Faculty of Natural and Applied Sciences Journal of Basic and Environmental Research
Print ISSN: 3026-8184 e-ISSN 3043-6338
www.fnasjournals.com
Volume 2; Issue 2; March 2025; Page No. 47-68.

Comparative Assessment of Heavy Metals in Soils of Designated Institutions in Rivers State, Nigeria

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Abstract
This study was based on assessment of heavy metal levels in soils of designated Institutions in Rivers State, Nigeria. Ten (10) heavy metals of Cd, Pb, Cr, Ni, Fe, Cu, Ag, Zn, Co and As. The assessment was achieved through a pure experimental study design but adopted the probability cluster sampling technique. Heavy metal concentration analysis was done using the atomic absorption spectrophotometer (ASTMD 1971/4691). The ranges for Cd concentration in the soil in were; Uniport (0.54±0.06-0.63±0.01), IAUE (0.84±0.01-0.86±0.01) and RSU (0.72±0.01-0.75±0.01); Pb, Uniport (1.25±0.02-1.32±0.03), IAUE (1.00±0.06-1.15±0.05) and RSU (1.32±0.01-1.36±0.01); Cr, 0.33±0.01-0.37±0.01 (Uniport), 0.32±0.03-0.40 ±0.03 (IAUE) and 0.33±0.01-0.36±0.01 (RSU); Ni, 0.50±0.02-0.55±0.01 (Uniport), 0.32±0.03-0.40±0.01 (IAUE) and 1.56±0.01-1.60±0.01 (RSU); Fe, 150±2.88-156±1.41 (Uniport), 265±2.12-2.70±1.41 (IAUE) and 286±1.41-290±1.41 (RSU); Cu, 1.75±0.01-1.79±0.01 (Uniport), 1.54±0.04-1.62±0.02 (IAUE) and 1.56±0.01-1.60±0.01 (RSU); Ag, 0.74±0.02-0.80±0.02 (Uniport), 1.30±0.04-1.40±0.04 (IAUE) and 1.16±0.03-1.24±0.03 (RSU); Zn, 51.8±0.64-53.7±0.71 (Uniport), 53.4±0.14-53.8±0.14 (IAUE) and 46.0±0.14-46.4±0.14 (RSU); Co, 1.25±0.01-1.28±0.01 (Uniport), 1.30±0.04-1.40±0.04 (IAUE) and 1.45±0.02-1.50±0.01 (RSU); but As recorded a uniform concentration of < 0.002mg/kg in the three university campuses. There was low concentration of these heavy metals in the designated soils though gradually building up as the concentrations were below permissible limits (WHO, DPR-EGASPIN, NJDEP, MHSPE). Spatial variation for the three campuses using a one-way ANOVA showed no significant difference ($p<0.05$) as f-ratio was 0.08734 and p-value of 0.916654. Similarly, t-test was used to compare the mean values of two campuses Up/IAUE (t = -0.37829), Up/ RSU (t = -0.40194), IUAE/RSU (t = -0.03585). The greatest threats of soil heavy metal contamination due to future accumulation in the soils were found in Cd, Cr, Zn and Co. The potential variation of heavy metals in the study was of the trend, Fe>Zn>Ni>Cu>Co>Pb>Ag>Cd>Cr>As. There should be deliberate attempt to regulate unfriendly and harmful anthropogenic activities within the campuses especially sanitary habits.

Keywords: Heavy metals, anthropogenic, Uniport, IAUE, RSU, metalloids, contamination

Introduction

Contamination of soils may emanate from the accumulation of heavy metals and metalloids through so many anthropogenic activities such as disposal of high metal wastes, leaded gasoline and paints, land application of fertilizers, animal manures, sewage sludge, pesticides, wastewater irrigation, coal combustion residues, spillage of petrochemicals, and atmospheric deposition etc (Khan et al., 2008; Zhang et al., 2010). Molecular understanding of plant metal accumulation has numerous biotechnological implications and also the long-term effects which might not be known yet (Singh et al., 2011). Heavy metals such as Co, Cu, Fe, Mn, Mo, Ni, and Zn are plant essential elements as most plants have the ability to accumulate them (Jadia & Fulekar, 2009). These metals are causes 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). According to Wuana and Okieimen (2011), the review of likely sources, chemistry, potential biohazards and best available remedial strategies for a number of heavy metals such as lead, chromium, arsenic, zinc, cadmium, copper, mercury and nickel found in contaminated soils are common. Heavy metal refers to any metallic chemical element that has a comparatively high density and is toxic or poisonous at low concentrations such as mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl), and lead (Pb). Metals of specific densities greater than 5g/cm^3 and high molecular mass have negative effects on the living things and the ecosystem are considered as heavy metals (Järup, 2003; Koller & Saleh, 2018). Koller and Saleh (2018) defined heavy metal as one of the common transition metals, such as copper, lead, and zinc and characterized by relatively high density and high relative atomic weight with an atomic number greater than 20 though other meanings of atomic mass exceeding twentythree (23) also exist. The major sources of heavy metals include fertilizers, pesticides, biosolids and manures, wastewater, metal mining, milling processes and industrial wastes and air-borne (Wuana & Okieimen, 2011).

Currently, pollution has increased due to increasing anthropogenic inputs such as burning of fossil fuels, industrial and automobile exhaust emissions which were identified as primary sources of atmospheric metallic burden (Khan et al., 2008; Zhang et al., 2010). Research has shown that different motor vehicles introduced various kinds of toxic metals into the ecosystem (GWRTAC, 1997). Research results exist of the deadly and disease-causing effect of heavy metals and other materials on living things such as Pb, Fe, Cd, Cr, Mn, Co (Kirpichtchikova, 2006). According to Singh et al. (2011), though heavy metals are natural components of the earth's crust, anthropogenic inputs have drastically affected their geochemical cycles and biochemical balance. Prolonged exposure to certain heavy metals such as Cd, Cu, Pb, Ni, and Zn can lead to adverse health effects in humans (Singh et al., 2011). Any metal or metalloid specie 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 (Singh et al., 2011; McIntyre, 2003).

According to Chronopoulos et al. (1997), all metals are toxic at higher concentrations, but excessive levels can be dangerous to the organism. Tchounwou et al. (2012) posits that bioaccumulation of heavy metals in human bodies is very detrimental due to their toxicity and cause multiple damages to organs which was supported by Araujo et al. (2013) stating that; “the presence of heavy metals in the environment, even in moderate concentrations, is detrimental to human health that produces variety of illnesses of the central nervous system (Mg, Hg, Pb As), the kidneys or liver (Hg, Pb, Cd, Cu) and skin, bones, or teeth (Ni, Cd, Cu, Cr)”. According to Kuo et al. (1983) supported by Kaasalainen and Yli-Halla (2003), heavy metals in the soil from anthropogenic sources tend to be more mobile, hence bioavailable than pedogenic, or lithogenic ones. Similarly, heavy metals occur naturally in the soil environment from the pedogenetic processes of weathering of parent materials at levels that are regarded as trace (<1000 mg kg^{-1}) and rarely hazardous (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 heavy metals high enough to cause adverse effects to human health, plants, animals, ecosystems, or other media (D'Amore et al., 2005). Yusuf et al. (2015) studied heavy metals of Fe, Cr, Cd, Zn and Pb and found that their concentrations were generally higher than the tolerable limit for safe environment as prescribed by Nigerian Federal Environmental Protection Agency (FEPA) and World Health Organization (WHO).

According to GWRTAC (1997), heavy metals makes up an ill-defined group of inorganic chemical hazards and commonly found at contaminated sites are lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu), mercury (Hg), and nickel (Ni). Soils are the major sinks for heavy metals released into the environment from anthropogenic activities and unlike organic contaminants which are oxidized to carbon (IV) oxide by microbial action, most metals do not undergo microbial or chemical degradation (Kirpichtchikova et al., 2006). Heavy metal total concentration in soils persists for a long time after their introduction (Adriano, 2003).

Though according to Wuana and Okieimen (2011), phytostabilization can occur through the process of sorption, precipitation, complexation, or metal valence reduction, this technique is useful for the cleanup of Pb, As, Cd, Cr, Cu, and Zn (Jadia & Fulekar, 2009). There are possible sources of contamination, basic chemistry, and the associated environmental and health risks of priority heavy metals like Pb, Cr, As, Zn, Cd, Cu, Hg, and Ni which can provide insight into heavy metal speciation and bioavailability (Wuana & Okieimen, 2011).

Heavy metal pollution of soils has global focus in most environmental researches (Singh et al., 2003). Heavy metals are environmental pollutants which emanate from human activities and are leached into lakes and rivers by acid rain

(A dictionary of Chemistry, 2000). For wastewater, Lead (Pb), Zn, Cu, As, Cd, Cr, Ni and Hg are the most observed (Ahmed & Ahmaruzzaman, 2016; Akpor & Muchie, 2010). Any metal (or metalloid) species is a "contaminant" if found where it is unwanted, or in a form or concentration that causes a detrimental human or environmental effect (Singh et al., 2011). Heavy metals are both precious noble elements and also toxic to man and the environment (Duruibe et al., 2007; Rao & Reddi, 2000). Similarly, heavy metals are highly persistent, toxic in small amounts, and can potentially induce severe oxidative stress in aquatic organisms (Singh & Kalamdhad, 2011). The impact of heavy metals on human growth and development cannot be over-emphasized especially environmental health (Goyer, 1997; Fergusson, 1990; Msaky & Calvet, 1990; Ma et al., 1994). The soil pollution is mainly due to disposal of industrial and urban wastes including the use of agrochemicals (Buchauer, 1973; McBride, 2003; Demirezen & Aksoy, 2006). Water pollution is mostly as a result of indiscriminate industrial wastes disposal, poor sewage disposal, petroleum contamination, and agricultural drainage water, surface and groundwater (Santos et al., 2005; Midrar-Ul-Haq et al., 2005; Tariq et al., 2006). Many growing populated areas in developing countries are prone to air pollution from heavy metals containing aerosols usually deposited on soil surfaces and plants (Voutsa et al., 1996). Extreme high concentration of Cd, Pb, and Zn has been found in plants and soils by smelting works (Wuana & Okieimen, 2011). Another major source of soil contamination is the aerial emission of Pb from the combustion of petrol containing tetraethyl lead which contributes substantially to the content of Pb in soils in urban areas and in those adjacent to major roads (Wuana & Okieimen, 2011). Zn and Cd may also be added to soils adjacent to roads through sources tyres and lubricant oils (USEPA, 1996). Heavy metal total concentration in soils persists for a long time after their introduction and so very dangerous (Adriano, 2003).

According to Wuana and Okieimen (2011), the proper protection and restoration of soil ecosystems contaminated by heavy metals need characterization and remediation. Contemporary legislation respecting environmental protection and public health, at both national and international levels, are based on data that characterize chemical properties of environmental phenomena, especially those that reside in our food chain (Kabata-Pendias & Pendias, 2001).Though soil characterization provides an insight into heavy metal speciation and bioavailability, attempt at remediation of heavy metal contaminated soils would entail expertise on the source of contamination, basic chemistry, environmental and associated health effects and risk assessment of these heavy metals (Wuana & Okieimen, 2011). Therefore, risk assessment is significant hence an effective scientific tool which enables decision makers to manage sites so contaminated in a cost-effective manner while preserving public and ecosystem health (Zhao & Kaluarachchi, 2002). From time immemorial, agriculture was the first major human influence on the soil (Scragg, 2006). According to Wuana & Okieimen (2011) plants must acquire macronutrients and essential micronutrients. Some soils lack enough heavy metals such as Co, Cu, Fe, Mn, Mo, Ni, and Zn that are essential for healthy plant growth (Lasat, 2000). Therefore, these deficiencies can be replenished to the soil or as a foliar spray (Wuana & Okieimen, 2011). Heavy metals such as Co, Cu, Fe, Mn, Mo, Ni, and Zn are plant essential metals so most plants have the potential to accumulate them (Jadia & Fulekar, 2009). According to Wuana and Okieimen (2011), heavy metals are significant due to their roles in crop production but the most common heavy metals found at contaminated sites in order of abundance are Pb, Cr, As, Zn, Cd, Cu, and Hg (USEPA, 1996). Their ability to decrease crop production resulting from the threat of bioaccumulation and biomagnification in the food chain is major environmental concern (Wuana & Okieimen, 2011). According to Canet et al. (1998), the potential of biosolids contaminating soils with heavy metals has raised serious concern on their application in agricultural practices (Canet et al., 1998). The common heavy metals found in biosolids are Pb, Ni, Cd, Cr, Cu, and Zn whose concentrations are governed by the nature and the intensity of the industrial activity (Mattigod & Page, 1983). Certain situations of metals added to soils in applications of biosolids can be leached downwards through the soil profile hence potentially contaminate groundwater (McLaren et al., 2005). Recent studies on some New Zealand soils treated with biosolids have shown increased concentrations of Cd, Ni, and Zn in drainage leachates (Keller et al., 2002; McLaren et al., 2004). This is also supported by the study of Iyama and Edori (2019) on leachates from Port Harcourt dumpsites in Nigeria.

According to Knight et al. (1997), large amounts of heavy metals like copper (Cu), cobalt (Co), and zinc (Zn) are basically required for typical body development while the high groupings of different metals like cadmium (Cd), chromium (Cr), manganese (Mn), and lead (Pb) are considered profoundly dangerous for human and aquatic life. According to Durowoju et al. (2018) health risk based on the concentration of toxic metals (Pb, Cr, Cd and Mn) in soil/dust from playgrounds/classrooms in selected primary schools in Lagos State was evaluated and some of the heavy metals in the soil were higher than permissible limits set by DPR, FEPA and WHO. Relative abundance of heavy metals across locations and all samples around quarry sites at located at Isiagwu, Ebonyi State, Nigeria was in the order Fe > Mn > Zn > Pb > Cu > Cd (Onyedikachi et al., 2018).

The introduction of numerous biosolids such as livestock manures, composts, and municipal sewage sludge to land for crop improvement leads to the accumulation of heavy metals such as As, Cd, Cr, Cu, Pb, Hg, Ni, Se, Mo, Zn, Tl, Sb, and so forth, in the soil (Basta et al., 2005). Some animal wastes (poultry, cattle, and pig manures) produced during farming are usually applied to crops and pastures either as solids or slurries (Sumner, 2000). In the pig and poultry industry, the Cu and Zn added to diets as growth promoters and as contained in poultry health products may also have the ability to cause metal contamination of the soil (Sumner, 2000; Chaney & Oliver, 1996). Repeated application of animal manures with high concentrations of As, Cu, and Zn to restricted land areas can lead to bioaccumulation of these metals in the soil in the long run (Wuana & Okieimen, 2011). Ezejiofor (2013) studied the environmental metals pollutants load of a densely populated and heavily industrialized commercial city of Aba, Nigeria and discovered they were high especially as it relates to high human activities around the study area. The rapid development of industrialization and urbanization in recent years has resulted in increased emissions of both metal and organic pollutants rendering the environment especially defenseless to ecological degradation and pollution (Kreimer, 1992). Heavy metals are non-degradable and accumulate in the environment with no known homeostasis mechanism for their removal (Tong & Lam, 2000).

Gržetić and Ghariani (2008) studied the potential health risk assessment for soil heavy metal contamination in the central zone of Belgrade (Serbia) and found out that there is no particularly dangerous single heavy metal, but their cumulative effect, expressed as Child Soil Ingestion Hazardous Index, is for concern. In the present case, Cd, Cr, Co, Cu, Pb, Mn, Ni and Zn were identified as potentially hazardous agents in the soil at different locations in Belgrade which are relevant to human health (Gržetić & Ghariani, 2008). Though there is no particularly dangerous single heavy metal in the study of Gržetić and Ghariani (2008) but from rare literature, data soils contain heavy metals. The prevalence of toxic heavy metals such as Cd, As, Pb, Zn, Cu, Cr, Ni, Fe, Ag, Co and others in the ecosystems at elevated levels continues to be of great concern considering the challenges (Hange & Awofoluu, 2017). According to Singh et al. (2011), the earth crust is known to contain natural levels of heavy metals, however, as a result of rapid development and industrialization, anthropogenic activities have introduced substantial amount of these metals into the environment at an unprecedented level (Armah et al., 2014). Some of these activities include mining operations, metal foundries, vehicular use, petrochemicals and agricultural such use application of inorganic fertilizers, sewage sludge, pesticides etc (Hange & Awofoluu, 2017). Heavy metals easily found associated to soil contamination by anthropogenic inputs are copper (Cu), zinc (Zn), lead (Pb), cadmium (Cd), manganese (Mn) chromium (Cr) mercury (Hg), arsenic (As) etc (Tahar & Keltoum, 2011; Yan et al., 2012; Aslam et al., 2013). Heavy metals are the main group of inorganic contaminants and a considerable large area of land is contaminated with them due to use of sludge or municipal compost, pesticides, fertilizers, and emissions from municipal wastes incinerates, exudates, residues from metalliferous mines and smelting industries (Halim et al., 2002). Heavy metals pollution of the soil is caused by various metals, especially Cu, Ni, Cd, Zn, Cr and Pb (Karaca et al., 2010).

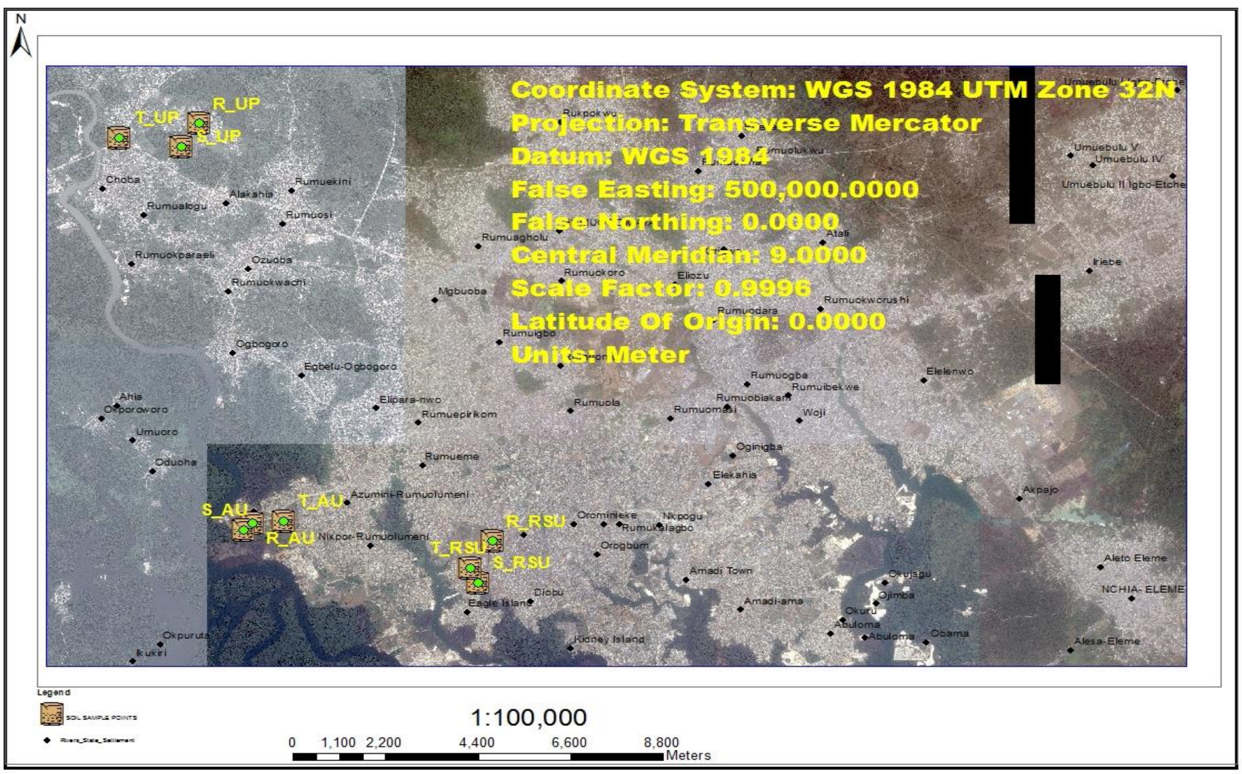
The implications of heavy metal on humans and wide-life are demonstrated by the uptake of metals by plants, the consumption of metal absorbing plants by ruminants and the eventual consumption of ruminant by human (Hange & Awofoluu, 2017). According to Cai et al. (2012), continued monitoring and assessment of toxic heavy metals in soils is of uttermost significance considering that the soil is a repository of heavy metals. Kaasalainen and Yli-Halla (2003) posits that anthropogenic generation or nature of heavy metals in the soil tend to be more mobile and readily bioavailable when compared to the pedogenic or lithogenic forms. As a result of this bioavailability, the metals can be taken up by plants with further distribution and accumulation across the food chain (Hange & Awofoluu, 2017). Research has showed the transfer of heavy metals from soil to organisms (Lavelle et al., 2004; Ting-li et al., 2014). Similarly, migration of heavy metals from soils to plants is also available (Lato et al., 2012; Aktaruzzaman et al., 2013). According to Tchounwou et al. (2012) elevated level of heavy metals above the natural constituents in soil has been attributed to anthropogenic inputs which facilitated and necessitated this study. Iyama and Edori (2019) determined the levels of heavy metals in sewage effluent emanating from the nearby abandoned dumpsite of the Rivers State Government, Nigeria. This study is aimed at assessing the levels of heavy metals in the soils of Uniport, IAUE, RSU and also determine the risk assessment for ten (10) heavy metals of Cd, Pb, Cr, Ni, Fe, Cu, Ag, Zn, Co and As.

Cite this article as:
Edori, O.S., Iyama, W.A., & Edori, E.S. (2025).Comparative assessment of heavy metals in soils of designated institutions in Rivers State, Nigeria.. *FNAS Journal of Basic and Environmental Research*, *2*(2), 47-68.

Materials and Methods

This study was conducted basically in Port Harcourt and Obio-Akpor local government areas of Rivers State, Nigeria where the three institutions are found. Port Harcourt is known as port town and capital of Rivers State, Niger Delta, Southern Nigeria. It lies along the Bonny River (eastern distributary 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 which is 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 study locations are located primarily though Uniport extends into Ikwerre Local Government.

The research study was carried out in three campuses of the Universities of Port Harcourt (UNIPORT), the Rivers State University (RSU), and the Ignatius Ajuru University of Education (IAUE). The UNIPORT is of three campuses Choba, Delta and Abuja, all located in Obio-Akpor and Ikwere Local Government and located on latitude 4053' 14"N through 4054' 42"N and longitude 6054' 00"E through 6055'50"E (Ijeomah et al., 2013). This is within the coordinates of 4.90690N and 6.91700E. The University has three campuses namely: Abuja, Delta and Choba from which soil samples were taken to constitute the composite sample. The three campuses are separated by road networks, although, Abuja and Delta Campuses are closer to each other in terms of distance. Figure 1 is the map of University of Port Harcourt showing the threeas. This study only collected samples from the Abuja campus. Soil samples were taken at three points labelled RUP, SUP, and TUP within the Abuja campus to form the composite sample. The sampling stations were selected based on areas of high population density, waste bins and mechanical works around the campuses. The geographical location is shown in Table 1 using the geographic positioning system (GPS) from Techno android phone.



Similarly, Rivers State University (RSU) is located in Port Harcourt City Council, the hub of the capital city. Rivers State University (or RSU), formerly Rivers State University of Science and Technology(UST) is a university located in the Diobu area of Port Harcourt, Rivers State, Nigeria. Rivers state university was established as a College in 1972 but transformed into full-fledged University in 1980. It is located within latitude 4º 47'58" N through 4⁰ 48'8"N and longitude 6⁰58'37"E through 6º59'3"E (coordinates of 4.7974ºN and 6.9803⁰E). Samples here were collected at same three points of R_{RSU}, S_{RSU} and T_{RSU} at the main gate, hostel C/D and faculty of engineering block area respectively. Finally, soil samples were also collected from the Ignatius Ajuru University of Education (IAUE) located at Rumuolumeni in Obio-Akpor local government of Rivers State, Nigeria. Ignatius Ajuru University of Education (formerly Rivers State University of Education) is a Nigerian university based in Rumuolumeni Port Harcourt, Rivers State. Founded in 2010, Ignatius Ajuru University of Education is a non-profit public higher education institution located in the metropolis of Port Harcourt (population range of 1,000,000-5,000,000 inhabitants), Rivers and officially accredited by the National Universities Commission, Nigeria. Ignatius Ajuru University of Education (IAUE) is a coeducational higher education institution and offers courses and programs leading to officially recognized higher education degrees such as bachelor degrees, master degrees, and doctorate degrees in several areas of study. IAUE lies within the geographical coordinates of 4.8045ºN and 6.9324ºE. The stations were labelled R_{AU}, S_{AU} and T_{AU} respectively. The Institution, co-ordinates and descriptions of study locations is shown in Table 1 using Techno Android Phone.

Table 1: Sampling Locations and Description

Institution		Study Location	Description
Uniport	R_{UP}	4º54'14''N/6º55'18''E	Ofrima/ Convocation Arena
	S_{UP}	4º51'18''N/6º55'43''E	Choba Park
	T_{UP}	4º54'01''N/6º54'17''E	Delta Park/ Ecobank ATM
IAUE	R_{AU}	4º48'22''N/6º56'01''E	Main Gate/ Fidelity Bank
	S_{AU}	4º48'16''N/6º55'54''E	Wike Halls
	T_{AU}	4º48'24''N/6º56'25''E	2nd Gate/ Abandoned dumpsite
RSU	R_{RSU}	4º48'07''N/6º59'06''E	Maingate/Catholic church
	S_{RSU}	4º47'30''N/6º58'55''E	Hostel C/D
	T_{RSU}	4º47'43''N/6º58'49''E	Engineering/ Deeper life Church

Soil Samples Collection and Analysis

Soil samples were collected randomly from the sampling points located by an android phone with installed GPS to determine the contamination levels of the ten (10) heavy metals at a depth of about 0–20cm to form composite samples after thorough mixing from three locations (for each campus) using a stainless-steel hand auger. The samples were then stored in polyethylene bags and transported to the laboratory and later oven-dried, ground and sieved using a 1.18 mm sieve sized mesh and stored in polythene bags for further analysis. The soil samples collected from the campuses after being oven-dried, thoroughly mixed to form a composite sample were oven-dried at 105°C for six hours until constant weight was attained.

Afterwards, thorough digestion of the representative samples was done. For each sample, 1g was digested in 10mL of 1:1 HNO_3 and heated to 95°C to dry and thereafter refluxed for 10 minutes without boiling. After cooling, 5mL of concentrated HNO_3 was once again added and refluxed for 30 minutes till brown fumes were produced. The process of adding 5mL of concentrated HNO_3 was repeated over and over till white fumes appeared. The solution was vaporized to about 5 on mantle set at 95°C with a watch glass over it. After cooling the resulting sample, 2mL of H_2O and 3mL 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 5mL at 95°C. Later, addition of 10mL 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. Finally, the digestate was filtered using Whatman No. 42 filter paper into a 100 mL volumetric flask and topped up to the mark with distilled water and the filtrate collected for analysis. Heavy metal analysis was done using the Atomic Absorption Spectrophotometer (ASTMD 1971/4691). The AAS was fitted with specific lamp of a particular heavy metal, while the other conditions were the same.

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Research and Sampling Designs

The pure experimental and longitudinal survey designs were adopted for the study. This study adopted the probability cluster sampling technique.

Statistical Analysis

The mean, standard deviation, one-way ANOVA and the t-test were used to determine the existing spatial relationships within the study stations and also for that between two different stations respectively at 95% confidence level ($p \leq 0.05$). Similarly, line graphs and histograms were used to illustrate existing trends around the three campuses of UNIPORT, RSU and IAUE, Port Harcourt.

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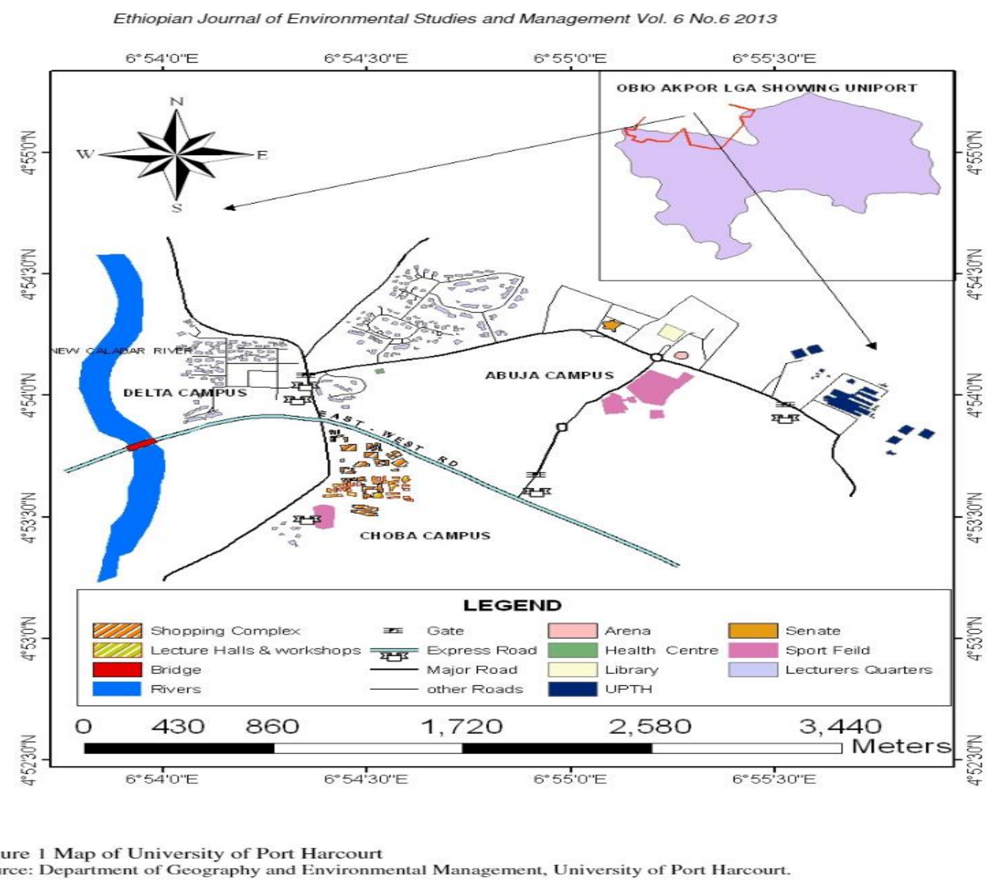

Figure 1: Map of the University of Port Harcourt

Source: Department of Geography and Environment Management, University of Port Harcourt

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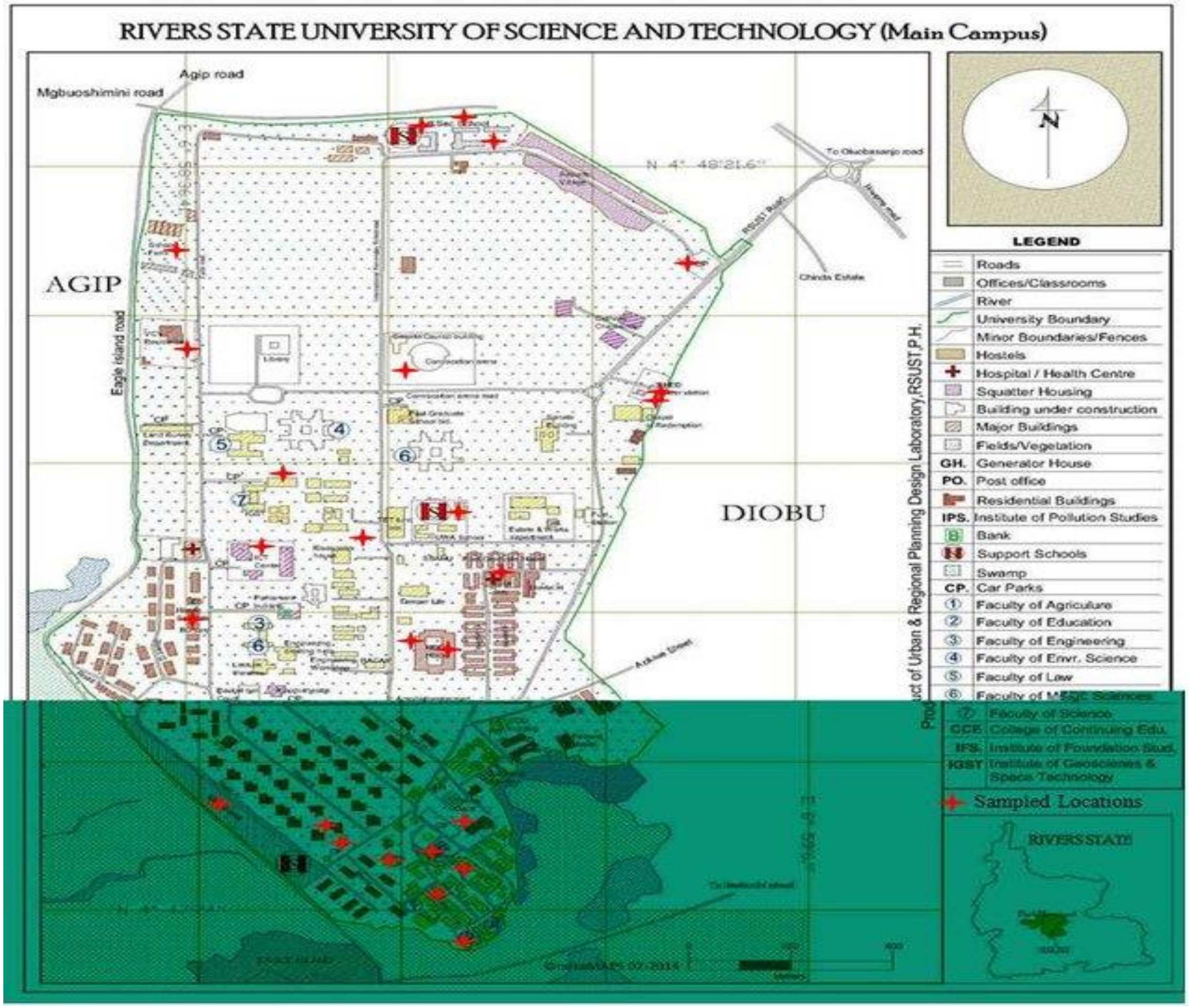

Figure 2: Map of Rivers State University (main campus)
Source: Ideriah and Ikoro (2015)

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Results

Table 2: Heavy Metal Concentration for Soils of Uniport, Port Harcourt, Nigeria

Heavy Metals (mg/kg)	Study Stations			Mean±SD
	R_{UP}	S_{UP}	T_{UP}	
Cd	0.54±0.06	0.70±0.06	0.63±0.01	0.62±0.08
Pd	1.32±0.03	1.25±0.02	1.27±0.01	1.28±0.04
Cr	0.37±0.01	0.36±0.01	0.33±0.01	0.35±0.00
Ni	0.55±0.01	0.50±0.02	0.53±0.00	0.53±0.23
Fe	154±0.71	156±1.41	150±2.83	153±59.0
Cu	1.78±0.01	1.79±0.01	1.75±0.01	1.77±0.08
Ag	0.77±0.00	0.80±0.02	0.74±0.02	0.77±0.24
Zn	52.6±0.07	53.7±0.71	51.8±0.64	52.7±1.34
Co	1.25±0.01	1.27±0.00	1.28±0.01	1.27±0.06
As	<0.002	<0.002	<0.002	<0.002

The results of soil concentration for the University of Port Harcourt (Uniport) are shown in Table 2. The results for the mean concentration of heavy metals in mg/kg are Cd (0.62±0.08), Pd (1.28±0.04), Cr (0.35±0.00), Ni (0.53±0.23), Fe (153±59), Cu (1.77±0.08), Ag (0.77±0.24), Zn (52.7±1.34), Co (1.27±0.06) and As (<0.002) respectively.

Table 3: Heavy Metal Concentration for Soils of IAUE, Port Harcourt, Nigeria

Heavy Metals (mg/Kg)	Study Stations			Mean±SD
	R_{AU}	S_{AU}	T_{AU}	
Cd	0.86±0.01	0.84±0.01	0.85±0.00	0.85±0.08
Pd	1.00±0.06	1.15±0.05	1.10±0.01	1.08±0.11
Cr	0.36±0.00	0.32±0.03	0.40±0.03	0.36±0.01
Ni	0.38±0.00	0.40±0.01	0.35±0.02	0.38±0.33
Fe	265±2.12	270±1.41	268±0.00	268±22.6
Cu	1.60±0.01	1.54±0.04	1.62±0.02	1.59±0.04
Ag	1.30±0.04	1.35±0.00	1.40±0.04	1.35±0.17
Zn	53.4±0.14	53.6±0.00	53.8±0.14	53.6±1.98
Co	1.30±0.00	1.28±0.01	1.32±0.01	1.30±0.04
As	<0.002	<0.002	<0.002	<0.002

The results of soil concentration for Ignatius Ajuru University of Education (IAUE) are shown in Table 3. The results for the mean concentration of heavy metals in mg/kg are Cd (0.85±0.08), Pd (1.08±0.11), Cr (0.36±0.01), Ni (0.38±0.33), Fe (268±22.6), Cu (1.59±0.04), Ag (1.35±0.17), Zn (53.6±1.98), Co (1.30±0.04) and As (<0.002) respectively.

Cite this article as:
Edori, O.S., Iyama, W.A., & Edori, E.S. (2025).Comparative assessment of heavy metals in soils of designated institutions in Rivers State, Nigeria.. *FNAS Journal of Basic and Environmental Research*, *2*(2), 47-68.

Table 4: Heavy Metal Concentration for Soils of RSU, Port Harcourt, Nigeria

Heavy Metals (mg/Kg)	Study Stations			Mean±SD
	R_{RSU}	S_{RSU}	T_{RSU}	
Cd	0.72±0.01	0.75±0.01	0.74±0.00	0.74±0.00
Pd	1.36±0.01	1.34±0.00	1.32±0.01	1.34±0.08
Cr	0.33±0.01	0.36±0.01	0.35±0.00	0.35±0.00
Ni	1.56±0.01	1.59±0.01	1.60±0.01	1.58±0.52
Fe	286±1.41	289±0.71	290±1.41	288±36.8
Cu	1.58±0.00	1.60±0.01	1.56±0.01	1.58±0.05
Ag	1.20±0.00	1.16±0.03	1.24±0.03	1.20±0.06
Zn	46.4±0.14	46.2±0.00	46.0±0.14	46.2±3.25
Co	1.48±0.00	1.50±0.01	1.45±0.02	1.48±0.09
As	<0.002	<0.002	<0.002	<0.002

The results of soil concentration for the Rivers State University (RSU) are shown in Table 4. The results for the mean concentration of heavy metals in mg/kg are Cd (0.74±0.00), Pd (1.34±0.08), Cr (0.35±0.00), Ni (1.58±0.52), Fe (288±36.8), Cu (1.58±0.05), Ag (1.20±0.06), Zn (46.2±3.25), Co (1.48±0.09) and As (<0.002) respectively. The summary of Heavy Metals Concentration in Soils of Uniport, IAUE and RSU, Nigeria is shown in Table 5 below.

Table 5: Summary of Heavy Metals Concentration in Soils of Uniport, IAUE and RSU, Nigeria

Heavy Metals (mg/Kg)	Study Stations		
	Uniport	IAUE	RSU
Cd	0.62±0.08	0.85±0.08	0.74±0.00
Pd	1.28±0.04	1.08±0.11	1.34±0.08
Cr	0.35±0.00	0.36±0.01	0.35±0.00
Ni	0.53±0.23	0.38±0.33	1.58±0.52
Fe	153±58.7	268±22.6	288±36.8
Cu	1.77±0.08	1.59±0.04	1.58±0.05
Ag	0.77±0.24	1.35±0.17	1.20±0.06
Zn	52.7±1.34	53.6±1.98	46.2±3.25
Co	1.27±0.06	1.30±0.04	1.48±0.09
As	<0.002	<0.002	<0.002

Discussion

Cadmium (Cd)

The result of Cd level for the three campuses of Uniport, IAUE and RSU were 0.62±0.08, 0.85±0.08 and 0.74±0.00 respectively. The ranges for Cd concentration in the soil in were; Uniport (0.54±0.06-0.63±0.01), IAUE (0.84±0.01-0.86±0.01) and RSU (0.72±0.01-0.75±0.01) respectively. The result recorded higher Cd concentration in IAUE than the other two campuses. These results were higher than the lower range limit but lower than the upper range limits in earlier research by Mohammed and Folorunsho (2015) in Makera Drain soils, Kaduna, Nigeria. These results were absolutely lower than those recorded by Fosu-Mensah et al. (2017) in their similar study but in similar range for the work of Edet and Ukpong (2014) on the concentrations of potentially toxic elements and total hydrocarbon in soils of Niger Delta Region, Nigeria. The concentration levels of Cd as recorded in this study were lower than the various regulatory standard limits (WHO, 1996; Denneman & Robberse, 1990; MHSPE, 2000; DPR-EGASPIN, 2002; Riley et al., 1992; NJDEP, 1996).

This can be emanating from the presence of dumpsite around the study site where abandoned batteries from domestic wastes and soil chemistry. According to Wuana and Okieimen (2011) the most significant use of Cd is in Ni/Cd batteries, as rechargeable or secondary power sources. Cadmium (Cd) is inorganic chemical, hazardous and those most commonly found at contaminated sites and it is non-essential element (GWRTAC, 1997; Shah et al., 2013; Khan et al., 2008). Cadmium does not easily undergo microbial or chemical degradation (Kirpichtchikova, 2006), and the

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total concentration in soils persists for a long time on introduction (Adriano, 2003). The overall mean concentration of Cd ranged from 0.62±0.08 to 0.85±0.08 which was found in Uniport and IAUE respectively.

These values were though higher than those found in common ranges of soils (0.01-0.7 mg/kg) but lower than threshold and permissible limits (Toth et al., 2016; UNEP, 2013). The concentrations recorded in this study were all bellow those in similar research studies by Nafiu et al. (2011) on the vertical distribution of heavy metals in wastewater-irrigated vegetable garden soils of three West African cities. The upper limit of the range was close to the WHO target value of soils (0.8 mg/kg) but relatively higher than the permissible values of plants (0.02mg/kg) though comparatively lower than the intervention limit values for soils of 12mg/kg (Denneman & Robberse, 1990; Shah et al. (2013) showed similar lower limit ranges in experimental results for Cd concentration in soil samples which occurred between the range of 0.15 and 1.99mg/kg but lower than the upper limit ranges from this study. These values were the permissible limits for heavy metals in soils and plants (WHO, 1996). The outcome of studies showed the influence of anthropogenic activities on the level of heavy metals in soil samples (Hange & Awofoluu, 2017). According to Masona et al. (2011), wastewater increases heavy metal concentrations in soils which agreed with the earlier research result of Schmidt (1997) that toxic heavy metals in particular Cd is frequently present in high concentrations in wastewater. The health implication of elevated Cd level especially as an endocrine disruptor and carcinogenicity in human cannot be underestimated (Kartenkamp, 2011; Pollack et al., 2011; Ali et al., 2012). Similarly, Cd being a a non-essential heavy metal and extremely toxic even at low concentration causes learning disabilities and hyperactivity in children (Hunt, 2003). All the mean concentrations of Cd were lower than the threshold limit of 1.4 mg/kg prescribed by UK but within the 0.8 mg/kg level by the Dutch’s guideline (MHSPE, 2000). Cadmium (Cd) has no physiological benefits; hence their transfer across the food chain and resultant health implication forms the basis of concern as in this study (Hange & Awofoluu, 2017). According to Wuana and Okieimen (2011), Cd is very bio-persistent but has few toxicological properties so once absorbed by any organism, remains resident for many years.

Though levels of Cd contamination were relatively low, contamination factor of 1.3 was recorded for Cd by Hange and Awofoluu (2017) which indicated moderate level of pollution and so considered minimal. Potential contributing sources of Cd include atmospheric deposition from mining activities, wastes from Cd-based batteries and runoff from agricultural soils; and as common impurity in phosphate fertilizers as according to Benson et al. (2014) are used. According to Wuana et al. (2010) changes in Cd speciation and uptake by maize in a sandy loam before and after washing with three chelating organic acids indicated that EDTA and citric acid appeared to offer greater potentials as chelating agents for remediating the permeable soil.

Lead (Pb)

The result of Pb level (mg/kg) for the three campuses of Uniport, IAUE and RSU were 1.28±0.04, 1.08±0.11 and 1.34±0.08 respectively. The ranges for Pb concentration in the soil in were; Uniport (1.25±0.02-1.32±0.03), IAUE (1.00±0.06-1.15±0.05) and RSU (1.32±0.01-1.36±0.01) respectively. The result recorded higher Pb concentration in RSU, followed by Uniport before IAUE. These results were under similar ranges with those observed in drain soils in Kaduna, Nigeria (Mohammed & Folorunsho, 2015). But these results were lower than those recorded in earlier similar works (Fosu-Mensah et al., 2017; Kacholi & Sahu, 2018; Edet & Ukpong, 2014). This may be attributed to the human activities around RSU study sites such as the mechanical engineering laboratory where vehicle servicing and repair activities take place. The average concentrations of Pb in the three study stations were found to be lower than the target value (85 mg/kg), permissible limits of WHO for heavy metals in plants (2mg/kg) and intervention limit value of 530 mg/kg (WHO, 1996; Denneman & Robberse, 1990; MHSPE, 2000; DPR-EGASPIN, 2002; Riley et al., 1992; NJDEP, 1996). According to Kabata-Pendias and Pendias (2001), typical mean concentration of Pb for surface soils worldwide is 32mgkg^{-1} and ranges between 10 and 67mgkg^{-1}. The result showed similar range for the lower limits but lower than the upper limit by Nafiu et al. (2011) for the vertical distribution of heavy metals in wastewater-irrigated vegetable garden soils of three West African cities. The soil analysis showed that the concentration of Pb was lower than that obtained heavy metals concentration and distribution in soils and vegetation at Korle Lagoon area in Accra, Ghana, 184.44 mg/ kg and in Yelu, Bauchi state, Nigeria respectively (Fosu-Mensah et al., 2017; Sanusi et al., 2017). Lead (Pb) is inorganic chemical, hazardous and those most commonly found at contaminated sites and it is non-essential element (GWRTAC, 1997; Shah et al., 2013; Khan et al., 2008). Similarly, Masona et al. (2011) posits that wastewater increases heavy metal concentrations in soils. This agrees with the earlier research result of Schmidt (1997) that toxic heavy metals in particular Pb is frequently present in high concentrations in wastewater. Lead (Pb) is a non-essential heavy metal and causes oxidative stress, contributing to the pathogenesis of lead poisoning through the disruption of the delicate antioxidant balance of the mammalian cells (Shah et al., 2013). According Rehman et al. (2013), high level accumulation of Pb in the body system causes anemia, colic, headache, brain damage, and central nervous system damage.

Lead (Pb) is a metal of group IV and period 6 of the periodic table with atomic number 82, atomic mass 207.2, density 11.4gcm^{-3}, melting point 327.4°C, and boiling point 1725°C. In terms of the industrial production of metals, Lead is fifth (5th) after behind Fe, Cu, Al, and Zn. Hange and Awofoluu (2017) recorded higher values than those of this study and hence high contamination factor as possible sources of Pb in the environment include atmospheric particulate deposition, lead-based wastes such as painted materials, used dry-cell batteries and mine tailings. Lead (Pb) can be assessed easily through absorption by plants and subsequent consumption of these plants by ruminants (Hange & Awofoluu, 2017). Lead (Pb) contaminant may be as a result of adjacent traffic activities and use of agrochemicals (Kananke et al., 2014). The lower soil organism (earthworms and insects0 could be affected with high risk of biodiversity loss. Soils affected by Pb could be ingested by children through the inhalation of dust $PM_{2.5}$ containing Pb hence cardiovascular and respiratory complications (Laumbach & Kipen, 2012). Lead (Pb) can also affect cognitive development in children (Bellinger, 2008). And is probably carcinogenic to human and the compound on prolonged exposure can damage human organs (Towle et al., 2017). One of the common heavy metals found in biosolids is Pb whose concentration is controlled by the type, intensity of industrial activity and kind of process applied in biosolids treatment (Mattigod & Page, 1983). The most striking challenges of Lead are serious injury to the brain, nervous system, red blood cells, and kidneys (Baldwin & Marshall, 1999). According to Wuana et al. (2010) changes in Pb speciation and uptake by maize in a sandy loam before and after washing with three chelating organic acids indicated that EDTA and citric acid appeared to offer greater potentials as chelating agents for remediating the permeable soil. According to Wuana and Okieimen (2011), though more than 1000 organolead compounds are known, those of commercial and toxicological significance are actually limited to the alkyl lead compounds and their salts such as tetraethyllead found in gasoline.

Chromium (Cr)

The mean result of Cr level (mg/kg) for the three campuses of Uniport, IAUE and RSU were 0.35±0.00, 0.36±0.01 and 0.35±0.00 respectively. These stations recorded concentration ranges of 0.33±0.01-0.37±0.01 (Uniport), 0.32±0.03-0.40 ±0.03 (IAUE) and 0.33±0.01-0.36±0.01 (RSU). All the stations sampled have values below the target value ranges and intervention limits for soils as well as for plants (WHO, 1996; Denneman & Robberse, 1990; MHSPE, 2000 DPR-EGASPIN, 2002; Riley et al., 1992; NJDEP, 1996). The values were relatively highest in the IAUE station though in a very negligible difference. The results were generally lower than those earlier recorded by Nafiu et al. (2011) on the vertical distribution of heavy metals in wastewater-irrigated vegetable garden soils of three West African cities but higher than the lower range limits as observed by Edet and Ukpong (2014) in Calabar, Nigeria. Chromium (Cr) is the 4th element in first transition series of d-block of atomic number 24, atomic mass 52, density 7.19gcm^{-3}, melting point 1875°C, boiling point 2665°C and of the less common elements and does not occur naturally in elemental form but only in compounds (Wuana and Okieimen, 2011). Though the relatively low concentration of Cr observed in sample site does not reflects its association with parent granite and ultramafic rocks as earlier reconfirmed by Mohammed and Folorunsho (2015), other human inputs must be of great concern. The primary sources of Cr-contamination include releases from electroplating processes and the disposal of Cr containing wastes. Smith (1995) especially Chromium (VI) which is the form Cr is commonly found in contaminated sites. On the average, IAUE recorded the highest concentrations of Cr while RSU and Uniport were almost the same. This may be an indication of soil types and high probability of similar anthropogenic inputs for the study areas in RSU and Uniport. These results are lower than those obtained by Yusuf et al. (2015) in Sokoto sampled soils and similar to those obtained by Ezejiofor (2013) on the study of environmental metals pollutants load of a densely populated and heavily industrialized commercial city of Aba, Nigeria. Similarly, those obtained in the analysis of soil heavy metal pollution and pattern in Central Transylvania were again higher than those in this study (Suciu et al., 2008). Chromium (Cr) plays a significant role in the metabolism of cholesterol, fat, and glucose (Shah et al., 2013). Its deficiency causes hyperglycemia, elevated body fat, and decreased sperm count but at high concentration it is toxic and carcinogenic (Chishti et al., 2011). According to the research by Shah et al. (2013), the Cr contents in the soil samples were found between the range of 2.63 and 32.53mg/kg which is higher than those of the present study.

Nickel (Ni)

The mean result of Ni level (mg/kg) for the three campuses of Uniport, IAUE and RSU were 0.53±0.23, 0.38±0.33 and 1.58±0.52 respectively. These stations recorded concentration ranges of 0.50±0.02-0.55±0.01 (Uniport), 0.32±0.03-0.40±0.01 (IAUE) and 1.56±0.01-1.60±0.01 (RSU). The soil values showed relatively higher variations in RSU compared to IAUE and Uniport. All the stations sampled have values below the target value ranges and intervention limits for soils as well as for plants (WHO, 1996; Denneman & Robberse, 1990; MHSPE, 2000; DPR-EGASPIN, 2002; Riley et al., 1992; NJDEP, 1996). These relatively lower values than the standard limits is an indication of man-made inputs which must be checked to avoid gradual accumulation and threat to life of both plants and organisms including man. The concentration of Ni in the study is far lower than those observed in earlier research works (Wuana & Okieimen, 2011; Fosu-Mensah et al., 2017; Shah et al., 2013; Adagunodo et al., 2018; Nafiu et al., 2011). These results were though lower (Ni) but higher in terms of the lower limit ranges by Edet and Ukpong (2014) in Calabar, Nigeria. According to Masona et al. (2011), the study revealed that wastewater increases heavy metal concentrations in soils. This agrees with the earlier research result of Schmidt (1997) that toxic heavy metals in particular Ni is frequently present in high concentrations in wastewater. According to research studies, nickel is occurs in the environment at very trace amount levels and is essential in small doses but can be toxic when the maximum tolerable amounts are exceeded and may result to different kinds of cancer on sites within the bodies of animals especially those that live near refineries (Wuana & Okieimen, 2011). The most common application of Ni is additive in steel and other metal production processes, the major sources of nickel contamination in the soil being metal plating industries, combustion of fossil fuels, and nickel mining and electroplating (Khodadoust et al., 2004)). Nickel (Ni) can be released into the air by power plants and trash incinerators which settle to the ground after undergoing precipitation reactions and Ni is persistent in the atmosphere (Wuana & Okieimen, 2011). According to Basta et al. (2005), certain agricultural animal wastes are the applications of numerous biosolids such as livestock manures, composts, and municipal sewage sludge to land leading to the accumulation of heavy metals such as Ni and so forth in the soil. Nickel is a first transition series element with atomic number 28 and atomic weight 58.69g. In low pH regions, the metal exists in the form of the nickelous ion, Ni(II). In neutral to slightly alkaline solutions, it precipitates as nickelous hydroxide, $Ni(OH)_2$, which is a stable compound. According to Adagunodo et al. (2018), soils pose health risk (HR) or ecological risk (ER) as long as the soil exceeds permissible limits indicating contamination (Toth et al., 2016; UNEP, 2013; Awasthi, 2000). According to research earlier works such as Wuana and Okieimen (2011), microorganisms can develop resistance to Ni but undergo growth decline at the earlier stages. Nickel is not known to accumulate in plants or animals and so has not been found to biomagnify up the food chain but Ni is known to be an essential foodstuff in trace quantities (Wuana & Okieimen, 2011).

Iron (Fe)

Iron (Fe) is the 6th element of the first transition series of atomic number 26 and atomic weight of 55.847g falling immediately after manganese but before cobalt. The mean result of Fe level (mg/kg) for the three campuses of Uniport, IAUE and RSU were 153±58.7, 268±22.6, 288±36.8 respectively. The values were relatively higher at the RSU and IAUE campuses compared to Uniport soil. These stations recorded mean concentration ranges of 150±2.88-156±1.41 (Uniport), 265±2.12-2.70±1.41 (IAUE) and 286±1.41-290±1.41 (RSU). The mean range of Fe in the three main study stations is 153±58.7-288±36.8 and all the stations sampled have values below the target value ranges and intervention limits for soils as well as for plants (WHO, 1996; Denneman & Robberse, 1990; MHSPE, 2000; DPR-EGASPIN, 2002; Riley et al., 1992; NJDEP, 1996). The concentration of Fe in this study is far below that recorded for soils of Illela Garage in Sokoto State, Nigeria which was as high as 1771±112.73 μg/g, oil impacted soil of the Niger Delta and Abattoir soils, Port Harcourt, Nigeria (Yusuf et al., 2015; Iwegbue et al., 2006; Edori & Iyama, 2017; Kacholi & Sahu, 2018). Similarly, the result of this study was relatively lower by upper limit ranges but higher in terms of lower limit range (Edet & Ukpong, 2014). Results of the atomic absorption spectrophotometric (AAS) analysis of samples of the soils revealed that Fe concentrations in the soils are below background levels and permissible limits recommended for soils in some countries but above those recorded by Sanusi et al. (2017) as indicated by the following mean concentration range of 0.583- 0.781mg/kg in their study. The concentration of Fe is highest on the RSU campus soil followed by IAUE but lowest in Uniport. This is likely due to natural Fe content in soil especially for both RSU and IAUE which lie on very similar terrain of soil structure and texture.

Though human activities may be contributing but minimal when compared to the similar trend found in RSU and IAUE. The concentrations so obtained were generally higher than the tolerable limit for safe environment as prescribed by Nigerian Federal Environmental Protection Agency, FEPA and World Health Organization WHO (WHO, 1971;

FEPA, 1998). Several studies have shown that Fe is amongst other metals responsible for certain diseases that have lethal effects on man, animals and plant (Kanmony, 2009). Averagely, Fe content in both soils and plants are usually high as shown by Shah et al. (2013) in their Comparative Study of Heavy Metals in Soil and Selected Medicinal Plants. Iron (Fe) remains the most abundant and an essential constituent for all plants and animals, Shah et al. (2013) and results to anemia and neurodegenerative conditions in human being (Fuortes & Schenck, 2000). The observed levels in soil samples studied were higher than the permissible limits in agricultural soils suggesting that the studied soil sample is severely contaminated by the referred heavy metal. The high observed Fe levels could be attributed to the nature of the parental material of soils in the study site as earlier affirmed by Kacholi and Sahu (2018) in soil study in Tanzania. Also, Fe could be emanating from phosphate fertilizers, waste water disposal, organic wastes dumping, use of sludge, and burning of the fossil fuels in the area (Tasrina et al., 2015).

Copper (Cu)

The mean result of Cu level (mg/kg) for the three campuses of Uniport, IAUE and RSU were 1.77±0.08, 1.59±0.04 and 1.58±0.05 respectively. These stations recorded mean concentration ranges of 1.75±0.01-1.79±0.01 (Uniport), 1.54±0.04-1.62±0.02 (IAUE) and 1.56±0.01-1.60±0.01 (RSU). The heavy metal contents were higher at the Uniport station compared to IAUE and RSU. The overall mean range of Cu in the three main study stations was 1.58±0.05-1.77±0.08 and all the stations sampled have values below the target value ranges and intervention limits for soils as well as for plants (WHO, 1996; WHO, 2008; Denneman & Robberse, 1990; MHSPE, 2000; DPR-EGASPIN, 2002; Riley et al., 1992; NJDEP, 1996). The concentration of Cu recorded in this study is below that observed in earlier research studies (Adagunodo et al., 2018; Sanusi et al., 2017; Suciu et al., 2008; Fosu-Mensah et al., 2017; Nafiu et al., 2011; Kacholi & Sahu, 2018). Similarly, the result of this study was relatively lower by upper limit ranges but higher in terms of lower limit range (Edet & Ukpong, 2014). Results of the atomic absorption spectrophotometric (AAS) analysis of soils samples revealed that for heavy metals, the concentrations in the soils are above background levels and permissible limits recommended for soils in some countries as indicated by the following mean concentration range (Cu, 42.01- 111.60 mg/kg). The low concentration of Cu in soils could be attributed to slow travel rate after release, its speciation and other geochemical characteristics in soil (Ezeh & Chukwu, 2012). This could also be linked to its mobility in weathering environment and ability to adsorb onto interstices of soil constituents surfaces through ion exchange process (Wuana & Okieiman, 2011). Copper (Cu) may be emanating from from nearby traffic activities and use of agrochemicals (Kananke et al., 2014). According to Masona et al. (2011), the study revealed that wastewater increases heavy metal concentrations in soils. This agrees with the earlier research result of Schmidt (1997) that toxic heavy metals in particular Cu is frequently present in high concentrations in wastewater. Heavy metals in the soil from anthropogenic sources tend to be more mobile and so bioavailable compared to the pedogenic or lithogenic ones (Kuo et al., 1983; Kaasalainen & Yli-Halla, 2003). Copper (Cu) is an essential trace element and very essential for many enzymes as well as normal growth and development (Shah et al., 2013). High concentration of Cu causes metal fumes fever, hair and skin decolorations, dermatitis, respiratory tract diseases, and some other fatal diseases in human beings (Khan et al., 2008) permissible limit of copper in medicinal plants is 10mg/kg while its intake level in food is 2-3mg/day.

Silver (Ag)

The mean result of Ag level (mg/kg) for the three campuses of Uniport, IAUE and RSU were 0.77±0.24, 1.35±0.17 and 1.20±0.06 respectively. These stations recorded mean concentration ranges of 0.74±0.02-0.80±0.02 (Uniport); 1.30±0.04-1.40±0.04 (IAUE) and 1.16±0.03-1.24±0.03 (RSU). The soils recorded relatively higher concentrations at the IAUE location than the others though followed closely by that of RSU. The overall mean range of Ag in the three main study stations was 0.77±0.24-1.35±0.17 and all the stations sampled have values below the target value ranges and intervention limits for soils as well as for plants (WHO, 1996; WHO, 2008; Denneman & Robberse, 1990; MHSPE, 2000; DPR-EGASPIN, 2002; Riley et al., 1992; NJDEP, 1996). Silver (Ag) is a metallic element that has been valued for its use in currency, jewelry, photo-processing, electronics, and in the medical field (VandeVoort & Arai, 2012). Silver is an ornamental element of atomic number 47 and atomic weight, 107.868g. According to Saeki et al. (1995), the Ag values ranged from 0.27 to 6.89 mg kg^{-1} which were much higher than the values of the unpolluted soils and also within the range of the results of this study especially the lower limit of 0.27mg/kg.

Zinc (Zn)

The mean result of Zn level (mg/kg) for the three campuses of Uniport, IAUE and RSU were 52.7±1.34, 53.6±1.98 and 46.2±3.25 respectively. These stations recorded mean concentration ranges of 51.8±0.64-53.7±0.71 (Uniport), 53.4±0.14-53.8±0.14 (IAUE) and 46.0±0.14-46.4±0.14 (RSU). The soils recorded relatively higher concentrations at the IAUE location than the others though least at the RSU study station. The overall mean range of Zn in the three main study stations was 46.2±3.25-53.6±1.987 and all the stations sampled have values below the target value ranges and intervention limits for soils but not for plants, 0.60mg/kg (WHO, 1996; WHO, 2008; Denneman & Robberse, 1990; MHSPE, 2000; DPR-EGASPIN, 2002; Riley et al., 1992; NJDEP, 1996). Similarly, the result of this study was relatively lower by upper limit ranges but higher in terms of lower limit range (Edet & Ukpong, 2014). The highest mean values of Zn were found in the composite soils of IAUE and Uniport but least in the RSU station. This variation is a threat due to the trend of RSU not closer to those of IAUE since both are closest in terms of soil structure and texture. This implies that certain human activities may be responsible. The observed concentrations for Zn fall below both lower and upper limits of common ranges in soils (10-300mg/kg) meaning within safety limits whose gradual increase must be properly monitored. The results of this study showed higher mean concentration compared to the works of earlier researchers in soils (Yusuf et al., 2015; Mohammed & Folorunsho, 2015; Dan'Azumi & Bichi, 2010; Fosu-Mensah et al., 2017; Nafiu et al., 2011) but within similar range to that of Shah et al. (2013) on the comparative study of heavy metals in soil and selected medicinal plants and lower than those of Kacholi and Sahu (2018) on the levels and health risk assessment of heavy metals in soil, water, and vegetables of Dar es Salaam, Tanzania.

According to Masona et al. (2011), the study revealed that wastewater increases heavy metal concentrations in soils even zinc. This agrees with the earlier research result of Schmidt (1997) that toxic heavy metals in particular Zn is frequently present in high concentrations in wastewater. Zinc is one of the heavy metals commonly found in contaminated soils (Wuana & Okieimen, 2011). Soils serve as sink for heavy metals released into the environment by anthropogenic activities but different from organic contaminants which are oxidized to carbon (IV) oxide by microbial action, most metals do not undergo microbial or chemical degradation (Kirpichtchikova, 2006). Therefore, their total concentrations in soils remain recalcitrant and persist for a long time after their introduction (Adriano, 2003). Zinc is a transition metal belonging to period 4; group IIB of atomic number 30, atomic mass 65.4, density 7.14gcm^{-3}, melting point 419.5°C, and boiling point 906°C. According zinc occurs naturally in soil, about 70mgkg^{-1} in crustal rocks (Davies & Jones, 1988). Zn concentrations are rising unnaturally due to anthropogenic inputs such as industrial activities from mining, coal and waste combustion and steel processing (Wuana & Okieimen, 2011). Many foodstuffs contain certain concentrations of Zn as well as drinking water which may be higher when it is stored in metal tanks (Wuana & Okieimen, 2011). Zinc accumulates in soils and plants extract it which may not be easily controlled (Wuana & Okieimen, 2011). Zinc (Zn) influences the performance of microorganisms and earthworms thereby distorting the activity in soils and retarding the breakdown of organic matter (Greany, 2005). According to Kuo et al. (1983) and Kaasalainen and Yli-Halla (2003), heavy metals in the soil from anthropogenic sources tend to be more mobile and so bioavailable compared to the pedogenic or lithogenic types.

Cobalt (Co)

The mean result of Co level (mg/kg) for the three campuses of Uniport, IAUE and RSU were 1.27±0.06, 1.30±0.04 and 1.48±0.09respectively. These stations recorded mean concentration ranges of 1.25±0.01-1.28±0.01 (Uniport), 1.30±0.04-1.40±0.04 (IAUE) and 1.45±0.02-1.50±0.01 (RSU). The soils recorded relatively higher concentrations at the RSU location than the others. The overall mean range of Co in the three main study stations was 1.27±0.06-1.30±0.04 and all the stations sampled have values below the target value ranges and intervention limits for soils as well as for plants (WHO, 1996; WHO, 2008; Denneman & Robberse, 1990; MHSPE, 2000; DPR-EGASPIN, 2002; Riley et al., 1992; NJDEP, 1996). The average cobalt concentration in European soils is between 1-20mg/kg dry weight. The observed concentrations of Co were far below those of threshold and permissible limits from similar regulatory standards (Toth et al., 2016; UNEP, 2013). The concentration of Co in this study was lower than those earlier recorded by Suciu et al. (2008) in Central Transylvania. Similarly,m the result of this study was relatively lower by upper limit ranges but higher in terms of lower limit range (Edet & Ukpong, 2014). Cobalt in soils throughout the world results from a combination of natural and anthropogenic activities and adversely affects wildlife and biodiversity. Cobalt soil concentrations is dependent on factors such as geology, atmospheric deposition of cobalt-containing dust, land use and associated amendments, mineral particle distribution, soil age, and climactic and transport factors affecting localised concentrations (Wendling et al., 2009). Cobalt being a transition element is an essential component of several enzymes and co-enzymes. It has been shown to affect growth and metabolism of plants, in different degrees, depending on the concentration and status of cobalt in rhizosphere and soil but also cancerous (Syamasri et al., 1994).

Cite this article as:
Edori, O.S., Iyama, W.A., & Edori, E.S. (2025).Comparative assessment of heavy metals in soils of designated institutions in Rivers State, Nigeria.. *FNAS Journal of Basic and Environmental Research*, *2*(2), 47-68.

Arsenic (As)

The concentration of Arsenic in the soil showed similar trend in all the study campuses of Uniport, IAUE and RSU respectively as < 0.002mg/kg. Therefore, all the stations sampled have values below the target value ranges and intervention limits for soils and plants, 0.60mg/kg (WHO, 1996; WHO, 2008; Denneman & Robberse, 1990; MHSPE, 2000; DPR-EGASPIN, 2002; Riley et al., 1992; NJDEP, 1996). The concentrations recorded in all the study stations were similar and almost constant and negligible. This is a clear indication of lack of anthropogenic input of materials capable of increasing its content in soils not minding the toxic impact of As. Arsenic is a metalloid in group VA, period 4 and occurs in a wide variety of minerals, mainly as As_2O_3, and can be recovered from processing of ores containing mostly Cu, Pb, Zn, Ag and Au. According to Wuana and Okieimen (2011), As is also present in ashes from coal combustion. Arsenic has atomic number 33, atomic mass 75, density 5.72gcm^{-3}, melting point 817°C, and boiling point 613°C. According to Smith (1995), As exhibits fairly complex chemistry and can be present in several oxidation states of −III, 0, IV/ and V as a typical transition metal. Scragg (2006) posited that many as compounds adsorb strongly to soils hence transported only over short distances in groundwater and surface water and its presence is associated with skin damage, increased risk of cancer, and problems with circulatory system. Arsenic (As) being one of the most toxic metals has low tolerable limit hence care must be taken to monitor its resurgence in later periods. The one-way ANOVA was used to determine the spatial variations in the composite sampled stations for Uniport, IAUE and RSU which were found not significant at $p< 0.05$ (f-ratios of 0.00069, 0.0001 and 0.00005) respectively. Similarly, the relationship amongst the campuses of Uniport, IAUE and RSU were found to have no significant relationship at $p<0.05$ (f-ratio of 0.08734). This is a clear indication of the existence of similar soil composition, texture, structure and anthropogenic disturbances. Metal-bearing solids found in contaminated sites can emanate from various anthropogenic sources either as metal mine tailings, disposal of high metal wastes in improperly protected landfills, leaded gasoline and lead-based paints, land application of fertilizer, animal manures, biosolids (sewage sludge), compost, pesticides, coal combustion residues, petrochemicals or atmospheric deposition (Zhang et al., 2010; GWRTAC, 1997; Basta et al., 2005).

Conclusion

This study showed that there were variations in the heavy metal contents of the various soils from the different university campuses even though they have similar services and within same alluvial soil environment. The levels of all the heavy metals were observed to be below the target, intervention and permissible regulatory limits for soils and plants (WHO, DPR-EGASPIN, USEPA *etc)* though Zinc level exceeded that of plants. Comparatively, Cd was highest in IAUE and least at Uniport, Pb was highest at the RSU station and least at IAUE, Cr was highest at the IAUE but least at both RSU and Uniport, Ni showed highest variation at the RSU station compared to the others, Fe was highest in RSU soil and least at the Uniport study site, Cu was highest in Uniport sampled soils and least at the IAUE and RSU, Ag was highest at the IAUE study soils and least at Uniport soil, Zn recorded highest concentrations at both IAUE and Uniport, Co was highest in RSU and least at Uniport study soil sites and finally As was of uniform concentration in all three study stations showing limited anthropogenic inputs. On the average, RSU study station recorded the highest levels of heavy metals followed by IAUE station probably due to their site location being closer to the heart of the city and some oil refining processes. The greatest threats of soil heavy metal contamination due to future accumulation in the soils were found in Cd, Cr, Zn and Co. The potential variation of heavy metals in the study was of the trend, Fe>Zn>Ni>Cu>Co>Pb>Ag>Cd>Cr>As. Therefore, there is need to formulate and execute policies that could help ameliorate the human input of heavy metal contaminants due the gradual build up within the campuses of the study locations. The student and staff population should be enlightened on the level of heavy metal contamination and possible health implications and hazards. There is the ardent need to have periodic monitoring system to ascertain the input rate on a yearly basis especially as technological advancements and indiscriminate waste dumping cannot be absolutely controlled.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this article.

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