Naturally Occurring Radioactive Materials and Heavy Metal Contamination Around a Super Phosphate Fertilizer Company

A. S. Arabi[*1,2] and **A. M. Muhammad**[2]

[1]Department of Geology, Faculty of Earth and Environmental Sciences, Bayero University, Kano, Nigeria

[2]Centre for Energy Research and Training, Ahmadu Bello University, Zaria, Nigeria

A research paper presented during the 9th International Conference of Naturally Occurring Radioactive Materials (NORM IX) in Denver, Colorado, USA , 22nd to 27th September, 2019

OUTLINE

- ✓Introduction
- ✓Materials and Methods
- ✓Results and Discussions
- ✓Conclusion and Suggestions

✓Introduction

Phosphate rocks are known to harbor high degree of radioactivity due to the presence of naturally occurring U, K and Th, and their daughter isotopes Ra, Rn and Po.

During fertilizer production process, phosphate ore is treated with sulfuric acid and as a result the fertilizers become somewhat enriched in uranium (up to150% relative to the ore), while 80% of the ^{226}Ra, 30% of ^{232}Th and 5% of uranium are left in phosphogypsum (UNSCEAR, 2008).

During processing of phosphates, gaseous and particulate emissions are generated which contain ^{238}U and ^{226}Ra and when these are discharged to the environment, the population are exposed to radiation hazards, and toxic and heavy metals contamination of soils, water bodies and air

✓Introduction

This study sets out to assess the levels of radio-elements, REE, heavy and toxic metals in soil and other materials around an abandoned super phosphate fertiliser company and to evaluate the risks and hazards associated with the deposition of these contaminated industrial waste and there use by inhabitants of the area sometime as soil fertility supplement on farmland.

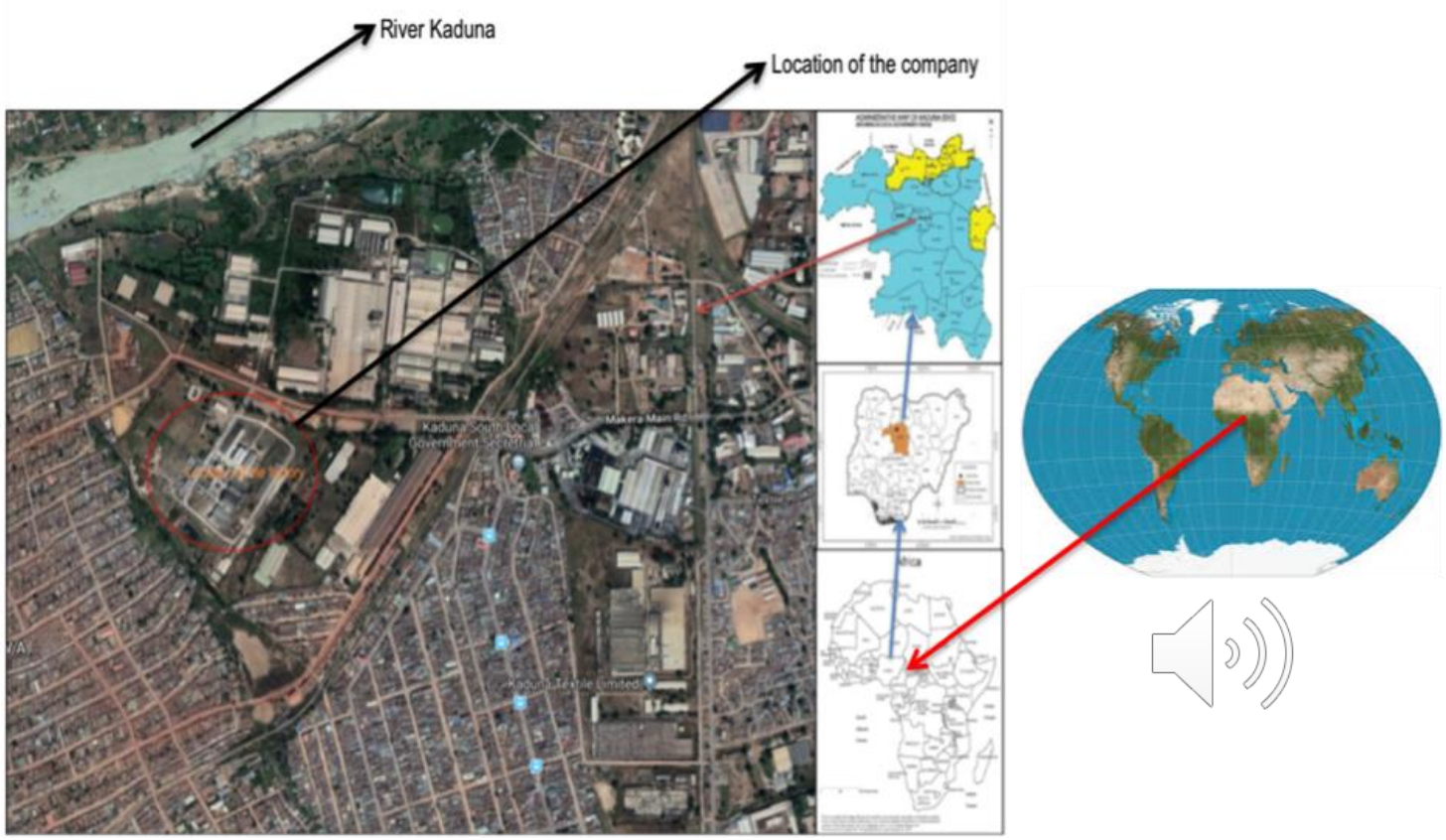

Fig. 1: The area is located in a densely populated area of Kaduna metropolis in northwester Nigeria.

Analysis of all the samples were carried out with a Miniature Neutron Source Reactor (MNSR), using Instrumental Neutron Activation Analysis (INAA) technique.

INAA has the capabilities for the analysis of trace, minor and major elements in different sample types. It uses high-enriched uranium as fuel and light water as moderator and coolant.

High-resolution gamma-ray spectrometers were used in this study. 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 2003) was employed in the analysis.

.

✓Introduction

✓**Materials and Methods**

✓Results and Discussions

✓Conclusion and Suggestions

The sample together with the standard were pulverized, sealed and irradiated at a flux of 5x1011ncm-2 s-1for 6 hours and counted for 1800s and 3600s after 4 and 14 days of cooling period respectively.

Identification of gamma ray of product radionuclide through their energies and quantitative analysis of their concentrations were achieved using the gamma-ray spectrum analysis software

Annual Effective Dose Equivalent (μSv/y),

$$H_R\,(\mathrm{mSvy^{-1}}) = D_R\,(\mathrm{nGh^{-1}}) \times 24\ \mathrm{h} \times 365.25\ \mathrm{dx}\ 0.2 \qquad \text{Equation 1}$$

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

$$H_{in} = \frac{A_{Ra}}{185Bq/kg} + \frac{A_{Th}}{259Bq/kg} + \frac{A_k}{4810Bq/kg} \qquad \text{Equation 2}$$

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

$$H_{in} = \frac{A_{Ra}}{185Bq/kg} + \frac{A_{Th}}{259Bq/kg} + \frac{A_k}{4810Bq/kg} \qquad \text{Equation 3}$$

$$H_{ex} = \frac{A_{Ra}}{370Bq/kg} + \frac{A_{Th}}{259Bq/kg} + \frac{A_k}{4810Bq/kg} \le 1 \qquad \text{Equation 4}$$

Annual Gonad Dose Equivalent (μSv/y),

$$\mathrm{AGDE\ (mSv\ y^{-1})} = 3.09\ A_{ra} + 4.18\ A_{th} + 0.31 A_K \qquad \text{Equation 5}$$

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

$$\mathrm{Ra_{eq}\ (Bq\ kg\ )} = A + 1.43A + 0.077A\ (1) \qquad \text{Equation 5}$$

Absorbed gamma ray dose rate (nGy/h),

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

Activity Utilization Index (AUI)

$$AUI = \frac{A_{Ra}}{50Bq/kg} f_U + \frac{A_{Th}}{50Bq/kg} f_{Th} + \frac{A_k}{500Bq/kg} f_K \qquad \text{Equation 7}$$

Gamma representation index (Iγ)

$$I\gamma = \frac{C_{Ra}}{300Bq/kg} + \frac{C_{Th}}{200Bq/kg} + \frac{C_K}{3000Bq/kg} \qquad \text{Equation 8}$$

Excess lifetime cancer risk (ELCR)

$$\mathrm{ELCR} = \mathrm{AEDE} \times \mathrm{DL} \times \mathrm{RF}\ (5) \qquad \text{Equation 9}$$

✓Introduction

✓Materials and Methods

✓**Results and Discussions**

✓Conclusion and Suggestions

Results indicates that highest values (6388±40 (Bq/g)) for ^{40}K was recoded in sediment sample while the average value for all the samples is 1241.9Bq/g. ^{238}U and ^{232}Th has values (Bq/g) ranging from 1.6±0.3-7.2±0.2 and 2.3±0.1-8.1±0.3, and a mean value of 35.38 and 4.4, respectively.

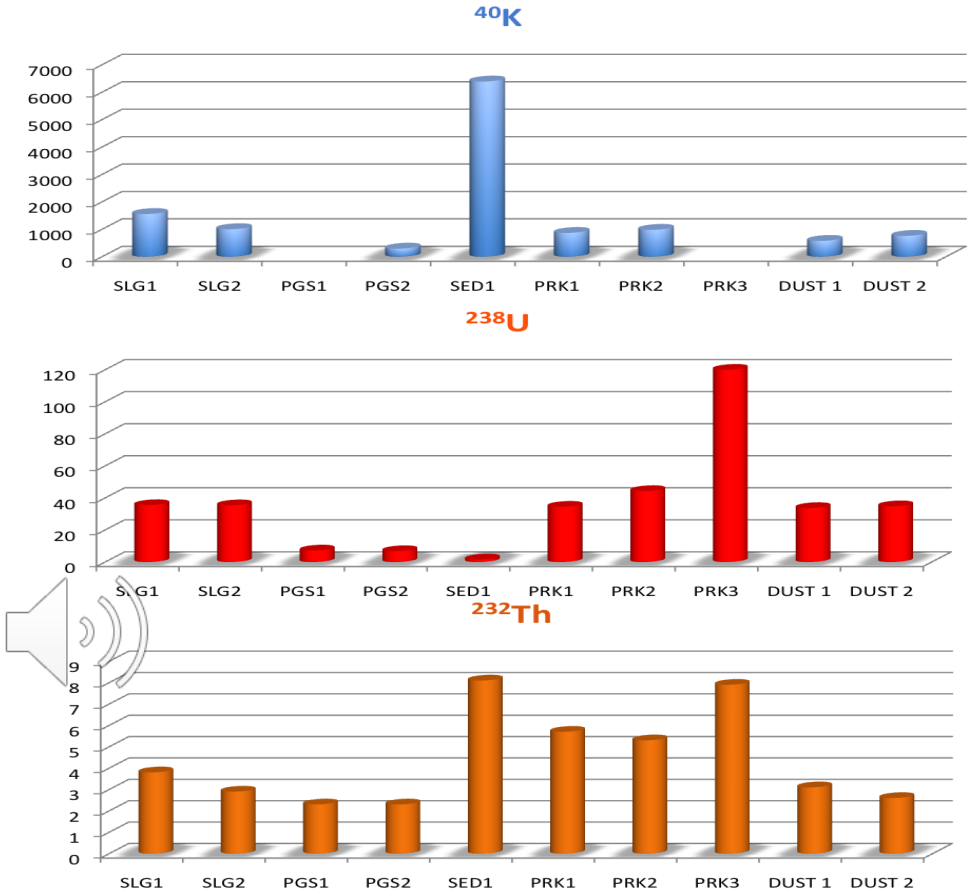

Figure 2: A plot of NORM values for all the sample

✓Introduction

✓Materials and Methods

✓**Results and Discussions**

✓Conclusion and Suggestions

^{238}U and ^{232}Th values are within the average while ^{40}K was higher than what obtains in most of the samples compared with

Table 1: Comparison of activity concentration of ^{238}U, ^{232}Th, and ^{40}K in phosphate rock sample with other values around the world

Location	Reference	Phosphate Rock Activity (Bq/kg)			
		^{226}Ra	^{238}U	^{232}Th	^{40}K
Morocco	Guimond and Hardin (1989)	1.6	1.7	0.01	0.02
Taiba-Togo		1.1	1.3	0.03	0.004
Syria	Attar et al (2011)	0.3	1.0	0.002	-
Florida	Guimond (1990)	1.6	1.5	0.02	-
India	Shahu et al (2014)	1.29	1.34	0.09	0.01
Nigeria (this study)		0.21	0.082	0.006	0.923

Table 2: Comparison of activity concentration of ^{238}U, ^{232}Th, and ^{40}K in phosphogysum sample with other values around the world

Location	Reference	Phosphogypsum Activity (Bq/kg)			
		^{226}Ra	^{238}U	^{232}Th	^{40}K
Brazil	Mazzilli et al (2000)	0.6	0.04	0.1	0.02
Egypt	Ahmed (2005)	0.1	-	0.04	0.5
Syria	Attar et al (2011)	0.3	0.03	0.002	-
Florida	Olszewska (1995)	0.9	0.069	0.01	-
India	Shahu et al (2014)	0.3	0.03	0.01	0.005
Nigeria	(this study)	0.07	0.007	0.0023	0.294

✓Introduction

✓Materials and Methods

✓Results and Discussions

✓Conclusion and Suggestions

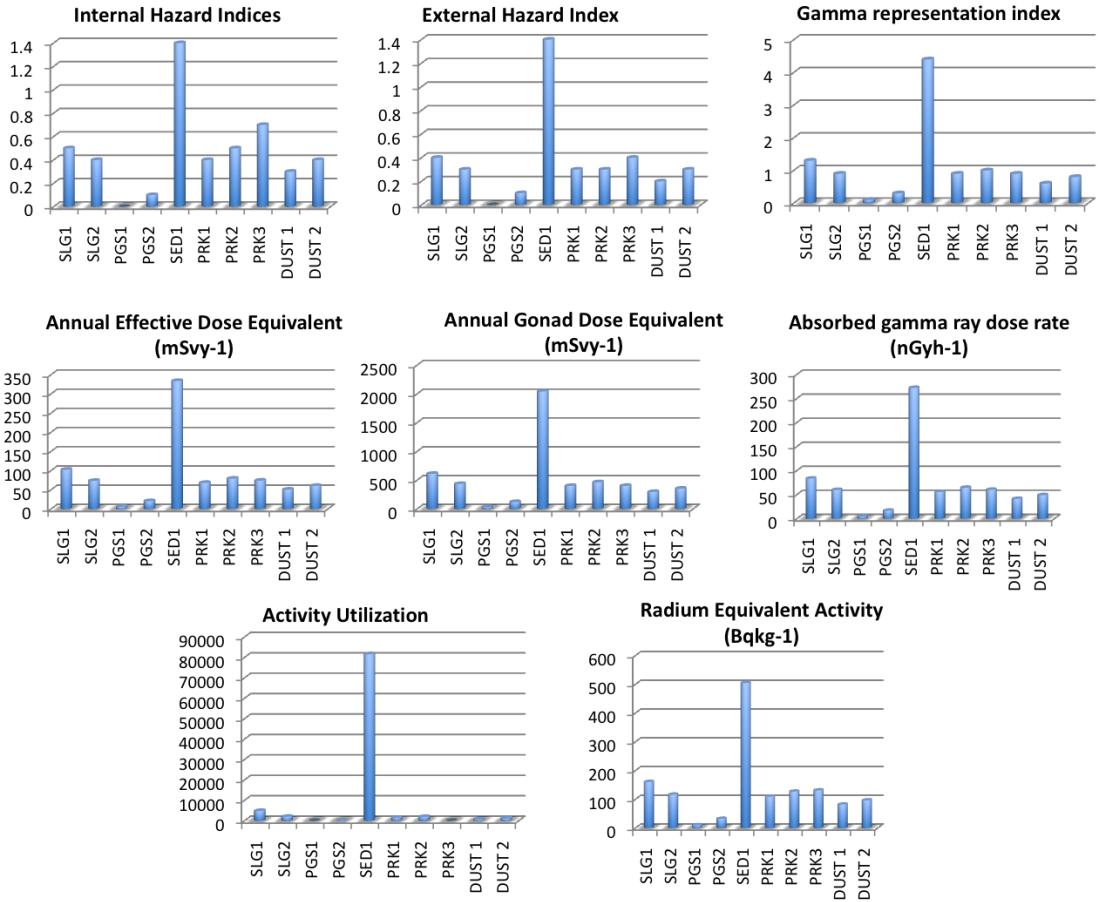

Figure 3: A plot of Annual Effective Dose Equivalent ($mSvy^{-1}$), internal Hazard Index, External Hazard Index, Annual Gonad Dose Equivalent ($mSvy^{-1}$), radium equivalent activity ($Bqkg^{-1}$) values for all the samples

✓Introduction

✓Materials and Methods

✓**Results and Discussions**

✓Conclusion and Suggestions

All the samples studied had values far greater than the 0.05 recommended by the ICRP, 1994. The range of values recorded are 20.6 – 1169 and a mean of 304.57

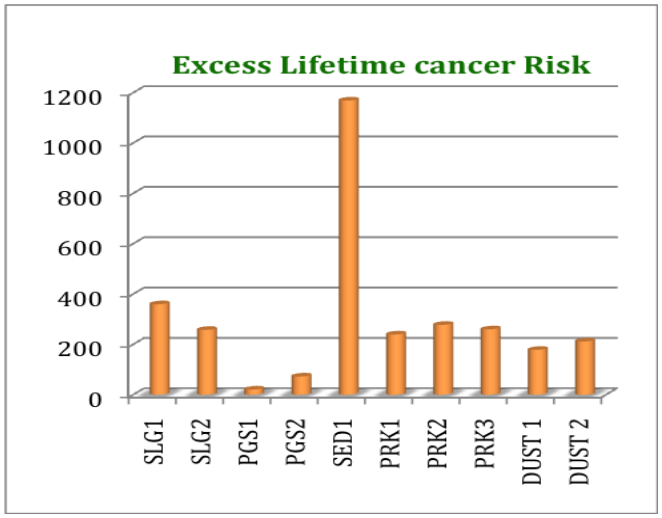

Figure 4: A plot of Excess Lifetime Cancer Risk for all the sample

✓Introduction

✓Materials and Methods

✓Results and Discussions

✓Conclusion and Suggestions

Table 3: Radiological parameters calculated for all the samples

Gamma Representation 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 ($mSvy^{-1}$)	SAMPLE ID
1.3	4842.6	83.7	160.7	614.2	0.5	0.4	102.7	**SLG1**
0.9	2012.2	60.0	116.8	436.5	0.4	0.3	73.6	**SLG2**
0.1	0.1	4.8	10.5	31.9	0.0	0.0	5.9	**PGS1**
0.3	173.0	16.9	32.7	122.9	0.1	0.1	20.7	**PGS2**
4.4	81631.2	272.3	505.1	2044.6	1.4	1.4	334.0	**SED1**
0.9	1504.0	55.7	109.4	402.7	0.4	0.3	68.4	**PRK1**
1.0	1917.4	64.7	127.3	466.4	0.5	0.3	79.3	**PRK2**
0.9	1.3	60.5	131.3	403.8	0.7	0.4	74.2	**PRK3**
0.6	661.4	41.5	82.4	297.6	0.3	0.2	50.9	**DUST 1**
0.8	1146.2	49.3	96.8	356.1	0.4	0.3	60.5	**DUST 2**
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	**RANGE**
1.1	9388.9	70.9	137.3	517.7	0.5	0.4	87.0	**MEAN**

✓Introduction

✓Materials and Methods

✓**Results and Discussions**

✓Conclusion and Suggestions

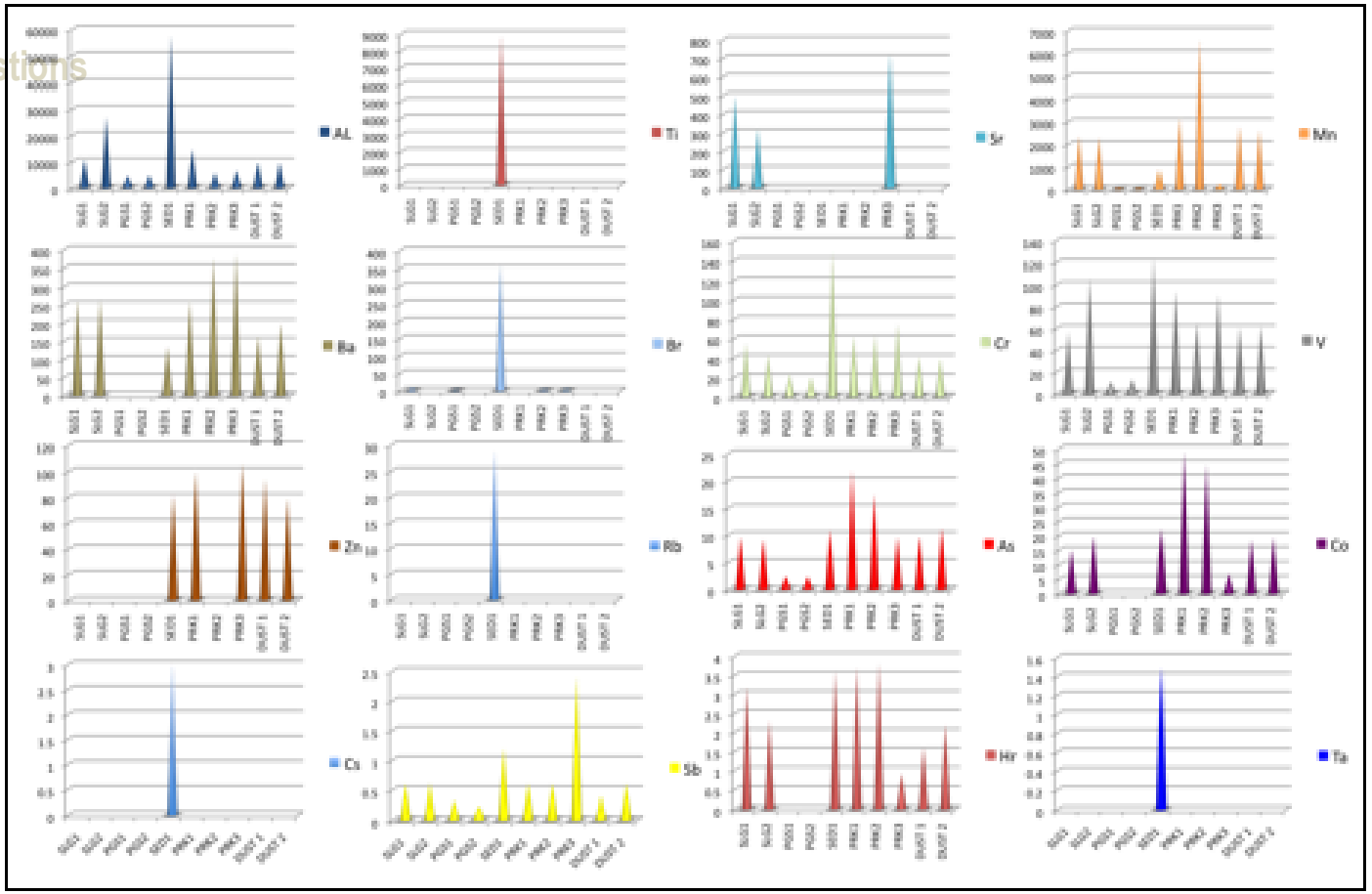

Figure 5: Plot of levels of Heavy metals in all the samples studied

✓Introduction

✓Materials and Methods

✓Results and Discussions

✓Conclusion and Suggestions

Table 4: Ranges of metal elements in studies samples compared with common ranges in soils around the World

METAL	This study	Common Range in Soils mg/kg
Aluminum (Al)	4587±21-2680±3	10,000-300,000
Arsenic (As)	2.3±0.1 - 21.9±0.3	1-50; 1-4010
Antimony (Sb)	0.23±0.04 - 2.4±0.1	
Barium (Ba)	BDL - 263±41	100-3,00010
Beryillium(Be)		
Cadmium (Cd)		0.01-0.7
Chromium (Cr)	20±2 - 149 ± 4	1-1,000; 5-3,00010
Copper (Cu)		2-100
Iron (Fe)		7,000-550,000
Lead (Pb)		2-200
Manganese(Mn)	12.1±0.4 - 6610 ± 7	20-3,000
Mercury (Hg)		0.01-0.3
Nickel (Ni)		5-500
Selenium (Se)		0.1-2.0
Silver (Ag)		0.01-5.0
Thallium (Tl)	BDL - 1.5±0.2	
Zinc (Zn)	BDL - 106±9	10-300

✓Introduction

✓Materials and Methods

✓Results and Discussions

✓Conclusion and Suggestions

Table 5: Comparison of Levels and ranges of Concentrations of Some Heavy Metals in Studied Sample and FAO/WHO Guidelines

METAL	This study	FAO/WHO Guidelines (mg/kg)	Soil (SED 1) (This study)	Common Range in Soils mg/kg
Aluminum (Al)	4587±21-26803		4587 – 26803	10,000-300,000
Arsenic (As)	2.3±0.1 - 21.9±0.3	20	2.3 – 21.9	1-50; 1-4010
Antimony (Sb)	0.23±0.04 - 2.4±0.1			
Barium (Ba)	BDL - 263±41		BDL – 263	100-3,00010
Beryillium(Be)				
Cadmium (Cd)		3		0.01-0.7
Chromium (Cr)	20±2 - 149 ± 4	100	20 – 149	1-1,000; 5-3,00010
Copper (Cu)		100		2-100
Iron (Fe)				7,000-550,000
Lead (Pb)		100		2-200
Manganese(Mn)	12.1±0.4 - 6610 ± 7		12.1 – 6610	20-3,000
Mercury (Hg)				0.01-0.3
Nickel (Ni)		50		5-500
Selenium (Se)				0.1-2.0
Silver (Ag)				0.01-5.0
Thallium (Tl)	BDL - 1.5±0.2			
Zinc (Zn)	BDL - 106±9	300	BDL - 106	10-300

- ✓Introduction
- ✓Materials and Methods
- ✓Results and Discussions
- ✓Conclusion and Suggestions

This study was set out to evaluated the levels of NORM and heavy metals in some material within and around the vicinity of a phosphate fertilizer factory and to ascertain the health hazard both from radiological and toxicity perspective in relation to the use of these materials on farms and as building material and also its implications on surface and groundwater resources in and around the area.

Levels of all the parameter evaluated varied from one sample to the other with sediment sample recording the highest of all the parameters. This is also an indication that the environment especially around the factory is very vulnerable to all these contamination.

Soil around the factory has indicated high level of contamination as marked by these high levels in sediment sample. The irony is that it is this same soil that is being use for construction of dwelling, farming and a transit of these radioactive and toxic to groundwater through percolation/infiltration.

The major River around the factory, River is therefore not spared by this contamination because run off and drains from and around the factory will 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

ON A SAD NOTE

Late Dr. Auwal Musa Muhammad

Late Dr. A. M. Muhammad is a co-author of this presentation, who after a brief illness recently passed away at the National Hospital in Abuja, Nigeria

He is a regular participant of NORM conferences. He was at NORM VI, NORM VII and NORM VIII

Finally, I want to thank the organizers of NORM IX for their efforts

The IAEA for the award of travel grant, though I could not make it because of the visa issue

I also want to suggest that for future NORM conferences, letters be sent to embassies to intimate and provide them with further information on events and participants

THANK YOU FOR LISTENING AND FOR THE OPPORTUNITY OF PLAYING MY PRESENTATION