Activity Concentrations of Naturally Occurring Radioactive Materials And Dose Calculation of Soils And Rocks Materials From A Superphosphate Industry

Arabi Suleiman (✉ asabdullahi.geo@buk.edu.ng)

Bayero University Kano

A. M. Muhammad

Ahmadu Bello University Zaria

A. D. Bajoga

Gombe State University

A. M. Ali

Bayero University Kano

S. I. Babale

Bayero University Kano

M. S. Abdulhamid

Bayero University Kano

Attahiru A. Jaoji

Ahmadu Bello University Zaria

Simon Kasidi

Adamawa State University

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Abstract

Activity concentration of Naturally Occurring radioactive Materials in samples from superphosphate industry was determined using Neutron Activation Analysis and radiological parameters calculated. Mean Annual Effective-Dose Equivalent(mSv/y), External and Internal Hazard, Annual Gonad Dose Equivalent(mSv/y), Radium Equivalent (Bq/kg), Absorbed Gamma Ray Dose(nGy/h), Potential Toxic Elements, Activity Utilization, and Gamma Representation Index are 87.0, 0.4, 0.5, 517.7, 137.3, 70.9, 20101.3, 9388.9, and 1.1, respectively. Most of the sample had activity concentrations of naturally occurring radioactive materials exceeding world average, indicating that activities of the industry impact on the environment. These results are good baseline data for future follow-up on activities of company.

Introduction

Phosphate rocks shelters high levels of radioactivity due to their composition of naturally occurring uranium, potassium and thorium, and their daughter isotopes radium, radon and polonium. Marine-deposited phosphate typically has a higher level of radioactivity than igneous phosphate deposits because of the presence of uranium in seawater (Abou El-Anwar et al., 2017). Long-live radioactive elements such as uranium (^{238}U), thorium (^{232}Th) and potassium (^{40}K) and any of their decay products, such as radium and radon are examples of naturally occurring radioactive materials (NORMs) (Arabi et al., 2016).

Phosphates are used extensively, as a source of phosphorous for fertilizers and for manufacturing phosphoric acid and gypsum. Phosphate ores typically contain about 1500 Bq/kg of uranium and radium (Anselmo S P and J. M. Godoy (2002)). In most cases during the production process of fertilizer, phosphate ore is treated with sulfuric acid, thus enriching the fertilizers in uranium by up to 150% relative to the ore, while 80% of ^{226}Ra , 30% of ^{232}Th and 5% of uranium are left in phosphogypsum (UNSCEAR, 2008). Also, the gaseous and particulate emissions generated during processing of phosphates contain ^{238}U and ^{226}Ra . The discharge of these emissions to the environment leads to exposure of the population to radiation hazards, and metal element contamination of soils, water bodies and air (UNSCEAR, 2000).

Toxic metals elements are relatively dense metals or metalloids that are associated with potential toxicity, especially in environmental contexts (Srivastava, S and Goyal, P. (2010)). These metals include cadmium, mercury, lead, arsenic, manganese, chromium, cobalt, nickel, copper, zinc, selenium, silver, antimony and thallium. They are found naturally in the earth and can become concentrated as a result of human activities.

This study sets out to determine the concentration levels and risks associated with the use of phosphate rock in the production of super phosphate fertilizer. This is achieved by assessing the concentration levels of radio-elements and metal elements in soils, sludge, dust, phosphate rock and phosphogypsum samples collected from around the super phosphate fertiliser company located within the Kaduna metropolis in northwest Nigeria (Fig. 1). The risks and hazards associated with the deposition of these contaminated industrial waste and their use by inhabitants of the area, sometimes as soil fertility supplement on farmland were evaluated. The area is located in a densely populated area of Kaduna metropolis (Fig. 1), therefore, the results obtained will go a long way in coming up with proactive mitigative measures by authorities e.g the National Environmental Standards and Regulations Enforcement Agency (NESREA) whose responsibility it is, to regulate the activities of corporate organization with regards to environmental implications of their activities.

Materials And Methods

2.1 Sampling and sample preparation

Two samples each of sludge, soil sediment, dust, phosphate rock and phosphogypsum were randomly collected within and around the super phosphate fertilizer company using EPA standard sampling procedure. Sludge samples were collected from the only two tanks in the industry premises, soil samples were collected one from the premises of the industry and another outside the premise, dust samples were collected from roofs around the premises, phosphate rock samples were collected from the rock pile freshly brought from the phosphate quarry, while phosphogypsum samples were collected from another pile approved for collection by the authorities of the industry. The industrial area was a restricted area and authority has to be sort before samples were collected. Areas approved for the team to collect samples were only accessible at the time of collection as major work was already going on around the company. All the samples collected were carefully packed into a polythene bag and transported to the laboratory at the Center for Energy Research and Training (CERT), Ahmadu Bello University, Zaria for analysis.

IAEA soil-7 was used as standard reference material relevant to the sample matrix and included as additional sample for irradiation. Before sample were sent into the reactor through the pneumatic system, 0.2000g of each sample was carefully placed in a high-density polyethylene bag, heat sealed and store in the desiccator. For short lived irradiation, one sample was packaged per capsule, while for long-lived irradiation, five to seven samples were packed in one capsule as required by the Nigeria Research Reactor 1 (NIRR-1) protocol for geological samples. The sealed capsules were made air tight ready for irradiation. Clean spatula and forceps were cleaned with acetone in-between samples handlings.

2.2 Instrumentation

The samples were analyzed at Reactor Engineering Section of the Centre for Energy Research and Training (CERT), Ahmadu Bello University (ABU), Zaria, Nigeria using a Miniature Neutron Source Reactor (MNSR) by means of Instrumental Neutron Activation Analysis (INAA) technique. INAA can analyse NORMs, race, minor and major elements in different sample types (Arabi et al., 2016). The reactor uses high-enriched uranium as fuel, and light water as a moderator and coolant. The natural radioactivity in these samples were determined using High-resolution gamma-ray spectrometers. The High Purity Germanium (HPGe) detector (model GEM 30P4-76) with a resolution of 1.74keV FWHM, operated at 1332.5keV of Co- 60, H.V. biased supply model 659 Ortec, 5kV, spectroscopy amplifier model 672 Ortec, acquisition interface card with computer and basic spectroscopy software (WINSPAN) was employed in the analysis. The samples were pulverized together with the standard, and then sealed and irradiated at a flux of $5 \times 10^{11} \text{ ncm}^{-2} \text{ s}^{-1}$ for 6 hours. Afterwards, the samples were counted for 1800s and 3600s after 4 and 14 days of cooling, respectively. Identification of gamma ray of product (uranium, thorium and potassium) radionuclide

through their energies and quantitative analysis of their concentrations were achieved using the gamma-ray spectrum analysis software. The activation product's half-life and energy of the photopeak are detailed in (Ahmed, 2005).

2.3 Calculation of risks and hazard indices

The risks and hazard indices were calculated from values obtained and analyzed from results of INAA. These indices are discussed below.

2.3.1 Annual Effective Dose Equivalent ($\mu\text{Sv/y}$)

To estimate the annual effective dose rate, it is necessary to use the conversion coefficient from the absorbed dose in air to the effective dose (0.7 SvGy^{-1}) and the outdoor occupancy factor (0.2 mSvy^{-1}) proposed by (UNSCEAR, 2000). Therefore, the effective dose rate is determined as follows as obtainable in (UNSCEAR, 2000).

$$H_R (\text{mSvy}^{-1}) = D_R (\text{nGh}^{-1}) \times 24 \text{ h} \times 365.25 \text{ d} \times 0.2 \quad \text{Eq. 1}$$

$$(\text{Out-door occupancy factor}) \times 0.7 \text{ SvGy}^{-1} (\text{conversion factor}) \times 10^{-6}$$

$$H_R = D_R \times 8766 \times 0.2 \times 0.7 \times 10^{-6} = D_R \times 0.00123$$

Where: D_R = estimated dose rate

D (nGyh^{-1}) is given by Eq. 6

2.3.2 External and Internal Hazard Index, (H_{ex} , H_{in})

In addition to the external radiation hazard they pose; radon and its short-lived daughters are also hazardous to the respiratory organs. The internal exposure caused by radon and its daughter products is quantified by the internal hazard index (H_{in}), which is defined in UNSCEAR, 2000, Eq. 2 below:

$$H_{in} = A_{Ra}/185 \text{Bqkg}^{-1} + A_{Th}/259 \text{Bqkg}^{-1} + A_K/4810 \text{Bqkg}^{-1} \quad \text{Eq. 2}$$

The internal hazard index is defined to reduce the acceptable maximum concentration of ^{226}Ra to half the value appropriate for external exposure alone. This criterion was proposed by Krieger, R. (1981), to assess the safety of use of materials in the construction of dwellings. $H_{in} \leq 1$

The external hazard index is a criterion used to assess the radiological suitability of a material. Using the relation given in UNSCEAR, 2000, Eq. 3 below (Beretka, J. and P.J. Mathew (1985)).

$$H_{ex} = A_{Ra}/370 \text{Bqkg}^{-1} + A_{Th}/259 \text{Bqkg}^{-1} + A_K/4810 \text{Bqkg}^{-1} \leq 1 \quad \text{Eq. 3}$$

Where:

A_{Ra} , A_{Th} and A_K are the activities of ^{226}Ra , ^{232}Th and ^{40}K in BqKg^{-1} .

2.3.3 Annual Gonad Dose Equivalent ($\mu\text{Sv/y}$)

In UNSCEAR (1988), the activities of bone marrow and bone surface cells are considered to be organs of interest, therefore, the Annual Gonadal Dose Equivalent (AGDE) was introduced to take care of the specific activities arising from Ra, Th and K. The AGDE was calculated using the following formula given in Eq. 4 (UNSCEAR, 2000).

$$\text{AGDE} (\text{mSvy}^{-1}) = 3.09A_{Ra} + 4.18A_{Th} + 0.31A_K \quad \text{Eq. 4}$$

2.3.4 Radium Equivalent Activity (Ra_{eq}) (Bq/kg)

A common radiological index referred to as radium equivalent was used in this study to evaluate the actual activity level of ^{226}Ra , ^{232}Th and ^{40}K in the samples and the radiation hazards associated with these radionuclides. This is as a result of the fact that distribution of natural radionuclide in the samples under investigation is not uniform and is assumed that 10Bqkg^{-1} of Ra, 7Bqkg^{-1} of Th and 130Bqkg^{-1} of K produce an equal gamma-ray dose (Krisiuk, 1971; Stranden, 1976).

This index is usually known as radium equivalent activity (UNSCEAR, 2008) and formula used to calculate radium equivalent is given in UNSCEAR, 2000 as:

$$Ra_{eq} = A_{Ra} + 1.43A_{Th} + 0.077A_K \quad \text{Eq. 5}$$

2.3.5 Absorbed gamma ray dose rate (nGy/h)

Estimation of the Absorbed Gamma Dose Rate (D_R) was calculated to take care of mean values of gamma dose rate in air at the distance of 1 m from the ground surface for different kinds of building materials. These values were calculated using the relation given in Eq. 6 (UNSCEAR, 2000).

$$D_R (\text{nGyh}^{-1}) = 0.92A_{Ra} + 1.1A_{Th} + 0.0807A_K \quad \text{Eq. 6}$$

2.3.6 Activity Utilization Index (AUI)

Because of the fact that building materials are mostly of geologic origin, they act as sources of radiation and also as shields against outdoor radiation (UNSCEAR, 1993). In houses constructed from different building materials, the factor that most strongly affects the indoor absorbed dose is the activity concentrations of natural radionuclide in those materials, while the walls absorb the radiation emitted by outdoor sources. Consequently, dose rates in indoor air will be elevated according to the concentrations of naturally occurring radionuclide in the construction materials used. To calculate dose rates in air from ^{226}Ra , ^{232}Th and ^{40}K in building materials and by applying the appropriate conversion factors, another parameter referred to as activity utilization index (AUI) was obtained using the formula as provided in Eq. 7 according to UNSCEAR, 2000 as follows:

$$AU = (A_{\text{Ra}}/50\text{Bqkg}^{-1}) f_U + (A_{\text{Th}}/50\text{Bqkg}^{-1}) f_{\text{Th}} + (A_{\text{K}}/500\text{Bqkg}^{-1}) f_{\text{K}} \quad \text{Eq. 7}$$

Where:

in our samples when they are considered for use as building materials; f_{Th} , f_{Ra} and f_{K} are the fractional contributions to the total dose rate in air attributed to gamma radiation from the actual concentrations of these radionuclide. In the NEA-OECD (1979), report, some typical activities per unit mass of ^{232}Th , ^{226}Ra and ^{40}K in building materials, are reported as 50, 50 and 500 Bqkg $^{-1}$, respectively.

2.3.7 Gamma representation index (I_γ)

Another radiation hazard index, the gamma activity concentration index, (I_γ), defined by Righi, S. and Bruzzi (2006) and the (European Commission, 1990) given as Eq. 8 below was used and correlated with the annual dose rate attributed to excess external gamma radiation (UNSCEAR, 2000), caused by superficial material.

$$I_\gamma = (C_{\text{Ra}}/300\text{Bqkg}^{-1}) f_U + (C_{\text{Th}}/200\text{Bqkg}^{-1}) f_{\text{Th}} + (C_{\text{K}}/3000\text{Bqkg}^{-1}) f_{\text{K}} \quad \text{Eq. 8}$$

Values of $I_\gamma \leq 2$ correspond to a dose rate criterion of 0.3mSv y^{-1} , whereas $2 < I_\gamma < 6$ corresponds to a criterion of 1 mSv y^{-1} (European Commission, 1990; Anjos, R.M., 2005). Thus, the activity concentration index should be used only as a screening tool for identifying materials that might be of concern when used as construction materials; although materials with $I_\gamma > 6$ should be avoided, these values correspond to dose rates higher than 1mSv y^{-1} value recommended for the population (European Commission, 1999).

2.3.8 Excess lifetime cancer risk (ELCR)

Excess lifetime cancer risk (ELCR) was calculated using the following equation and presented in UNSCEAR, (2000), as Eq. 9 below.

$$\text{ELCR} = \text{AEDE} \times \text{DL} \times \text{RF} \quad (5) \quad \text{Eq. 9}$$

Where:

AEDE, DL and RF are the annual effective dose equivalent, duration of life (70 years) and risk factor (Sv $^{-1}$), fatal cancer risk per Sievert. For stochastic effects, ICRP60 uses values of 0.05 for the public (Stranden, 1976).

2.3.9 Potential Heavy and Toxic Elements

Potential heavy and toxic elements in the samples were evaluated, plotted and analysed for compliance with world averages and standard as presented in the appropriate Tables together with corresponding figures that allows for pictorial variability of the element in each of the samples as provided in the discussions chapter.

Results And Discussion

3.1 Radionuclide Concentrations

The activity concentrations of ^{238}U , ^{232}Th , and ^{40}K in all the samples have been measured using Instrumental Neutron Activation Analysis (INAA) and the results presented and plotted (Table 1 and Fig. 2a-c). The highest value (6388 ± 40 (Bq/g)) for ^{40}K was recorded in the sediment sample while the average value for all the samples is 1241.9Bq/g. The ^{238}U and ^{232}Th values (Bq/g) range from 1.6 ± 0.3 – 35.5 ± 0.4 and 2.3 ± 0.1 – 8.1 ± 0.3 , and mean values of 35.38 and 4.4, respectively. The relatively higher radionuclide activity concentration values recorded in the sediment sample can be attributed to the fact that soil around the factory receives most of the waste, i.e. settling dust, dumped waste (sludge) or even some fragments of the phosphate rocks used inside the factory. The movement and long queues of transporting trucks within the vicinity of the factory also contributes to this higher radionuclide concentration in soils.

Table 1
Activity concentration (Bq/g) of ^{238}U , ^{232}Th and ^{40}K in the different matrices studied

NORM	SAMPLE ID										Range	Mean
	SLG1	SLG2	PGS1	PGS2	SED1	PRK1	PRK2	PRK3	DUST 1	DUST 2		
^{40}K	1556 ± 34	1003 ± 29	BDL	294 ± 90	6388 ± 4	867 ± 14	979 ± 16	BDL	575 ± 13	757 ± 15	BDL-6388 ± 40	1241.9
^{238}U	35.5 ± 0.4	35.4 ± 0.5	7.2 ± 0.2	6.8 ± 0.2	1.6 ± 0.3	34.5 ± 0.4	44.3 ± 5	120 ± 1	33.7 ± 0.4	34.8 ± 0.4	1.6 ± 0.3–7.2 ± 0.2	35.38
^{232}Th	3.8 ± 0.2	2.9 ± 0.2	2.3 ± 0.1	2.3 ± 0.1	8.1 ± 0.3	5.7 ± 0.2	5.3 ± 0.3	7.9 ± 0.3	3.1 ± 0.2	2.6 ± 0.2	2.3 ± 0.1–8.1 ± 0.3	4.4
Key: SLG = Sludge, PGS = Phosphogypsum, SED = Sediment, PRK = Phosphate Rock NB: all values are in mg/g, BDL = Below Detection Limit												
*Minimum Detectable Activity are 1.0×10^{-2} Bq kg ⁻¹ for ^{232}Th and ^{238}U , and 4.0×10^{-2} Bq kg ⁻¹ for ^{40}K												

The activity concentration values of the radionuclides in the studied phosphate rock and Phosphogypsum samples (Tables 2 and 3) were compared with values obtained in different locations around the world. The ^{238}U and ^{232}Th concentrations of the samples are observed to be slightly less than the earlier reported values, while ^{40}K is relatively higher.

Table 2
Comparison of activity concentration of ^{238}U , ^{232}Th and ^{40}K in phosphate rock of this study with other values around the world.

Location	Reference	Phosphate Rock Activity (Bq/kg)			
		^{226}Ra	^{238}U	^{232}Th	^{40}K
Morocco	[18]	1.6	1.7	0.01	0.02
Syria	[19]	0.3	1.0	0.002	-
Florida	[20]	1.6	1.5	0.02	-
India	[21]	1.29	1.34	0.09	0.01
Nigeria	Present study	0.21	0.082	0.0066	0.923

Table 3
Comparison of activity concentration of ^{238}U , ^{232}Th , and ^{40}K in phosphogypsum sample with other values around the world

Location	Reference	Phosphogypsum Activity (Bq/kg)			
		^{226}Ra	^{238}U	^{232}Th	^{40}K
Brazil	[23]	0.6	0.04	0.1	0.02
Egypt	[22]	0.1	-	0.04	0.5
Syria	[19]	0.3	0.03	0.002	-
Florida	[24]	0.9	0.069	0.01	-
India	[21]	0.3	0.03	0.01	0.005
Nigeria (present study)		0.07	0.007	0.0023	0.294

3.2 Radiological Parameters

Radiological parameters such as Annual Effective Dose Equivalent (mSvy⁻¹), Internal Hazard Index, External Hazard Index, Annual Gonad Dose Equivalent (mSvy⁻¹), Radium Equivalent Activity (Bqkg⁻¹), Absorbed Gamma Ray Dose Rate (nGyh⁻¹), Activity Utilization and gamma representation index were also calculated from the activity concentration values of the different radionuclide and the result presented in Table 4.

3.2.1 Annual Effective Dose Equivalent (AEDE)

The annual effective dose for the public is 1mSvy⁻¹ as set by Arabi et al., 2016. This is the effective dose that can be received by the public with fewer risks from the effect of ionizing radiation, though cumulative value could be higher when added to the dose received from cosmic radiation. The AEDE values recorded for the entire samples are greater than the permissible limit. For all the samples studied, the range of values recorded is 5.88–333.95mSvy⁻¹ with a mean value of 87.0mSvy⁻¹.

3.2.2 Internal and external hazard

The external hazard index is an evaluation of the hazard of the natural gamma radiation (Arabi et al., 2016; Mujahid, S. A. et al., 2008), while the internal exposure to radon and its daughter products are quantified by the internal hazard index (H_{in}), (Mujahid et al., 2008; Xinwei, 2004). A plot of these parameters (Fig. 3) indicates that Internal and External Hazard index (H_{in} and H_{ex}) are relatively higher in the sediment sample (range of 0.028–1.36, and a mean value of 0.4) than any other sample, and lowest in the phosphogypsum samples (range of 0.048–1.37 and a mean value of 0.5).

3.2.3 Annual Gonadal Dose Equivalent ($mSv\cdot y^{-1}$)

The Annual Gonadal Dose Equivalent (AGDE) covers the dose received by certain organs resulting in the effect of ionizing radiation. These organs include gonads, female breast, active bone marrow and bone surface cells (UNSCEAR, 1988). The results indicate that the sediment sample has the highest AGDE (2044.6) with a range of 31.86–2044.63 obtained for all the samples and a mean value of 517.7.

3.2.4 Radium Equivalent Activity ($Bq\cdot kg^{-1}$)

Radium equivalent activity is a common radiological index employed in this study to evaluate the actual activity level of ^{226}Ra , ^{232}Th , and ^{40}K since the distribution of NORM in the samples is not uniform. The variation observed for radium equivalent activity followed the same pattern as the other parameters, where the sediment sample and phosphogypsum have the highest and lowest values, respectively. The radium equivalent activity values range from 10.49 to 505.06 with a mean value of 137.3.

3.2.5 Absorbed Gamma Ray Dose Rate ($nGy\cdot h^{-1}$)

The absorbed gamma ray dose quantifies the mean gamma dose rate in air at a distance of 1 m from the ground surface when samples are used as building material. The global average value is about $84nGy\cdot h^{-1}$. However, the value obtained is lower than the global average for all the samples, except the sediment sample ($272.3\ 84nGy\cdot h^{-1}$). The mean value for all the samples is $70.9nGy\cdot h^{-1}$. The phosphogypsum sample recorded the lowest value of 31.86 (Fig. 3).

3.2.6 Activity Utilization Index (AUI)

Building materials can serve as sources of radiation and as shields against outdoor radiation (UNSCEAR, 1993). Indoor air can be elevated, depending on the concentration of NORM in the building material used for construction. Materials with Activity Utilization Index (AUI) of < 2 has been recommended for construction. The AUI values for most of the samples were found to be greater than < 2 except for Phosphogypsum 1 (PGS1) and phosphate rock 3 with AUI values of 0.1 and 1.3, respectively. AUI for the entire sample ranged from 0.11–81631.22 with a mean value of 9388.9, while the sediment sample has the highest value of 81631.22.

3.2.7 Gamma Representation Index ($I\gamma$)

The gamma activity concentration index, ($I\gamma$), has been defined by the European Commission (EC) (Eq. 9) as another radiation index used as a screening tool for identifying hazardous construction materials. Materials with gamma index > 6 correspond to dose rate higher than $1mSv\cdot y^{-1}$ and therefore must be avoided. The gamma representative index for all the samples ranged from 0.071–4.35, with sediment sample recording the highest value of 4.35. The average gamma representative index is 1.1. Based on this parameter, the samples can be used for construction since their values are < 6 . The European Commission, 1999 suggests that building materials with gamma activity concentration index with < 6 should be exempted from all restrictions concerning their radioactivity provided that the excess gamma radiation originating from them does not increase the annual effective dose to member of the public by more than $0.3mSv$ (Anjos, 2005).

3.2.8 Excess lifetime cancer risk (ELCR)

Excess lifetime cancer risk (ELCR) was calculated using Eq. 10. The values obtained are presented in Table 4 and plotted (Fig. 4). This risk factor is defined as the fatal cancer risk per Sievert. For stochastic effect, the ICRP 60 document (Xinwei, L. and China. J. (2004) recommends a value of 0.05 from the public.

For this parameter (ELCR), all the samples studied had values significantly greater than the 0.05 recommended by the (ICRP (1994). The values range from 20.6 to 1169, with a mean of 304.57.

It is evident that the radiological parameters of the studied materials exceed the world averages. Although these studied materials are not used in the construction of dwellings, except the soil sediment sample, and the phosphate rock to some extent, the materials contribute a lot to environmental radioactivity.

3.2.9 Metal elements

Result of analysis of all the heavy metals in soil sample (Table 5) indicates that all the element concentrations fall within common ranges in soils as it is around the world, except manganese (Mn) whose concentration is 6610 mg/kg, almost twice the highest value (3,000 mg/kg) for the world average (Table 5, Fig. 5). Also, the sediment sample (SED1) has the highest values recorded for Al, Ta, Cs, Hf, Ta, Rb, Br, Cr and V, while samples of phosphate rocks (PRK1 and PRK2) has the highest level of As, Mn, Sr, Hf, Sb, Zn, Ba, with almost all the samples having Ta, Cs, Rb, Ti, and Br levels lower than the detection limit, except SED1. Sample of phosphate rock (PRK1) had the highest value of 21.9 mg/kg for arsenic (As) which is twice the value obtained in soil sample (SED1) as obtained from the study area. Also, chromate (Cr) value obtained in SED1 sample (149 ± 4 mg/kg) has the highest value as can be observed from the Table, followed by all samples of phosphate rocks (PRK1, PRK2 and PRK3), with values 62, 63 and 75 mg/kg, respectively. This might be the source of high value recorded in SED1 around the study area. Comparing these values with the FAO/WHO guidelines for maximum allowable limit for concentration of heavy metals in soil (mg/kg) and other values worldwide (Table 3, 6), results obtained from heavy metals (As) (21.9 mg/kg), Cr (149 mg/kg) and Mn (6610 mg/kg) are greater than the FAO/WHO guidelines (Table 6) of 20 mg/kg, 100 mg/kg and 5000 mg/kg for the As, Cr, and Mn, respectively, while values for Zn is exactly the same with maximum allowable limit.

Table 4 Radiological parameters calculated for all the samples

SAMPLE ID	Excess Lifetime Cancer Risk	Gamma Representati on Index	Activity Utilization	Absorbed Gamma Ray Dose Rate (nGyh ⁻¹)	Radium Equivalent Activity (Bqkg ⁻¹)	Annual Gonad Dose Equivalent (mSvy ⁻¹)	Internal Hazard Indices	External Hazard Index	Annual Effective Dose Equivalent (mSvy ⁻¹)
SLG1	359.5	1.3	4842.6	83.7	160.7	614.2	0.5	0.4	102.7
SLG2	257.6	0.9	2012.2	60.0	116.8	436.5	0.4	0.3	73.6
PGS1	20.7	0.1	0.1	4.8	10.5	31.9	0.0	0.0	5.9
PGS2	72.5	0.3	173.0	16.9	32.7	122.9	0.1	0.1	20.7
SED1	1169	4.4	81631.2	272.3	505.1	2044.6	1.4	1.4	334.0
PRK1	239.4	0.9	1504.0	55.7	109.4	402.7	0.4	0.3	68.4
PRK2	277.6	1.0	1917.4	64.7	127.3	466.4	0.5	0.3	79.3
PRK3	259.7	0.9	1.3	60.5	131.3	403.8	0.7	0.4	74.2
DUST 1	178.2	0.6	661.4	41.5	82.4	297.6	0.3	0.2	50.9
DUST 2	211.8	0.8	1146.2	49.3	96.8	356.1	0.4	0.3	60.5
RANGE	20.6 - 1169	0.071 - 4.35	0.11 - 81631.22	4.8 - 272.3	10.49 - 505.06	31.86 - 2044.63	0.048 - 1.37	0.028 - 1.36	5.88 - 333.95
MEAN	304.57	1.1	9388.9	70.9	137.3	517.7	0.5	0.4	87.0

Table 5 NAA results (Bq/g) for levels of metal elements in all samples

SAMPLE ID	Hf	Ba	Cs	Sb	Sr	Rb	Zn	Co	Cr	Br	As	Mn	V
SLG1	3.2±0.3	263±41	0.00	0.6±0.1	499±95	0.00	0.00	15.2 ± 0.5	55 ± 4	5.1±0.4	9.6±0.3	2350±5	56±6
SLG2	2.3±0.3	264±36	0.00	0.6±0.1	319±63	0.00	0.00	19.9±0.5	43±3	0.00	9.2±0.3	2287±5	106±6
PGS1	0.00	0.00	0.00	0.33±0.05	0.00	0.00	0.00	0.00	23±2	0.3±0.1	2.4±0.1	14.4±0.4	11±2
PGS2	0.00	0.00	0.00	0.23±0.04	0.00	0.00	0.00	0.00	20±2	0.00	2.3±0.1	12.1±0.4	13±2
SED1	3.6±0.3	134±36	3.0±0.4	1.2±0.1	0.00	29±6	82±8	22.3±0.5	149±4	361±1	10.9±0.4	847±3	124±9
PRK1	3.7±0.3	259±39	BDL	0.6±0.1	0.00	0.00	100±11	49.1±0.6	62±4	0.00	21.9±0.3	3160±6	94±6
PRK2	3.8±0.3	376±54	0.00	0.6±0.1	0.00	0.00	0.00	44.8±0.7	63±4	1.5±0.2	17.5±0.3	6610±7	65±2
PRK3	0.9±0.2	388±39	0.00	2.4±0.1	725±73	0.00	106±9	6.8±0.4	75 ± 4	2.3±0.3	9.6±0.3	202±2	91±6
DUST 1	1.6±0.2	163±35	0.00	0.4±0.1	0.00	0.00	94±10	18.5±0.5	41±3	0.00	9.8±0.2	2778±6	61±4
DUST 2	2.2±0.3	199±35	0.00	0.6±0.1	0.00	0.00	79±10	19.3±0.5	39.5±0.1	0.00	11.3±0.3	2607±5	62±3
Mean	2.1	204.6	3.0	0.8	154.3	29	46.1	19.6	57.1	37	10.5	2086.8	57.1

Key: ELE = Elements, SLG = Sludge, PGS = Phosphogypsum, SED = Sediment, PRK = Phosphate Rock **NB:** all values are in mg/g, BDL = Below Detection Limit

Table 6
Comparison of Levels and ranges of Concentrations of Some metal elements in Studied Sample and FAO/WHO Guidelines

METAL	This study (mg/kg)	FAO/WHO Guidelines (mg/kg)	Soil (SED 1) (This study) (mg/kg)	Common Range in Soils (mg/kg)
Aluminium (Al)	57440 ± 12-4587 ± 21		57440 ± 12	10,000–300,000
Arsenic (As)	2.3 ± 0.1–21.9 ± 0.3	20	10.9 ± 0.4	1–50; 1–4010
Antimony (Sb)	0.23 ± 0.04–2.4 ± 0.1			
Barium (Ba)	BDL – 388 ± 39		134 ± 36	100–3,000
Chromium (Cr)	20 ± 2–149 ± 4	100	149 ± 4	1–1,000; 5 – 3,000
Manganese (Mn)	12.1 ± 0.4–6610 ± 7		847 ± 3	20 – 3,000
Thallium (Tl)	BDL – 1.5 ± 0.2			
Zinc (Zn)	BDL – 106 ± 9	300	82 ± 8	10–300

Conclusion

This study was set out to evaluate the levels of NORM and metal elements in some materials within and around the vicinity of a phosphate fertilizer factory to ascertain the radiological risks and metal element levels as compared to levels elsewhere around the world. The levels of all the evaluated parameters varied from one sample to the other, with the sediment sample recording the highest values for all the parameters, which indicated that the environment especially around the factory is highly vulnerable to all the contaminants studied. The major River around the factory, River Kaduna therefore, might not be spared by these contaminants, as run off and drains from and around the factory certainly flow into the river while partly percolates/infiltrate down to groundwater water level which may end up in wells and finally in homes as drinking water. It is therefore recommended that a more detailed study to cover areas not included/covered in this study especially down stream of River Kaduna be carried out and the outcome be transmitted to the National Environmental Standards and Regulations Enforcement Agency (NESREA) for closer monitoring of the activities of the industry in terms of environmental standard enforcement.

Declarations

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DECLARATION OF INTEREST

The authors wish to declare that there is no conflict of interest with regard to this wok title “**Assessment of NORMs and associated dose from different materials within and around a superphosphate industry**”

AUTHORS CONTRIBUTION/ASSIGNMENTS

A. S. Arabi drafted the manuscript, A. M. Muhammad and A. A. Jaoji conducted the NAA analysis, A. D. Bajoga, A. M. Ali, S. I. Babale and M. S. Abdulhamid conducted the field work while Kasidi Simon reviewed the manuscript and calculations therein

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Figures

Figure 1

Areal view of part of Kaduna Metropolis depicting the location of the study area (red circle (smaller = inner perimeter, Bigger = outer perimeter) (Google map, visited 20-10-2020)

Figure 2
a Variation of activity concentration of 238U, 232Th and 40K in the samples b Variation of activity concentration of 238U, 232Th and 40K in the samples c Variation of activity concentration of 238U, 232Th and 40K in the samples

Figure 3
A plot of Annual Effective Dose Equivalent (mSvy-1), internal Hazard Index, External Hazard Index, Annual Gonad Dose Equivalent (mSvy-1), radium equivalent activity (Bqkg-1) values for all the samples

Figure 4

A plot of Excess Lifetime Cancer Risk for all the sample

Figure 5

Plot of levels of metal elements in all the samples studied