediment balance, more erosion than sediment.

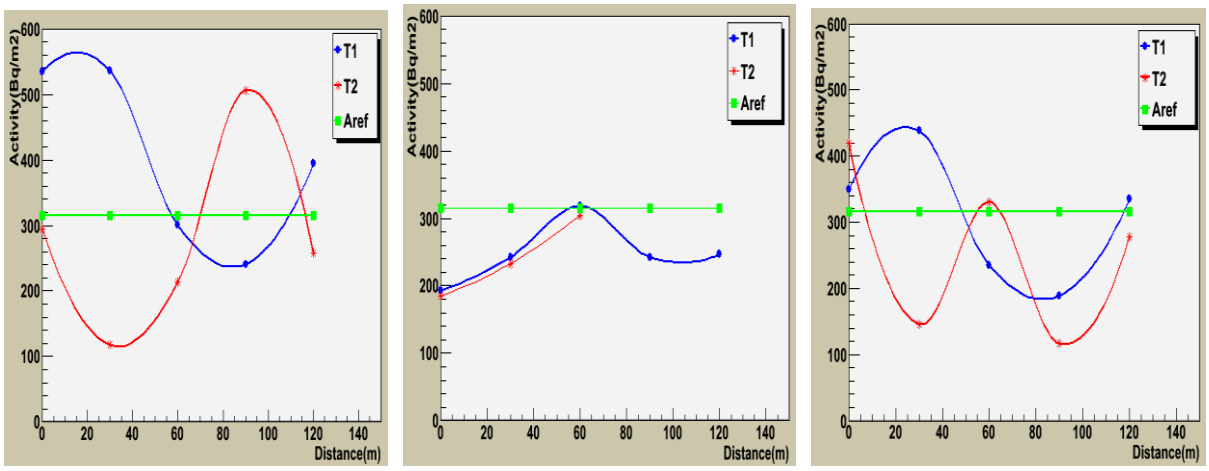
The variation in ^{7}Be activity with the distance from upslope to downslope long the transect for tow years is presented in Fig.3 and Fig.4. Usually the longitudinal variation in ^{7}Be activity, related to the soil loss or deposition, depends on the variations of the topography and the position of the sampling point from hilltop.

For vine field, we can see from transect 2 that ^{7}Be inventory decreases rapidly with distance until 30 m starting from the top. Then ^{7}Be activity loss becomes lower. This can be explained by the convexity of the middle. At 90 m, the ^{7}Be activity increases and reaches a value of 506.5 Bq m^{-2}, indicating a deposition of soil. Then ^{7}Be activity deposition becomes lower with distance. This can be explained by the concavity of the middle. On the other hand the transect 1 presents a great increase of ^{7}Be inventory, it reaches 535.4 Bq m^{-2} at 30 m. This can be explained by the concavity of the middle. Then ^{7}Be activity decreases with distance until 90 m with a value of soil loss reaches 240.8 Bq m^{-2}.

For field planted with wheat culture, variations of ^{7}Be inventory loss are observed to be significant along the transect 1 and 2. The ^{7}Be inventory maximum is about 184.8 Bq m^{-2}.

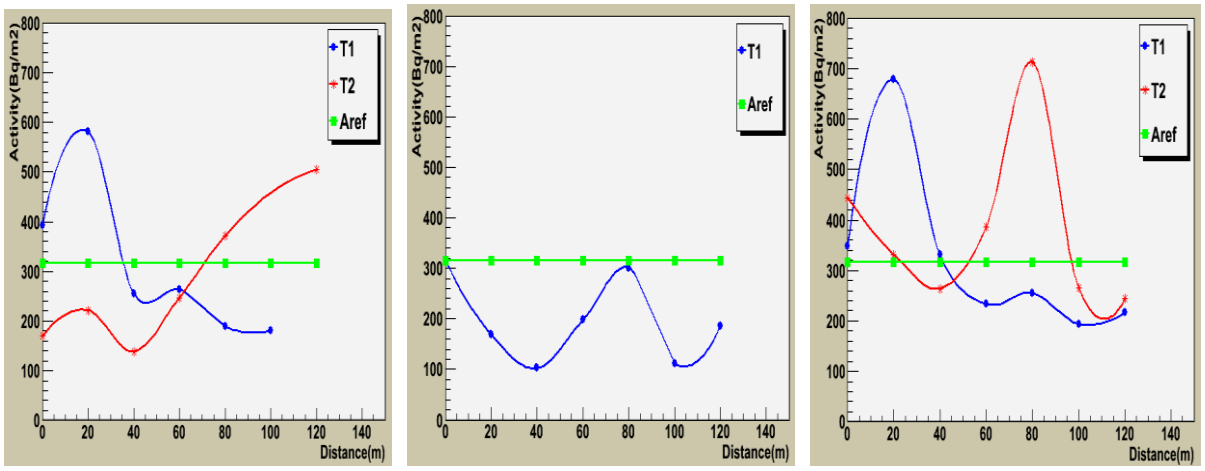
The field cultivated with bean culture, we can see similar behaviour in transect 1 for vine field. The transect 1 shows an increase in ^{7}Be activity, it reaches 438.1 Bq m^{-2} at 30 m. Then a value of soil loss reaches 116.2 Bq m^{-2}. This can be due to the influence of the topography (concavity and convexity) of the two points. On the other hand, the transect 2 shows an irregular and oscillating behaviour of ^{7}Be activity loss suggesting a variation of soil loss along the transect.

In 2010, we can see similar behaviour in two agricultural fields planted with vine monoculture and wheat/barley rotations. The fallow field presents more deposition than erosion soil.



Vine field Wheat field Bean field

FIG. 3. ^{7}Be activity redistribution for three agricultural fields in April 2009.



Vine field Barley field Bean field

FIG. 4. ^{7}Be activity redistribution for agricultural fields in June 2010.

Table 1 summarise the gross erosion rate, gross deposition rate, net erosion rate and sediment delivery rate estimated in three agricultural fields for two years 2009 and 2010 using profile distribution model.

TABLE 1. THE EROSION AND DEPOSITION RATES OF SOIL ESTIMATED IN THE STUDIED SITE USING ^{7}BE TECHNIQUE

Erosion / deposition	April 2009			June 2010		
	Vine	Wheat	Bean	Vine	Barley	Bean
Gross erosion rate	-5	-6.8	-7.6	-7.4	-13.9	-4.2
Gross deposition rate	5.9	0.0	1.8	4.1	0.0	5.9
Net erosion rate	0.9	-6.7	-5.8	-3.3	-13.9	1.7
Sediment delivery rate	-18%	100%	77%	45%	100%	41%

The results show a negative sediment balance, more erosion than sedimentation, particularly for field cultivated with wheat/barely rotation for tow years see table. Vine site present the lowest assessed erosion rate for 2009 but in 2010 the field cultivated with bean present the lowest assessed erosion rate because this site was fallow.

6. CONCLUSION AND PERSPECTIVE:

The study of the Sehoul region, Morocco, has demonstrated the potential of the ^{7}Be technique to provide erosion rate data. The detailed study and sampling method using several transect have allowed us to obtain on one hand the spatial distribution of ^{7}Be in the soil and to highlight the impact of the agricultural practices and on the other hand to contribute to the assessment of short term erosion rates. The net erosion rate was estimated to be 6,7 t/ha and 13,9 t/ha for field planted with wheat/barely rotation in 2009 and 2010 respectively. 5,8 t/ha for the field cultivated with Bean on 2009 and 1,7 t/ha for the same site in 2010 which was fallow. 0,9 t/ha and 3.3 t/ha with vine monoculture on two years 2009 and 2010 respectively. Site with wheat/barely rotation present more erosion than site was neglected for more than 15 years and in 2009 this site cultivated by bean rotation followed vine monoculture rotation. In 2010, we find the same results except at the filed planted with vine monoculture that undergoes more soil loss than the bean rotation; this can be explained that the soil was left fallow in 2010.

In perspective we plan to study those sites with ^{137}Cs technique for validate successful conservation techniques in this region.

ACKNOWLEDGEMENT

I thank all members who helped me for making this research.

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REMEDIATION OF A PHOSPHOGYPSUM DISPOSAL AREA IN TUNISIA: A NEW CONCEPT

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Abstract

Can we rehabilitate a phosphogypsum stack to a new use that is environmentally safe, financially robust and which adds an economic and social value to the local area? This was the main goal of the project on remediation of a phosphogypsum disposal area of 260 ha initiated in 2006 in the city of Sfax which is the 2nd economical pole of Tunisia. Providing a better quality of life for the citizen of the city with the rehabilitation and the reclaim of 6 km of beaches and thereby creating a new urban zone was envisaged. On shore and of shore works were conducted with the depollution of the sea, the removal of the phosphogypsum plaque surrounding the stack, the backfilling with new soil and sand and the confinement of the stack. Simultaneously, a radiological monitoring programme was carried out before, during and after the site remediation. External exposure to gamma radiation and internal exposure due to the inhalation of dusts and radon gas were assessed to evaluate occupational and public exposure. A comprehensive program for site and environmental sampling analysis was conducted to estimate the internal exposure due to the ingestion. The evaluation of the radiation survey resulted in a level of public and workers exposures of less than 1 mSv/y. Communication with the public and the interested parties have been addressed at all stages of the project by the regulatory authority (CNRP) and the operator (SEACNVS). Along with a description of the project, some of the details of radon measurements are included in the paper.

1. INTRODUCTION

Tunisia is ranked the fifth largest phosphate rock producer in the world and one of the world's leading producers of phosphate derivatives. Sfax is an open coastal city on the Mediterranean and the second industrial city of Tunisia. It has the largest and the leading port in the export of phosphate rock and products.

The Sfax plant which started production in 1947, was the first phosphate rock processing facility in Tunisia. Industrial activities have left behind a huge deposit of phosphogypsum on the coast, near the centre of the city. The stack was about 50 ha with a height of 8 meters above the sea level surrounded by a plaque of 90 ha of phosphogypsum.

Due to the pollution problems, the beaches were closed and swimming was forbidden in 1978.

2. PROJECT GOALS

An important project was launched by the government of Tunisia in 2006 with two main steps:

a. The Clean up of the site pollution with a total of 260 ha and a further 160 ha recovered from the sea. A total of 6 km of beaches has been restored.

b. The safe and sustainable development of a new urban zone with 420 ha for public and private activities such as, beaches, parks, museum, educational and health infrastructures.

3. REMEDIATION PROCESS

3.1. Scientific studies

A variety of comprehensive studies were carried out during the 1990's at the site for the chemical and radiological characterisation.

- Characterisation of the site: to determine the extent of polluted areas and the quantities of materials to be removed. The pollution was assessed on the land and the surrounding sea of the stack. The chemical pollutant determination concerned heavy metals and arsenic with using Dutch reference levels related to ecological risk criteria.
- Radiological Impact Assessment: a comprehensive study was carried by Algade and CNRP in 1998-1999. Gamma dose rates, radon exhalation rates, radon and dust in outdoor air, radionuclide in fishes and phosphogypsum residues. The activity concentration of Ra226 was 0.4 Bq/g in phosphogypsum. With the identification of the important exposure pathways, external exposure to gamma and internal exposure due to the inhalation of dusts and radon and due to the ingestion were evaluated to estimate the doses to the public and to the workers for different exposure scenarios. The natural background was estimated to be 0.8 mSv/y. The exposure to workers was estimated to be 1.22 mSv/y and to public closed to 1 mSv/y depending on the exposure scenario. The CNRP, which is the regulatory authority in radiation protection, has defined a level of public exposure of less than 1 mSv/y above natural background for the future use of the remediate site. The future requirement was that the containment should be a green park. Reference levels were derived from IAEA's Basic Safety Standard n°115 [1], ICRP 60 [2] and the Council Directive 96/29/ Euratom [3], as NORM industries were excluded from the national regulation of radiation protection.

3.2. Remediation works

The remediation plan selected was to excavate the polluted material from the land and the sea and incorporate it after de-watering into the phosphogypsum stack. This one was reshaped to a circular form and surrounded by a vertical barrier of HPDE panels filled with bentonite-concrete mixture, in order to confine the pollutant material. The total area was then covered by a land based material (figure 1). Surface run off is collected and channelled into the flood control canal discharging into the harbour. The groundwater level underneath the stack is constantly monitored by automatic systems. In this city, the groundwater is only used for industrial purposes.

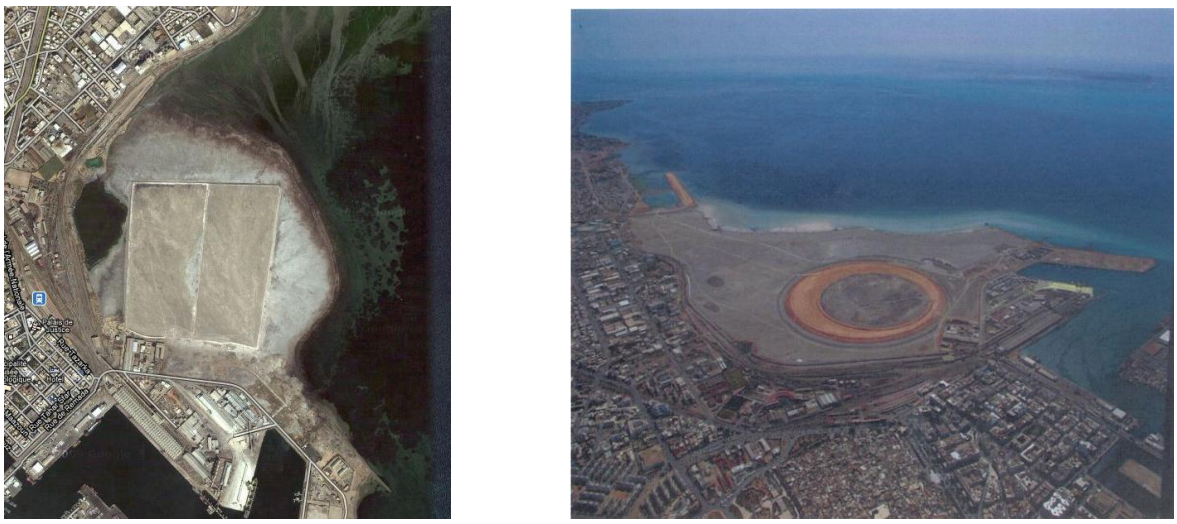

FIG. 1. The project before and after remediation

3.3. Monitoring programme

A comprehensive radiation surveys have been carried out before, during and after the site remediation to assess exposure of the public and the workers. Individual and workplace monitoring were performed by TLDs, radon dosimeters (dust and gas) and portable instruments. Public exposure was assessed by 3 on site environmental stations and another one in the centre of the city to control gamma exposure by TLDs and internal exposure by radon dosimeters. A comprehensive program for site and environmental sampling analysis was conducted by the Centre National des Sciences et Techniques Nucleaires (CNSTN) to estimate the internal exposure due to the ingestion. Results analysis was compared to UNSCEAR 2000 [4]. A gamma grid radiation survey was carried after the excavation, after the backfilling and at the end of the guarantee period. The average natural background gamma doserate is now estimated to be 0.05 $\mu Sv.h^{-1}$. The evaluation of the radiation survey has confirmed the initial predictions with a level of public and workers exposures of less than 1 mSv/y. Quality assurance objectives were met through internal controls implemented by the operator (SEACNVS) and external audits implemented by the CNRP.

3.4. Radon Campaign

During the remediation works, the local population has been involved to participate in a campaign for the evaluation of radon gas concentration in 50 dwellings surrounding the site. The overall average annual concentration was 32 Bq.m-3. This value is comparable to the national average for Tunisia of 36 Bq.m-3 [5].

3.5. Public Opinion

Communication with the public and the interested parties groups has been addressed at all the stages of the project by the operator (SEACNVS) and the regulatory authority (CNRP), through meetings, radiation protection training for workers, website, brochures and media.

3.6. Guarantee period

This period extends from 2009 to 2013. The radiation monitoring program was adapted to control the gamma external exposure, radon gas and seepage water discharged to the channel and the sea. In addition, the structure has been monitored for its stability and compliance with the design criteria. A comprehensive radiological, chemical, biological and

bacteriological study has been conducted to evaluate the marine ecological system and the opening of the new beaches to swimming.

4. FUTURE CHALLENGES

The success of the first part of the project is due to the engagement of the government, the operator, the interested parties and the public opinion. Now, we are face to the biggest challenge to ensure a sustainable and a safe development for an attractive urban zone which will offer an important socio-economical impact for the city. Once again, stakeholder engagement and public communication are required.

5. CONCLUSION

In this project, the reduction of the doses to the individuals and reduced environmental impacts has been achieved by actions applied to the source by means of the removal of contamination and the isolation of the contaminant.

A series of thorough and comprehensive radiation surveys and assessments have been carried out before, during and after the site remediation. The dose to the public has been achieved and confirmed the initial predictions.

The stability of the containment and the long term integrity of the capping layer are the important aspects that require to be controlled, in addition to the flood release.

It has been demonstrated from this experience that a graded approach to regulation is required and is important when dealing with NORM and it is important to involve all interested parties.

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UPTAKE OF RADIUM BY GRASS AND SHRUBS GROWN ON MINERAL HEAPS: A PRELIMINARY STUDY

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Abstract

A preliminary study of the uptake of ^{226}Ra and ^{228}Ra by grass and shrubs grown on mineral heaps was carried out. Activity concentrations of ^{226}Ra and ^{228}Ra in grass and shrubs were measured using gamma spectrometry. The result showed that grass and shrubs grown on mineral heaps contained elevated levels of radium compared to grass and shrubs grown on normal soils. Thus, these plants might be used for phytoremediation of radium contaminated soil.

1. INTRODUCTION

Malaysia used to be the world largest tin producer and this tin industry was once a major contributor to the economic, social and industrial development until late 1970s. Nowadays, there are a few companies in Malaysia still involves in tin mining activities. One of the by-products generated from the tin mining activity is amang. Basically, amang which also known as a tin tailing consist of natural occurring radioactive materials (NORM) such uranium, thorium and other radionuclides from their decay series [1]. However, amang has been found to contain valuable minerals such as ilminite (61-86%), monazite (0.5%) and zircon (<0.5-5.5%) [2]. Thus, amang is treated to extract these valuable minerals in which they are classified as radioactive [3].

At minerals processing plant in Malaysia, usually amang, ilminite or zircon are stored outdoor in very large conical piles. Sometimes these minerals are dump for many years before further processing. Accordingly, there are certain type of plants can grow on these minerals and therefore NORM can be taken up by these plants. For example, some of the grass and shrubs can be found growing on these minerals as shown in Fig. 1. The concentration of radium in minerals and tin ores separated at amang plant was reported by Omar et al. [1].They reported that ilminite, monazite and zircon were contained of ^{226}Ra about 3460 $Bqkg^{-1}$, 20975 $Bqkg^{-1}$ and 11303 $Bqkg^{-1}$, respectively. Thus, any plants that grow on these minerals may contain elevated levels of radium and possibly can be used for phytoremediation. According to Peer et al. [4], plants growing in metal-contaminated and metalliferous soils developed three basic strategies of survival: metal excluders, metal indicators and metal accumulators. Many researchers also have studied the uptake of specific radionuclides by various plants species growing in environments where there are in contact with radionuclides [5]. Most studies found significantly elevated ^{226}Ra levels in plants at or near mining and milling operations [6]. In general, many studies were done closely related to the safety of human food chain and remediation studies [5, 7, 8, and 9]. In view of this, study on uptake of radionuclides by plants assumed important.

Radium generally is a naturally occurring radioactive element and present radiological hazard to human by replacing calcium in bone structure [6].Thus, understanding the processes that govern the uptake of radionuclides is very important in environmental control and surveillance [10]. If plant uptake and accumulation are sufficiently high, plants can be used in cleaning soils, sediments and waters contaminated by low and moderate levels of radionuclides [10]. Therefore, the work described here presents our investigations on the

uptake of ^{226}Ra and ^{228}Ra by grass and shrubs grown on mineral heaps. This information can be used for selecting the plants for phytoremediation, especially for radium contaminated soil.

FIG. 1. Grass and shrubs grown on mineral heap at mineral processing plant.

2. MATERIALS AND METHODS

2.1 Sampling and sample preparation

Samples of plants (Fig. 2), namely jointhead grass (*Arthraxon hispidus)*, cogongrass (*Imperata cylindrica*), siam weed (*Chromolaena odorata)* and chinese violet (*Asystasia gangetica)* grown on mineral heaps were collected at mineral processing plant located in Perak, Malaysia. The minerals i.e. zircon and amang from the plants area collection were also collected at the root zone (the upper 10 cm) to ensure that the sample were representative. Samples from the same plant species were collected from the controlled sites (which were grown on non radioactive soils). All the samples were brought to the laboratory for processing and analysis. The plants samples were washed gently with tap water to remove the minerals and soil adhered. In the laboratory the samples were dried at room temperature for about 1 week and then were cut into small pieces. The plant samples were oven dried at 105°C to reduce bound water. The dried samples were then ashed at 350°C for about 12h in furnace, cooled and weighted. The data in this study was reported in dry weight basis (350°C). The soil samples were dried in oven at 105°C for about 10 -15 h to obtain a constant dry weight and then passed through 2 mm mesh sieve. All the samples were packed in 30 ml of polyethylene container air-tight sealed and kept for at least 3 weeks in order to reach secular equilibrium between ^{222}Rn and ^{226}Ra.

*FIG. 2 Types of plant samples analyzed in this study: top from left, Jointhead grass (Arthraxon hispidu and Cogongrass (Imperata cylindrica) grown on zircon, bottom from left; Siam weed (Chromolaena odorata), Chinese violet (*Asystasia gangetica) and *Cogongrass (Imperata cylindrica) grown on amang.*

2.2. Analytical Methods

The leachability tests of minerals were investigated by adding 100 ml of rain water to each 100 g of zircon and amang respectively. The mixtures were left overnight at room temperature and followed by the separation of solution by vacuum filtration. The pH and conductivity were measured immediately using pH meter (Trans Instrument Model BP3001) and conductivity meter (Trans Instrument HC3010) respectively. The experiments were done in duplicate and the average result was reported. The samples were also subjected to measurement for radionuclides content using gamma spectrometer system.

Nitric acid digestion was performed before zircon and amang were analyzed for Ca, Mg, K, Na, Fe, Mo, Fe, Cu, Zn and Mn contents. 0.30g of zircon , amang and soil samples were placed in a 100 ml beaker and 5 ml of 65% concentrated HNO_3 were added to each beaker. The samples were left for about one hour at room temperature. Then, the samples were heated for about 45 hours at 70ºC. After cooling, 20 ml of distilled water were added to the samples. The solutions were filtered through No. 1004 filter paper and transferred to 30 ml plastic container. The concentrations of for Mg, K, Na, Fe, Mo, Fe, Cu, Zn and Mn in the final solution were determined by inductively coupled plasma mass spectrometry (ICP-MS) (Perkin Elmer Model ELAN 6000) and Atomic absorption spectroscopy (AAS) (Perkin Elmer AAS Analyst 800).

2.3. Measurement by gamma spectrometry

All samples were counted for about 24 hours using a Canberra n-type high purity germanium (HPGe) γ-spectrometry system (with 30% relative efficiency and a resolution of 1.9 keV at 1332.5 keV of ^{60}Co). For detector efficiency calibration, a standard source in 30 ml plastic container (containing certified concentrations of ^{210}Pb, ^{241}Am, ^{109}Cd, ^{57}Co, ^{123m} Te, ^{51}Cr, ^{113}Sn, ^{85}Sr, ^{137}Cs, ^{88}Y dan ^{60}Co) was prepared using in house prosedure.This calibration source was obtained by spiking a 10.5g of a commercially available multinuclides standard solution (purchased from Isotopes Product Laboratories, USA) into alumina with same density of sample to be assayed. A Genie-2000 analysis software was used to analyse the spectrum of the samples. The photopeaks with energy level 295 keV (19.2 %), 352 (37.1%) keV from ^{214}Pb and 609keV (46.50 %) from ^{214}Bi were used to obtain the activity concentration of ^{226}Ra and 911 keV (27.7%) for ^{228}Ra. The activity concentration of the radionuclides was measured in per unit weight or volume (i.e. Bqkg^{-1} and BqL^{-1}).

3. RESULTS AND DISCUSSION

Rain is assumed to be the only primary source of water for plants grown on mineral heaps and thus, it may affect the solubility of radium in mineral. Table 1 presents the properties of pH, conductivity and activity concentration of radium in filtrates from the mixture of mineral and rain water after 24 hours of leachability test. The pH values of filtrates presented in Table 1 classified them as acidic. Consequently, under this acidic condition ^{226}Ra was highly mobile [10] and therefore more likely to be available for root uptake. The conductivity of filtrates was ranged from 148 to 302 (μS) which indirectly indicates the presence of dissolved ion during leaching test. As shown in Table 1, ^{226}Ra were detected in all filtrates. However, for ^{228}Ra were only detected in filtrates from the mixture of amang and rain water and not detected in filtrates from the mixture of zircon and rain water.

The result of selected essential plant nutrients determined in zircon, amang and soil is presented in Table 2. The result indicated that zircon and amang were found contained of macronutrients (Ca, K and Mg) and micronutrients (Co, Cu, Fe, Mn, Na and Zn), in which those elements are essential for plant growth. In general, plant roots play an important role in absorbing water and nutrients needed for plant growth. However, root has no power to reject any soluble element and thus, absorption by roots is also the main pathway of trace elements to plants [11] including radionuclides. Most metals enter root cells primarily through particular transport system such as carrier or ion channels [12]. The plasma membrane divalent-cation channels, which pass cations including Ca could be the transport for certain metal contaminant into root cells [13]. With regard to this, radium ions may be absorbed by root through this ion channel. Moreover, Ra is considered to be approximate chemical and physiological analogues of Ca [14]. In the case of plants grown on mineral heaps, ^{226}Ra may be act as analogue to Ca. Therefore, as analogue to this element ^{226}Ra is assumed to be readily incorporated by biological tissues.

Table 3 shows the activity concentration (Bqkg^{-1}) of radium in minerals and soils. It is seen that both ^{226}Ra and ^{228}Ra activity concentration in minerals were significantly higher than in soils. The activity concentrations of ^{226}Ra and ^{228}Ra in minerals were ranged from 796.69 - 1132.1 Bqkg-^{1} and 626.16-1362.89 Bqkg^{-1}, respectively. While, the activity concentrations of ^{226}Ra and ^{228}Ra in soils were ranged from 97.45 - 150.49 Bqkg-^{1} and 68.3 - 249.94 Bqkg-^{1}, respectively. The activity concentration of ^{226}Ra in Malaysian soils as reported in UNSCEAR [15] ranged between 38 and 94 Bqkg^{-1} but slightly lower than this study. However, between the two minerals, the activity of both ^{226}Ra and ^{228}Ra in zircon were found considerably higher than amang.

TABLE 1. pH, CONDUCTIVITY AND ACTIVITY CONCENTRATION OF RADIUM IN FILTRATES FROM THE MIXTURE OF MINERAL AND RAIN WATER AFTER 24 HOURS OF BATCH LEACHING TEST

Sample Types	pH	Conductivity (μS)	Activity concentration (BqL^{-1})	
			^{226}Ra	^{228}Ra
Filtrate 1 (from the mixture of zircon 1 + rain water)	5.40 ± 0.04	148.2 ±0.02	5.47±2.09	< MDA*
Filtrate 2 (from the mixture of zircon 2+ rain water)	5.96 ± 0.06	302.0 ±0.04	8.76±2.04	< MDA*
Filtrate 3 (from the mixture of amang 1+ rain water)	5.42 ± 0.02	240.0 ±0.03	5.59±2.20	<MDA*
Filtrate 4 (from the mixture of amang 2 + rain water)	5.50 ± 0.02	255.0 ±0.02	9.81±2.05	11.28±5.48
Rain water	7.71 ± 0.01	104.5 ±0.03	4.77±2.20	6.33±5.61

*MDA –Minimum Detectable Activity

TABLE 2 CONCENTRATION OF SELECTED ESSENTIAL PLANT NUTRIENTS ($mgkg^{-1}$) IN ZIRCON, AMANG AND SOIL

Element	Concentration of selected essential plant nutrients ($mgkg^{-1}$)								
	Zircon 1	Zircon 2	Amang 1	Amang 2	Amang 3	Soil 1 (control)	Soil 2 (control)	Soil 3 (control)	Soil 4 (control)
Ca	7.71	13.60	29.89	39.41	3427.25	47.90	51.72	55.09	56.44
Mg	21.35	15.20	102.20	46.24	8.85	5221.18	76.18	66.25	66.51
K	57.63	27.13	38.05	19.09	44.25	151.71	90.28	63.86	78.67
Na	24.69	7.75	8.19	78.51	18.60	61.42	240.59	62.47	107.4
Fe	804	12932	21041	673	3867	6195	4232	3772	2684
Mn	517.54	338.52	2834.8	2342	232.17	68.87	104.66	54.65	3.61
Cu	16.72	14.17	38.55	34.10	15.83	4.39	6.95	5.51	5.43
Zn	129.35	134.91	220.46	156.2	99.08	120.95	231.41	116.49	<5.30
Co	7.23	4.25	17.58	41.74	1.40	0.68	3.09	0.88	0.28

TABLE 3 ACTIVITY CONCENTRATIONS OF RADIUM IN MINERALS AND SOILS ($Bqkg^{-1}$)

Sample Types	Activity Concentration ($Bqkg^{-1}$)	
	^{226}Ra	^{228}Ra
Zircon 1	1132.10 ± 2.33	1362.89± 30.34
Zircon 2	2631.38 ± 54.12	6213.75 ±133.31
Amang 1	885.73 ± 18.23	589.83 ± 14.20
Amang 2	796.69 ±16.39	626.16 ± 14.65
Amang 3	1001.91 ± 11.56	812.57 ± 14.60
Soil 1(Control)	150.49± 3.07	249.94±9.01
Soil 2 (Control)	105.76±3.0	154.91±6.52
Soil 3(Control)	97.45 ± 2.78	68.30 ± 5.18
Soil 4(Control)	106.69 ± 2.88	107.18 ± 5.43

The activity concentration of ^{226}Ra and ^{228}Ra in grass and shrubs grown on mineral heaps and soils are presented in Fig. 3 and Fig. 4, respectively. Significantly differences were observed in the activity concentration of ^{226}Ra and ^{228}Ra in all plants. Grass and shrubs grown on mineral heaps were found contained higher concentration of radium compared to those grown on soils. This suggests that both isotopes may be associated to a considerable degree with their respect parent (^{238}U and ^{232}Th) minerals, and consequently isotopic exchange is not expected to occur in soil [6]. Besides that, the differences might depend on plant species, the radionuclides and on substrate characteristics [16]. Activity concentration levels found in different species grown on mineral heaps also differed largely, ranging from 311-603 Bqkg^{-1} for ^{226}Ra and 464-13937 Bqkg^{-1} for ^{228}Ra. Among all the plant species analyzed the highest uptake of ^{226}Ra and ^{228}Ra were found in grass species which grown on zircon. The highest uptake of ^{226}Ra and ^{228}Ra were found in jointhead grass (*Arthraxon hispidus)* and cogongrass (*Imperata cylindrica*in), respectively. This higher uptake may be associated with strong absorbing-powers of the root in those species compared to other species. The different respond to the radium uptake among species might be also related to metabolic rate differences between plant species due to their size and structure and maturity of the plant [17]. Therefore, it seems that jointhead grass (*Arthraxon hispidus)* and cogongrass (*Imperata cylindrica*in can be considered for phytoremediation of radium contaminated soil.

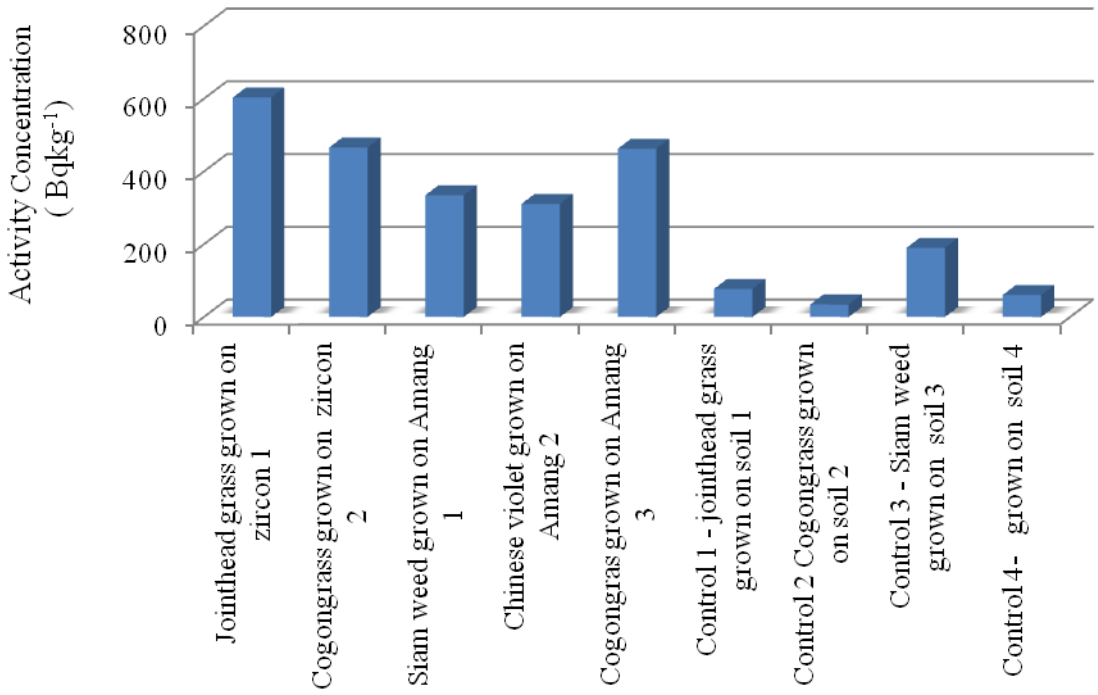

FIG. 3. Activity concentration of ^{226}Ra in grass and shrubs grown on mineral heaps and soils.

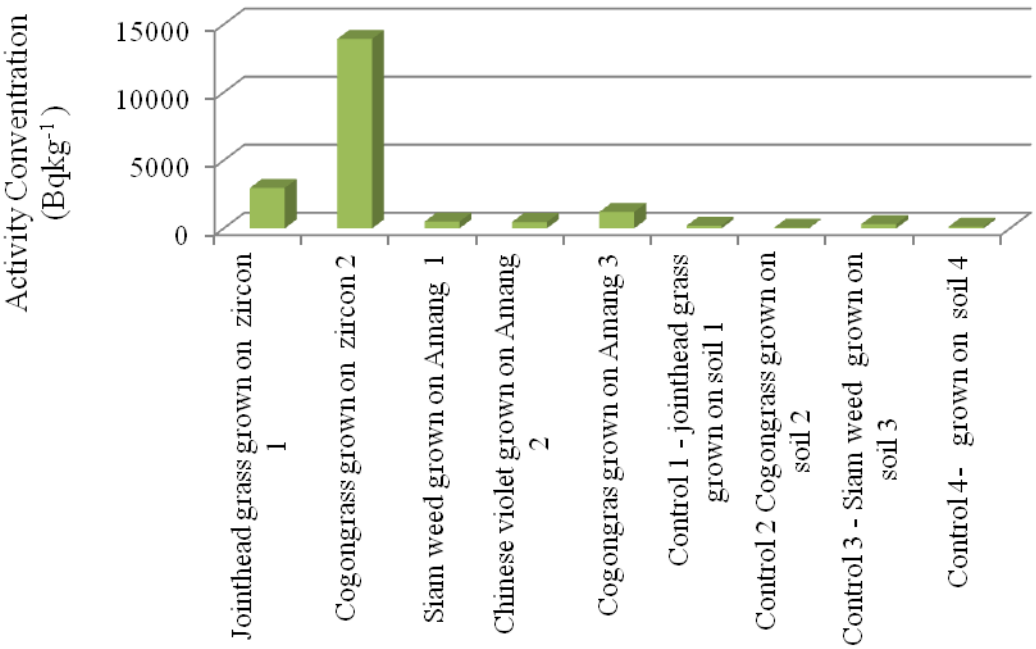

FIG. 4. Activity concentration of ^{228}Ra in grass and shrubs grown on mineral heaps and soils.

4. CONCLUSION

This preliminary study indicated that grass and shrubs grown on mineral heaps contained elevated levels of radium compared to those grown on normal soils. The uptake of ^{226}Ra and ^{228}Ra among the grass and shrubs grown on mineral heaps were differed largely and this suggests that the uptake of radium was depending on plant species. Based on this study, jointhead grass (*Arthraxon hispidus)* and cogongrass (*Imperata cylindrica*in) contained high activity concentration of ^{226}Ra and ^{228}Ra. Hence, further studies should be conducted considering these species for phytoremediation of radium contaminated soil.

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AIRBORNE SURVEY CAPACITY BUILDING OF NATIONAL NUCLEAR SAFETY ADMINISTRATION (MEP) IN CHINA

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Abstract

Airborne survey is being paid more and more attention in the nuclear and radiation environment monitoring due to its unique advantages, especially after the nuclear accident of Fukushima Japan. Thus, National Nuclear Safety Administration is strengthening to build airborne survey capacity. The administration has set up an advanced airborne survey system and established an expert team. This airborne survey system here is fixed under a capable helicopter, which has a monitoring volume of 75.6 liters, independent advanced digital spectrometer and intelligent data processing functions. In this paper, a way that is applied for wireless data real-time transmission is presented, and our research works on calibration and the survey methods are also included. The airborne survey system can be widely used in the nuclear and radiation accidents monitoring and relative radiation monitoring in NORM.

1. INTRODUCTION

Airborne gamma ray spectrometer surveying techniques had been applied in radiation environment survey for about half a century and has evolved significantly from continuing advances in instrumentation, field procedures, and calibration and data processing procedures. The use of gamma ray spectrometry as a tool for mapping radioelement concentrations has found widespread acceptance in diverse fields. Gamma ray spectrometry is widely used for environmental mapping, geological mapping and mineral exploration [1], invited more attention in the radiation environment monitoring following the nations concern on nuclear and radiation events.

Airborne survey can play a special role in space radiation monitoring due to its characteristics of high speed and broad coverage. An airborne surveying system was established in Nuclear and Radiation Safety Center as a part of the “2011 Fukushima nuclear accident responding radiation environment emergency capacity building program” of the National Nuclear safety Administration after the Fukushima nuclear accident. The function modification and development of this system has been done and will be illustrated below.

2. AIRBORNE GAMMA-RAY SPECTROMETRY

2.1. System basic configuration

The system adopts big volume scintillation detectors, which is made of sodium iodide treated with thallium, in the form of single crystals of up to 4.2 L in volume. Each individual crystal detector have its own multi-channel analyzer (MCA) mounted on the photomultiplier tube (PMT) directly. There are totally 18 such kind of crystal detectors , they are fixed in four detector cases, two of the four cases consist of 4 downward-looking crystal detectors , other two cases consist of 4 downward-looking crystal detectors and one upward-looking crystal detector.

The detector case is constructed as a carbon fiber ‘sandwich’ with the necessary thermal insulation acting as the filler. The inner part of the case is lined with shock absorbing material. The mechanical assembly on the front of the case holds the detector processing electronics

(DPU).

Fig.1 show the components of this airborne gamma ray spectrometer (AGRS). In addition to the gamma spectrometer itself, the system configuration also contains a number of ancillary or additional instruments，such as radar altimeter for height corrections with changes in altitude, Air Pressure and Temperature sensor for ‘air column’ measurement corrections, GPS based flight navigation system with Survey Planner and Pilot Steering Indicator, Power Distribution Unit (PDU) .

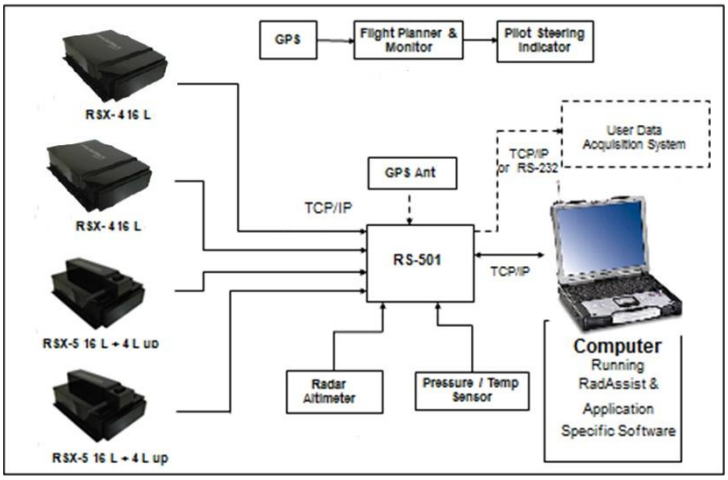

FIG. 1. Basic Configuration.

2.2. System installation

The system was designed for helicopter. It was fixed underneath and away from the fuel-tank for better sensitivity. The loading capacity、the size of detector、center of gravity and the passengers were also concerned. The easy-loading framework was made from titanium alloy so that it can afford all the four detector cases, see Fig. 2. The system can also be fixed in the cabin of helicopter or fixed wing aircraft which is relative easy.

FIG. 2. Airborne Gamma-Ray Spectrometry (AGRS) Fixed Setting.

3. FUNCTION OF AIRBORNE GAMMA-RAY SPECTROMETRY

There are several unique advantageous functions which make it one of the most advanced airborne survey system. The main advantageous functions are:

3.1. Advanced digital spectrometer

The Advanced Digital Spectrometer (ADS) is a high performance Multi-Channel Analyzer (MCA) with very low dead time and very high count rate capability. The spectrometer operates up to 250,000 cps without any spectral distortion and with less than 20% dead time. It will operate up to 1,000,000 cps with some spectral distortion. The AGRS have a resolution of around 8.5% (to the 662KeV photopeak of ^{137}Cs), a measuring rate of dose equivalent covering the rage of 10 nSv/h to 0.1Sv/h, can be used in the rage of –30°C to +60°C in temperature, All detectors can be started synchronously to work within 20 microseconds.

3.2. Spectral stabilization

Automatic spectral stabilization ensures accurate and reliable data using the naturally occurring isotopes. There is no need for external sources to either 'kick-start' or to assist stabilization. Fig.3 illustrates a detector case (4x 4.2L NaI detectors) with an advanced gain correction algorithm that will track and correct for any thermal or electronic changes. The performance is identical within one detector (1 x 4.2L NaI detector).Fig.3 illustrates the automatic gain stabilization of four individual crystals to a step change in temperature over the range of -20^0 C to +50^0 C in a 24 hour period.

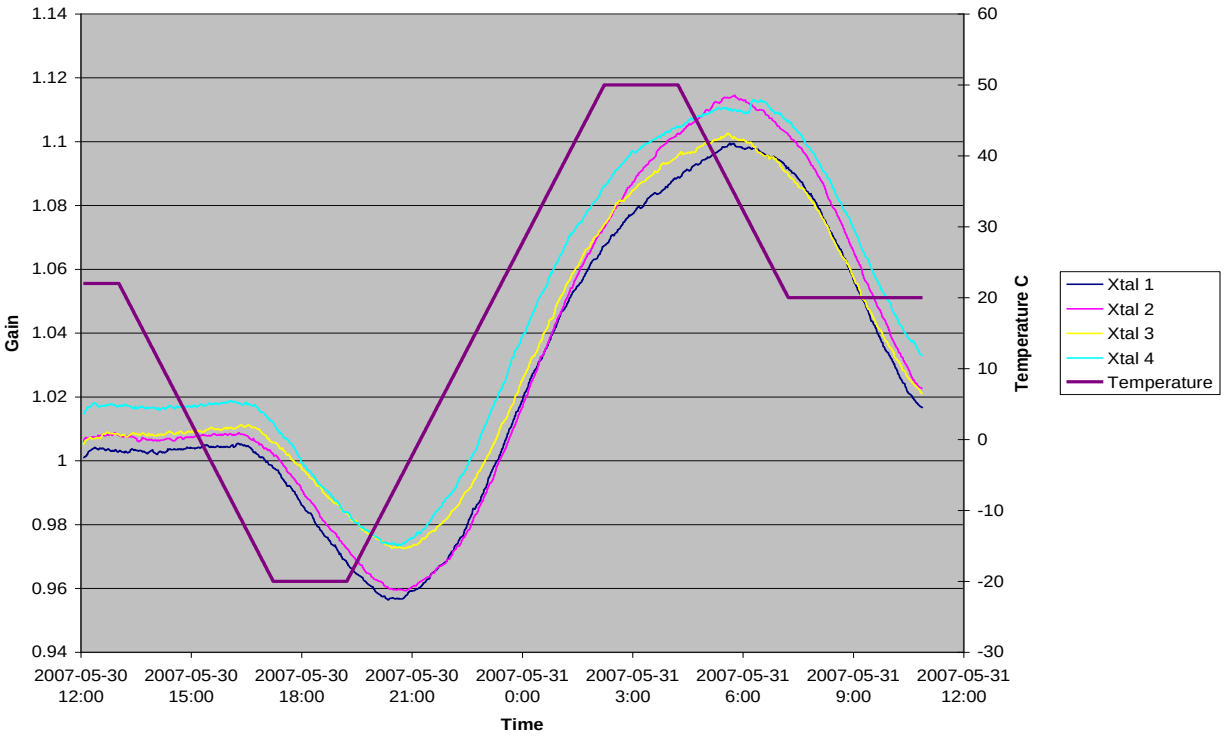

FIG. 3. Temperature Response functions of 4 NaI(Tl) Scintillation Detectors'

The auto stabilization occurs approximately every two minutes greatly minimizing drift and maintaining the peak position +/- 0.2% over 1024 channels. The 1024 channel spectrum is fully linearized and combining this with the accurate stabilization ensures that any number of crystals can be summed together with essentially no spectral degradation for subsequent data analysis.

3.3. Powerful utility software and data processing functions

The AGRS is supplied with powerful utility software, which can monitor and record all data from detectors and ancillary or additional instruments previously mentioned as well as their status, finally show them in computer operation interfaces. Operation staff use the software to check monitoring data and carry out data processing and analytical work. the system software also serves the following purposes.1) Set up of Operating and Device Parameters 2) Control the System 3) Monitor the data, spectral, strip chart format, map view with breadcrumb trail etc. 4) Perform Nuclide Identification 5) The Recording and Exporting and replying of data 6) Event Log 7) Various 'toolbox' utilities to ensure system performance

3.3.1. Energy channels and windows

The system gamma ray spectrum over the rage of 15KeV to 3.0MeV is resolved by Advanced Digital Spectrometers (ADS) into 1023 channels, each one ranging from 2.5 to 3.2 KeV in width. A separate channel records all high energy radiation from 3.0MeV to 6.0MeV, caused by cosmic radiation. the counts can be summed over groups of channels to produce up to 10 energy windows as you like, each window is particularly sensitive to energies of the interested radioactive nuclides, such as ^{40}K, or 137Cs ,or the U or Th decay series and so on[2].

3.3.2. Custom script function

The system software has a powerful function of graphics displaying and monitoring data editing. According to the different actual need, Operation staff can edit the counts of total and different energy windows, set different abnormal alarms and their expected values to find abnormal occurrence, for instance, artificial radionuclide or high radioactivity level of natural background or radioactive plume, etc.

3.4. Upward-looking detectors

Because of the presence of radon and its decay products in the atmosphere and Radon is a decay product in the uranium decay series, and being a gas can diffuse out of the ground. the effect of radon and its gamma ray emitting decay products can be significant and cause serious errors in the measurement of ground concentrations of uranium[1] [2].

Airborne detector packages could usually be configured with an additional NaI crystal mounted above the four main crystals (downward-looking detector) in the northern hemisphere where there is significant 137Cs contamination[2] [3]. It is called the upward-looking detector method. The main crystals then partially shield the additional crystal from radiation from the ground. The additional crystal (the upward-looking detector) gives the detector a directional sensitivity. These detectors give the spectrometer a directional sensitivity capable of distinguishing between atmospheric radon or atmospheric radioactive plume and terrestrial sources of radiation[1]. In the installations here there is no lead sheet shield between upward-looking detectors and downward-looking detectors.

3.5. Data wireless transmission

Airborne survey data is normally recorded for further analysis while in our case the data is conveyed to a ground server at the same time, there for the real-time analysis is possible. It is achieved via two parts:1、a Wireless Local Area Network (WLAN) between aircraft and ground monitoring vehicle based on radio-frequency transmissions；2、a Virtual Private

Network(VPN) between vehicle and monitoring command centre. A 3G wireless router is used to connect the two parts as showed below.

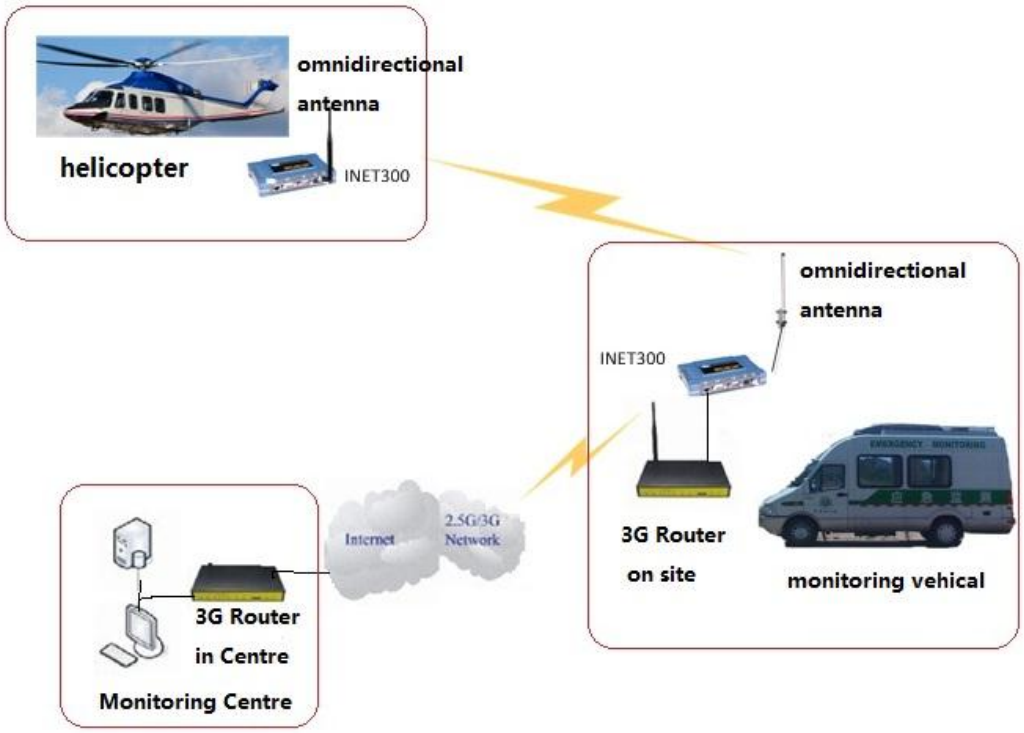

FIG. 4. Wireless data communication between the Ground Monitoring Centre and the helicopter.

4. CALIBRATION

This airborne gamma ray spectrometer survey system is designed to be applied during radiological emergency and environment monitoring [4]. The system calibrations (in process) will include the following parts:

(1) Calibrations for Natural background [2] [5] [6], including
---- Determination of aircraft、equipment and cosmic background
---- Determination of U、Th、K standard spectrum、stripping ratios and system sensitivity
---- Determination of radon background
---- Determination of height attenuation coefficient
---- Radar altimeter calibration
---- Calibration of barometric pressure transducer
This part of work is aimed to determinate the sensitivity coefficient of ground natural elemental concentrations and total dose rate at 1 meter aboveground for natural radionuclide finally.
(2) Calibrations for Nuclear and radiation accidents/incidents monitoring[1] [4] [7].
There are two kind of calibration models for nuclear accidents/incidents monitoring which are radioactive fallout monitoring and radioactive source searching. The calibration is concentrate on artificial radioactive nuclide、height correction factor、aerial sensitivity、the ratio of total counts /dose on different height and system angle response function. In this case ^{137}Cs surface sources were used to simulate an infinite flat surface instead of a radiocontaminated ground after a real accident. Beyond that, the impact of radioactive plume is hypothesized to be linear dependence on time of flight in this paper.

5. SYSTEM SET OUT AND TESTING

Nuclear and Radiation Safety Center was assigned to the airborne survey system operation by National Nuclear safety Administration. An experts team was set up then acceptance checking、 research work and functional test in a SUV and under a helicopter respectively were carried out in turn during about 6 month, afterwards data transmission system and GIS system were updated. Since then, several tasks were carried out by the team successfully. Fig.5 are one result map of one of those tasks.

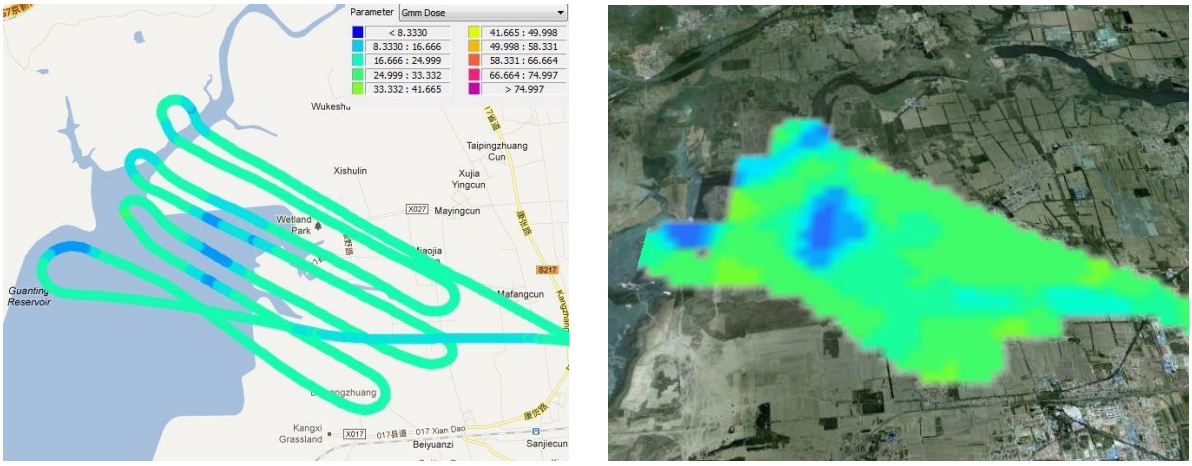

FIG. 5. Gamma ray radiation map, showing no contamination in a given region . All flight lines are shown.

The team have different plans of survey and analytical methods for radiation accident、nuclear explosion、environment monitoring and mine searching. They are experienced and prepared for their duties.

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DISTRIBUTION AND FRACTIONATION OF URANIUM ISOTOPES IN WATER FROM SAN MARCOS DAM, CHIHUAHUA, MEXICO

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Abstract

The aim of this work was to assess the fractionation and distribution of isotopic uranium contained in both, suspended matter and water. Uranium was measured in three points along the San Marcos dam: water input, midpoint, and near to dam wall. Every water sample was separated in suspended particulate matter fraction and in dissolved fraction. Likewise, suspended particulate matter was divided and analyzed in three particle size fractions: coarse, medium, and fine. The results show that most uranium was in the suspended particulate matter. The distribution coefficient k_d ranged between $1.6 \cdot 10^1$ to $1 \cdot 10^3$ L/g. In dissolved fraction, high concentrations of ^{234}U were found, where the activity ratio (AR, $^{238}U/^{234}U$) ranged from 2.1 to 3.5. In average, uranium contents tend to be concentrated in coarse fraction, with AR near to unit. Medium and fine fractions showed ^{238}U concentration higher than ^{234}U. The highest uranium concentration was at water input point. The highest ^{238}U concentrations were found: in the coarse fraction at the input point, in the medium fraction at the midpoint of the dam, and in the fine fraction by the nearest point of the dam wall.

1. INTRODUCTION

To assess the radiological contamination from natural sources, it is important to understand the behavior of radionuclides released to the environment [1]. The concentration of radioisotopes in water are influenced by the lithology of the region [2], and in addition, are strongly affected by its interaction with the suspended particulate matter (inorganic and organic), and by the sedimentation. Sedimentation and resuspension are important processes in the migration of radioisotopes from water to sediment and vice versa. Thus, the main physical processes that have the control on the migration of radioisotopes in the different water bodies are: diffusion and dispersion in water transport, exchange phases solid/solution, deposition and remobilization in sediments, both suspended and precipitates [3]. In most of the rivers, the suspended and dissolved materials are an excellent source of information about the history of the material from its source to its transport through the water [4].

According to the chemical properties of the various radioisotopes, their behavior in natural waters depends on three main factors: a) the chemical speciation of radioisotopes in solution, b) interactions with mineral or organic solids and c) reaction with colloidal material. The chemical speciation of uranium in solution has been the most extensively studied, where the pH and redox potential (Eh) are the main parameters that affect their chemical form. Thus, uranium under reducing conditions has valence of +4 and it is insoluble, but under oxidation conditions it takes valence of +6 which is its soluble form, being the most common the uranyl ion UO_2^{+2}. The solubility of uranium depends on its ability to form compounds; for example, compounds with carbonates inhibit the adsorption of uranyl, especially in alkaline solutions. In oxidized waters, uranyl compounds may predominate with hydroxides, carbonates, fluorides, sulfates or phosphates [5]. Moreover, the actinides have high reactivity with mineral surface and with organic compounds, and results in the removal of these from the solution [6].

It is also known that colloids affect the mobility of radioisotopes in water and soils, and thereby influencing the division of these within surface environments [7]. Studies about uranium contamination levels in ground and surficial water have been performed in many countries around the World. In San Marcos zone located in Chihuahua, Mexico, it has been found that in water from San Marcos dam the activity concentration of ^{238}U has been of up 7.7 Bq/L [8]. In addition, in coarse suspended solids (particles size >25 μm) from water of that dam, the values of uranium ranged from 0.022 to 1.9 Bq/g [9]. In most of the researches, surface water is filtered at 0.2 or 0.45 microns to separate nominally the particulate phase, which represents the products of physical and chemical weathering. The "dissolved phase" (<0.2 or 0.45 μm) of surface water is enriched with solutes derived from weathering and may also contain colloidal material [10]. Therefore, knowing how the distribution and fractionation of uranium is in the suspended particulate matter from surface water is the goal in this scientific work.

The aim of this work was to assess the fractionation and distribution of isotopic uranium contained on both, suspended matter and water.

2. MATERIALS AND METHODS

2.1. Study Area

In Figure 1 is showed the area of study. This study was carried out in the San Marcos-Sacramento area, which is located at northwest of Chihuahua city, Mexico. San Marcos area is a rhyolitic volcanic system, showing mainly rhyolitic tuffs and some Upper Cenozoic intermediate volcanic sequences [11]. Its uranium mineralogical characterization showed the following radioactive species: uranophane, metatyuyamunite, uraninite, bequerelite and masuyite [12]. San Marcos range formation includes a river (San Marcos River), a dam (San Marcos dam), and at least two outcrops of uranium minerals. These outcrops are named Victorino and San Marcos I, which are of hydrothermal origin [11]. The river passes close to the outcrops, firstly river water crosses Victorino mineral outcrop, and secondly next to the San Marcos I mineral outcrop, finally the river reaches to the dam where most water is stored.

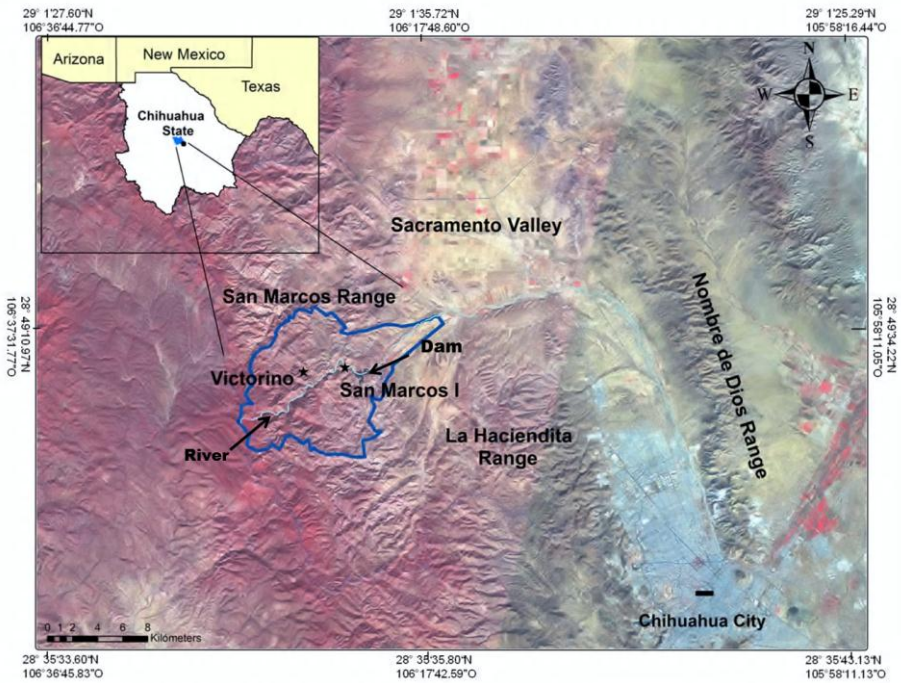

FIG. 1. Location of the area of study, San Marcos region.

2.2 Sampling

Sampling was carried out in May 2011; five water samples were taken from different points of the dam. Three sampling points were taken at the surface level along the dam: first at input water point (1S), the second at middle point of dam (2S) and third the nearest point to the dam well (3S). This last point was sampled at the deepest place of dam of 19 m. The other two sample points were taken in depth from point 3S: first to 8 meters (3M) and the second to 16 meter (3P). In Figure 2 is showed the sampled points inside the San Marcos dam.

FIG. 2. Sampling points in San Marcos dam.

The surface water samples were collected in polyethylene 5 L containers. Geographic coordinates, temperature, total dissolved solids (TDS), redox potential (Eh) and pH parameters were measured in situ. The water samples were filtered to different pore diameter to obtain size particle fractions of: >25 μm (coarse fraction, CF), 11 to 25 μm (medium fraction, MF), and 1 to 11 μm (fine fraction, FF) from suspended matter. Uranium within water that passed through the last filtration was called "dissolved uranium" (dissolved fraction).

2.3. Experimental

U-isotopes concentration was determined by liquid scintillation counting (LSC). ^{238}U and ^{234}U specific activities were determined using a PERALS (photon/electron rejecting alpha liquid scintillation) spectrometer [13]. In this methodology, U is extracted with URAEX extracting cocktail [14]. For accuracy, an artificial water sample was prepared using a certified reference material of uranium (solution from High Purity Standards no. 100064), and for its quantification it was spiked with ^{232}U (SRM 4324B from NIST). Results for ^{238}U and ^{234}U were 0.601Bq and 0.571 Bq, respectively, with relative uncertainty of 3%, while those reported from the reference material were 0.617± 0.002 Bq for ^{238}U and 0.599 ± 0.002 Bq for ^{234}U.

3. RESULTS AND DISCUSSION

3.1. Size fraction contents

In figure 3 is showed the size particle contents (%) of samples. At surface level, contents of CF, MF, and FF ranged from 55 to 93 %, from 6 to 35 %, and from 1 to 9 %, respectively. The contents of coarse fraction tend to enhance from input water to the dam wall, whereas the medium and fine fraction tend to decrease.

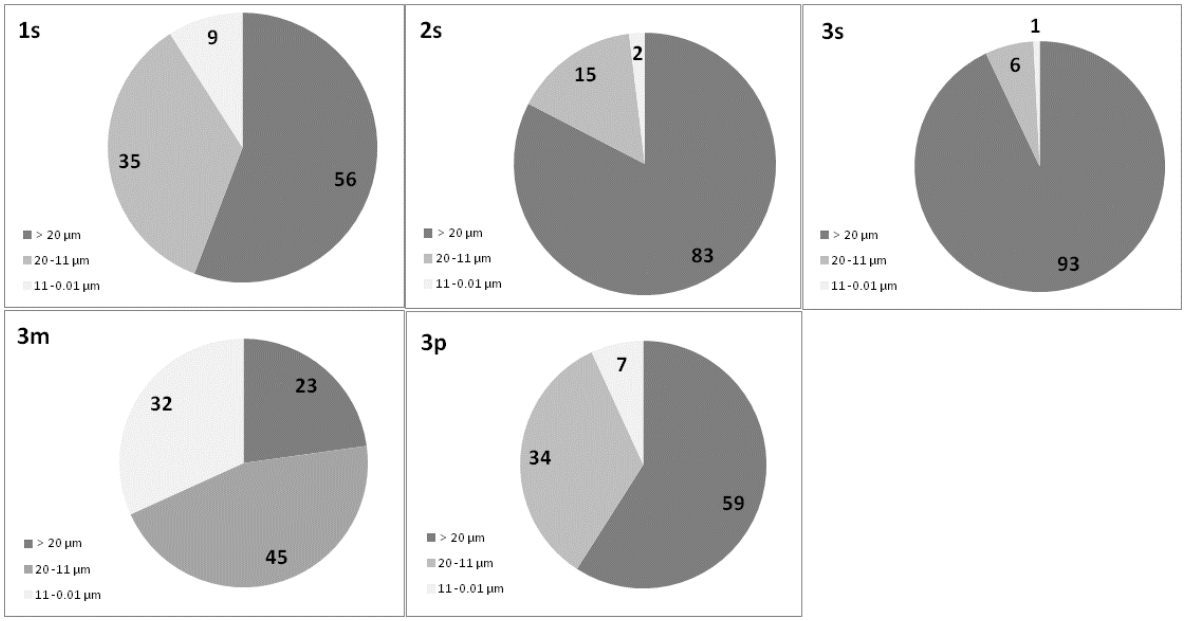

FIG. 3. Samples contents (in % weight) of coarse, medium, and fine fraction.

Otherwise, the contents of coarse fraction, medium fraction, and fine fraction in different sample depths ranged from 23 to 93 %, from 6 to 45, and from 1 to 32, respectively. In these samples, a tendency was not showed about the content of size particles; however, the point to 8 depth meters shows the most uniformly distributed particle fraction contents.

3.2. Uranium concentration

In Table 1 are shown the activity concentrations of ^{238}U and ^{234}U isotopes, as well as their $^{234}U/^{238}U$ activity ratios (AR), in suspended particulate matter and in dissolved fractions of surface water samples from San Marcos dam.

In suspended particulate matter, U was fractionated depending of particle size. In average, uranium contents tend to be concentrated in coarse fraction, with AR near to unit. The highest U content in surficial CF was found at input water point (1s), and the highest ^{238}U was in the deepest sampling point (3p). AR in the point 1s suggests that coarse fraction is composed of sediments from the river, whereas the high ^{238}U content in point 3p can be attributed to sediments resuspended from the dam bottom. In addition, the $^{234}U/^{238}U$ AR increase along the surface flux from input water to the dam wall, reaching to 1.35. In medium fraction the high concentration of U was at point 2s. On the contrary to behavior of $^{234}U/^{238}U$ in coarse fraction the AR in medium fraction decreases along surface flux. The medium size particles, at depth, showed concentration of ^{238}U higher than ^{234}U. In fine fractions ^{238}U concentrations were also higher than those ^{234}U at surface level. However, fine size particles increase their concentration of ^{234}U with depth, where the highest content was at 8 meter depth.

TABLE 1 SPECIFIC ACTIVITY OF ISOTOPIC URANIUM AND THEIR UNCERTAINTY, AS WELL AS THE ACTIVITY RATIOS IN DISSOLVED FRACTION FROM SURFACE WATER.

Size particle fraction	^{238}U	^{234}U	AR ($^{234}U/^{238}U$)	*Ut	Kd (L/g)
Coarse (>20 µm, mBq/Kg)					
1S	4.80±0.11	4.79±0.11	1.00	9.59	$1.7 \cdot 10^2$
2S	2.20±0.19	2.30±0.21	1.05	4.50	$2.7 \cdot 10^2$
3S	2.65±0.21	3.59±0.26	1.35	6.25	$4.5 \cdot 10^2$
3M	1.65±0.12	2.52±0.16	1.53	4.17	$2.3 \cdot 10^2$
3P	11.28±0.60	3.44±0.31	0.31	14.72	$1.0 \cdot 10^3$
Medium (20 - 11 µm, mBq/Kg)					
1S	0.35±0.01	0.51±0.02	1.47	0.86	$1.6 \cdot 10^1$
2S	1.46±0.14	1.32±0.09	0.90	2.78	$1.7 \cdot 10^2$
3S	0.73±0.09	0.01±0.001	0.02	0.74	$5.4 \cdot 10^1$
3M	1.38±0.16	0.25±0.03	0.18	1.63	$9.0 \cdot 10^1$
3P	0.58±0.08	0.09±0.01	0.16	0.67	$4.7 \cdot 10^1$
Fine (11 - 0.01 µm, mBq/Kg)					
1S	2.32±0.14	5.02±0.32	2.17	7.34	$1.3 \cdot 10^2$
2S	2.45±0.00	0.82±0.07	0.33	3.27	$2.0 \cdot 10^2$
3S	5.17±0.79	1.92±0.33	0.37	7.09	$5.1 \cdot 10^2$
3M	0.16±0.03	8.24±0.88	51.28	8.40	$4.7 \cdot 10^2$
3P	0.19±0.01	5.91±0.24	31.29	6.10	$4.3 \cdot 10^2$
Dissolved (mBq/L)					
1S	12±1	41±5	3.4	0.06	
2S	5±0.1	13±1	2.6	0.02	
3S	3±0.1	10±1	3.3	0.01	
3M	5±0.1	12±2	2.4	0.02	
3P	6±0.1	7±1	1.2	0.01	

*Ut was determined by the sum of ^{238}U and ^{234}U

On the other hand, dissolved fraction showed higher contents of ^{234}U than ^{238}U, showing the highest values of AR at surface level, as was expected. At surface level, the highest AR was found at input water point whereas in depth this AR decreases from 3 to 1.

According to the above, the results showed that most uranium was in the suspended particulate matter. The distribution coefficient k_d, calculated by the activity concentration ratio between suspended particulate matter and dissolved fractions, ranged between $1.6 \cdot 10^1$ to $1 \cdot 10^3$ L/g.

4. CONCLUSIONS

Size particles contents were different for each sampling point, being the coarse fraction with highest percent in every sample. The highest uranium concentration was at water input point. The highest ^{238}U concentrations were found: in the coarse fraction at the input point, in the medium fraction at the midpoint of the dam, and in the fine fraction by the nearest point of the dam wall. According to the distribution coefficient k_d, most of uranium was in the suspended particulate matter. In suspended particulate matter, U was fractionated depending of particle size. In average, uranium contents were concentrated in coarse fraction. Therefore, in medium and fine fractions ^{238}U concentration were higher than those of ^{234}U. Uranium distribution varied according to sampling point. The highest uranium concentration was at

water input point. The highest ^{238}U concentrations were found: in the coarse fraction at the input point, in the medium fraction at the midpoint of the dam, and in the fine fraction by the nearest point of the dam wall.

For all the aforementioned, the results have shown a possible lixiviation of uranium from geological substrate into the surface water and an important fractionation of isotopic uranium, which has in consequence that uranium is distributed non homogeneously along San Marcos dam.

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ELEMENTAL DISTRIBUTION IN DEPTH AS WELL AS THEIR FRACTIONATION RELATED TO PARTICLE SIZE, IN PHOSPHOGYPSUM FROM PHOSPHORIC ACID PRODUCTION (HUELVA, SW SPAIN)

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Abstract

In this work, we assessed uranium and some toxic elements distribution according to particle sizes in phosphogypsum cores, in order to improve the knowledge behavior of radioactive (^{238}U and ^{234}U) and toxic elements (Cd, Cr, Cu, Zn, Ag, Zr, Pb, Y, and Sr) Elemental concentration was measured in two phosphogypsum cores, which were separated in three depth intervals. Every sample also was divided in three particle size fractions. Results show that most of elements are not distributed homogeneously in phosphogypsum cores. The differences in distribution of elements suggest that there are fluxes of elements. On the other hand a high fractionation of elements was observed, where most of those were concentrated in fine particles in comparison with coarse and medium particle sizes. The main consequence of that most of these elements are concentrated in the fine fraction (particles <20 μm), is that make them easily mobilized by leaching and/or erosion.

1. INTRODUCTION

In recent years, the assessment of pollution, risk and impact caused by radionuclides released into the environment by non nuclear industries has given great importance. Most of these industries have generated large quantities of wastes with several pollutants, which have forced them to become aware of the impact caused to the environment. In Spain, factories related to phosphoric acid and fertilizer manufacture were located in the estuary of the Tinto and Odiel rivers. It is well established that these industries used phosphate rock of marine sedimentary origin, mainly from Morocco and Senegal, as raw material [1]. This rock is affected by high concentrations of some trace elements and naturally-occurring radionuclides [2, 3]. The industrial processes used allow that high concentrations of toxic elements are also present in both products and wastes. Hence, the presence of trace elements and natural radionuclide concentrations, at higher than natural levels, would be considered as environmental contamination. These industries used the "di-hydrated" process to obtain phosphoric acid as main product and, as by-products hydrogen fluoride and calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$), which is a by-product called Phosphogypsum (PG) [3]. This PG is also composed, in lesser 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]. Previous studies, the fluxes and contents of U in the phosphoric acid production process have been determined that more than 80 % of the U content is in phosphoric acid while the U content in phosphogypsum is lower [1, 5-7]. However, the 23 % of U is bounded to the bioavailable fraction of phosphogypsum particles [8].

It is estimated that annually 2.5 million tons of phosphogypsum were deposited and stored in open-air piles near to the factories. 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].

In this work, we assessed uranium and some toxic elements distribution according to particle sizes as well as to determine the elemental fluxes in phosphogypsum cores, in order to improve the knowledge behavior of radioactive and toxic elements.

2. MATERIALS AND METHODS

Phosphogypsum cores (PG) were taken from a stack belonging to a phosphoric acid industry, located next to the Tinto river (37º 15.3'N, 6 º 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 homogenized to 100 µm diameter by grinding and sieving and, these were then dried at 50 ºC for 48 h. Elemental concentration was measured in samples from two phosphogypsum cores (total depth of 90 cm), which were separated in three depth intervals: 0-30 cm, 30-60 cm, and 60-90 cm. Every sample also was divided in three particle size fractions: coarse (>53 µm), medium (53-20 µm) and fine (<20 µm).

Concentrations of trace elements and radioisotopes were obtained by X-ray fluorescence (XRF) and alpha spectrometry, respectively. Concentrations of Cd, Cr, Cu, Zn, Ag, Zr, Pb, Y, and Sr were obtained by XRF analysis, using a Panalytical AXIOS with an Rh tube. Isotopic uranium concentrations were carried out by alpha spectrometry. Samples were spiked with ^{232}U and put under the radioanalytical analysis procedure. Total sample dissolution was performed by atmospheric acid digestion using 8M HNO_3 and H_2O_2. UTEVAS ion-exchange resins were used to isolate uranium (Michel H. et al., 2008). Then, uranium was electrodeposited on stainless steel planchets (Hallstadius, 1984). An alpha spectrometry chain Alpha Analyst (CANBERRA) was used for alpha activity measurements. Radiochemical yield was determined by the ^{232}U counting rate.

3. RESULTS AND DISCUSSION

3.1. Particle size fractionation

Average values of phosphogypsum granulometry showed that the medium fraction (20-53 µm) was the dominant size fractions by up 40 %, whereas coarse (> 53 µm) and fine (> 20 µm) were of 30 and fine 28 %, respectively, of the sample masses.

3.2. XRF characterization

Table I shows the concentration of the some trace elements, along the cores, found in three different particle size fraction, coarse (CF), medium (MF), and fine (FF). According to our results, the concentrations of trace elements were found in the following order of abundance: Sr > Y > Ba > Cr >Cu > Ag > Zn> Cd> Zr.

From results of Table 1, trace elements are not distributed homogeneously in phosphogypsum cores. In general, most of those elements tend to be concentrated in the deepest zones. Thus, in core I elements such as Cr, Cu, and Zr, increase with depth, whereas Ag and Cd tend to decrease with depth. In core 2 elements such as Cr, Ag, Cd, and Zr, tend to be concentrated in the interval from 0 to 60 cm. Otherwise, in both cores, elements that increase with depth Zn, Ba, Sr, and Y while Pb tends to be concentrated in the first two intervals.

On the other hand, a high fractionation of elements was observed, where most of those were concentrated in fine particles in comparison with coarse and medium particle sizes, nevertheless, elements as Cd showed to be concentrate in medium fraction.

3.3. Alpha spectrometry

In Table II is shown the concentration of ^{234}U and ^{238}U along the cores, found in same three different particle size fractions.

From results, the behavior of both ^{234}U and ^{238}U is the same along of both cores; the value of ratio $^{234}U/^{238}U$ is 1, for all samples. At the same way of trace elements, most of uranium is concentrated in the deepest samples of cores. In core I, the high concentration of uranium is in the interval from 60 to 90 cm of depth, whereas in core 2 it also tends to be concentrated in the sample from 0 to 60 cm. In addition, also the highest contents of uranium were presented in fine particles that those found in coarse and medium particle sizes.

TABLE 1. TRACE ELEMENT CONCENTRATIONS (PPM) OF PG CORES SAMPLES DIVIDED IN THREE SIZE PARTICLE FRACTIONS: COARSE (>53 μm), MEDIUM (53-20 μm) AND FINE (<20 μm).

Sample/element	Y	Ba	Sr	Cr	Cu	Zn	Ag	Cd	Zr	LOI*
Core I										
P14(0-30)										
CF	131.2	69.7	641.2	11.2	10.7	6.9	10.0	6.7	3.2	8.4
MF	134.1	74.6	628.3	12.6	8.3	6.5	10.7	7.3	4.4	7.4
FF	202.6	100.6	644.1	18.4	16.2	7.9	10.7	6.9	7.1	8.0
P14(30-60)										
CF	139.8	77.9	617.6	15.0	13.8	7.3	8.1	5.9	3.0	7.5
MF	134.1	61.9	666.3	12.2	9.4	8.1	9.0	6.6	3.8	7.5
FF	138.5	69.7	663.4	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	7.5
P14(60-90)										
CF	133.5	115.8	704.6	22.4	11.2	8.2	6.6	5.0	3.3	4.7
MF	136.9	129.2	737.7	22.4	12.0	8.5	7.1	5.2	4.8	7.9
FF	211.2	225.4	775.5	36.0	12.1	12.6	6.3	3.4	9.0	7.5
Core II										
P19(0-30)										
CF	133.7	73.6	627.5	8.31	13.3	6.2	7.3	5.0	4.1	4.2
MF	131.9	71.6	633.8	10.9	11.6	6.6	7.4	4.3	5.9	7.4
FF	191.9	91.5	661.6	11.03	13.7	8.2	8.9	7.6	6.7	8.2
P19(30-60)										
CF	165.5	72.4	672.2	15.2	8.9	7.2	10.0	7.0	3.9	2.3
MF	177.8	72.6	688.2	13.23	7.9	7.1	8.3	5.8	8.7	9.2
FF	259.5	98.0	742.6	16.73	13.7	9.0	15.6	10.5	8.2	2.4
P19(60-90)										
CF	134.6	125.5	776.6	13.7	11.8	7.5	8.4	5.9	1.4	7.9
MF	182.0	181.5	856.9	13.65	9.6	8.5	1.9	0.2	3.9	10.6
FF	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	8.9

*Loss on ignition (% weight). n.m. not measured

TABLE 2. ISOTOPIC URANIUM CONCENTRATIONS (Bq/kg), AS WELL AS THEIR ACTIVITY RATIO ($^{234}U/^{238}U$) IN PG CORES SAMPLES.

Sample/isotope	^{234}U	^{235}U	^{238}U	$^{234}U/^{238}U$
Core I				
P14(0-30 cm)				
CF	116.8 ± 9.0	3.1 ± 0.9	114.0 ± 8.9	1.0
MF	128.1 ± 7.2	1.2 ± 0.4	116.0 ± 6.9	1.1
FF	226.4 ± 13.8	8.1 ± 1.1	210.0 ± 12.8	1.1
P14(30-60)				
CF	111.5 ± 9.4	3.3 ± 1.1	112.0 ± 9.4	1.0
MF	127.4 ± 7.2	2.6 ± 2.9	125.0 ± 7.1	1.0
FF	143.7 ± 8.1	4.6 ± 0.9	142.0 ± 8.0	1.0
P14(60-90)				
CF	175.5 ± 5.6	3.4 ± 0.6	167.0 ± 5.5	1.1
MF	138.4 ± 7.8	3.8 ± 2.9	126.0 ± 7.1	1.1
FF	244.9 ± 13.8	7.1 ± 6.9	240.0 ± 13.6	1.0
Core II				
P19(0-30)				
CF	75.2 ± 2.3	1.7 ± 0.3	73.3 ± 2.3	1.0
MF	114.1 ± 9.6	3.3 ± 1.1	115.0 ± 9.6	1.0
FF	122.1 ± 4.8	114.6 ± 9.6	110.0 ± 4.6	1.1
P19(30-60)				
CF	118.9 ± 6.7	3.6 ± 2.0	118.0 ± 6.7	1.0
MF	150.0		148.0	
FF	211.1 ± 7.1	5.5 ± 1.0	193.0 ± 6.8	1.1
P19(60-90)				
CF	85.7 ± 6.0	2.3 ± 0.5	76.6 ± 5.5	1.1
MF	124.5 ± 8.4	3.9 ± 0.8	115.0 ± 7.9	1.1
FF	144.3 ± 9.9	5.6 ± 1.1	133.0 ± 9.3	1.1

In these samples, there was no correlation between any element and the organic material (this taken as LOI). The differences in distribution of elements suggest that there are vertical flux of elements: in core 1 the flux is from up to down in depth and concentrate in the deepest zone (90 cm), whereas in core 2 the movement behavior of most of elements is only until the first 60 cm, excepting Cr that is concentrated in de last interval from 60 to 90 cm. However, it is not possible to determine a horizontal flux because only two cores were taken.

The higher activity concentration of U-isotopes generally occurs in the fine fraction (244.9 Bq/kg of ^{238}U). Lowest value is observed in the coarse fraction (75.2 Bq/kg of ^{238}U). The $^{234}U/^{238}U$ activity ratio is close to the unity in all the samples and there is not dependent of granulometry.

4. CONCLUSIONS

Concentration of toxic elements (Cd, Cr, Cu, Zn, Ag, Zr, Pb, Y, and Sr) and activity concentration of U-isotpoes (^{238}U, ^{235}U, ^{234}U) were measured in two cores of phosphogypsum. Different samples were separated from each core in three depth intervals: 0-30 cm, 30-60 cm, and 60-90 cm. Every sample also was divided in three particle size fractions: coarse (>53

μm), medium (53-20 μm) and fine (<20 μm). Results show that most of elements are not distributed homogeneously in phosphogypsum cores. In core 1 elements such as ^{238}U, Cr, Cu, and Zr, increase with depth, whereas Ag and Cd tend to decrease with depth. In core 2 elements such as ^{238}U, Cr, Ag, Cd, and Zr, tend to be concentrated in the interval from 0 to 60 cm. Otherwise, in both cores, elements that increase with depth Zn, Ba, Sr, and Y while Pb tends to be concentrated in the first two intervals. The differences in distribution of elements suggest that there are flux of elements: in core 1 the flux is from up to down in depth and concentrate in the deepest zone (90 cm), whereas in core 2 the movement behavior of most of elements is only until the first 60 cm, excepting Cr that is concentrated in de last interval from 60 to 90 cm. On the other hand a high fractionation of elements was observed, where most of those were concentrated in fine particles in comparison with coarse and medium particle sizes, nevertheless, elements as Cd showed to be concentrate in medium fraction. The main consequence of that most of these elements are concentrated in the fine fraction (particles <20 μm), is that make them easily mobilized by leaching and/or erosion.

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IMPACT OF NATURAL RADIOACTIVITY IN A THERMAL WATERS SPA: THE CASE OF ELGUEA SPA IN CUBA

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Abstract

The use of thermal waters coming from deep geologic structures in spas has been identified as typical scenarios of exposure to radiation of natural origin. In general these scenarios can affect tourists and/or patients under treatment, as they can be in direct contact with the materials carrying radionuclides, as well as the workers whose permanency in sites with increased levels of radiation is greater than that of the patients. By this reason studies for assessing the radiological impact of these exposure scenarios over these population categories have been carried out worldwide. The spa Elguea, located in the north coast of Villa Clara, Cuba, is considered one of the most important spas in Latin America. This spa is equipped with three swimming pools, individual bathtubs with motors for massages, sauna, hydrotherapy and mud therapy. All these services use, in one way or another, the existent in the area of the spa thermal waters and mud. The waters of this spa are rich in chlorine, sodium and bromine salts, sulphides and they also contain significant levels of radon. Present paper shows the dose estimations made for both patients and worker based on the radiological characterization of the spa and its surroundings and for identified exposure scenarios. Dose values are in the range 1.0 to 180 μSv/year for workers, the most irradiated group, and these results suggest that it is not necessary to adopt any additional regulation or measure for protection.

1. INTRODUCTION

The problem of non-controlled exposures to natural radiation sources due by reasons of work or health treatments is today subject of debate among specialists and regulators as, although associated with these activities received doses are usually greater than doses received by people involved in controlled activities, activities related with the use and exposure to material containing natural radionuclides are not, in general, considered as practices since the regulator point of view. Some countries have adopted normative and criteria regarding the exposure to this kind of sources [1], but today this question is still raised. By this reason the scientific community is dedicating efforts to the study of the radiological impact of scenarios of exposure to radioactive materials of natural origin. Among others, the natural thermal spas, in which often the levels of radioactivity of natural origin are relatively high, have been object of study due to the exposure to radon, thoron and gamma radiation [2-7].

In Cuba there have been identified five scenarios of possible significant exposure to radiation of natural origin, and they appear as candidates to be assessed for the adoption of control measures. Spas located in zones of higher radioactivity levels are considered among these scenarios. As a first step in the characterization and assessment of impact of this kind of sources, the “Elguea” spa was selected. “Elguea” spa is located in the North coast of the Villa Clara province, central region of the country, and is considered one of the most important spas in Latin America. Thermal waters of this spa are rich in chlorine, sodium and bromine salts, sulphur compounds and radon. These waters are used for different therapeutic procedures as: relaxation, revitalization, anti-stress treatments, treatment of obesity and diseases of locomotive, respiratory and circulatory systems, as well as support in case of neurological health problems. With these purposes, the spa is equipped with three swimming pools, jacuzzis for therapeutic massages, sauna, and facilities for therapy with thermal water and with thermal muds.

With the aim of characterizing this spa scenario, measurements of gamma dose rates in different zones of the spa were carried out and dose levels received by workers and patients under treatment by different pathways were assessed. Present paper summarizes obtained results.

2. MATERIALS AND METHODS

The possible exposure scenarios inside the facilities of the "Elguea" spa were assessed and identified based on the routine of their functioning (see Table 1). For the evaluation of gamma dose rate levels LiF thermoluminiscent dosemeters were used, placing them in the different areas of the spa for periods of two months during one year. These measurements were complemented with in-situ measurements carried out with the use of a portable gamma spectrometric system based on a HPGe detector. Radon in air levels were assessed using a portable radon measuring system SARAD RM2000 and results were complemented with the use of passive track-etch detectors based on LR-15 films, which were exposed by periods of six months during the same year.

TABLE 1. IDENTIFIED EXPOSURE SCENARIOS

No.	Scenario	Exposure type	Exposed group[a]
1	Stay in closed premises	External	W & P
2	Radon inhalation	Internal	W & P
3	Thermal muds treatment	External	P
4	Muds manipulation	External	W
5	Immersion in thermal waters	External	P

[a]W – workers, P – patients under treatment (public)

For each identified exposure scenario doses were evaluated as follows.

For the exposure scenario No. 1 "Stay in closed premises" conservative occupancies of 192 hours per month for workers and 20 h per one-week stay for patients under treatment were assumed. For the estimation of doses, the highest dose rate value measured in each location was used. Doses were estimated using the expression:

$$E = \dot{E} \times t \quad (1)$$

where E – effective dose by external exposure (μSv); $\dot{E}$ – maximal gamma dose rate measured in the assessed location (μSv h^{-1}); t – integration time for the doses, one year for workers and one treatment season for patients (h).

For the case of the scenario No. 2 "Radon inhalation" assumed occupancies were the same as for the previous scenario and for the dose estimations the highest value of measured radon concentrations was used. Doses were estimated using the equation:

$$E = 0.4 \times C_{air,radon} \times DF_{inh,radon} \times t \quad (2)$$

where E – committed effective dose due to radon inhalation (μSv); $C_{air,radon}$ – maximal measured radon concentration in air (Bq m^{-3}); $DF_{inh,radon}$ – dose conversion coefficient for radon inhalation (9 x 10^3 μSv Bq h^{-1} m^{-3}, according the model proposed by UNSCEAR [6]); t – occupancy time for locations with presence of radon (h). The value 0.4 in the expression is the recommended by UNSCEAR default value for the equilibrium factor between radon and daughters for indoors occupancy [6].

The estimation of dose for scenario No. 3 “Thermal muds treatment” was carried out provided the information by the personnel of the spa according which a whole treatment can include until nine sessions of application of mud over the skin thirty minutes duration each. In the estimations the maximal values of Ra-226 and K-40 concentrations measured in used thermal muds were used. The contribution of radionuclides of Th-232 series was not considered, as the measurements indicated concentration values of these radionuclides more than twenty times lower than the concentrations measured for the selected for the estimation radionuclides. For the estimation of doses to the skin due to Ra-226 it was assumed that radionuclides in the segment Ra-226 – Po- 210were in secular equilibrium, assumption that maximizes the estimation. Doses were estimated using the expression:

$$E = A_{sup} \times DF_{sup} \times t \qquad (3)$$

where E – equivalent dose to skin by irradiation form the mud deposited over it (μSv); A_{sup} – surface activity of radionuclides deposited with the mud (Bq cm^{2}); DF_{sup} – equivalent dose rate by unit surface contamination, values taken from [8] (μSv Bq h^{-1} cm^{-2}); t – integration time (h). Same assumptions for considered radionuclides were made for the scenario No. 4 “Muds manipulation”. For this scenario a time of fifty minutes per day was assumed, for considering not only the time spent by the worker applying the muds to the patient, but also the mud preparation time. This time, for an average of twelve working days per month for each worker, as workers in this area alternate one week of work with another week off. A particular case was identified in the person in charge of collecting muds in the place of origin, as this person carry out this operation daily and for which a total manipulation time of twenty four hours per month was assumed. The expression for dose calculations is the same as for the scenario No. 4.

Finally, for the scenario No. 5 “Immersion in thermal waters”, the existing for these treatments protocol establishes that patients should remain immersed into the water in a time sequence, starting from five minutes first, and increasing each time five more minutes until a final permanence in water of thirty minutes, which represent a total time of 1.75 hours per treatment. The used for the calculations radionuclide concentrations in water were the ones obtained from measurement of previously taken water samples, assuming again equilibrium in the segment Ra- 226 – Po-210. Doses were estimated using the expression:

$$E = C_{water} \times DF_{immersion} \times t \qquad (4)$$

where E – effective dose due to immersion in water (μSv); C_{water} – radionuclide concentrations in water (Bq m^{-3}); $DF_{immersion}$ – effective dose rate due to immersion in water, values taken from [9] (μSv h^{-1} Bq m^{-3}); t – dose integration time (h).

Once estimated doses for each of selected scenarios and for each involved persons group (workers or patients), contributions of each scenario to each group of persons were summed, assuming conservatively that the most exposed person in each group receives all the doses from all the possible for this group scenarios.

3. RESULTS AND DISCUSSION

The results obtained on the basis of measurements made are shown in Tables 2 and 3. With these results dose estimations were carried out, following the methodology described before.

TABLE 2. MEASURED VALUES USING TL DOSIMETERS FOR ESTIMATING GAMMA DOSE RATE IN PREMISES

Place	Ambient dose equivalent (mSv)
Infirmary	0.20
Electrotherapy	0.20
Director's office	0.17
Massage room	0.20
Muds preparation room	0.22
Interior swimming pool	0.14

TABLE 3. ACTIVITY CONCENTRATIONS OF GAMMA EMITTERS OF NATURAL ORIGIN IN COLLECTED SAMPLES.

Sample	Ac-228 (Bq kg^{-1})	Ra-226 (Bq kg^{-1})	K-40 (Bq kg^{-1})	Pb-210 (Bq kg^{-1})
Thermal mud (pool 2)	15 ± 2	711 ± 36	116 ± 8	395 ± 21
Thermal mud (pool 3)	19 ± 3	480 ± 24	121 ± 13	127 ± 12
Thermal mud (pool 4)	19 ± 3	473 ± 24	119 ± 13	128 ± 12
Thermal waters	-	6.3 ± 0.4	-	-

The dose estimations results are shown in Tables 4 and 5, for workers and patients respectively. As it can be appreciated for the case of workers, the permanence in premises (54%) and radon inhalation are the most important exposure pathways. Despite the fact that the workers conform the most exposed group, as expected due to their greater occupancy of exposure scenarios, dose are not significant, representing only a 20% increase over the average dose – 1.1 ± 0.3 mSv y^{-1} – received by Cuban population due to environmental sources [10]. In the case of radon, it is important to emphasize the influence of high ventilation rates of studied facilities, as it is traditional in the country due to specific of climate conditions.

For the case of patients, doses are practically non-significant (0.3% of the representative value of doses for Cuban population due to environmental sources), due mainly to the low occupancies for assessed facilities, as they stay in the premises only during the time of the treatments.

TABLE 4. DOSE ESTIMATIONS FOR WORKERS IN DIFFERENT SCENARIOS.

Exposure scenario	Dose, µSv y^{-1}
Stay in closed premises	
Radon inhalation	330 ± 160
Muds manipulation (previously to the treatments)[b]	
Muds manipulation (collecting and conditioning)[b]	

[b]To be summed alternatively.

TABLE 5. DOSE ESTIMATIONS FOR PATIENTS IN DIFFERENT SCENARIOS.

Exposure scenario	Dose, μSv per whole treatment
Stay in closed premises	1.7 ± 0.7
Radon inhalation	1.4 ± 0.7
Thermal muds treatment	0.46 ± 0.03
Immersion in thermal waters	$(2.1 \pm 0.1) \times 10^{-9}$
Total dose	4 ± 1

4. CONCLUSIONS

With the aim of evaluating the radiological impact of natural radionuclides present in the "Elguea" spa, a study was carried out for characterizing the site. Measurements made indicated the prevailing presence of radionuclides form the U-238 series, with important concentrations of Ra-226 and Rn-222 in muds and waters used for patients treatments. Received by both workers and patients doses were estimated for identified exposure scenarios. Estimated dose values range between 1.01 and 180 μSv y^{-1} for workers and 0.46 to 1.7 μSv per whole treatment for patients. Obtained values, even for workers as most exposed group, do not indicated the need for adoption of special radiation protection measures.

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PUBLIC AND OCCUPATIONAL EXPOSURE TO NATURALLY OCCURING RADIOACTIVE MATERIALS FROM MINING AND MINERAL PROCESSING IN SIERRA LEONE

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Abstract

Mining has been identified as one of the potential sources of exposure to naturally occurring radioactive materials (NORM). However, mining companies are not being regulated for NORM in Sierra Leone until when recently the Protection from radiation Act 2001 was revised and repeated as recommended by the International Atomic Energy Agency's Integrated Regulatory Review Service mission in Sierra Leone. Now Sierra Leone can be proud of one of the best laws in radiation protection that is the Nuclear Safety and radiation protection act, 2012. This law gave enforcement powers to the regulatory authority and a wider scope of control not excluding NORMS. Whilst the developed countries have identified NORM as potential problems and measures are being taken to address the issues, very little is being done in the developing countries.

1. INTRODUCTION

Naturally occurring radioactive material (NORM) such as ^{238}U and ^{232}Th series and ^{40}K, are essential constituents of the earth's crust. NORM can be found in higher than normal concentrations in some regions of the planet, known as "high natural radiation". NORM is a characteristic of many geologic materials. In Sierra Leone NORMS are encountered during mining and mineral processing. Work has not been done for NORM in offshore oil and gas as oil companies are still on exploration. Some of the metal ores associated with NORM include rutile, Zircon, tantalum pent oxide and niobium, bauxite and gold occurrences. Although the concentration of NORM in most natural materials is low, any activity in which any material is extracted from the earth and processed can concentrate NORM.

Uncontrolled activities associated with enhanced levels of NORM can contaminate and pose risk to human health. The risks can be alleviated by the adoption of adequate regulatory controls to identify NORM areas and also strategically control NORM-contaminated equipment and waste to protect the workers, the environment and the general public. In recent times, the awareness about radiation doses due to NORM has been an increased concern and it is widely acknowledged that both workers and the general public may be at risk of radiation exposure resulting from NORM.

2. NORM INDUSTRIES

However, most of the NORM industries such as mining and mineral processing are located in developing countries like Sierra Leone. Currently, there are over one hundred (100) registered mining companies operating small, medium and large scale mining in Sierra Leone. Cluff Gold is one of the largest gold mining companies in Sierra Leone and has been in operation for a number of years with no data on radioactivity levels. Gold mining produce large volume of tailings and waste that may contain NORM. Tantalum pent oxide is at present exported on small commercial scale and it is produced from artisanal mining areas. The Sierra Rutile mines undertake both wet and dry mining and also produce large volume of tailings containing NORM. The workers and the public are exposed to the NORMS with limited supervision.

The exposure of the public to NORM from processing of gold ore at the goldmine, rutile, tantalum and iron ore mining sites were analyzed for U/Th series and K-40 in soil, rock and particulate (dust) samples from the mining environment. An example site where measurements were carried out are shown in Fig.1 and Fig.2. The mean activity concentrations measured for ^{238}U, ^{232}Th and ^{40}K in the soil/rock samples were 15.2 Bq/kg, 26.9 Bq/kg and 157.1 Bq/kg respectively. The average annual dose for the public was estimated to be 0.74 mSv. The results indicate an insignificant exposure of the public to NORM from the activities of the mines.

Studies from oil producing countries have shown that Offshore Oil and Gas exploration and production produces large volume of waste containing significant amount of NORM. Some of the NORM are soluble in water and have the tendency to leach into water bodies and farm lands. NORM leaching water can be swallowed by fish and other aquatic animals making them radioactively contaminated. When these contaminated aquatic animals such as fish, shrimps etc. are sold in the market, and then the public is affected. This is in fact a global concern as contaminated fish can be sold all over the world if measures are not taken to combat the risk.

3. REGULATORY CONTROL AND REQUIREMENT

The Nuclear Safety and Radiation Protection Authority has made considerable effort and now been devoted to identifying and quantifying the radiological risks to individuals exposed to natural radiation at various mining sites and putting in place at the national level regulatory measures for the control of these risks. The authority ensure that radiation doses from mineral processing industries are kept ALARA and members of the public must not exceed 1millisievert (mSv) per person in a year.

The Authority conducted investigations for exposure to natural radiation nationwide at various mining sites. An investigation for exposure to natural radiation is now a continuous process in Sierra Leone. The concentrations of natural radiation sources are low and the exposure of workers is within the acceptable standards.

The newly revised legislation which has already been enacted and regulation in radiation protection and safety makes provision for natural radiation sources (e.g. uranium, thorium, etc) and prescription of measures for the protection of workers, public and environment. Putting in place at the national level regulatory measures for the control of these risks as the new act gives mandate to the Regulatory Body to perform such a task section 5 subsection 2 clause iv in the new regulation.

Currently, minerals and raw materials in Sierra Leone are exported on a commercial scale. The authority issue clearance certificate for exportation of mineral and raw materials to ensure that radiation emitted by the mineral to be exported meets the basic safety requirements.

4. PUBLIC AND OCCUPATIONAL EXPOSURES

During industrial processes, naturally occurring radioactive materials (NORM) deposits exists in many facilities in the industry, causing increased levels of radiation exposure. Increased levels of NORM concentrates are also detected in the waste materials.

A conducted study on exposures to NORM at various mining sites indicates an estimated average annual radiation dose of 0.74 mSv. Members of the public are residing over 800m away from the tailings, stock piles and NORM leaching streams.

According to the Regulations for Radiation Protection, the action levels concerning the effective dose to workers at work places due to natural radiation sources is 1mSv in a year.

FIG.1 Dose rate measurement to identify NORM present in an industrial site.

FIG.2 Survey carried out at a NORM residue area in Sierra-Leone.

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RADIATION DOSE ASSESSMENT IN INSTALLATION OPERATING MINERALIZED HEAVY SAND IN MADAGASCAR

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Abstract

Among the major sectors affected by NORMs industries are the manufacturing of titanium dioxide pigment (TiO2). Mineral sands operated by Rio Tinto QMM (Quit Madagascar Mineral) contain Ilmenite and heavy minerals such as monazite and zircon. The extraction process of the Ilmenite takes place exclusively by physical separations. The process begins with the enrichment of heavy sand ore by gravity spiral, followed by separation by electrostatic and magnetic fields. Radioactivity in the sand gradually increases as the ore beneficiation process advance. It reached the maximum residue with magnetic, which are composed mainly of residues RER. The results show that the process of extraction of Ilmenite greatly increases the concentration of radionuclide in products with higher levels of the original soil and these products can be considered as radioactive materials and radiation protection measures are necessary. The gamma dose rate emitted by products depends not only on the concentration of the radionuclide, but also on their quantity. The accumulation of products in one place can increase the gamma dose rate in this place. Although no particular product is stored inside the plant, debris can accumulate on the floor. This area is classified as a controlled area.

1. INTRODUCTION

Among the sources of radiation in industry, there are the naturally occurring radioactive materials (NORM). They are processed or unprocessed materials containing natural substances. A wide variety of industries is affected by the NORM. In fact, all major industries with significant activities must take into account NORM. The concentration of radioactive material in the initial soil may be insignificant, but when hundreds of thousands of tons of materials are exploited every year, the concentration of radionuclide causes a radiological concern. It has launched an operation to extract mineralized sands near Fort Dauphin (Tolagnaro), at the South-East of Madagascar. Over the past 40 years, Rio Tinto QMM intends to extract Ilmenite and zircon from heavy mineral sands in an area of about 60 km² along the coast (see Fig. 1). The Ilmenite extracted contain a titanium dioxide (TiO_2 at 60 %) giving it a higher quality than most other deposits in the world.

2. METHODS, EQUIPMENTS AND RESULTS

2.1. Extraction process of ilmenite

NORM operated by Rio Tinto QMM is initially present in the soil. In the natural environment, their concentration is low. The extraction process of the Ilmenite sand increases their concentrations. A typical floating dredge plant is shown in Fig.2. The extraction process of the Ilmenite takes place exclusively by physical separations. The process begins with the concentration of heavy mineral sand with spirals gravity (see Fig.3), followed by separation by electrostatic (see Fig.4) and magnetic fields (see Fig.5).

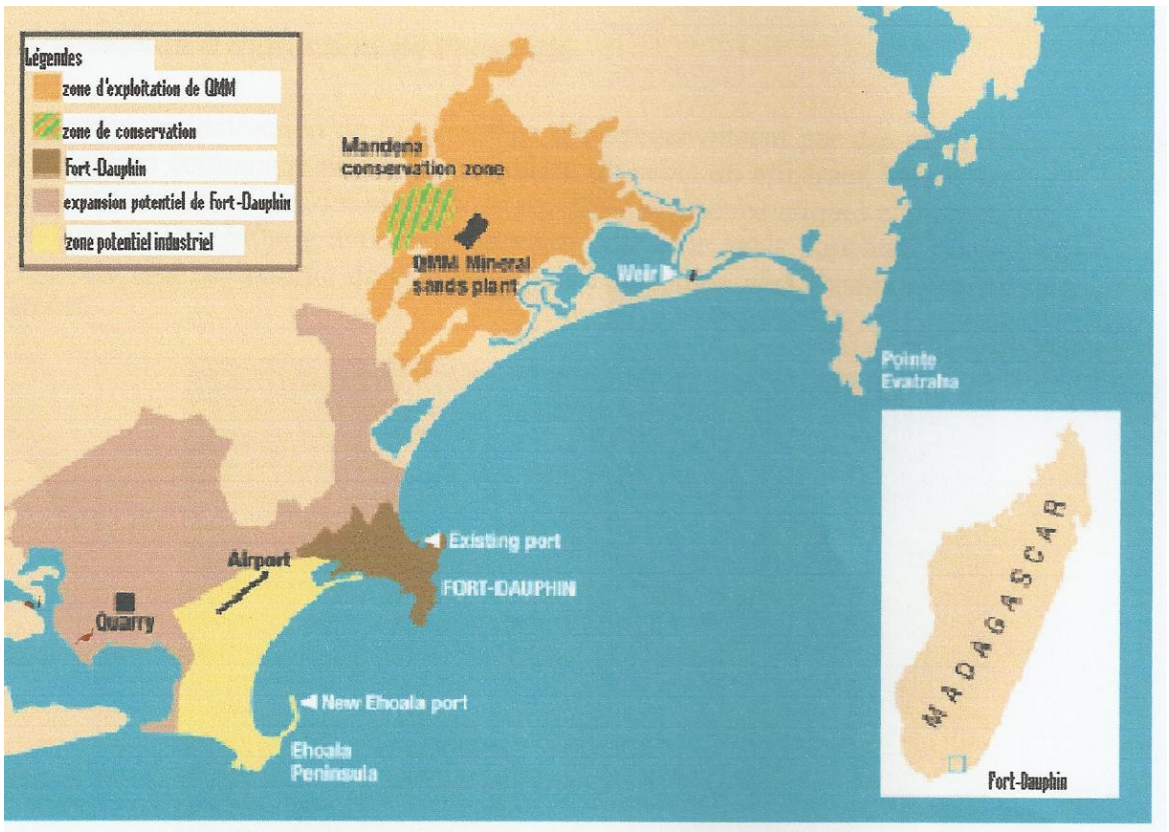

FIG. 1. Map of Rio Tinto QMM Exploitation Fort-Dauphin, Madagascar.

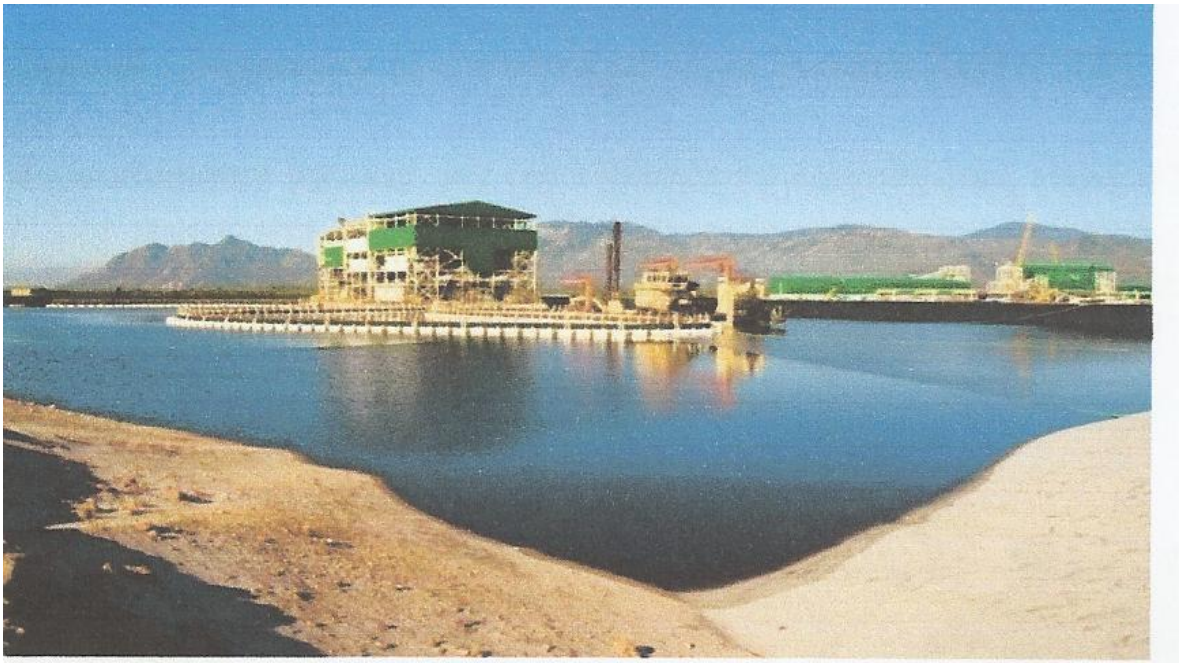

FIG. 2. Floating dredge plant.

FIG. 3. Spiral gravimetric.

FIG. 4. Electrostatic separator (high tension roll HTR).

FIG. 5. Magnetic separator (high intensity rare earth roll).

Sand operated by Rio Tinto QMM contains Ilmenite and heavy minerals such as monazite and zircon. Exposures due to the extraction of small quantity of these NORM are not important. However, the production quantities are typically several thousand tons. The concentrations of radionuclide in the sand then cause concern from radiation exposure point of view. The radioactivity of the ground comes from these two minerals containing thorium and uranium. In the wild, these minerals are dispersed and their concentration is low. However, the process of the extraction of Ilmenite increases with their concentration in the sand. Radioactivity in the sand gradually increases as the ore beneficiation process advance. It reached the maximum residue with magnetic, which are composed mainly of monazite residues.

2.2. Results

The gamma spectrometry analysis of the samples was used to determine the amount of radionuclide presents in the various products of the process of extraction of Ilmenite such as, uranium-238 and thorium-232. The results are presented in Table 1.

2.3. Gamma dose rate on the site

To quantify the risk of worker exposure, measurements have been focused in the main areas of work. Among these places include the mineral separation plant and the storage products from the concentration process. Radiation detector used: Thermo Scientific with alpha and beta probe. Table 2 provides the results of gamma dose rates in the mineral separation plant at various locations.

TABLE 1. RESULTS OF SAMPLES CONCENTRATIONS BY GAMMA SPECTROMETRY ANALYSIS

Type of product	Radionuclide	Average activity (Bq/g)
Dry Mining	Th-232	0.81 ± 0.07
	U-238	0.07 ± 0.31
Heavy Mineral Concentrate	Th-232	5.83 ± 0.40
	U-238	2.36 ± 0.44
Non conductive	Th-232	10.78 ± 1.93
	U-238	27.48 ± 1.48
Magnetic release	Th-232	14.26 ± 9.45
	U-238	8.76 ± 12.9
Ilmenite	Th-232	0.64 ± 0.06
	U-238	0.73 ± 0.40
Zirsill	Th-232	0.42 ± 0.06
	U-238	12.77 ± 0.83

These results show that the process of extraction of Ilmenite increases greatly the concentration of radionuclide in products at higher levels than the original soil. Elevated concentrations of radionuclide may increase the emission of radiation by extractives products. They are in the same time increase the risk of contamination and internal exposure. The products issued to the process of extraction of Ilmenite increase also the risk of exposure of the workers. The results of concentration analysis indicate that these products can be considered as radioactive materials and radiation protection measures required. During the process of extraction of Ilmenite, the amount of treated product decreases once the process moves forward and the quantity of products such as HMC (Heavy Mineral Concentrate) that is located upstream of the process is much more important than that is downstream. Approximately 23 million tonnes of HMC products per year is processed and obtain nearly 750,000 tons of Ilmenite per year.

3. CONCLUSIONS

The gamma dose rate emitted by products does not depend only on the concentration of radionuclide but also their quantity. Accumulation of products in one place can lead to an increase in the gamma dose rate in this place. The process of concentrating ores by electrostatic and magnetic concentrators happens inside the plant. Although no particular product is stored inside, residues can accumulate on the plant floor. This area is classified as a controlled area.

TABLE 2. GAMMA DOSE RATE IN THE MINERAL SEPARATION PLANT

Place of storage	Gamma dose rate ($\mu Sv.h^{-1}$)	Average ($\mu Sv.h^{-1}$)
HMC	4.97 – 6.74	5.92
Non conductive	20.10 – 26.5	23.56
Mids	3.43- 4.06	3.72
Magnetic release	25-36.5	3.72
Zirsill	1.88-2.07	1.96
Ilmenite	0.55-0.92	0.75
Packaging Zirsill	6.57-7.93	7.07
Mineral Separation Unit (SMU) Floor	3.65-7.04	5.06

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RADIOACTIVE LEVELS IN LIQUID EFFLUENTS OF SOME NORM INDUSTRIES IN CHINA

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Abstract

Material giving rise to those enhanced exposures has become known as naturally occurring radioactive material (NORM) and it has been a broad consensus that the environmental radioactive impact NORM brings is greater than nuclear facilities cause. This paper focuses on NORM radioactive level and emissions of liquid effluents in China, and compares them with relevant provisions of national standards.

1. INTRODUCTION

From the end of 2006 to 2009, the State organized the first national suvey of pollution sources. The pollution sources associated with radioactivity is one of the major survey objects.Environmental radiation monitoring stations in every province surveyed the facilities using 11 types of mineral resource, including rare earths, niobium/tantalum, zirconium, zirconium oxide/zinc, copper, iron, phosphates, coal, aluminium and vanadium, and screened 1433 facilities to monitor and analysis of U, ^{232}Th和^{226}Ra in samples.

However, the survey is not enough adequate. For the phosphate industry, monitoring data of wastewater are relatively small, and has no analysis of ^{210}Po and ^{210}Pb in ^{238}U series, ^{228}Ra and ^{224}Ra in Th series, not to mention monitoring gaseous effluents. There is a great exploit of Petroleum and natural gas in China. However, the possible radioactive harm to the environment and radiation protection for the staff in mining and production are not caused enough attention, and radiological survey data of the petroleum and natural gas industries are rare.

This article has major collection in radioactive survey data of liquid effluents in the rare earth industry, coal industry and other NORM industry, and compares them with the related standards in China.

2. RADIOACTIVE LEVEL IN LIQUID EFFLUENTS OF SOME NORM INDUSTRIES

2.1. Rare-earth industries

Rare earth minerals are one of minerals associated with radioactivity but it is a valuable strategic resource of scarcity. Shandong province in China has only a Fluorocarbon- Cerium-Lanthanum rare earth ore with less titanium, iron and phosphorus.

A rare-earth mine in Shandong province has an area of 81,630 m^2 and annual production capacity of 39,600 tons. The mining method is underground mining with shrinkage, mining depth is from-10 m elevation to -100 m elevation, and mineral processing method is flotation. The main product is concentrate Fluorocarbon- Cerium- Lanthanum ore with an annual output of more than 2,600 tons. The discharge capacity of wastewater is 302,000 tons every year and 1,080 tons per day on average. There are a treatment facility with three levels of sedimentation tanks, with design capacity of 750 tons per day. However, the settlers has not been used until now and wastewater is directly discharged. Survey results for natural radionuclides' concentrations in waste water from the rare earth facility is given in Table 1.

TABLE 1. SURVEY RESULTS FOR NATURAL RADIONUCLIDE CONCENTRATIONS IN WASTE WATER [1]

Wastewater sampling locations	natural radionuclide concentrations(Bq/L)				
	^{238}U	^{232}Th	^{226}Ra	总α	总β
Sedimentation tank	3.87	0.40	986	10.7	2.20
Wastewater in mine tailing	0.24	$7.69*10^{-3}$	8.5	0.67	0.14
drained waste water	0.91	$1.05*10^{-2}$	6.0	4.03	0.33
river nearby	0.667	$2.24*10^{-2}$	0.476	10.0	2.62

Table 1 shows that concentrations of natural radionuclides in waste water discharged in the rare earth mine in Shandong province are rather high, which of ^{238}U, ^{232}Th and ^{226}Ra in the Sedimentation tank is the highest. The averaged total alpha radioactivity level in drained waste water exceeds about 4 times of 1Bq/L of emission standard values given in Integrated Wastewater Discharge Standard (GB8978 -1996) .

2.2. Associated ores

Actual investigation of radioactivity of associated ores in Chongqing, showed that it was not necessary for some mines that mined ores were screened or processed. Those ores were directly carried out as products, so the produced radioactive wastewater was less. There were no waste minerals or waste residue in some mines, which were temporarily placed or immediately carried out or reused. Research results of samples showed that radioactive wastewater produced in the mine utilization process was mainly from of excluded water in mine pit. The findings were shown in the Table 2.

TABLE 2. SURVEY RESULTS FOR NATURAL RADIONUCLIDE CONCENTRATIONS IN WASTE WATER [2]

Unit name	Survey object	^{238}U mBq/L	^{226}Ra mBq/L	^{232}Th mBq/L	^{40}K mBq/L	总α Bq/L	总β Bq/L
Coal mine 1	Water in mines	84.29	78.42	2.31	89.23	0.54	0.77
	Drinking water	21.79	18.42	1.17	98.53	0.02	0.03
Coal mine 2	Water in mine pits	31.87	28.56	3.45	127.34	0.23	0.38
Coal mine 3	Effluent in mines	35.76	29.37	3.44	110.51	0.24	0.39
Coal mine 4	Water in mine pits	54.75	56.65	3.56	98.64	0.35	0.47
Coal mine 5	Liquid effluents in mines	39.27	51.82	6.17	88.72	0.37	0.38
	Drinking water nearby	15.42	14.29	2.17	70.22	0.06	0.06
Coal mine 6	Water in mine pits	50.39	53.67	3.38	112.41	0.31	0.78
Coal mine 7	Liquid effluents in mines	45.23	38.27	5.33	93.91	0.25	0.74
	River nearby	6.20	11.7	0.92	71.21	0.01	0.03
	Drinking water nearby	17.01	12.7	1.53	74.19	0.04	0.07

Bayan Obo mine has a deposit of iron and rare earth ores that is renowned as a large rare earths deposit. The ores are rich in radioactive elements, with a 0.01–0.05% concentration of

ThO2 and a 0.0005–0.002% of U_3O_8. The deposit has been mined for more than 50 years. The ores are transported by train to the refinery plants in Baotou to process for products of iron and steel, rare earths and their compounds. Meanwhile, a large amount of NORM residue produced is being regulated and controlled. By the end of the year 2007, about 288 million tons of mined ores has been mined. Most of the wastewater, after being treated, is discharged into the tailings pond and then pumped to the milling plant for reuse. Many of the liquid effluents are produced by the wet process method (alkali and acid melting) and are discharged into the tailings pond after treatment. The total liquid effluent is about 17 million m3 with a gross alpha activity concentration of 5.39 Bq/L and a gross beta activity concentration of 1.58 Bq/L (See Table 3). The liquid effluent discharged into the tailings pond was recorded at 65 875 000 t in 2006, of which 64 572 100t have been recovered. The effluent contains, in addition to thorium radionuclides, fluorine, nitrogen (as ammonia) and a large amount of sulphate and chlorine ions.

TABLE 3. SURVEY RESULTS FOR NATURAL RADIONUCLIDE CONCENTRATIONS IN WASTE WATER [3]

Waste water	Waste water emission（m3）	Total α（Bq/L）	Total β（Bq/L）
Waste water from tailings pool	1.7×10^7 (The accumulated mount)	5.39	1.58
Wastewater ischarged from alkali melting		0.46	2.77
Wastewater discharged from acid melting		6.13	1.86

China Institute of Atomic Energy selected nine NORM enterprises, from which waste water had higher radioactivity concentration for Uranium, Thorium and Radium, and analysed radioactivity of wastewater. The survey results were shown in Table 4. The results indicated that certain concentration of radioactive waste water reached dozens of Bq/L.

TABLE 4. RADIOACTIVITY CONCENTRATIONS OF ^{238}U, ^{232}Th AND ^{226}RA IN SAMPLES [4]

Sample location	^{232}Th（Bq/L）	^{238}U（Bq/L）	^{226}Ra（Bq/L）
Baotou Steel Concentrator	0.13	0.03	0.01
Rare-earth plant 1	0.14	0.06	0.01
Rare-earth plant 2	28.10	51.28	0.31
A chemical factory (sulphur -phosphor salts)	0.38	0.13	0.01
Coal mine 1	0.24	0.09	0.01
A columbium-tantalum plant	1.19	1.46	0.75
A tin plant	0.03	0.02	0.024
Rare-earth plant 3	0.03	0.38	0.037
A germanium plant	0.23	0.19	0.99

2.3. Hot spring

At Tengchong county in Western Yunnan province, there are widely typical Cenozoic volcanic and geothermal area, of which the most famous one was Rehai hot spring scenic spot. The survey of radionuclides' concentrations was carried out for thermal springs In Rehai

scenic, such as “Da Gunguo”、 “Huai Tai well” and “Pearl spring” , and local drinking water. The results see Table 5.

TABLE 5. CONTENTS OF NATURAL RADIONUCLIDES IN WATER（mBq/L）[5]

Sample Location	^{238}U	^{232}Th	^{226}Ra	^{40}K
Da Gunguo	0.97	4.41	23	3070
Huai Tai well	15.79	4.41	36	2440
Pearl spring	46.16	1.80	317	630
Drinking water	0.002	0.70	14	65
Average values of the springs in Yunnan province	3.90	0.65	265	402
Average values of the drinking water in Yunnan province	6.90	0.50	4	45

Except for "Da Gunguo” springs, the results of uranium and thorium in other springs are higher than the average results obtained for hot springs in the province. Particularly for the Pearl spring, not only the content of ^{238}U in the water is obviously on the high, but also ^{226}Ra is higher than the average of the province. Natural radionuclides contents of "Roll Pan" hot spring are all lower than the average of the province. Except that ^{226}Ra is slightly higher but still within the fluctuation of the environmental results, the contents of natural radionuclides, in drinking water from dozens of miles away, are close to the average of drinking water across the province.

3. CONCLUSIONS

As NORM exposure has caused widespread concern in recent years, our country has also carried out a survey and evaluation. However, in terms of effluents from NORM industries, only a few investigations have been carried out. There are still many issues about regulatory controls, monitoring and assessment, pollution recovery, and so on and recommend further studies in the future.

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RADIOGENIC AND DOSIMETRIC CHARACTERISTICS OF ARTISANAL MINING OF A HIGH BACKGROUND RADIATION AREA (HBRA) 'CONFLICT MINERAL' COLUMBITE-TANTALITE

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Abstract

The paper reports on the radiogenic and dosimetric study of extraction and processing of a 'conflict mineral' columbite-tantalite (coltan) in Rwanda using gamma-ray spectrometry and multivariate chemometrics. The study was motivated by the need for evidence-based development of a radiological regulatory framework for artisanal mining of conflict minerals in high background radiation areas (HBRA), which is widespread in Eastern Africa; and for furnishing a rapid method for forensic and quality assurance of coltan mining and trade utilizing coltan ore gamma-ray spectra as unique geochemical fingerprints. The mean activity concentrations of ^{238}U and ^{232}Th in mined coltan were 513 Bq kg^{-1} and 57 Bq kg^{-1} respectively, while that of ^{40}K was 267 Bq kg^{-1}. Measured absorbed dose rates varied 518.34 - 796.92 nGy h^{-1}, 522.4 - 820.7 nGy h^{-1} and 563.8 - 845.7 nGy h^{-1} in Muhanga, Ruli and Ngoma respectively; these values are 11 times higher than world average, showing Rwanda's coltan mining belt is a HBRA. Measured dose rates were twice higher than computed rates based on measured radionuclide activities, indicating the significance of gamma dose from radioactive dust and radon. Calculation of effective doses according to exposure pathways and working scenarios showed that total effective doses vary 0.0173 - 0.272 mSv y^{-1} in Muhanga, 0.013 - 0.525 mSv y^{-1} in Ruli and 0.022 - 0.255 mSv y^{-1} in Ngoma; inhalation of coltan bearing dust accounts for 98 % of the total exposure. It was found that processing coltan enhances the concentration of ^{232}Th and ^{238}U by a factor of 3 and 2 respectively, while it reduces that of ^{40}K by a factor of 15. Principal component analysis (PCA) of the radionuclides source-apportioned coltan accurately to the respective mining areas and differentiated extracted from processed coltan. Although PCA also showed that artisanal mining practices hardly contribute to radiogenic pollution of the environment, results of this study raise important radiological and quality assurance concerns.

1. INTRODUCTION

"Conflict minerals", which are widely used in a wide variety of products such as mobile phones, medical devices and jewelry, are commercially valuable resources mined in areas of armed conflict or human rights abuses. Unregulated artisanal mining of conflict minerals is widespread Eastern Africa. This poses radiological and radiogenic quality assurance concerns particularly in HBRA. In HBRA, local geology and geochemical effects have resulted in highly enhanced background radiation levels [1-3]: In these areas the external dose to inhabitants > 4 mSv y^{-1} and radon concentration of the atmosphere > 40 Bq m^{-3} [4]. From the environmental point of view, unregulated discharges from mining activities in HBRA constitute low-medium level radioactive waste. HBRA in Eastern Africa include Lambwe, Mrima Hill [5-7], Rangwa, Soklo, Kuge, and Gwasi in Kenya [8] and Minjingu in Tanzania [9] among others. In Mrima Hill for instance external gamma radiation doses are ~ 50 times the normal background. This is as a result of the deeply weathered thorium-enriched

carbonitite rocks in the area. Levels of NORM at a place depend on the distribution of rocks and soils from which they originate and processes which concentrate them. Mineral extraction in HBRA therefore needs to be considered for radiogenic and radiological quality assurance necessitated by the likely enhancement of radionuclides in the mineral product and immobilization of NORM in the environment [10-11].

Funtua and Elegba [12] estimated the radiological impact of processing cassiterite and columbite from different mills of Jos Plateau, Nigeria, at different processing points and locations at the mills and found dose that rates ranged 5 μSv h^{-1} - 80 μSv h^{-1} in the premises and processed zircon respectively. The enhanced activity and ambient radiation (1375 - 1475 nGy h^{-1}, which is 28 times higher than the global average) that was observed in Manjingu phosphate mine of Tanzania are due to the high concentration of ^{226}Ra in phosphate (5,760 Bq kg^{-1}) and waste (4,250 Bq kg^{-1}) rock [9]. In the eastern Democratic Republic of Congo (DRC) which borders Rwanda the occupational exposure dose due to grinding and sieving of columbite-tantalite (coltan) was observed to reach 18 $mSvy^{-1}$ [10, 13]. The activity concentrations of ^{226}Ra and ^{232}Th in tantalite were 7.06 Bq g^{-1} and 1.75 Bq g^{-1} respectively. Although knowledge of the activity concentration of NORM in the various matrices associated with mining is important, dosimetric and radiogenic quality assurance with respect to the mineral products and artisanal miners' working environment is more informative to the development of appropriate product quality assurance protocols and radiological regulatory frameworks.

The highly mineralized Kibaran Belt of Rwanda is composed of folded and metamorphosed sediments - mainly schists and quartzites intruded by granites. The most exploited minerals here are cassiterite, wolfram and coltan. These minerals are extracted mainly from Muhanga, Ruli and Ngoma areas from open pits and exported to the EU and USA. During processing (digging the ore, sloshing in washtubs to separate coltan from soil, drying the coltan in open air, and grinding and sieving the dried coltan), the miners suffer from both radiogenic and radiation exposure. Further, the final mineral product lacks radiogenic quality assurance. Exposure of the public living near the mines also arises, from immobilized radionuclides which may be directly ingested through drinking contaminated water or through the food chain, or may result from the reuse of mine wastes (tailings and waters) [14]. We report on the occupational radiation doses and radiogenic fluxes from different working scenario received by mine workers in Muhanga, Ruli and Ngoma coltan-mining areas of Rwanda. Thousands of other small unregulated artisanal mines are being worked in northern Burundi, eastern Congo, other areas of Rwanda and southwestern Uganda. The interest in coltan in the areas is similar to the "goldrush" of the past.

2. MATERIALS AND METHODS

2.1. Sampling preparation and spectrometric analysis

Processed and extracted coltan ore, sediment and soil samples from various mines located in Muhanga (Southern Province), Ruli (Northern Province) and Ngoma (Eastern Province) areas of Rwanda were collected (5 sites per region). Control sites in areas not associated with coltan ore was also sampled. The samples were prepared to dry fine powder and stored in sealed plastic beakers for one month to allow ^{238}U and ^{232}Th and their decay daughters (^{214}Bi and ^{214}Pb) to reach secular equilibrium. Analysis was done using HPGe-based gamma-ray spectrometry (144 mm^3 detector active volume and 76 mm diameter, efficiency: 31.6 %; resolution: 1.8 keV). Samples were measured in 500 cm^3 malineri beakers for 10,000-50,000 s depending on sample activity. The activity of ^{40}K was evaluated from the 1460 keV line; that of ^{238}U from 351 keV line of ^{214}Pb and that of ^{232}Th from 238 keV line of ^{212}Pb. IAEA Soil 375 CRM was similarly analyzed for method validation. Spectra were

processed and analyzed using PCA 2 (version 1.00) software [15]. The activity concentration was calculated using the comparative method. Chemometrics analysis via PCA was used to explore the multivariate relationships between measured quantities and evaluate the sources of coltan in relation to its radiogenic characteristics. The Unscrambler version 9.5 software was used for analysis.

2.2. Absorbed and effective dose

Dose rates were measured using the Sensor Meter (Model G/B) survey meter. Absorbed dose rates in air in $nGyh^{-1}$ were computed from the measured dose rates in $\mu Sv\ h^{-1}$ according to UNSCEAR (2000) [16] recommendations. The radiation doses that are likely to accrue from the various working or exposure scenarios were calculated using existing generic models that closely describe the scenarios. Input parameters comprised of activity concentrations of the radionuclides, working habit data (e.g. exposure duration, breathing rates, etc.) and the dose coefficients [17, 18]. The model used for external dose due to gamma-rays emitted by radionuclides contained in ground is that of a volume target at a specified distance from an infinitely large volume source [2, 7, 19] assuming a uniform spatial distribution of the radionuclides both across the surface and within the source. Calculation of internal dose due to inhalation of air contaminated with radioactive dust was based on the method proposed by Oatway and Mobbs [20]: the dust load values (in $g\ m^{-3}$) used were 10^{-3} for manual digging and handling coltan in open mine, 10^{-2} for crushing and sieving coltan in the mills, and $5x10^{-3}$ for drying coltan. The inhalation rates ($m^3\ h^{-1}$) were 1.2 for drying and 1.69 for rest of the scenarios. Internal dose due to inadvertent ingestion of the radionuclide was also calculated. Inadvertent ingestion was assumed to occur through hand to mouth transfer of contaminated soil and dust present on the skin and clothing [20]. The time was taken to be 2500 hrs y^{-1} for a miner working for eight hours for six days in a week for 52 weeks for the digging, crushing and panning scenarios and for external exposure due to submersion in contaminated air.

3. RESULTS AND DISCUSSION

3.1. Activity concentration and absorbed dose

The measured gamma doses are shown in Table 1. Extracted coltan is the raw ore taken from soil; processed coltan is obtained after separating soil and coltan. The values vary 666.2 - 696.6 nGy h^{-1} (mean: 685.1±104.2 nGy h^{-1}), which is ≈ 11 times the world average value of 60 nGy h^{-1} [16]. The activity concentration of ^{40}K, ^{238}U, and ^{232}Th in each sample class and region relative to the control are shown in Table 2. The range in activity concentrations for extracted coltan are 258.29 - 334.76 Bq kg^{-1} for ^{40}K (mean: 304.1 Bq kg^{-1}), 481.69 - 792.29 Bq kg^{-1} (mean: 638.9 Bq kg^{-1}) for ^{238}U and 21.15 - 37.53 Bq kg^{-1} (mean: 26.9 Bq kg^{-1}) for ^{232}Th. Sediment had 289.43 - 489.49 Bq kg^{-1} (mean: 405.04 Bq kg^{-1}) for ^{40}K, 50.20 - 7 0.76 Bq kg^{-1} (mean: 61.70 Bq kg^{-1}) for ^{238}U and 27.45 - 55.99 Bq kg^{-1} (mean: 44.18 Bq kg^{-1}) for ^{232}Th. The activity concentration of ^{238}U even in control samples exceeded the world average of 35 Bq kg^{-1} while those of ^{40}K were generally below the world average of 400 Bq kg^{-1} [16] (except for control samples and sediment), with processed coltan having the lowest (< 30 Bq kg^{-1}).

TABLE 1. MEASURED ABSORBED DOSES

Muhanga	Abs. dose (nGy h^{-1})	Ruli	Abs. dose (nGy h^{-1})	Ngoma	Abs. dose (nGy h^{-1})
Mean	666.26	Mean	696.61	Mean	692.44
Control	650.55	Control	507.43	Control	552.06

This implies that ^{40}K is preferentially contained in the soil compared to coltan. The mean activity concentration of ^{232}Th for processed coltan and sediments was higher than the word average, while for extracted coltan it was lower. It may be concluded that artisanal mining of coltan enhances ^{232}Th and ^{238}U by 300 % and 200 % respectively; but reduces the concentration of ^{40}K by 1500 %. This is not unusual with artisanally processed minerals from HBRA: analysis of mineral sands mined from Erasama beach in India showed that the monazite and zircon components are highly radioactive [1] - in mozanites especially of granitic origin, the actinide incorporation into the crystal lattice is dominated by thorium. Sediments were however depleted of ^{232}Th and ^{238}U, implying insignificant radiological impact of the environment from the extraction and processing of Rwanda's coltan.

The absorbed dose rates were calculated from ^{238}U, ^{232}Th and ^{40}K activity concentrations neglecting other radionuclides as they contribute very little to the total dose from the environment [21]. The mean absorbed in air was found to be 6 times the world average but comparable with the other HBRA around the world [1, 3, 9, 22-27]. The higher measured absorbed dose rates (compared with calculated) may be attributed to radon and the fact that measured dose may not have come only from NORM in coltan ore but also the ambient radioactive aerosols and dust at the mining sites.

TABLE 2. MEAN NORM ACTIVITY CONCENTRATION (Bq kg^{-1}) IN RWANDAN COLTAN MINING

Region	Sample Type	^{40}K (Bq kg^{-1})	^{238}U (Bq kg^{-1})	^{232}Th(Bq kg^{-1})
Muhanga	Processed coltan	25.06	972.89	67.43
	Extracted coltan	258.29	642.86	21.15
	Sediments	289.43	50.20	27.45
	Control samples	*186.99*	*69.03*	*39.45*
Ruli	Processed coltan	16.72	2011.81	68.01
	Extracted coltan	319.08	481.69	22.03
	Sediments	436.29	64.33	55.99
	Control samples	*590.21*	*69.74*	*73.38*
Ngoma	Processed coltan	16.58	853.36	91.06
	Extracted coltan	334.76	792.29	37.53
	Sediments	489.41	70.76	49.12
	Control samples	*245.92*	*71.33*	*132.49*
World average		400	35	30

3.2. Effective dose

Exposure pathway and working scenario doses are shown in Table 3. D_{ext} is the external dose due to gamma-rays emitted by radionuclides in the environment; D_{inh} is the internal dose due to inhalation of air contaminated with dust from the ore; D_{ing} is the internal dose due to inadvertent ingestion of radionuclides; D_{subm} is external dose due to submersion in contaminated air.

The total effective doses varied 0.0173 - 0.272 mSv y^{-1} in Muhanga, 0.013 - 0.525 $mSvy^{-1}$ in Ruli and 0.022 - 0.255 mSv y^{-1} in Ngoma as a result of the variations in coltan ore radiogenic quality and mining practices. The most significant exposure pathway (98 %) was found to be inhalation of coltan bearing dust; the least significant was exposure from submersion in radiogenically contaminated air.

TABLE 3. CALCULATED EFFECTIVE DOSES ACCORDING TO THE EXPOSURE PATHWAYS AND WORKING SCENARIOS

Area	Working scenario	Dose (□Svy^{-1})				Total effective dose (mSvy^{-1})
		D_{ext}	D_{inh}	D_{ing}	D_{subm}	
Muhanga	Digging	0.611	16.55	0.121	1.9 E-07	0.017
	Drying	1.741	23.79	0.056	4.6 E-06	0.026
	Crushing and sieving	3.277	268.5	0.223	1.9 E-05	0.271
Ruli	Digging	0.476	12.72	0.097	2.3 E-07	0.013
	Drying	3.256	45.99	0.095	3.2 E-06	0.049
	Crushing and sieving	6.29	518.98	0.379	1.3 E-05	0.525
Ngoma	Digging	0.767	20.98	1.162	2.4 E-07	0.022
	Drying	1.475	22.30	0.058	3.1 E-06	0.024
	Crushing and sieving	2.799	251.6	0.233	1.2 E-05	0.254

3.3. Exploratory analysis of radiogenic characteristics of coltan

An accurate classification of processed coltan according to geographical origin was achieved via multivariate chemometrics using principle component analysis (PCA) of ^{238}U, ^{232}Th and ^{40}K activity concentrations. Three clusters were obtained (Fig 1). Similar results were obtained with extracted coltan (Fig 2). However the classification was more efficient in processed coltan where radionuclide concentration accounted for 91% on PC1 compared with 87 % for extracted coltan.

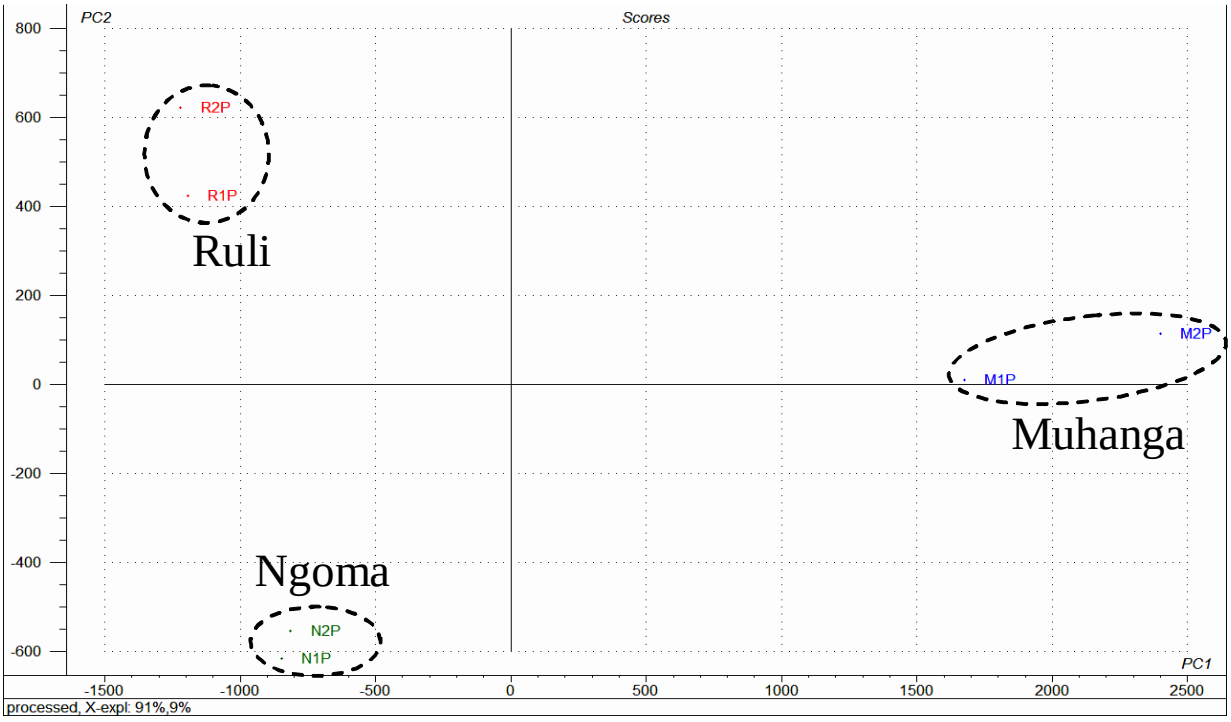

FIG. 1. PCA score plot for processed coltan using radionuclides.

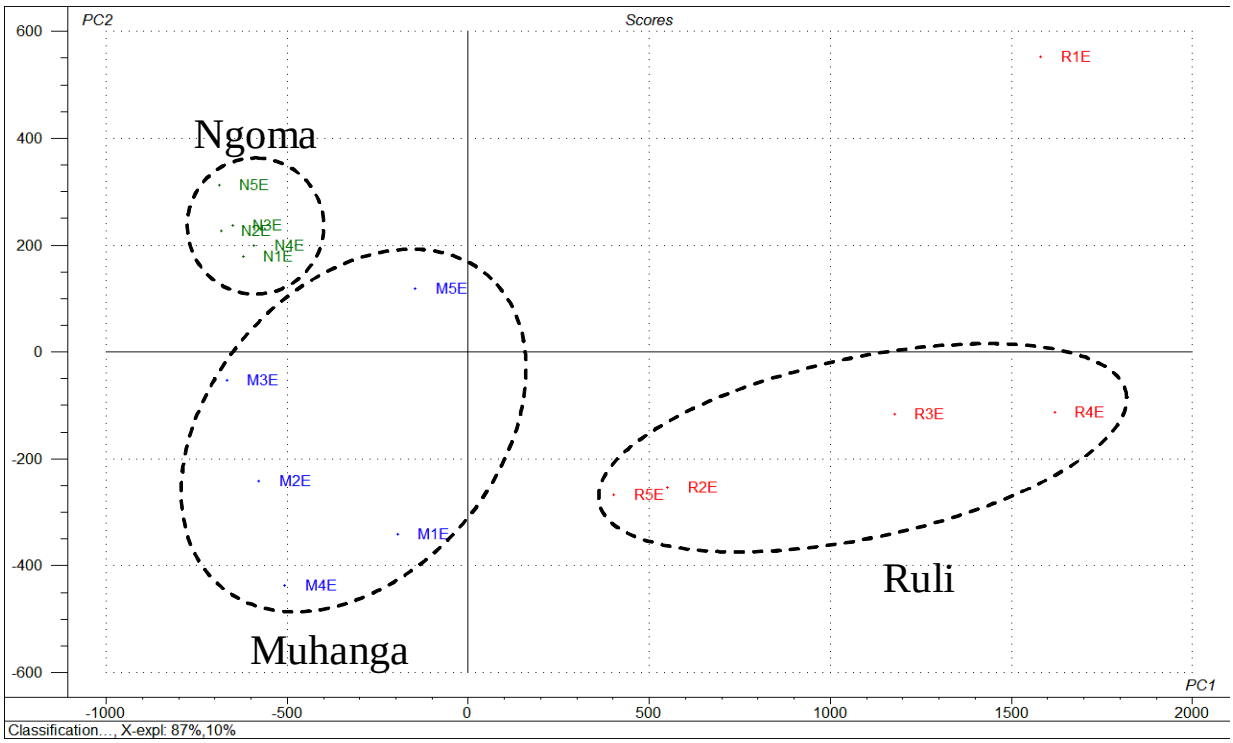

FIG. 2. PCA score plot for extracted coltan using radionuclides.

It was also possible, for each region, to distinguish processed and extracted coltan, and to demonstrate that there no significant radiogenic pollution of the environment from artisanal mining of coltan in Rwanda (Fig 3): in the score plot the first group comprises of processed ores (N1P and N2P) in blue; the second comprises of extracted ores (N1E, N2E, N3E, N4E, and M5E) in light blue; and the third, sediments and soil in red (M1S, N2S, N3S, N4S, and N5S) and soil from control point (CPN) in green. The groups represent coltan type. It should be noted that PCA was not able to separate sediments and soil from the controls, because after processing the coltan ore, the sediments have the same radiogenic characteristics as the soil drawn from a control location not associated with the coltan underlying rock. PCA of activity concentrations of ^{238}U, ^{232}Th and ^{40}K and concentrations of coltan associated elements (Ta, Nb, Sn) was also tested, to explore the additional role of these elements whose levels in the coltan is a measure of quality as a factor contributing to sample discrimination. The results showed the potential of the combined utility of radionuclides and these coltan mineral quality elements in simultaneous source apportionment and quality assurance of coltan applicable to coltan types with more geographical diversity. Ore gamma-ray spectra may directly be used as unique geochemical fingerprints applicable to the forensic and radiological control and quality assurance of coltan.

4. CONCLUSION

Activity concentration of ^{40}K, ^{238}U and ^{232}Th in coltan (extracted, processed), sediments and soils from three artisanal mining areas of Rwanda were determined. Absorbed dose was also determined by both measurement and model calculation. The mean activity concentration were 267.4 Bq kg^{-1}, 521.5 Bq kg^{-1} and 57.1 Bq kg^{-1} in coltan ore, sediments and soil respectively. The activity concentration of ^{238}U was 15 times higher than world average. In extracted coltan the activity of ^{232}Th was below word average. In processed coltan the activity concentration of ^{40}K was below the world average. Based on the high levels of dose compared to the world average (55 nGy h^{-1}), the coltan mining belt of Rwanda may be regarded as HBRA. Calculated effective dose showed most significant exposure pathway (0.27 mSv y^{-1} in

Muhanga, 0.52 mSv y^{-1} in Ruli, 0.25 mSv y^{-1}in Ngoma) is inhalation of coltan bearing dust. Processing coltan enhances the concentration of ^{232}Th and ^{238}U by a factor of 3 and 2 respectively, while it reduces that of ^{40}K by a factor of 15. Rwanda's artisanally mined coltan has thus important quality assurance and radiological regulatory concerns. Nonetheless the mining practices were found to hardly contribute to radiogenic pollution of the environment.

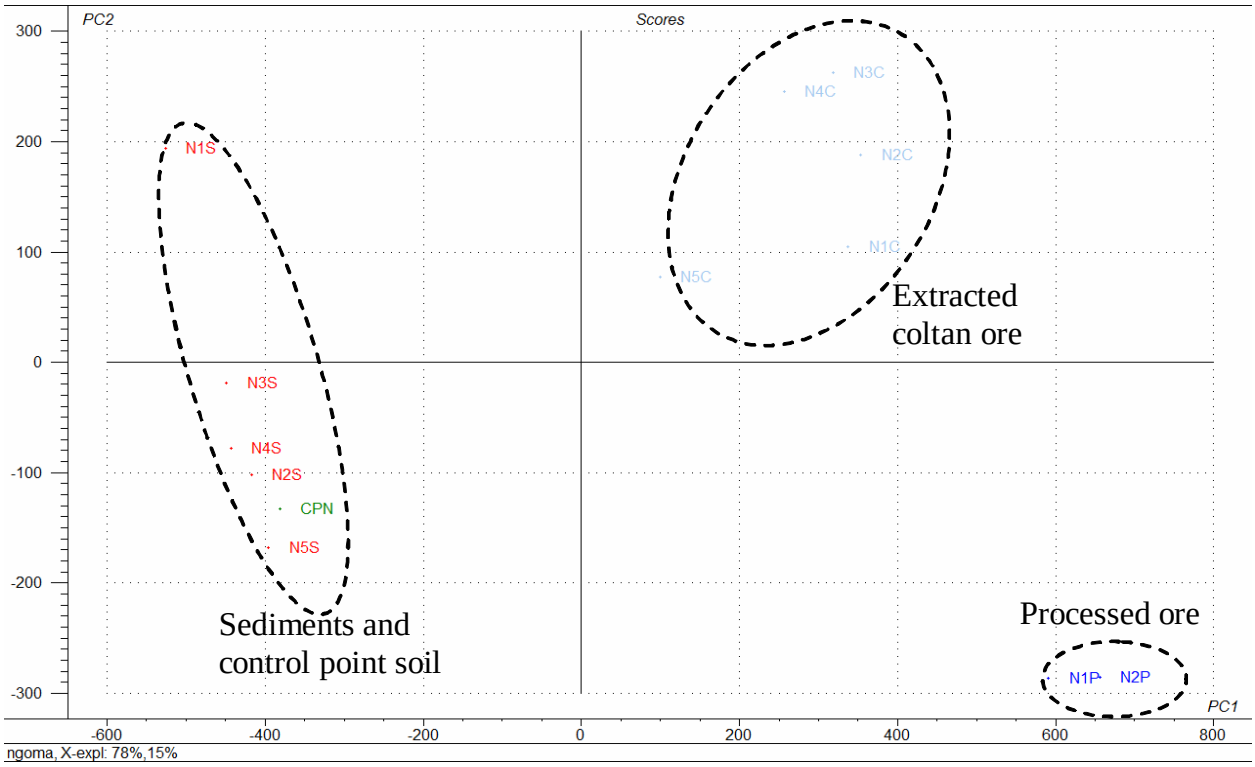

FIG. 3. PCA score plot of various radionuclides of samples from Ngoma.

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