Assessment of Levels and Safe Factor Index of Heavy Metals in Soils Around Diobu, Port Harcourt, Nigeria

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Abstract*: This study was aimed at determining the variations of some heavy metals in soil sample between Mile 3 (M_3) and Mile 4 (M_4), all in Diobu, which are both primarily business and residential areas when compared to the control represented by the Rivers State University (RSU), Port Harcourt. The Azuka Index (A_i) was used to determine the Safety Factor Index. The levels and distribution of seven heavy metals (Fe, Pb, Cu, Cd, Cr, Ni, As) in soil (0–25 cm depth) from the area using Atomic Absorption Spectrometer (AAS, Perkin Elmer 2380) were assessed. The results showed that in M_3, Fe (1418.303), Cd (2.692), Pb (7.646), Ni (7.412) and M_4, Fe (1162.011), Cd (1.436), Pb (7.372), Ni (5.384) were above WHO/FAO/FEPA recommended permissible limits for soils. High percentage variations occurred between the study stations and the controls, M_3/RSU for Fe, Cd, Cr, Ni, As and M_4/ RSU for Cd, Cr, Ni, As respectively. Though, the result of the ANOVA showed p-value of 0.2845 (α=0.05) meaning no significant difference within the M_3, M_4 and RSU stations was also corroborated by the t-test result for M_3/ RSU control and M_4/ RSU control which were 1.013 and 1.037 respectively at 0.05 significant levels. The mile 3 study station was observed to have more anthropic inputs which also showed in the variations from the Mile 4 results. The above results showed that only Cu in the Mile 4 study station certified a safe range while all the heavy metals exceeded safe limits especially Cd, As and Ni. The concentration distribution trend for the heavy metals studied were; M_3 (Fe>Cr>Cu>Pb>Ni>As>Cd); M_4 (Fe>Pb>Cr>Cu>Ni>As>Cd); RSU (Fe>Cu>Pb>Cr>Ni>As>Cd). The increasing concentrationss of these heavy metals in the soils of these areas stands a threat to health of the inhabitants; hence must be monitored and adequate measures taken by appropriate authorities of government*

Keywords: *Heavy metals, Azuka safe index, Mile3, Mile 4, Anthnropic, sample variation*

1. INTRODUCTION

According to Fergusson (1990), inorganic elements which are five times the specific gravity of water are considered as heavy metals. Heavy metals occur naturally in the ecosystem, most of them in trace quantities (Adamo *et al*., 2002). Any metal considered toxic may be called heavy metal not minding the weight, atomic mass or density (Singh, 2007). Heavy metals are a member of an ill-defined subset of elements that exhibit metallic properties. These include the transition metals, some metalloids, lanthanides, and actinides. One source defines heavy metal as one of the common transition metals, such as copper, lead, and zinc. These metals are a cause of environmental pollution from sources such as leaded petrol, industrial effluents, and leaching of metal ions from the soil into lakes and rivers by acid rain (Dictionary of Chemistry, 2000). Heavy metals are generally referred to as those metals which possess a specific density of more than 5 g/cm^3 and adversely affect the environment and living organisms (Järup, 2003). Heavy metals pollution of the soil is caused by various metals especially Cu, Ni, Cd, Zn, Cr, and Pb (Hinojosa *et al*., 2004). Similarly, heavy metals are characterized by relatively high density and high relative atomic weight with an atomic number greater than 20.

Heavy metals occur naturally in the soil environment from the pedogenetic processes of weathering of parent materials at levels regarded as *trace* ($<1000 mgkg^{-1}$) and seldom toxic (Kabata-Pendias & Pendias, 2001; Pierzynski *et al*., 2000). Due to the disturbance and acceleration of nature's slowly occurring geochemical cycle of metals by man, most soils of rural and urban environments may accumulate one or more of the heavy metals above defined background values high enough to cause risks to human health, plants, animals, ecosystems, or other media (D'Amore *et al*., 2005).

Similarly, Arsenic, lead, cadmium (Cd), and mercury have serious health implications within the heavy metals (Agency for Toxic Substances and Disease Registry, ATSDR, 2007; Csavina *et al*., 2012; Sharma *et al*., 2014; Gupta *et al*., 2015a). Arsenic, Cd, mercury, and lead have patho-physiological significance as their bioaccumulation in living systems may cause severe damage to vital organs (Sharma *et al*., 2014; Gupta *et al*., 2015b Heavy metals can damage and alter the functioning of organs such as the brain, kidney, lungs, liver, and blood. Heavy metal toxicity can either be acute or chronic effects.

Although plants require certain heavy metals for their growth and upkeep in the soil, excessive amounts of these metals can become toxic to plants. Some of the direct toxic effects caused by high metal concentration include inhibition of cytoplasmic enzymes and damage to cell structures due to oxidative stress (Duruibe *et al*., 2007; Young, 2005). Similarly, acid leaching and electrokinetics extract metals from soil. Heavy metals pollution is a menace to our environment as they are foremost contaminating agents of our food supply (Chauhan & Chauhan, 2014). Vegetables get contaminated by absorbing heavy metals from polluted air, soil, and water (Sharma *et al*., 2008; Singh *et al*., 2010). Heavy metals pollution in soil and water has a lot of adverse effects and thus is of great concern to public health, agricultural production, and environmental health (Goyer, 1997; Fergusson, 1990; Msaky & Calvet, 1990; Ma *et al*., 1994). Soil pollution results mainly from disposal of industrial and urban wastes as well as usage of agrochemicals (Buchauer, 1973; McBride, 2003; Demirezen & Aksoy, 2006). Many growing areas in the developing countries are vulnerable to air pollution due to the fact that heavy metals containing aerosols are normally deposited on soil surface and get absorbed by vegetables or sometimes get deposited on plant leaves (Duruibe *et al*., 2007). The absorption of heavy metals by the plants from the soil depends on different factors, including application of agrochemicals, solubility of heavy metals, soil pH, soil type, and plant species (Young, 2005; Gupta *et al*., 2013).

Heavy metals are one of the most widespread contaminants in the environment. They cause environmental pollution from sources such as industrial effluents, mine tailings, land application of fertilizers, atmospheric deposition and leaching of metal ions from the soil into lakes and rivers by acid rain (Chauhan & Chauhan, 2014; Sharma *et al*., 2008; Singh *et al*., 2010).

Research has shown that the main sources of heavy metals in the environment include geogenic, industrial, agricultural, pharmaceutical, domestic effluents, and atmospheric (Goyer, 1997). Environmental pollution is very prominent in point source areas of soil like mining, foundries and smelters, and other metal-based industrial operations (Goyer, 1997; Singh *et al*., 2010; Chauhan & Chauhan, 2014). The most common heavy metals found at contaminated sites, in order of abundance are Pb, Cr, As, Zn, Cd, Cu, and Hg (Gupta *et al*., 2013).

The advancing demand for information technology has resulted in large volumes of e-waste globally (Wagner, 2009). Accordingly, e-waste contains many different hazardous materials such as Cd, Pb, As, Be, Cr, Hg, polycyclic aromatic hydrocarbons (PAHs), chlorofluorocarbons, polybrominated diphenyl ethers and dioxin-like compounds and non-hazardous metals like Zn, Cu, Se, precious metals Ag, Au, Pt, among others. These significant harmful environmental impacts when not properly disposed-off especially to the soil (Lim, 2010; Tsydenova & Bengtsson, 2011). However, the dose, concentration and receptor organ can convert non-hazardous chemicals such as Zn, Cu and Se to hazardous ones in humans and ecosystems (Musee, 2011; Tchounwou *et al*., 2012; Itai *et al*., 2014).

Heavy metals are natural constituents of the earth's crust and soils, but indiscriminate anthropogenic inputs activities have altered their geochemical cycles and biochemical balance. This results in accumulation of metals in plant parts having secondary metabolites, which is responsible for a particular pharmacological activity. Research has also shown that prolonged exposure to heavy metals such as cadmium, copper, lead, nickel, and zinc can cause deleterious health effects in humans. All metals are toxic at higher concentrations (Chronopoulos *et al*., 1997). Excessive levels can be damaging to the organism. Any metal (or metalloid) species may be considered a "contaminant" if it occurs where it is unwanted, or in a form or concentration that causes a detrimental human or environmental effect. Heavy metals include lead (Pb), cadmium (Cd), mercury (Hg), arsenic (As), chromium (Cr), copper (Cu), selenium (Se), nickel (Ni), silver (Ag), and zinc (Zn). Other less common metallic contaminants include aluminium (Al), cesium (Cs), cobalt (Co), manganese (Mn), molybdenum (Mo), strontium (Sr), and uranium (U) (Mcintyre, 2003). Living organisms require varying amounts of heavy metals. Iron, cobalt,

copper, manganese, molybdenum and zinc are required by humans (Lane & Morel, 2009). Heavy metals such as mercury, plutonium, and lead are toxic metals that have no known significant effect on organisms, and their accumulation over time in the bodies of animals can cause serious illness. Certain elements that are normally toxic are for certain organisms or under certain conditions, beneficial. Examples include vanadium, tungsten, and even cadmium (Ernst, 2002; Lane *et al.*, 2005; Singh *et al*, 2010).

Metals concentration in soil can extend to as high as 100,000 mg/kg (Long *et al.*, 2002). Heavy metals are the major inorganic contaminants and relatively large area of land can be contaminated (Halim *et al.*, 2002). Notwithstanding the origin of the metals in the soil, excessive concentrations of many metals can lead to soil quality degradation, crop yield reduction, and poor quality of agricultural products, which poses significant hazards to human, animal, and ecosystem health (Long *et al.*, 2002). The knowledge of the present heavy metal concentration in the soil around this busy environment will guide the academic and government sectors to make rightful decisions and proffer adequate mitigating measures to protect the ecosystem and man. There is therefore the ardent need to assess the variations in soil heavy metal content so as to monitor its impact on the soil, plant and human health risk implications.
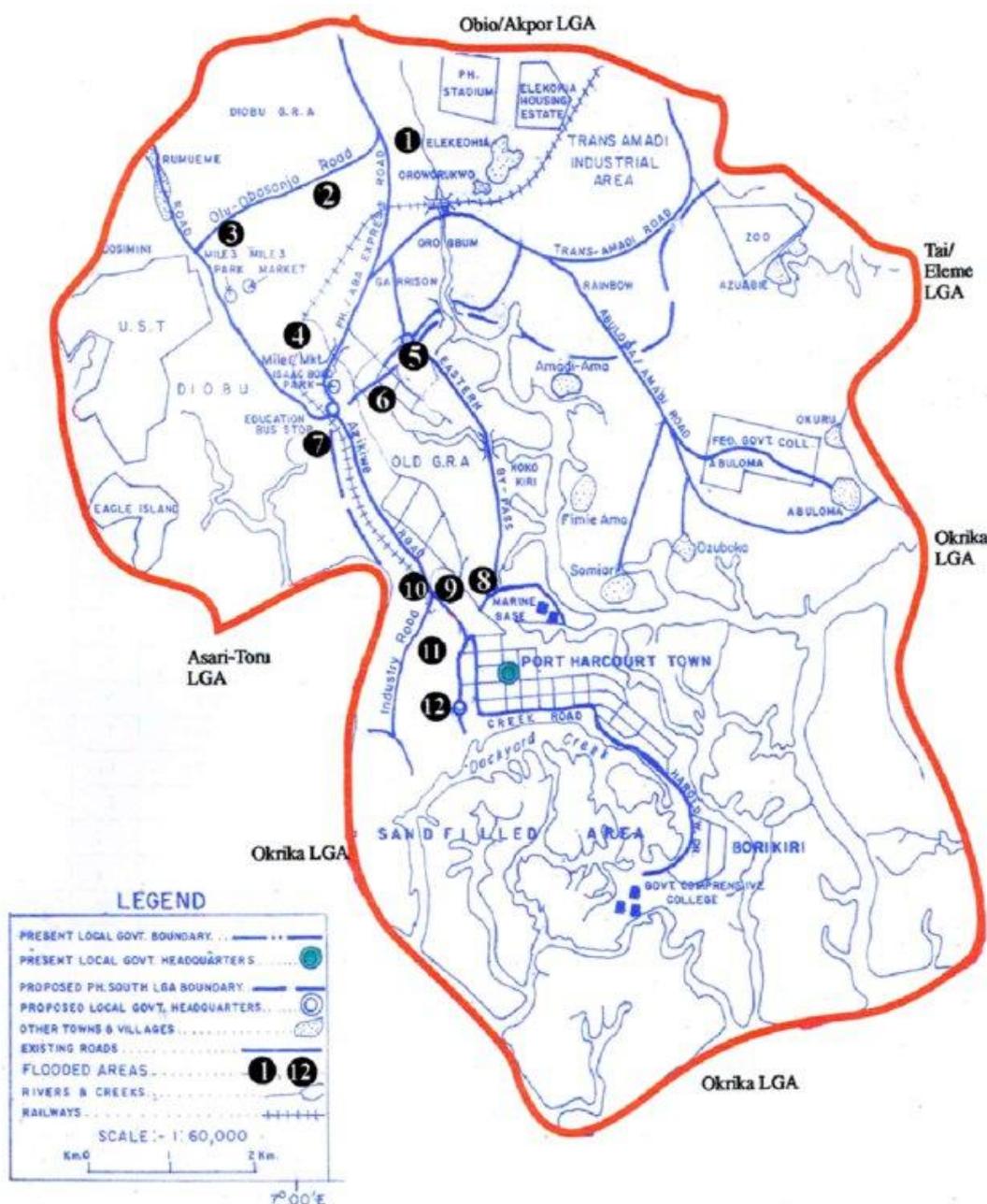

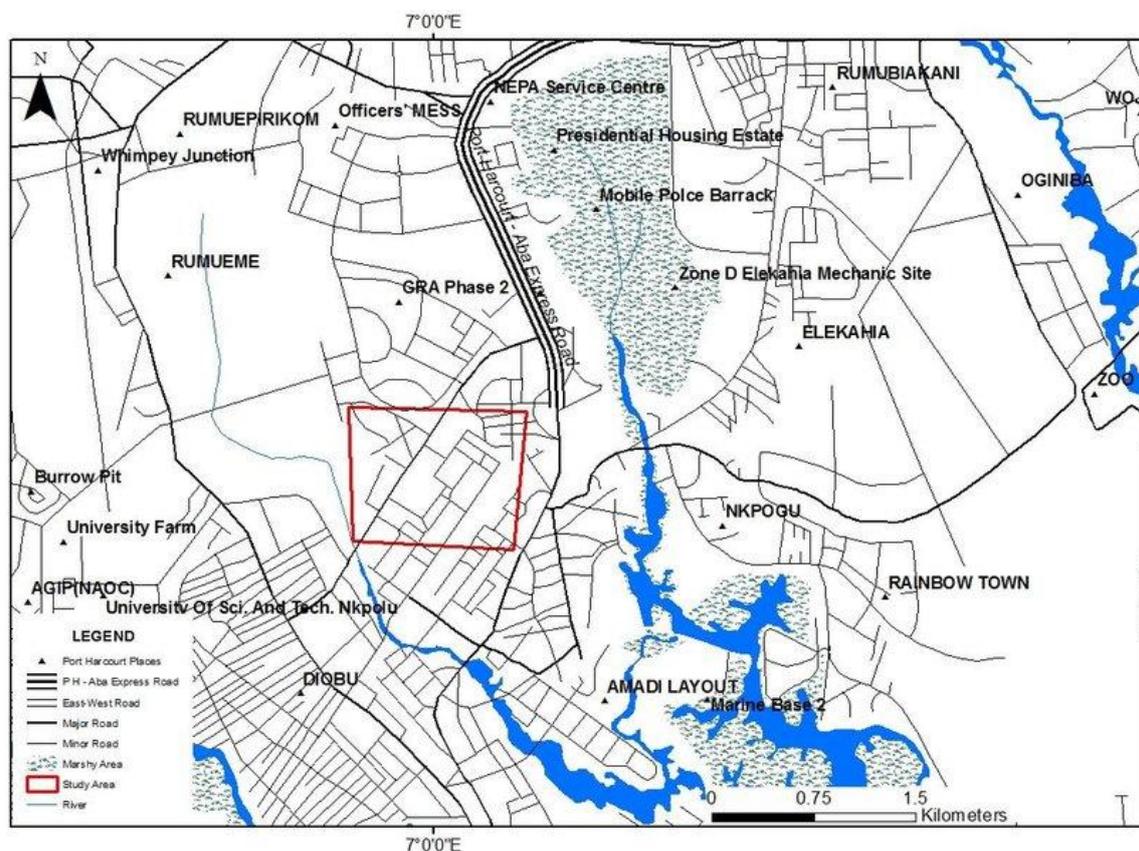**Figure1.** *Map of Port Harcourt (Nwankwoala & Warmate, 2014)*

Figure2. *Image Uploaded by Nwankwoala and Warmate (2014)*

2. MATERIALS AND METHODS

2.1. Study Area

This study was conducted in Port Harcourt and Obio-Akpor local government areas of Rivers State, Nigeria. Port Harcourt is known as port town and capital of Rivers State, Niger Delta, Southern Nigeria. It lies along the Bonny River (eastern tributary of the Niger River) 41 miles (66 km) upstream from the Gulf of Guinea. Port Harcourt was founded in 1912 in an area traditionally occupied by the Ijo (Ijaw), Okrikans, and Ikwere people. It began to serve as a port (named for Lewis Harcourt, then colonial secretary) after the opening of the rail link to the Enugu coalfields in 1916. Now one of the nation's largest ports, its deepwater (23 feet, about 7 metres) facilities handle the export of palm oil, palm kernels, and timber from the surrounding area, coal from Anambra state, tin and columbite from the Jos Plateau, and, since 1958, petroleum from fields in the eastern Niger River delta. Port Harcourt has bulk storage facilities for both palm oil and petroleum. In the 1970s the port was enlarged with new facilities at nearby Onne. Today, Port Harcourt is made up of two large local governments of Port Harcourt City and Obio-Akpor to which the two study locations are sited (Mile 3 and Mile 4 respectively).

The sample stations are basically areas designated as residential but due to increased population has become centre of business activities though no major industries are located. These areas are made up of Institutions such as the Rivers State University, the former School of Nursing and the Rivers State College of Health Science and Management Technology, Port Harcourt. The only major company of interest is the Nigerian Agip Oil Company (NAOC) whose office is located within the study stations. The map of Port Harcourt showing the areas of study are in Figures 1 and 2. The coordinates of the study stations were as follows; Control station of RSU for Ta, Tb, Tc (Chapel,4^0 47'58" N, 6^0 59'3"E; Convocation Arena, $4^0$48'3"N, 6^o58'49"E; VC lodge, 4^o48'8"N, 6^o58'37" respectively); Mile 3 for Ta, Tb and Tc (RSU Round About, 4° 48'19" N, 6^o59'16"E; Mile 3 Park, 4^o48'13"N, 6^o59'22"E; Ikoku, 4^o47'57"N, 6^o59'30" respectively) and Mile 4 for Ta, Tb, Tc (Agip Flyover, 4^o48'51" N, 6^o59'2"E; OCC Town Hall, 4^o49'10"N, 6^o58'56"E; Whimpey Junction, 4^o49'50"N, 6^o58'53" respectively).

2.2. Description of the Sampling Sites

The sampling sites were the Mile 3 (M_3) and Mile 4 (M_4) study Stations while the Rivers State University served as the Control station. The study area was divided into three (3) sites depending on the prevalent activity around the area. These areas are purely residential and business districts but the Rivers State University Site (control) was mainly areas where student population density was higher. Each sampling site was 350 m apart from the designated study station. The control station which was the University was 1.5km away from the Mile 3(M_3) station and 3km away from the Mile 4 (M_4) sampling site respectively.

2.3. Sample Collection

In each of the selected sites, three quadrats were marked. In each quadrat, three core soil samples were collected randomly at depth 0–25 cm using a soil auger and put together to form a composite sample. The composite samples were well-mixed and sub-samples taken (Qin *et al*., 2014). Three soil replicates were collected from each site, making a total of nine (9) soil samples from the study area. The soil samples were kept in zip-locked plastic bags, labelled and transported to the laboratory for further treatment and analysis. The soil samples were air-dried at room temperature for 4 days, and ground to fine powder. They were then sieved with a 2 mm sieve to remove the coarse soil components. Sub-samples of the sieved soils were then taken for soil heavy metals analysis.

2.4. Soil Sample Preparation and Analysis

The soil samples collected from the sub-stations were thoroughly mixed to form a composite sample; then, the samples were oven-dried at 105°C for six hours until constant weight was attained. The oven-dried samples were then crushed and sieved through 2.0 mm wire mesh. Afterwards, thorough digestion of the representative samples were done. For each sample, 1 g was digested in 10 mL of 1: 1 HNO_3 and heated to 95°C to dry and thereafter refluxed for 10 minutes without boiling. After cooling, 5 mL of concentrated HNO_3 was once again added and refluxed for 30 minutes till brown fumes were produced. The process of adding 5 mL of concentrated HNO_3 was repeated over and over till white fumes appeared. The solution was vaporized to about 5mL on mantle set at 95°C with a watch glass over it. After cooling the resulting sample, 2 mL of H_2O and 3 mL of 30% H_2O_2 were added and the solution was placed on the heating mantle to start the oxidation of peroxide until effervescence subsided. The vessel was cooled and the acid-peroxide digestate heated to about 5 mL at 95°C. Later, addition of 10 mL concentrated HCl to the sample digest was done and the solution was placed on the heating source and refluxed for 15 minutes at 95°C. The digested soil samples were analyzed for the heavy metals (Fe, Pb, Cu, Cd, Cr, Ni, and As) using atomic absorption spectrophotometer, Finally, the digestate was filtered and the filtrate collected for analysis of heavy metals in the Atomic Absorption Spectrophotometer (AAS, Perkin Elmer 2380). The AAS was fitted with specific lamp of a particular heavy metal, while the other conditions were the same as explained earlier (Welz & Sperling, 1999). Blanks were prepared to check for background contamination by the reagents used.

2.5. Data Analysis

- The Azuka Index was used to determine the safe limits of each metal in the various study stations.

$Ai = M_{ch} / M_{cc}$

A_i = Azuka Safe Index for heavy metals; M_{ch} = heavy metal mean concentration in the study station; M_{cc} = Heavy metal mean control concentration for the station

Interpretation:[< 1= safe condition; > 1= Risk zone; 1= moderate risk]

- % Variation= 100(H2-H1)/H2

[H2-Highest mean metal value; H1-Lowest mean metal value]

- [M3/M4= Mile 3/ Mile 4 variation; M3/RSU= Mile 3/ RSU variation; M4/RSU-Mile 4/RSU variations]

Table1. *Heavy Metals Concentrations in Soil Samples from Mile 3*

Heavy metals (Mg/Kg)	Stations			
	Ta	Tb	Tc	Control RSU
Fe	1,418.303 ± 0.000	1,418.301 ± 0.001	1,418.305 ± 0.001	890.453 ± 373
Pb	7.650 ±0.000	7.648 ±0.000	7.649 ± 0.000	5.603 ± 1.450
Cu	8.779 ±0.000	8.777 ± 0.000	8.778 ± 0.000	7.589 ± 0.840
Cd	2.691 ± 0.000	2.693 ± 0.000	2.692 ± 0.000	0.169 ± 1.780
Cr	9.379 ± 0.000	9.380 ± 0.000	9.375 ± 0.000	3.428 ± 4.210
Ni	7.414 ± 0.000	7.410 ± 0.000	7.409 ± 0.000	2.306 ± 3.610
As	3.704 ± 0.000	3.706 ± 0.000	3.705 ± 0.000	0.703 ± 2.120

Table2. *Heavy Metal Concentrations in Soil Samples from Kala (Mile 4) Study Station*

Heavy metals (Mg/Kg)	Stations			
	Ta	Tb	Tc	Control RSU
Fe	1,160.011 ± 1.410	1,164.012 ± 1.410	1,162.010± 0.001	890.453 ± 192
Pb	7.370±0.000	7.374 ±0.000	7.372 ± 0.000	5.603 ± 1.250
Cu	5.842 ±0.000	5.840± 0.000	5.844 ± 0.000	7.589 ± 1.240
Cd	1.434 ± 0.000	1.436± 0.000	1.438 ± 0.000	0.169 ± 0.900
Cr	6.486 ± 0.000	6.489 ± 0.000	6.492 ± 0.000	3.428 ± 2.160
Ni	5.382 ± 0.000	5.386± 0.000	5.384± 0.000	2.306 ± 2.180
As	1.893 ± 0.000	1.890 ± 0.000	1.896 ± 0.000	0.703 ± 0.840

Table3. *Heavy Metals Concentrations in Soil Samples from RSU Control Station*

Heavy metals (Mg/Kg)	Stations			
	Ta	Tb	Tc	Control RSU
Fe	890.450 ± 0.000	890.452 ± 0.000	890.453 ± 0.000	930.362 ± 28.220
Pb	5.603 ±0.000	5.600 ±0.000	5.606 ± 0.000	6.714 ± 0.790
Cu	7.589±0.000	7.589± 0.000	7.589 ± 0.000	8.572 ± 0.700
Cd	0.169 ± 0.000	0.170± 0.000	0.168 ± 0.000	1.373 ± 0.850
Cr	3.428 ± 0.000	3.425 ± 0.000	3.431 ± 0.000	5.433 ± 1.420
Ni	2.304± 0.000	2.306± 0.000	2.308 ± 0.000	3.272 ± 0.680
As	0.703 ± 0.000	0.700± 0.000	0.706 ± 0.000	1.630 ± 0.660

Table4. *Spatial Variation of Heavy Metals Concentrations in Soil Samples from Mile 3, Mile 4 and RSU Study Stations*

Heavy metals (Mg/Kg)	Stations			
	Mile 4	Mile 3	RSU	Mean
Fe	1,162.011 ± 3.600	1,418.303 ± 184	890.453 ± 188	1156.922
Pb	7.372 ±0.350	7.649 ±0.550	5.603 ± 0.900	6.875
Cu	5.842 ±1.100	8.778 ± 0.970	7.589 ± 0.130	7.403
Cd	1.436 ± 0.000	2.692 ± 0.890	0.169 ± 0.000	1.432
Cr	6.489 ± 0.030	9.378 ± 1.470	3.428 ± 1.500	6.432
Ni	5.384 ± 0.180	7.412 ± 1.190	2.306 ± 1.360	5.034
As	1.893 ± 0.100	3.705 ± 0.800	0.703 ± 0.700	2.100

Table5. *Percentage Variation of Heavy Metals in Soils of Study Areas*

Heavy metals %	Stations		
	M_3/M_4	M_3/RSU	M4/ RSU
Fe	18.07	79.02	23.37
Pb	3.62	26.75	24.00
Cu	33.45	13.55	23.02
Cd	46.65	93.72	88.23
Cr	30.81	63.45	56.85
Ni	27.36	68.89	57.17
As	48.91	81.02	62.86

Table6. *WHO Standard Permissible Limits for Heavy Metals*

Elements	*Target value of soil (mg/kg)	**Permissible value of plant (mg/kg)
Cd	0.8	0.02
Zn	50	0.60
Cu	36	10
Cr	100	1.30
Pb	85	2
Ni	35	10

*Target values are specified to indicate desirable maximum levels of elements in unpolluted soils. Source: Denneman and Robberse 1990; Ministry of Housing, Netherlands 1994 and **Source: WHO (1996)*

Table7. *Safe Limits of Heavy Metals in Soils of Study Areas*

Heavy metals %	Stations		
	M_3	M_4	RSU
Fe	1.59	1.30	1
Pb	1.36	1.31	1
Cu	1.16	0.77	1
Cd	15.93	8.50	1
Cr	2.74	1.90	1
Ni	3.21	2.33	1
As	5.27	2.69	1

3. DISCUSSION OF FINDINGS

3.1. Concentration of Iron (Fe)

The concentrations of Fe (mg/Kg) in the Mile 3 station were $1,418.303 \pm 0.000$, 1418.301 ± 0.001, 1418.305 ± 0.001 for Ta, Tb, Tc and mean of $1,418.303 \pm 184$ respectively. The control station of RSU was 890.453 ± 373. Similarly, the Mile 4 study station recorded for Ta, Tb, Tc as $1,160.011 \pm 1.410$, 1164.012 ± 1.410, and 1162.010 ± 0.001 while the mean concentration was $1,162.011 \pm 3.600$ respectively. The control station of RSU recorded Fe concentrations of Ta, Tb, Tc as 890.450 ± 0.000, 890.452 ± 0.000, 890.453 ± 0.000 while the mean concentration was 890.453 ± 188 respectively.

Thus, these findings suggest that the studied soil sample is severely contaminated by the Iron metal. The high observed Fe levels could be attributed to the nature of the parental material of soils in the study site (Sharma *et al*., 2008). Iron (Fe) is an element relatively abundant in many cultivated soils with an average total concentration of 20 to 40 g kg^{-1} (Cornell & Schwertmann, 2003). Research has shown that Iron (Fe) plays significant roles in plant physiology (Buchauer, 1973; Demirezen & Aksoy, 2006). The result from this study corroborates with those of similar researches confirming the high Fe content of the soil as they were higher than the FEPA maximum permissive limits (Mohammed & Folorunsho, 2015; Sahu, & Kacholi, 2016).

Comparatively, the mile 3 study stations (is of more human impact) showed results higher than those at the mile 4 but lower than those from the control station where conventional human activities are less in terms of business environment. This result can be attributed to the nature of anthropogenic inputs and soil structure, texture and parent rock prevalent around the study stations but most importantly by the nature of the parent material composition (Sahu, & Kacholi, 2016). This is verified by the percentage variations between the study stations, M_3/M_4, M_3/RSU and M_4/RSU as 18.07, 79.02 and 23.37 respectively and shown in Table 5. Most studies on heavy metals in soils were linked to common industrial, agricultural and human activities and which are not rife here (Ogedengbe & Akinbile, 2004; Tasrina *et al*, 2015).

The safety index (A_i) as in Table 7 shows that the Mile 3 study station was more polluted by increased concentration of Fe as it exceeded the safety limit of less than 1. Though the Niger Delta soils have high concentration of Fe, this must be checked to avoid deleterious effects on plants and animals including man as supported by Edet *et al*. (2014) in similar studies.

3.2. Concentration of Pb

Mile 3 study station recorded concentrations for Pb (mg/Kg) in Ta, Tb, Tc as 7.370 ± 0.000, 7.374 ± 0.000, 7.372 ± 0.000 and 7.649 ± 0.550 as mean respectively. Similarly, Mile 4 study station recorded Pb concentrations of 7.370 ± 0.000, 7.374 ± 0.000, 7.372 ± 0.000 and mean value of 7.372 ± 0.350 respectively. The control station of RSU recorded Pb concentrations of Ta, Tb, Tc as 5.603 ± 0.000, 5.600 ± 0.000, and 5.606 ± 0.000 while the mean concentration was 5.603 ± 0.900 respectively.

The concentration of Pb followed similar trend as they were higher than the WHO permissible limits (1.6mg/Kg) and higher than those obtained in Kaduna soil (Mohammed & Folorunsho, 2015). Similarly, Pb concentration was higher at the mile 3 study station but lowest at the control (RSU). This may be attributed to the high vehicular traffic, road runoff around the mile 3 axis compared to mile 4, whereas almost negligible at the RSU control station as supported by Kananke *et al*. (2014) and Tasrina *et al.* (2015) in similar studies. The concentration of Pb though lower than WHO (1996) standard was higher than FEPA standard (Now ministry of Environment, Nigeria). The percentage variation in the concentration of Pb by M_3/M_4, M_3/RSU and M_4/RSU are 3.62, 26.75 and 24.00 respectively, showing lower significant impacts (Table 5).

Heavy metals pollution in soil has a lot of negative impacts, hence, of great concern to public health, agricultural production, and environmental health (Fergusson, 1990; Ma *et al*., 1994; Goyer, 1997). The soil pollution is mainly due to disposal of industrial and urban wastes as well as usage of agrochemicals (McBride, 2003; Demirezen & Aksoy, 2006). Lead (Pb) remains one of the highly toxic metals in soils and stems from surrounding traffic activities and agrochemicals applications (Kananke *et al*., 2014).

The safety index (A_i) as in Table 7 showed that the Mile 3 study station was slightly more polluted by increased concentration of Pb as it exceeded the safety limit of less than 1. Though the Niger Delta soils have high impact of Pb due to prevailing anthropic activities, this must be checked to avoid deleterious effects on plants and animals including man as supported by Edet, *et al.* (2014) and Tsuwang, *et al.* (2014) in Northwestern Nigeria.

3.3. Concentration of Cu

Mile 3 study station recorded concentrations for Cu (mg/Kg) in Ta, Tb, Tc as 8.779 ± 0.000, 8.777 ± 0.000, 8.778 ± 0.000 and 8.778 ± 0.970 as mean respectively. Similarly, Mile 4 study station recorded Cu concentrations of 5.842 ± 1.100, 8.778 ± 0.970, 7.589 ± 0.130 and mean value of 5.842 ± 1.100 respectively. The control station of RSU recorded Cu concentrations of Ta, Tb, Tc as 7.589 ± 0.000, 7.589 ± 0.000, 7.589 ± 0.000 while the mean concentration was 7.589 ± 0.130 respectively.

The level of Cu in the study stations showed relatively lower values compared to permissible standard limits (FEPA, WHO/ UNEP, 1997). The mean concentrations of copper recorded were below the WHO/FAO (2001) permissible limit of 100 mg/kg for soils. These values were lower than those obtained by Mohammed and Folorunsho (2015) in Kaduna, Central Nigeria. The trend of percentage variation, M_3/M_4, M_3/RSU and M_4/RSU were 33.45, 13.55 and 23.02 respectively. This showed that the difference between the both study stations was high showing parent material and anthropogenic effects were influential (Tasrina *et al*., 2015). This relatively lower concentration recorded is in tandem with those of Sahu and Kacholi (2016) in related studies. Increased concentration of Cu in soils causes decreases in enzymatic action especially earthworms which increases proper aeration for plant growth (Malley *et al*., 2006).

Badilla-Ohlbaum *et al.* (2001) recorded higher soil Cu contents in Chile. Cultivation may cause soil contamination by heavy metals, specifically copper in vineyard areas (Facchinelli *et al*., 2001; Nachtigall *et al*., 2007; Fernandez-Calviño *et al*., 2009). The intensive use of agrochemicals with Cu in their composition may pollute the soil (Ramos & López-Acevedo, 2004; Gaw *et al*., 2006; Komárek *et al*., 2010).

The safety index (A_i) as in Table 7 showed that the Mile 3 study station was also more polluted by increased concentration of Cu as it exceeded the safety limit (< 1) whereas the Mile 4 station had A_i of 0.77 which showed a good safe limit condition. Though some Niger Delta soils have high concentration of Pb, this must be checked to avoid deleterious effects on plants and animals including man as supported by Edet, *et al.* (2014) in similar studies.

3.4. Concentration of Cd

Mile 3 study station recorded concentrations for Cd (mg/Kg) in Ta, Tb, Tc as 2.691 ± 0.000, 2.693 ± 0.000, 2.692 ± 0.000 and 2.692 ± 0.890 as mean respectively. Similarly, Mile 4 study station recorded Cd concentrations of 1.434 ± 0.000, 1.436± 0.000, 1.438 ± 0.000 and mean value of 1.436 ± 0.000 respectively. The control station of RSU recorded Cd concentrations of Ta, Tb, Tc as 0.169 ± 0.000, 0.170± 0.000, 0.168 ± 0.000 while the mean concentration was 0.169 ± 0.000 respectively.

The concentration of Cd in the study stations were above the permissible limits and hence needs adequate monitoring (WHO, 1996). The results for Cd in the RSU control station was within the permissible limit showing that not much of anthropogenic inputs (WHO/FAO, 2007). The Cd concentrations were found in excess of FAO/WHO recommended limits, respectively, this indicates potential health risk for human through the food chain (Okunola et $al.$, 2008). The concentration of Cd in the Mile 3 and Mile 4 stations fall within similar range with earlier researches (Okunola et $al.,$ 2008).

The percentage variation (%) of M_3/M_4, M_3/RSU and M_4/RSU were 46.65, 93.72 and 88.23 respectively. The values showed that there is high impact of activities within the M_3 and M_4 study areas as that of RSU was relatively low. This high percentage variation of study stations from the control is a great threat to human health as Cd can lead to so many health challenges. Researches have shown that metal pollutants can be harmful to roadside vegetation, wildlife and the neighboring human settlements (Turer & Maynard, 2003; Awofolu, 2005). Cadmium (Cd) concentrations were found in excess of FAO/WHO recommended limits which could be due to the nature of Cd, since Cd is known to be less retained by the soil than other toxic cations (Lokeshwari & Chandrappa, 2006) or the low organic matter contents of soils sampled could have also enhanced soil retention of metals (Okunola et $al.$, 2008).

However, considerably higher concentrations of Cd were detected when compared to 0.2 mg kg^{-1} (WHO/FAO, 2001) maximum critical limit above which toxicity is possible. Cadmium (Cd) showed higher concentration levels of contamination in the study areas than several mean values obtained in similar researches (Ndiokwere, 1984; Ho & Tai, 1988; Jaradat & Momani, 1999). The concentrations of Cd obtained in this study is far higher than earlier research result of 0.004 mg/Kg, which showed that anthropogenic inputs must be well monitored (Muyoma et $al.$, 2019).

The safety index (A_i) as in Table 7 shows that the Mile 3 study station was highly polluted as compared to the Mile 4 but both exceeded the safe limit (<1) by increased concentration of Cd. Though the Niger Delta soils have low concentration of Cd, this result showed a dangerous trend which must be checked to avoid deleterious effects on plants and animals (Edet, et $al.$, 2014; Ideriah et $al.$, 2005).

3.5. Concentration of Cr

Mile 3 study station recorded concentrations for Cr (Mg/Kg) in Ta, Tb, Tc as 9.379 ± 0.000, 9.380 ± 0.000, 9.375 ± 0.000 with mean of 9.378 ± 1.470 respectively. Similarly, Mile 4 study station recorded Cr concentrations of 6.486 ± 0.000, 6.489 ± 0.000, 6.492 ± 0.000 and mean value of 3.428 ± 2.160 respectively. The control station of RSU recorded Cr concentrations of Ta, Tb, Tc as 3.428 ± 0.000, 3.425 ± 0.000, and 3.431± 0.000 while the mean concentration was 3.428 ± 1.500 respectively.

The concentration of Cr in the M_3 study station (9.378± 0.000) showed that of relatively higher value than the control (3.428 ± 4.21). Similarly, the M_4 study station had a lower concentration of 6.489 ± 0.000 showing that the soil of M_3 is more contaminated with Cr. The concentration of Cr in the RSU study station is an indication of lower pollution potential as it is lower than the WHO/FAO (2007) permissible limit of 5.00-30.00mg/kg. Results from this study indicated that concentration value of Cr in the soil samples were generally higher than the FEPA maximum permissive limits but lower than WHO (1996) for plants and soil. Heavy metals such as Cr are exceptionally toxic and dangerous environmental pollutants (Buchauer, 1973; McBride, 2003). The percentage variations (%) showed that M_3/M_4, M_3/RSU and M_4/RSU were 30.81, 63.45 and 56.85 respectively. This means that the input to parent material from human activities for the M_3 study station is higher indicating that it has more human activities and impacts.

The concentration of chromium Cr ranged from 6.486-6.492 mg/kg at M_4 and 9.375-9.380 mg/Kg at M_3 with mean values 6.489 and 9.378 mg/Kg respectively. The high concentration of Cr recorded could be as a result of the recycling of e-waste such as used computers, cables, printers, photocopy machines and batteries at the sites. The absence of these wastes at the control station could have been the cause of lower concentrations of Cd around the RSU station. Adverse health effects associated with Cr (VI) exposure include occupational asthma, eye irritation and damage, perforated eardrums, respiratory irritation, kidney damage, liver damage, pulmonary congestion and edema, upper abdominal pain, nose irritation and damage, respiratory cancer, and skin irritation (Dayan & Paine, 2001). When inhaled, chromium compounds cause respiratory tract irritations and pulmonary sensitization. Chronic inhalation of Cr (VI) compounds increases the risk of lung, nasal, and sinus cancer. Severe dermatitis and usually painless skin ulcers can result from contact with Cr (VI) compounds. The concentration of Cr in the soils may vary considerably according to the natural composition of rocks and sediments that compose them (Kimbrough *et al*, 1999). The levels of chromium in the soil may increase mainly through anthropogenic deposition, as for example atmospheric deposition (Rosas *et al.*, 1989).

The safety index (A_i) as in Table 7 shows that the Mile 3 study station ($A_i = 2.74$) was more polluted by increased concentration of Cr as it exceeded the safety limit (<1). Though the Niger Delta soils have high concentration of Cr in certain areas, this must be checked to avoid deleterious effects on terrestrial organisms (Ideriah, *et al.* 2005; Edet, *et al.,* 2014).

3.6. Concentration of Ni

Mile 3 study station recorded concentrations for Ni (mg/Kg) in Ta, Tb, Tc as 7.414 ± 0.000, 7.410 ± 0.000, 7.409 ± 0.000 with mean of 7.412 ± 1.190 respectively. Similarly, Mile 4 study station recorded Ni concentrations of 5.382 ± 0.000, 5.386 ± 0.000, 5.384 ± 0.000 and mean value of 5.384 ± 0.180 respectively. The control station of RSU recorded Ni concentrations of Ta, Tb, Tc as 2.304 ± 0.000, 2.306 ± 0.000, 2.308 ± 0.000 while the mean concentration was 2.306 ± 1.360 respectively.

The percentage variations (%) for M_3/M_4, M_3/RSU, M_4/RSU study relationship were 27.36, 68.89, and 57.17 respectively. This showed that there was high input from human activities at the M_3/RSU which much be monitored to avoid Ni poisoning. The M_3 study station recorded the highest concentration of Ni as supported by the level of anthropogenic activities around the study locations such as mechanics, sales of old fridges (Belgium fridges) and wastes dumps. The poor drainage cum flooding situation around the study sites exposes it to potential of Ni availability. Though the concentration of Ni was lower than WHO (1996) permissible limit (35 mg/Kg) for plants and soils, it was found to relatively higher than WHO/FAO (2007) permissible limit for edible plant of 1.67mg/Kg and other standards (WHO, 1971; DPR, 1991; FEPA, 1991). This showed that there is a considerable increase in the amount of Ni available in the study sites. This abrupt rise in Ni concentration is a threat to plants to which humans depend on for livelihood hence effect on health of humans. Plants such as vegetables which are regular consumables are polluted by heavy metals like Ni both in soil and water and so pose a serious threat to public and environmental health and agricultural production (Fergusson, 1990; Ma *et al.*, 1994; Goyer, 1997). The concentration of Ni recorded in this study is below that observed in similar research in Kaduna (Inuwa *et al.*, 2007). Heavy metals pollution of the soil is caused by various metals especially Ni and many others (Karaca *et al.*, 2010).

The safety index (A_i) as in Table 7 showed that the Mile 3 study station was more polluted by increased concentration of Ni as it exceeded the safety limit (<1). Though the Niger Delta soils have relatively low concentration of Ni, this result is a threat and so must be checked to avoid negative effects (Iwegbue *et al.*, 2006).

3.7. Concentration of As

Mile 3 study station recorded concentrations for As (Mg/Kg) in Ta, Tb, Tc as 3.704 ± 0.000, 3.706 ± 0.000, 3.705 ± 0.000 with mean of 3.705 ± 0.800 respectively. Similarly, Mile 4 study station recorded As concentrations of 1.893 ± 0.000, 1.890 ± 0.000, 1.896 ± 0.000 and mean value of 1.893 ± 0.100 respectively. The control station of RSU recorded As concentrations of Ta, Tb, Tc as 0.703 ± 0.000, 0.700 ± 0.000, 0.706 ± 0.000 while the mean concentration was 0.703 ± 0.700 respectively as shown in Table 5.

The percentage variations (%) for M_3/M_4, M_3/RSU, M_4/RSU study relationship were 48.91, 81.02 and 62.86 respectively. The concentrations obtained were lower than those obtained in soils of Anka area of Northwestern Nigeria (Tsuwang et al., 2014). This result showed a high difference in the concentrations between the study stations and the control (RSU). This is a clear indication of high anthropogenic inputs and activities which may also be facilitated by parent materials of the study locations. Arsenic (As) is one of the very toxic metals in nature whose concentration must be periodically monitored. This is because heavy metals are potent enzyme inhibitors to which man cannot ignore and the uptake of heavy metals by plants and subsequent accumulation along the food chain is a potential threat to animal and human health. (Singh & Kalamdhad, 2011; Mustafa & Alsharif, 2018). Low concentration of heavy metals may inhibit the physiological metabolism of plants (Singh & Kalamdhad, 2011). Heavy metals exert toxic effects on soil microorganism hence leads to variations in diversity, population size and overall activity of the soil microbial communities (Ashraf & Ali, 2007). Arsenic is a natural component of the earth's crust and is widely distributed throughout the environment in the air, water and land. It is highly toxic in its inorganic form.

Inorganic arsenic is a confirmed carcinogen and is the most significant chemical contaminant in drinking-water globally. Arsenic can also occur in an organic form. Inorganic arsenic compounds (such as those found in water) are highly toxic while organic arsenic compounds (such as those found in seafood) are less harmful to health. Arsenic has both acute and chronic effects and WHO provisional guideline value of 10 μg/L were not exceeded but arsenic poisoning must be monitored since it is natural component of the earth crust (Ravenscroft *et al.*, 2009).

Research has shown that Arsenic (As) background concentrations in soil range from 1 to 40 mg/Kg, with mean values often around 5 mg/Kg. Naturally elevated levels of arsenic in soils may be associated with geological substrata such as sulfide ores (IPCS, 1981). Anthropogenic inputs in contaminated soils can have concentrations of arsenic up to several grams per 100 ml. Arsenic (As) from weathered rock and soil may be transported by wind or water erosion. However, as many arsenic compounds tend to adsorb to soils, leaching usually occurs during transportation over only short distances in soil (Moore *et al.*, 1988; Welch *et al.*, 1988).

The safety index (A_i) as in Table 7 showed that the Mile 3 study station was far contaminated by As from the increased concentration of Ni as it exceeded the safety limit (<1). Though the Niger Delta soils have relatively low concentration of As, this result is a threat and so must be checked to avoid negative effects (Hughes *et al.*, 1988; Iwegbue *et al.* (2006). This is because arsenic causes disquiet from ecological and personal points of view (Hughes *et al.*, 1988).

4. CONCLUSION

This study showed that the Mile 3 subsoil is contaminated by heavy metals more than the Mile 4 and RSU study stations as their concentrations are relatively higher than permissible limits for soil. This was attributed mostly to underlying parent materials, composition and anthropogenic inputs due to the busy and occupational activities around these study sites (mostly M_3 and M_4). Heavy metals are naturally present in the soil but geologic and anthropogenic activities can increase their concentration to amounts that are may be toxic to living things which must be checked. High percentage variations occurred between the study stations and the control, M_3/RSU for Fe, Cd, Cr, Ni, As and M_4/ RSU for Cd, Cr, Ni, As respectively. Though, the result of the ANOVA showed p-value of 0.2845 (α=0.05) meaning no significant difference within the M_3, M_4 and RSU stations was also corroborated by the t-test result for M_3/ RSU control and M_4/ RSU control which were 1.013 and 1.037 respectively at 0.05 significant levels.

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