Assessing the impact of rock phosphate storage on uranium and thorium concentration in soil samples from Richards Bay using neutron activation analysis

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Abstract. Determination of radionuclides in soil samples is important to estimate the radiation level to which persons are directly or indirectly exposed especially from a health physics point of view. In this study, the concentration of parent radionuclides ^{238}U, ^{232}Th and ^{40}K were measured in soil samples around a rock phosphate storage facility at Richards Bay. Ninety soil samples were collected from 30 sampling positions. Gross alpha and beta activity concentration measurements were first performed using a gas flow proportionality counter to estimate the total activity of each sample without regards to specific radionuclides. The samples were further analyzed for ^{238}U and ^{232}Th concentrations using neutron activation analysis (NAA) by irradiating with thermal neutrons flux of about 1×10^{14} n cm^{-2}.s^{-1} in a nuclear research reactor (SAFARI 1) at NECSA. The total mean values (mean±S.D) of elemental concentrations for ^{238}U, ^{232}Th and ^{40}K in all the samples studied were 2.29 ± 0.95 ppm, 7.77 ± 3.98 ppm and 0.44 ± 0.32 at % for uranium, thorium and potassium respectively. The elemental concentrations of ^{238}U, ^{232}Th and ^{40}K are lower than the corresponding values reported worldwide for natural sources by a factor of 0.15, 0.30 and 0.68 respectively.

1. Introduction

Despite their positive values and uses for the production of fertilizer, animal feed supplements and industrial chemicals [1], research [2, 3, 4, 5] has shown that phosphate rocks contain a substantial concentration of uranium, thorium and their decay products. When phosphate rocks are applied to soil, they elevate the radioactivity levels in the soils [2, 6, 7]. The radionuclides in soil can be incorporated into human bodies through inhalation of contaminated soil dust by workers, other site users or a member of the general public. Leaching of these radioactive nuclides is another source of dissemination and possible transfer to waters and finally to human beings and animals [4]. Gamma radiation from natural radionuclides and cosmic rays constitute external exposure while those derived from inhalation and ingestion through foods and drinking water constitute internal exposure to humans [8]. About 80% of radiological dose contributed from

the environment are derived from the natural radionuclides while the remaining 20% are from cosmic rays and nuclear processes [9]. The natural radionuclides of concern in the terrestrial environment are mainly Uranium-238, Thorium-232, Potassium-40 and the radioactive radon gas produced as a result of decay of the first two aforementioned parent nuclides [9].

Richards Bay is an industrial area located on latitude 28° 48' S and longitude 32° 02' E in KwaZulu Natal Province, South Africa. The area is well known for its harbour facility and industrial activities. Rock Phosphate mined in Phalaborwa in Limpopo is transported by rail about 750 km to Richards Bay where it is stored prior to export or used by Foskor Richards Bay as raw material. Environmental problems associated with naturally occurring radioactive materials (NORMs) in solid mineral mining and processing occurs during drilling, processing, transportation and storage. These usually lead to the spread of NORMs contaminating the environment and subsequently result in potential radiation exposure of workers and members of the general public. Although research has reported a low concentration of radionuclide in rock phosphate stored in this study area [10], and a good water quality of the area, no available literature is published about the distribution of radionuclides in soil. This study is aimed at surveying the concentration of NORMs in soil samples around the rock phosphates storage facility at Richards Bay with an intention to map out hot spots in terms of radioactivity concentration level.

Figure 1. Map of study area showing sampling positions

2. Material and methods

2.1. Sampling and sample preparations

Ninety soil samples were collected from 30 sampling positions (Figure 1) divided into the coal area (Area 1, four sampling positions), the rock phosphate storage area (Area 2, 17 sampling position) and the control area (Area 3, nine sampling position). It is worth mentioning that more samples were collected from Area 2 because it is the area of interest for this study. Collected samples were dried in an oven at a temperature of 105 °C for 24 hrs and then milled to powder. About 1.00 g of each powder soil sample was sealed in polythene ampoules and further encapsulated in polythene foil to avoid superficial contamination during irradiation and handling. Prepared samples were irradiated with thermal neutrons at NECSA (SAFARI 1) producing a neutron flux of about 1×10^{14} n.cm^{-2}.s^{-1} at the core of the reactor. During neutron activation in a reactor,^{238}U and ^{232}Th undergo the following nuclear process.

$$^{238}U(n,\gamma) \longrightarrow ^{239}U \longrightarrow ^{239}Np \tag{1}$$

$$^{232}Th(n,\gamma) \longrightarrow ^{233}Th \longrightarrow ^{232}Pa \tag{2}$$

The gamma rays emitted were measured using a closed end coaxial high-purity germanium (HPGe) detector with a relative efficiency of 25.1%, peak to Compton ratio of 40.2:1 and a resolution of 2.3 keV at 1332 keV of ^{60}Co. The detector was calibrated for energy and efficiency using ^{152}Eu with an activity of (18.6 ± 0.5) kBq at reference date of 2006 February 09 at 12.00 GMT. The activity concentration of ^{40}K was determined directly from the gamma energy line of 1460.8 keV without sample irradiation. Gamma energy peaks of 277.6 keV and 312.2 keV from the decay of ^{239}Np and ^{233}Pa were used for the identifications of ^{238}U and ^{232}Th respectively. Elemental content was determined relative to certified reference materials which were irradiated and counted under the same conditions as the samples. Reference materials were supplied by the South African National Bureau of Standards. The experiment was carried out in the Radio-analysis laboratory at the South African Nuclear Energy Corporation (NECSA), Pretoria, South Africa. The background was determined by treating an empty capsule as the sample. The uncertainty value reported is calculated mainly from counting statistics and it is not the standard deviation obtained from replicate measurements.

2.2. Activity calculations and determination of elemental concentration

Following the spectrum analysis, the specific activity of ^{233}U and ^{232}Th were determined in units of Bq.kg^{-1} and then converted into total elemental concentrations (F_E) in units of part per million (ppm) of ^{238}U, ^{232}Th and % of ^{40}K using equation (3) [11].

$$F_E = \frac{M_E C}{\lambda_E N_A f_{(A,E)}} \times A_E \tag{3}$$

Where, M_E,λ_E,$f_{(A,E)}$ and A_E are the atomic mass (kg.mol^{-1}), the decay constant (s^{-1}), the fractional atomic abundance in nature and the measured specific activity concentration (Bq.kg^{-1}) respectively of the corresponding element E. N_A is the Avogadro number 6.023 × 10^{23} atoms mol^{-1}, C is a constant with values of 10^6 for ^{238}U and ^{232}Th as well as 10^2 for ^{40}K that converts the ratio of the elements to soil mass into part per million of ^{238}U, ^{232}Th or a percentage of ^{40}K. Using equation (3), this yields the same results as the conversion factors of

$$\begin{gathered} 1\text{ppm} = 12.25\ \text{Bq.kg}^{-1}\ \text{of}\ ^{238}\text{U} \\ 1\text{ppm} = 4.06\ \text{Bq.kg}^{-1}\ \text{of}\ ^{232}\text{Th and} \\ 1\ \% = 131\ \text{Bq.kg}^{-1}\ \text{of}\ ^{40}\text{K} \end{gathered}$$

given in IAEA technical document 390 as utilized by [12].

3. Results and discussion.

3.1. Gross alpha and gross beta activities

The gross alpha and beta activity is a first order estimate performed to obtain the total activity concentration of radionuclides in a sample without considering specific nuclides. Figure 2 shows the total activity concentration of each sampling position.

3.2. Elemental concentrations in soil samples

The elemental concentrations of uranium, thorium and potassium obtained from the three areas where soil samples were collected are summarized in Table 1. The measured arithmetic mean and standard deviation of elemental concentrations for ^{238}U, ^{232}Th and ^{40}K in all the samples studied are 2.29 ± 0.95 ppm, 7.77 ± 3.98 ppm and 0.44 ± 0.32 at % respectively, while the revised median values obtained worldwide are 2.67 ppm, 11.08 ppm and 1.34 at % respectively. The above-mentioned worldwide mean values were derived by transforming the corresponding worldwide average concentrations of 33, 45 and 420 Bq.kg^{-1} for ^{238}U, ^{232}Th and ^{40}K radionuclides [9] into

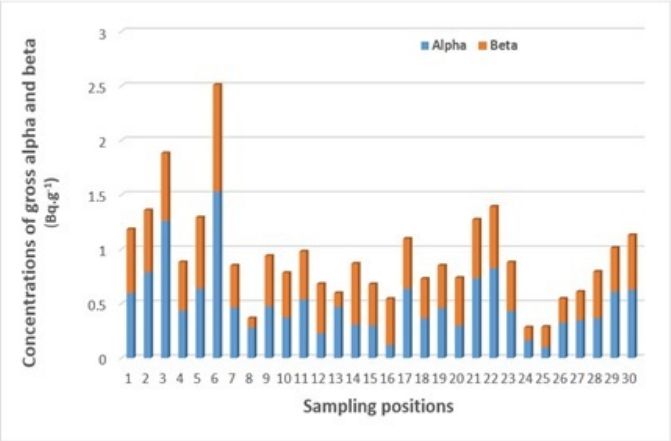

Figure 2. Gross alpha and gross beta activity concentrations of each sampling position from where soil samples were collected.

Table 1. Elemental concentrations of ^{238}U, ^{232}Th and ^{40}K in soil samples studied.

Sampling Area	Number of samples	Parameters	Elemental concentrations (ppm) ^{238}U (ppm)	^{232}Th (ppm)	^{40}K at (%)
Area 1	12	Min	2.48 ± 0.12	8.86 ± 0.34	0.36 ± 0.14
		Max	4.19 ± 0.17	18.58 ± 0.38	0.60 ± 0.15
		Ave ± S.D	3.39 ± 0.8	14.47 ± 4.58	0.47 ± 0.13
Area 2	51	Min	1.04 ± 0.07	1.44 ± 0.22	0.01 ± 0.001
		Max	3.76 ± 0.15	13.09 ± 0.33	0.88 ± 0.21
		Ave ± S.D	2.29 ± 0.92	7.30 ± 2.82	0.47 ± 0.20
Area 3	27	Min	0.84 ± 0.05	2.25 ± 0.09	MDA
		Max	2.81 ± 0.18	8.45 ± 0.25	0.99 ± 0.22
		Ave ± S.D	1.81 ± 0.69	5.69 ± 2.41	0.38 ± 0.32
Total	90	Min	0.84 ± 0.05	1.44 ± 0.22	MDA
		Max	4.19 ± 0.17	18.58 ± 0.38	0.99 ± 0.22
		Ave ± S.D	2.29 ± 0.95	7.77 ± 3.98	0.44 ± 0.32
World average			2.67	11.08	1.34

^{238}U, ^{232}Th and ^{40}K elemental concentrations respectively using Equation (3). This study reveals that the total mean concentration of ^{238}U, ^{232}Th and ^{40}K measured in soil samples from Richards Bay (this study area) are 85%, 70% and 32 at % of corresponding values reported worldwide. Hence they are all lower by a factor of 0.15, 0.30 and 0.68 compared to the corresponding worldwide average values for soil samples from non-mining areas.

From Table 1, area 1 exhibited the highest concentrations in uranium and thorium with an arithmetic mean value (mean ± S.D) of 3.39 ± 0.8 ppm and 14.47 ± 4.58 ppm respectively. As can be seen from Figure 3, columns 2 and 3, the highest concentration of ^{238}U, ^{232}Th and ^{40}K were measured in soil samples collected from area 1 and 2. This can be attributed to industrial activities and mined minerals handled within these area. Although comparable and within the range of some areas globally (see Table 2), the total mean elemental concentrations of ^{238}U,

Table 2. Concentrations of ^{238}U, ^{232}Th and ^{40}K in soil samples from different countries [11]

Countries	^{238}U (ppm)	^{232}Th (ppm)	^{40}K at (%)
Spain	1.1 - 13.8	1.7 - 50.3	0.2 - 5.2
Rajasthan, India	2.4 - 6.3	10.6 - 26.1	0.2 - 0.5
Italy	4.6 - 5.7	18.0 - 21.0	1.9 - 2.5
Russaifa, Jordan	3.9 - 42.4	2.1 - 6.7	0.1 - 1.0
Alps-Apennines, Italy	0.3 - 5.6	0.3 - 16.7	0.1 - 5.1
Cyprus	0.0004 - 3.2	0.003 - 9.8	0.0001 - 1.9
South Africa (Present study)	0.8 - 4.2	1.4 - 18.6	0.0 - 0.44

^{232}Th and ^{40}K observed in soil from the rock phosphate storage area (Table 1, Area 2) are still below the world mean elemental concentrations values of the same radionuclide reported in the UNCSCEAR 2000 report [9] for soil from non-mining areas. Furthermore, from Table 2 it is clear that the corresponding elemental concentration values of ^{238}U, ^{232}Th and ^{40}K obtained from this study fall within the lower range of most reported values from other areas globally. Since natural radioactivity is directly related to the content of radioactive elements in the soil, Richards Bay can be considered as one of the world areas that exhibit low level of natural radioactivity.

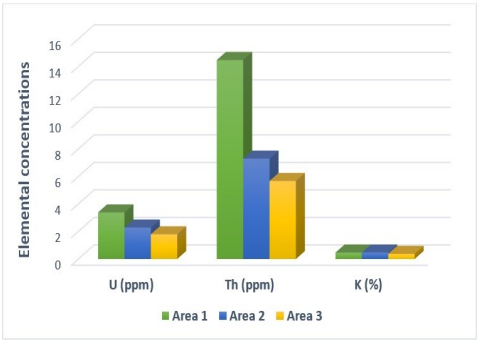

Figure 3. Mean values of ^{238}U, ^{232}Th, ^{40}K

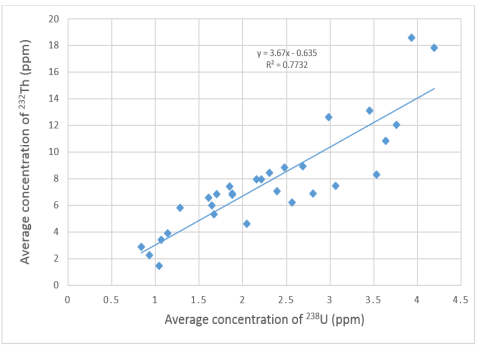

Figure 4. Correlation of ^{238}U and ^{232}Th

3.3. Correlation between ^{238}U and ^{232}Th

The relationship between uranium and thorium can be considered in terms of the thorium and uranium ratio [11]. Figure 4 show the correlation of Th/U with a fitting relation of a linear type yielding a correlation coefficient of 0.88. The theoretical expected ratio of Th/U is approximately 3.00 for normal continental crust [11]. Corresponding values obtained for this ratio in this study vary from 1.38 to 4.53 with an arithmetic mean and standard deviation of 3.30 ± 0.73 which is consistent with the continental crust. The high values of Th/ U ratio in some samples is an indication that the soil samples analyzed are thorium enriched or uranium depleted due to natural processes [9, 12] such as weathering and leaching in this area. However, thorium enrichment indicates the presence of a significant amount of monazites and zircon [13], and this is evident in the quantity of zircon mined by Richards Bay minerals company (RBM) in Richards Bay [14]. Hence, it is observed that Richards Bay is rich in Thorium concentration.

4. Conclusion

The concentration of ^{238}U and ^{232}Th in 90 soil samples collected around a rock phosphate storage facility were analyzed by means of neutron activation analysis and found to be of continental crust level. There were no hot spot identified with regards to radioactivity concentration level within this study area, however the concentrations of ^{238}U and ^{232}Th was found to be slightly enhance by anthropogenic activities within this area. The elemental concentration of ^{238}U, ^{232}Th and ^{40}K were found to be lower than their corresponding values reported worldwide for soil samples from non-mining areas by a factor of 0.15, 0.30 and 0.68 respectively. Therefore, the influence of rock phosphate storage in Richards Bay on the concentration of ^{238}U and ^{232}Th in soil of this area is at present negligible. Since the radioactivity level depends directly on the content of radionuclides within a given sample, Richards Bay in KwaZulu Natal, South Africa can be considered as one of the areas around the world that exhibit low level of radioactivity in soil. Furthermore, a strong correlation 0.88 was found between the concentrations of thorium and uranium, suggesting thorium enrichment in soil of this area.

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