

Evaluation of Toxicity Levels in Diverse Carriers around a Super Phosphate Fertilizer Company Using Instrument Neutron Activation Analysis (INAA)

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Abstract: This study is aimed at determining the levels, risks/hazards associated with the use of phosphate rock in the production of super phosphate fertilizer by a company in northwestern Nigeria. This was achieved through sampling and analysis of ten samples of diverse matrices namely; sludge, sediments, phosphate rock, phosphogypsum and dust obtained within and around the company and the results presented. Instrumental Neutron Activation Analysis was employed in the analysis of Rare Earth Element, toxic and heavy metals involving ten samples comprising of sludge, soil sediment, dust, phosphate rock and phosphogypsum, collected within and around the super phosphate fertilizer company using standard sampling procedure. The samples were irradiated in a research reactor for 6 hours then counted for 1800 secs and 3600 secs. for 4 and 14 days of cooling, respectively, under a neutron flux of flux of $5 \times 10^{11} \text{ n cm}^{-2} \text{ s}^{-1}$. Results obtained indicate the enrichment of some heavy and toxic metals in the materials sampled, with samples of sludge, sediment, dust and phosphate rocks having levels beyond world average while samples of dust had the lowest levels. The result obtained for the levels of REE indicates that the maximum concentration in the entire samples is due to the element Neodymium (Nd) with Sludge, Dust, and Phosphate rocks recording the highest values of 525 mg/g, 531 mg/g, 532 mg/g, respectively. The minimum and maximum levels in all the samples are due to the elements Antimony (Sb) and Nd at 0.8 mg/g and 341.7 mg/g, respectively. For the potential toxic elements, the range and mean value of the following: Al, V, As, Cr, Sb etc. are (4587 - 2603) mg/g and 9840 mg/g; (11 - 106) mg/g and 57 mg/g; (2.3 - 21.9) mg/g and 10.5 mg/g; (20 - 149) mg/g and 57.1 mg/g; (0.23 - 2.4) mg/g and 0.8 mg/g, respectively. It is concluded that the levels of these element indicate a potential health hazard to inhabitants of the area, possible impact on River Kaduna and the use of its water for irrigation and in homes, in addition to the use of material such as sludge as supplement for soil fertility improvement on farms as practice by some farmers around the area.

Key words: Environment; Risks; Nigeria; Phosphate rocks, INAA; Heavy metals, Rare elements

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Date of Submission: 26-07-2020

Date of Acceptance: 10-08-2020

I. Introduction

Heavy metals are relatively dense metals or metalloids that has been implicated for their potential toxicity, especially in environmental contexts (Srivastava and Goyal, 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. In humans, heavy metal poisoning is generally treated by the regulatory administrators as chelating agents. However, some elements otherwise regarded as toxic heavy metals are essential, in small quantities, for human health.

Rare Earth Elements (REE) on the other hand, are naturally found in very low concentration in the environment. Near mining and industrial sites, their concentrations can be highly elevated above normal background levels. Once in the environment, REEs can leach into the soil where their transport is determined by numerous factors such as erosion, weathering, pH, precipitation, ground water, etc. Acting much like metals they can speciate, depending on the soil condition being either motile or adsorbed to soil particles. Depending on their bioavailability REEs can be absorbed into plants and later consumed by humans and animals. The production of phosphate fertilizers also contributes to REE contamination due to their production and deposition around fertilizer production plants. Furthermore, strong acids are used during the extraction process of REEs, which can then leach out in to the environment and be transported through water bodies and result in the acidification of aquatic environments.

Several studies were carried out in different countries, to determine REE, toxic and heavy metals concentration in different samples and their effects on humans (Hannigan & Sholkovitz, 2001; Chirhakarhula, 2018; Mehmood *et al.*, 2009). Enhanced levels of metals such as lead, cadmium, and copper are potentially toxic can present an issue of concern for human health (Jarup, 2003; Tchounwou, *et al.*, 2012). Lead is a cumulative toxin affects the central nervous system and cardiovascular, including human cognitive abilities, among others (Flora, *et al.*, 2012; Jakubowski, *et al.*, 2011). Rare Earth Element (REE) found widespread applications, including their uses in high-performance magnets which are used in wind turbines; electronics for liquid crystal display and plasma screen, glass ceramics, and due to their thermal stability, in the manufacture of alloys which are used in jet engines. An increasing important area of their use is in low-carbon technologies (GSL, 2011). The REE are also used in scientific researches, for example in the earth sciences, where their unique properties have led them being successfully applied to a number of geological research problems. Some environmental issues associated with the REE occurrence is their frequent association with radioactive elements uranium and thorium. In particular, the heavy rare elements have great affinity with thorium deposits in the same geological environment, commonly found in monazite formed in granitic rocks and in the mineral sands derived from them.

REE, heavy and toxic element contamination of soil is one of the most pressing concerns in the debate about food security and food safety globally (CEC, 2006; Kong, 2014; Peralta-Videa *et al.*, 2009). During mining and processing, REE production uses a great amount of energy, which is derived from fossil fuels, that will eventually add to carbon emission, especially if it comes from coal-powered stations (GSL, 2011). Additional problems can arise due to extraction and processing of these elements, including environmental pollution from the chemicals used, especially if environmental regulation or enforcement is weak. This study therefore, sets out to assess the levels of REE, heavy and toxic metals in soil and other materials around a super phosphate fertiliser company and to evaluate the risks and hazards associated with the deposition of these contaminated industrial waste and their use by inhabitants of the area sometime as soil fertility supplement on farmland. The plant is located in a densely populated area of Kaduna metropolis in northwestern Nigeria, with the following co-ordinates: 10° 31'23"N 7°26'25"E (see Fig. 1).

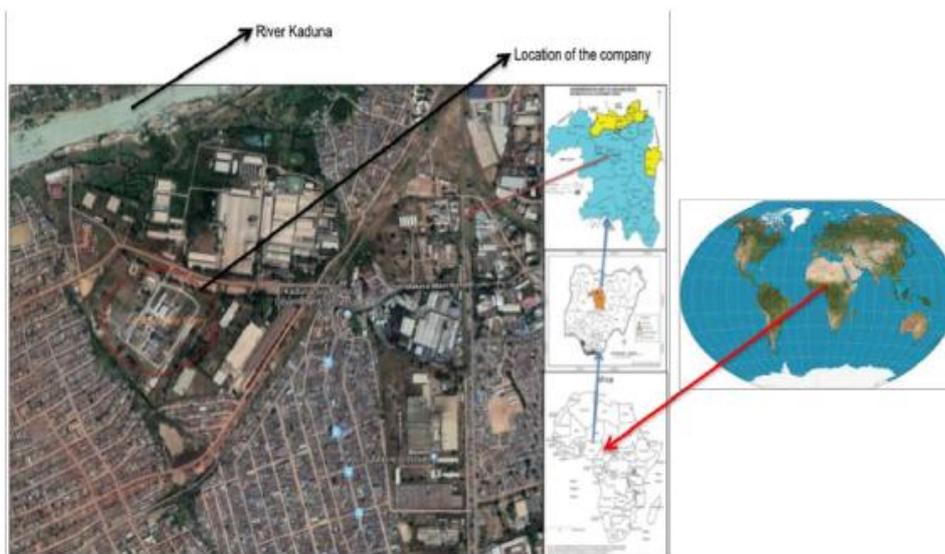


Fig. 1. Areal view of part of Kaduna Metropolis depicting the location of the study area.

II. Materials And Methods

2.1 Sampling

Ten samples comprising of sludge (SLG), soil sediment (SED), dust (DST), phosphate rock (PRK) and phosphogypsum (PGS), were collected within and around the super phosphate fertilizer company using standard procedure described in EPA sampling standard. Sludge sample was taken directly from most recent sludge pile using a hand spatula while phosphate rock was collected from rock chips brought from the field. Sediment samples were collected using plastic hand trowel within and outside the company. Dust sample was collected from

dust deposited on the roof of the security post at the entrance of the company and phosphogypsum collected from a storage facility of the company. All the samples collected were carefully packed into a polythene bag and transported to the laboratory for analysis.

2.2 Instrumentation

Analysis of all the samples were carried out at the Centre for Energy Research and Training (CERT), Ahmadu Bello University, Zaria-Nigeria, utilizing a Miniature Neutron Source Reactor (MNSR), Nigeria's first nuclear research reactor (NIRR-1) using Instrumental Neutron Activation Analysis (INAA) technique. The 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. The samples together with the standard were pulverized, sealed and irradiated at a flux of $5 \times 10^{11} \text{ ncm}^{-2}\text{s}^{-1}$ for 6 hours then counted for 1800 secs and 3600 secs. for 4 and 14 days of cooling, respectively.

2.3 Rare Earth and Heavy Elements

Rare earth elements and 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 section.

III. Results and Discussion

3.1 Levels of Rare Earth, Heavy and Toxic Elements

Measurement of Rare Earth, Heavy and Toxic metals in the samples provides us the opportunity to ascertain their levels and impact on the surrounding area of the factory (CLEA, 2018).

3.1.1 Rare Earth Element (REE)

REEs (e.g. Dy, La, Sm, Gd, Ho, Sc, Sb, Nd, Eu, Tb, Tm, Yb, Lu) are a large group of elements with different properties and levels in the environment, because of this unique nature and inadequate research; it has been difficult to determine safe levels of exposure for humans. A number of studies have been conducted with most of them focusing on risk assessment based on routes of exposure and variance from back ground levels related to nearby agriculture, mining, and industry. It has been reported that numerous REEs have toxic properties and are present in the environment or in work places. Exposure to some REE can lead to a broad range of harmful health outcomes such as cancer, respiratory issues, dental loss and even death (Vodyanitskii, 2016). However these elements are numerous and present in many different forms and at different levels of toxicity, as such it has been difficult to give straight-out warnings on cancer risk and toxicity as some of these are harmless while others pose a risk.

Of all the REE determined in the studied samples as listed in the following Table 1, Nd had the highest value ($> 500 \text{ mg/g}$) in sample SG1, SLG2, DUST2 and PRK1. This is followed by the element La with values $> 200 \text{ mg/g}$ in PRK2, $> 100 \text{ mg/g}$ in SLG1, SLG2, PRK1, DUST1 and DUST2. The element Sb has the lowest value which is less than the detection limit as indicated in Table 1 and Figure 2.

Table no 1: Levels of REE (mg/g) in the entire sample

| REE | S | | A | | M | | P | | L | | E | | I | | D | | R A N G E | MEAN |
|-----|-----------|-----------|-----------|-----------|-----------|------------|-----------|-----------|-----------|-----------|-----------------------|---|----|--|---|--|-----------|------|
| | SLG1 | SLG2 | PGS1 | PGS2 | SED1 | PRK1 | PRK2 | PRK3 | DUST1 | DUST2 | | | | | | | | |
| Dy | 42 ± 1 | 44.3±0.9 | 3.7±0.3 | 3.3±0.3 | 4.2±0.5 | 47.2±1.2 | 4.9 ± 2 | 18.5±0.6 | 4.5 ± 1 | 4.3 ± 1 | 3.3±0.3 - 49±2 | 3 | 0 | | | | | |
| La | 171.9±0.3 | 162.0±0.5 | 26.8±0.1 | 27.7±0.1 | 35.9±0.3 | 154.3±0.3 | 210.3±0.4 | BDL | 155.0±0.3 | 159.1±0.3 | BDL - 210.3±0.4 | 1 | 10 | | | | | |
| Sm | 57.2±0.1 | 53.5±0.1 | 6.00±0.02 | 6.13±0.02 | 5.62±0.03 | 49.70±0.05 | 61.2±0.1 | 32.5±0.1 | 47.7±0.1 | 53.5±0.1 | 5.62±0.03 - 61.2±0.1 | 3 | 7 | | | | | |
| Gd | 15 ± 3 | 22±4.0 | BDL | BDL | BDL | 1.4 ± 3 | 1.7 ± 3 | 5.0 ± 4 | 1.6 ± 2 | 1.5 ± 2 | BDL - 2.2±4.0 | 1 | 5 | | | | | |
| Ho | 21.7±0.4 | 19.6±0.3 | 1.1±0.1 | 0.7±0.1 | BDL | 9.6±0.3 | 22.9±0.3 | 9.3±0.5 | 21.9±0.3 | 11.2±0.3 | BDL - 22.9±0.3 | 1 | 2 | | | | | |
| Sc | 9.8 ± 0.1 | 9.2±0.1 | 3.05±0.04 | 3.05±0.04 | 11.5±0.1 | 11.2±0.1 | 11.8±0.1 | 5.9±0.1 | 8.7±0.1 | 8.9±0.1 | 3.05±0.04 - 11.8±0.1 | 8 | | | | | | |
| Sb | 0.6 ± 0.1 | 0.6±0.1 | 0.33±0.05 | 0.23±0.04 | 1.2±0.1 | 0.6±0.1 | 0.6±0.1 | 2.4±0.1 | 0.4±0.1 | 0.6±0.1 | 0.23±0.04 - 2.4±0.1 | 1 | | | | | | |
| Nd | 520 ± 12 | 525±12 | 5.1 ± 5 | 3.3 ± 4 | 6.6 ± 5 | 53.2±12 | 338±14 | 342±16 | 479±12 | 531±13 | 3.3±4 - 532±12 | 3 | 42 | | | | | |
| Eu | 127 ± 0.4 | 11.8±0.3 | 1.1±0.2 | 1.1±0.1 | 1.4±0.1 | 9.9±0.3 | 10.9±0.4 | 4.1±0.2 | 10.1±0.3 | 10.9±0.1 | 1.1±0.1 - 127±0.4 | 1 | 9 | | | | | |
| Tb | 7.1 ± 0.2 | 6.2±0.2 | 0.6±0.1 | 0.8±0.1 | 0.9±0.1 | 5.7±0.2 | 6.4±0.2 | 2.3±0.1 | 5.5±0.2 | 5.9±0.2 | 0.6±.1 - 7.1±0.2 | 4 | | | | | | |
| Tm | 127 ± 0.9 | 13.3±0.9 | BDL | 4.7±0.6 | BDL | BDL | BDL | BDL | 1.6 ± 1 | 1.3 ± 1 | BDL - 1.27±.9 | 1 | 7 | | | | | |
| Yb | 18.1±0.2 | 18.1±0.3 | 1.5±0.1 | 1.5±0.1 | 1.4±0.2 | 16.2±0.2 | 16.4±0.2 | 10.7±0.2 | 16.4±0.2 | 17.2±0.1 | 1.4±0.2 - 18.1±0.3 | 1 | 2 | | | | | |
| Lu | 3.47±0.05 | 3.25±0.05 | 0.35±0.02 | 0.28±0.2 | 0.22±0.02 | 2.74±0.04 | 3.4±0.1 | 1.69±0.04 | 2.91±0.04 | 3.16±0.3 | 0.22±0.02 - 3.47±0.05 | 2 | | | | | | |

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

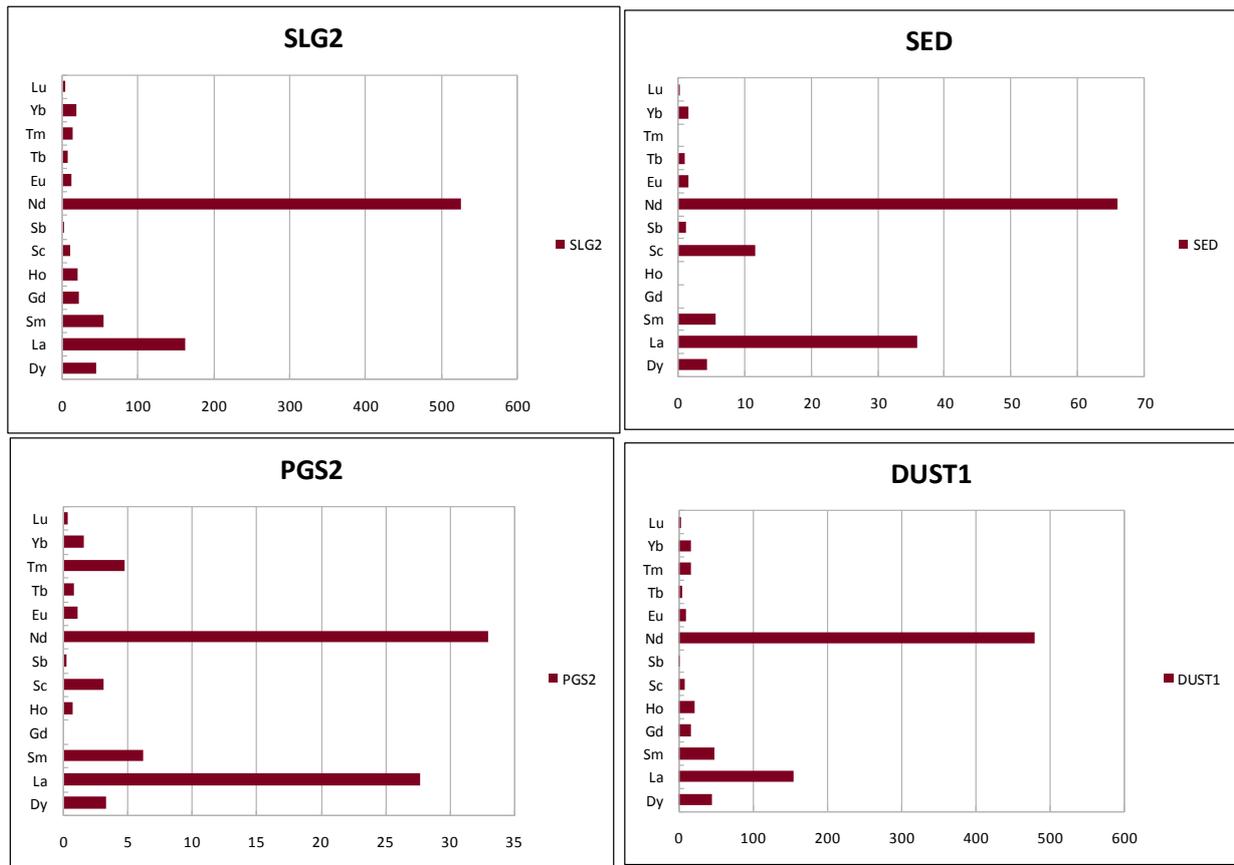


Fig. 2:A Plot of REE levels (mg/g) in some of the samples

3.1.2 Heavy and Toxic metals

The following heavy metals, i.e. Al, Ti, V, Mn, As, Br, Cr, Co, Zn, Rb, Sr, Sb, Cs, Ba, Hr and Ta, were studied in all the samples. Result of all the heavy metals analyzed in soil sample (SED1) indicates that all the element concentrations fall within common ranges in soils around the world, except manganese (Mn) (6610 mg/kg) which is almost twice the highest value (3,000 mg/kg) for the world average (Table 2, Figure 3).

From Table 2 and Figure 3 of the studied materials, the sediment sample (SED1) has the highest level recorded for Al, Ti, Cs, Hr, Ta, Rb, Br, Cr and V, while samples of phosphate rocks (PRK1 and PRK2) has the highest level of the following metals: As, Mn, Sr, Hr, Sb, Zn, Ba, with almost all the samples having Ta, Cs, Rb, Ti, and Br levels lower than the determination 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) recorded the highest obtained, 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 area.

Comparing these values with the FAO/WHO guidelines for maximum allowable limit of concentration of heavy metals in soil (mg/kg) (Table 3), 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 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 no 2: Results for levels of heavy metals in all samples

| ELE | S | | A | | M | | P | | L | | E | | I | | D | | R A N G E | MEAN |
|-----|----------|----------|-----------|-----------|----------|----------|----------|---------|----------|----------|---------------------|-------|---|--|---|--|-----------|------|
| | SLG1 | SLG2 | PGS1 | PGS2 | SED1 | PRK1 | PRK2 | PRK3 | DUST1 | DUST2 | | | | | | | | |
| A l | 10720±35 | 26800±43 | 4587±21 | 4741±18 | 57440±12 | 14610±37 | 5616±51 | 6519±42 | 9578±23 | 9486±11 | 4741±18 - 57440±12 | 15010 | | | | | | |
| T i | BDL | BDL | BDL | BDL | 8884±791 | BDL | BDL | BDL | BDL | BDL | BDL - 8884±79 | 888 | | | | | | |
| V | 56 ± 6 | 106 ± 6 | 11 ± 2 | 13 ± 2 | 124 ± 9 | 94 ± 6 | 65 ± 2 | 91 ± 6 | 61 ± 4 | 62 ± 3 | 11 ± 2 - 106 ± 6 | 68 | | | | | | |
| M n | 2350±5 | 2287±5 | 14.4±0.4 | 12.1±0.4 | 847 ± 3 | 3160±6 | 6610±7 | 202 ± 2 | 2778±6 | 2607±5 | 12.1±0.4 - 6610 ± 7 | 2087 | | | | | | |
| A s | 9.6±0.3 | 9.2±0.3 | 2.4±0.1 | 2.3±0.1 | 10.9±0.4 | 21.9±0.3 | 17.5±0.3 | 9.6±0.3 | 9.8±0.2 | 11.3±0.3 | 2.3±0.1 - 21.9±0.3 | 10 | | | | | | |
| B r | 5.1±0.4 | BDL | 0.3±0.1 | BDL | 361 ± 1 | BDL | 1.5±0.2 | 2.3±0.3 | BDL | BDL | BDL - 361 ± 1 | 37 | | | | | | |
| C r | 55 ± 4 | 43 ± 3 | 23 ± 2 | 20 ± 2 | 149 ± 4 | 62 ± 4 | 63 ± 4 | 75 ± 4 | 41 ± 3 | 39.5±0.1 | 20 ± 2 - 149 ± 4 | 57 | | | | | | |
| C o | 15.2±0.5 | 19.9±0.5 | BDL | BDL | 22.3±0.5 | 49.1±0.6 | 44.8±0.7 | 6.8±0.4 | 18.5±0.5 | 19.3±0.5 | BDL - 49.1±0.6 | 20 | | | | | | |
| Z n | BDL | BDL | BDL | BDL | 82 ± 8 | 100±11 | BDL | 106 ± 9 | 94 ± 10 | 79 ± 10 | BDL - 106 ± 9 | 46 | | | | | | |
| R b | BDL | BDL | BDL | BDL | 29 ± 6 | BDL | BDL | BDL | BDL | BDL | BDL - 29 ± 6 | 3 | | | | | | |
| S r | 499±95 | 319±63 | BDL | BDL | BDL | BDL | BDL | 725±73 | BDL | BDL | BDL - 725 ± 73 | 154 | | | | | | |
| S b | 0.6±0.1 | 0.6±0.1 | 0.33±0.05 | 0.23±0.04 | 1.2±0.1 | 0.6±0.1 | 0.6±0.1 | 2.4±0.1 | 0.4±0.1 | 0.6±0.1 | 0.23±0.04 - 2.4±0.1 | 1 | | | | | | |
| C s | BDL | BDL | BDL | BDL | 3.0±0.4 | BDL | BDL | BDL | BDL | BDL | BDL - 3.0±0.4 | 0 | | | | | | |
| B a | 263±41 | 264±36 | BDL | BDL | 134±36 | 259±39 | 376±54 | 388±39 | 163±35 | 199±35 | BDL - 388 ± 39 | 205 | | | | | | |
| H r | 3.2±0.3 | 2.3±0.3 | BDL | BDL | 3.6±0.3 | 3.7±0.3 | 3.8±0.3 | 0.9±0.2 | 1.6±0.2 | 2.2±0.3 | BDL - 3.8 ± 0.3 | 2 | | | | | | |
| T a | BDL | BDL | BDL | BDL | 2.2±0.3 | BDL | BDL | BDL | BDL | BDL | BDL - 2.2 ± 0.3 | 0 | | | | | | |

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

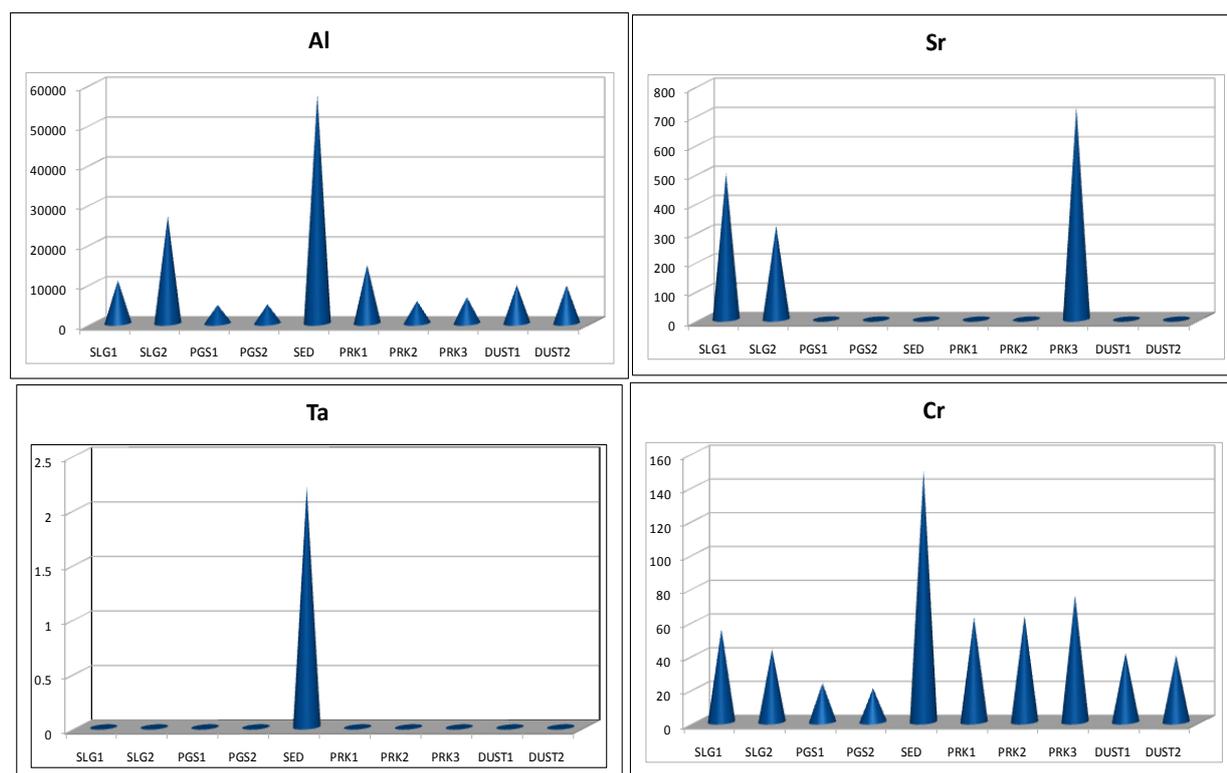


Fig. 3:A Plot of levels of some Heavy metals in the entire samples

Table no. 3: Comparison of Levels and ranges of Concentrations of Some Heavy Metals in Studied Sample and FAO/WHO Guidelines.

| M E T A L | This study | FAO/WHO Guidelines (m g / k g) | Soil SED1 (This study) | Common Range in Soils (m g / k g) |
|---------------|--------------------|----------------------------------|------------------------|-------------------------------------|
| Aluminum (Al) | 4587±21-26800±43 | | 4587 - 26803 | 10,000 - 300,000 |
| Arsenic (As) | 2.3±0.1 - 21.9±0.3 | 2 | 0 - 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 0 . 0 1 - 0 . 7 |
| Beryllium(Be) | | | | | | | | | | | | | | | | | | | | | |
| Cadmium (Cd) | | | | | | | | | | | | | | | | | | | | | 3 |
| Chromium (Cr) | 20±2 - 149 ± 4 | 1 | | | | | | | | | | | | | | | | | | | 0 0 2 0 - 1 4 9 1-1,000; 5-3,00010 |
| Copper (Cu) | | 1 | | | | | | | | | | | | | | | | | | | 2 - 1 0 0 |
| Iron (Fe) | | | | | | | | | | | | | | | | | | | | | 7,000 - 550,000 |
| Lead (Pb) | | 1 | | | | | | | | | | | | | | | | | | | 2 - 2 0 0 |
| Manganese(Mn) | 12.1±0.4 - 6610 ± 7 | | | | | | | | | | | | | | | | | | | | 12.1 - 6610 2 0 - 3 , 0 0 0 |
| Mercury (Hg) | | | | | | | | | | | | | | | | | | | | | 0 . 0 1 - 0 . 3 |
| Nickel (Ni) | | 5 | | | | | | | | | | | | | | | | | | | 5 - 5 0 0 |
| Selenium (Se) | | | | | | | | | | | | | | | | | | | | | 0 . 1 - 2 . 0 |
| Silver (Ag) | | | | | | | | | | | | | | | | | | | | | 0 . 0 1 - 5 . 0 |
| Tantalum (Ta) | BDL - 1.5 ± 0.2 | | | | | | | | | | | | | | | | | | | | |
| Zinc (Zn) | BDL - 106 ± 9 | 3 | | | | | | | | | | | | | | | | | | | 0 0 BDL - 106 1 0 - 3 0 0 |

The maximum allowable limits for heavy metal varies one from country to another, and are presented in Table 4. below. The results obtained indicate a maximum values of 60 mg/kg (Taiwan), 450 mg/kg (UK), 600 mg/kg (Taiwan) and 200 mg/kg (Taiwan) due to As, Pb, Zn and Ni, respectively, and which are all higher than the values obtained from this study (Nigeria).

Table no. 4: Maximum Allowable Limits of Concentration of heavy Metals in Soil for Different Countries

| Country | A | s | Pb | Hg | Cd | Cr | Cu | Zn | Co | Ni | Reference | | | | | |
|--------------------|-----------|-----|------|------|-----|----|----|----------|-----|------|-----------|------|------|-------------------------------|--------------------------------|------------------------|
| Germany | 5 | 0 | 70 | 0.5 | 1 | 6 | 0 | 40 | 1 | 5 | 0 | n.a. | 50 | (Lee and Lee, 2011) | | |
| Poland | n.a. | 100 | n.a. | 3 | 1 | 0 | 0 | 100 | 3 | 0 | 0 | 5 | 0 | 100 | (Mtunzi et al., 2015) | |
| UK | 3 | 2 | 450 | 1 | 0 | 10 | 1 | 3 | 0 | n.a. | n.a. | n.a. | n.a. | 130 | (Heavy Metal Guidelines, 2018) | |
| Australia | 2 | 0 | 300 | 1 | 3 | 5 | 0 | 100 | 2 | 0 | 0 | n.a. | 60 | Australian EPA accessed 2018) | | |
| Taiwan | 6 | 0 | 300 | 2 | 5 | 2 | 5 | 0 | 200 | 6 | 0 | 0 | n.a. | 200 | (Lee and Lee, 2011) | |
| Bulgaria | 1 | 0 | 26 | 0.03 | 0.4 | 6 | 5 | 3 | 4 | 8 | 8 | 2 | 0 | 46 | (Atanassov, 2007) | |
| Canada | 2 | 0 | 200 | 0.8 | 3 | 2 | 5 | 0 | 150 | 5 | 0 | 0 | n.a. | 100 | (CME, 2009) | |
| China | 3 | 0 | 80 | 0.7 | 0.5 | 2 | 0 | 0 | 100 | 2 | 5 | 0 | n.a. | 50 | (EPMC, 2015) | |
| Tanzania | 1 | 200 | 2 | 1 | 1 | 0 | 0 | 200 | 1 | 5 | 0 | n.a. | 100 | (He et al., 2015) | | |
| FAO/WHO Guidelines | 2 | 0 | 100 | n.a. | 3 | 1 | 0 | 0 | 100 | 3 | 0 | 0 | 5 | 0 | 50 | (Chiroma et al., 2014) |
| EU Guidelines | n.a. | 300 | n.a. | 3 | 1 | 5 | 0 | 140 | 3 | 0 | 0 | n.a. | 75 | (ECE, 2016) | | |
| South Africa | 5 | 8 | 20 | 0.93 | 7.5 | 6 | 5 | 16 | 2 | 4 | 0 | 3 | 0 | 91 | (GSA, 2006) | |
| Nigeria | .3 - 21.9 | | | | | | | 20 - 149 | | | | | | BDL - 106 | BDL - 49.1 | This Study |

3.2 Correlation between Rare Earth, Heavy and Toxic Element

Tables no. 5 and Table no. 6 gives a correlation coefficient of the measured REE and heavy metals as detected in the samples from the area of study. The coefficient gives the nature of relationships amongst the elements and ranges from -1 to 1; indicating negative and positive correlation, respectively, with 0 signifying no relationship.

From Table 5, a strong correlation were observed from between the elements La-Dy, Nd-Sm and Lu-Yb at 0.93, 0.922 and 0.922, respectively. Moderate correlation at 0.515, 0.502, and 0.543 was observed between Sc-Ho, Nd-Gd and Nd-Sc among other, respectively. In contrast to the above, the element Sb correlates negatively with the following elements in the samples: Eu, Tb, Tm, Yb, Lu.

Table no 5: Correlation between REEs in the entire measured samples.

| Elements | Dy | La | Sm | Gd | Ho | Sc | Sb | Nd | Eu | Tb | Tm | Yb | Lu |
|----------|--------|--------|--------|-------|--------|-------|-------|----|----|----|----|----|----|
| Dy | 1.000 | | | | | | | | | | | | |
| La | 0.932 | 1.000 | | | | | | | | | | | |
| Sm | 0.976 | 0.894 | 1.000 | | | | | | | | | | |
| Gd | 0.341 | 0.026 | 0.458 | 1.000 | | | | | | | | | |
| Ho | 0.875 | 0.833 | 0.901 | 0.410 | 1.000 | | | | | | | | |
| Sc | 0.656 | 0.687 | 0.619 | 0.081 | 0.515 | 1.000 | | | | | | | |
| Sb | -0.195 | -0.450 | -0.074 | 0.759 | -0.124 | 0.047 | 1.000 | | | | | | |

| | | | | | | | | | | | | | | | | | | |
|-----------------------|---------------------------------|-------|-------|-------|-------|-------|---|-------|-------|-------|-------|-------|-------|--|--|--|--|--|
| N d | 0.921 | 0.763 | 0.922 | 0.502 | 0.780 | 0.543 | 0.000 | 1.000 | | | | | | | | | | |
| E u | 0.322 | 0.379 | 0.412 | 0.040 | 0.473 | 0.232 | -0.110 | 0.394 | 1.000 | | | | | | | | | |
| T b | 0.976 | 0.943 | 0.979 | 0.298 | 0.896 | 0.651 | -0.221 | 0.915 | 0.497 | 1.000 | | | | | | | | |
| T m | 0.284 | 0.345 | 0.369 | 0.009 | 0.456 | 0.166 | -0.144 | 0.376 | 0.990 | 0.465 | 1.000 | | | | | | | |
| Y b | 0.977 | 0.871 | 0.987 | 0.463 | 0.890 | 0.590 | -0.082 | 0.967 | 0.412 | 0.977 | 0.384 | 1.000 | | | | | | |
| L u | 0.976 | 0.903 | 0.996 | 0.424 | 0.916 | 0.598 | -0.122 | 0.931 | 0.443 | 0.987 | 0.411 | 0.992 | 1.000 | | | | | |
| C o r r e l a t i o n | S t r o n g P o s i t i v e | | | | | | L a - D y , H o - S m , N d - D y , N d - S m , T b - N d , L u - Y b , e t c . | | | | | | | | | | | |
| | M o d e r a t e p o s i t i v e | | | | | | S c - H o , N d - G d , N d - S c , e t c . | | | | | | | | | | | |
| | N e g a t i v e | | | | | | S b - D y , S b - H o , E u - S b , e t c . | | | | | | | | | | | |

Similar trend was observed for the heavy metals as shown in Table 6. For example, strong positive correlation coefficients were found between Br-Al, Co-As and Cs-Cr at 0.913, 0.961, and 0.880, respectively. Conversely, a weak negative correlation was observed between Mn-Al, Sr-As and Ba-Al among others at -0.143, -0.101 and -0.063, respectively. However, a relationship cannot be established between Ti and Rb and the remaining heavy elements because they have only parameter as observed from Table 2 above.

Table no 6: Correlation between heavy metals in the entire measured samples.

| Metals | A l | T i | V | M n | A s | B r | C r | C o | Z n | R b | S r | S b | C s | B a | H r | T a |
|-----------------------|---------------------------------|-----|-------|--------|--------|--------|---|--------|-------|-------|--------|-------|-------|--------|-------|-------|
| A l | 1.000 | | | | | | | | | | | | | | | |
| T i | nc* | nc* | | | | | | | | | | | | | | |
| V | 0.724 | nc* | 1.000 | | | | | | | | | | | | | |
| M n | -0.143 | nc* | 0.195 | 1.000 | | | | | | | | | | | | |
| A s | 0.127 | nc* | 0.584 | 0.732 | 1.000 | | | | | | | | | | | |
| B r | 0.913 | nc* | 0.530 | -0.216 | 0.027 | 1.000 | | | | | | | | | | |
| C r | 0.827 | nc* | 0.766 | 0.012 | 0.365 | 0.883 | 1.000 | | | | | | | | | |
| C o | 0.169 | nc* | 0.512 | 0.823 | 0.961 | 0.057 | 0.317 | 1.000 | | | | | | | | |
| Z n | 0.221 | nc* | 0.511 | -0.099 | 0.418 | 0.254 | 0.433 | 0.231 | 1.000 | | | | | | | |
| R b | nc* | nc* | 0.529 | -0.217 | 0.027 | 1.000 | 0.880 | 0.058 | 0.256 | 1.000 | | | | | | |
| S r | -0.116 | nc* | 0.252 | -0.244 | -0.101 | -0.194 | 0.085 | -0.286 | 0.048 | nc* | 1.000 | | | | | |
| S b | 0.192 | nc* | 0.530 | -0.258 | 0.120 | 0.251 | 0.543 | -0.092 | 0.533 | nc* | 0.701 | 1.000 | | | | |
| C s | nc* | nc* | 0.529 | -0.217 | 0.027 | 1.000 | 0.880 | 0.058 | 0.256 | nc* | -0.204 | 0.246 | 1.000 | | | |
| B a | -0.063 | nc* | 0.579 | 0.584 | 0.675 | -0.178 | 0.280 | 0.559 | 0.247 | nc* | 0.561 | 0.556 | nc* | 1.000 | | |
| H r | 0.466 | nc* | 0.665 | 0.700 | 0.831 | 0.355 | 0.586 | 0.856 | 0.158 | nc* | -0.086 | 0.016 | nc* | 0.565 | 1.000 | |
| T a | nc* | nc* | 0.529 | -0.217 | 0.027 | 1.000 | 0.880 | 0.058 | 0.256 | nc* | -0.204 | 0.246 | nc* | -0.184 | 0.351 | 1.000 |
| C o r r e l a t i o n | S t r o n g P o s i t i v e | | | | | | B r - A l , C r - A l , C o - M n , C o - A s , R b - C r , C s - C r , H r - A s , e t c . | | | | | | | | | |
| | M o d e r a t e p o s i t i v e | | | | | | B r - V , C o - V , Z n - V , R b - V , S b - C r , S b - V , S b - Z n , C s - V , B a - C o , e t c . | | | | | | | | | |
| | N e g a t i v e | | | | | | M n - A l , S r - A l , B r - M n , Z n - M n , S r - C o , e t c . | | | | | | | | | |

In each case, a good correlation suggests same origin and similar geochemical behaviour or co-contamination between the elements (e.g. La-Dy, Nd-Sm, Lu-Yb, etc.), where as negative or inverse correlation between variable pairs (e.g. Mn-Al, Sr-As and Ba-Al, etc.) indicates they are of different geochemical dynamics and possibly different origin (Omoniyi *et al.*, 2013).

IV. Conclusion

This study was set out to evaluate the levels of toxic and heavy metals in some material within and around the vicinity of a phosphate fertilizer factory, compared with set guidelines, range of levels around the world and to ascertain their 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 (SED 1) recording the highest of all the parameters. This is also an indication that the environment especially around the factory is very vulnerable to all the contaminants studied. Soil around the factory has indicated high level of contamination as marked by the high levels in sediment sample (SED 1). A good correlation amongst the REE and heavier metals was also observed in the studied samples. The irony is that it is this same soil that is being used for construction of dwelling, farming and a transit of these radioactive and toxic/heavy metals to groundwater through percolation/infiltration. The major River around the factory, River Kaduna is therefore not spared by this contamination, because runoff 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.

Acknowledgement

The authors wish to acknowledge the contribution of anonymous reviewers whose contribution has helped a lot in putting this manuscript in its present state. The authors also wish to acknowledge the immense contribution of late Auwal Musa Muhammad who is also an author of this paper. May God the exalted in might, the merciful reward him with the best of paradise.

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