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Assessment of Soil Metals Status in parts of Rivers State, Nigeria

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ABSTRACT: The study evaluates levels of metals in soils of 9 locations in Port Harcourt and its environs in Rivers State in Nigeria. Composite samples were collected by random sampling from each of the 9 test locations, 3 control samples were also collected from each of the study areas. Concentration levels of (Lead) Pb, (Copper) Cu, (Cadmium) Cd, (Zinc) Zn, (Calcium) Ca, (Nickel) Ni, (Sodium) Na, (Potassium) K, (Chromium) Cr, (Magnesium) Mg, (Manganese) Mn, and (Sulphur) S in soil were measured using Atomic Absorption Spectrophotometry. The obtained mean levels of Pb, Cu, Cd, Zn, Ca, Ni, Na, K, Cr, Mn and Mg were 1.45±0.16, 0.22±0.04, 0.04±0.01, 2.61±0.51, 12.99±4.81, 0.75±0.08, 173.64±35.31, 6.06±1.58, 0.27±0.03, 4.21±0.61 and 11.87±2.10 ppm respectively. There were significant differences in levels of Pb among the test and control samples (p=.048). There was significant difference in levels of Cu among the test and control samples (p=0.001). There was significant difference in levels of Zn among the test and control samples (p=0.016). The study establishes that urbanization, industrialization and agricultural activities do affect the level of metals in the soils of the study areas. The pollution of soils with metals in the studied sites is within permissible limits, however, levels of Zn, Cd and Ni should be on close monitoring to in the industrial areas and urbanized areas. The study establishes that oil and gas activities variedly affect the levels of metal pollution in urbanized, industrialized and agricultural areas.

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Environmental pollution is an increase in the concentration of both biological and physicochemical parameters above the environmental baseline levels. These baseline levels may be determined in the environment. Environmental pollution is an aspect of environmental degradation (United Nations Interagency Framework Team for Preventive Action, 2012). Degradation of the environment may be expeditiously influenced by; rapid economic growth, population growth, urbanization, industrialization, unrestrained agricultural activities, rising energy consumption and transportation (Li and Ma, 2014). Therefore, human disturbance is a primary cause of environmental degradation and loss of soil ecosystem integrity. Despite being a major source of environmental degradation, population is an important aspect of development. A big population means voluminous wastes. Population, megacities and urban slams are rapidly emerging and consequently the environment continues to receive voluminous wastes that compromise its natural status (Prasad and Kaimin, 2016). The World Bank foresees that 2.2 billion tons of wastes will be produced by 2025, which is an increase of 69% and reflects urbanization and industrialization (Hoornweg and Bhada, 2012). It is not certain of all the areas that are contaminated in Nigeria and there is need for continuous monitoring of the environment in order to come up with the sites that are polluted. A risk assessment is thus vital for description and management of the environment. The scope of this study is limited to assess human influence on levels of physicochemical parameters in soils of Port Harcourt and its environs.

Ecological risks are of concern due to accumulation of heavy metals in the soil which compromises the soil ecosystem integrity (Islam *et al.,* 2017), and consequently calls for more ecological risk assessment (Islam *et al.*, 2017). Food that is contaminated with heavy metals is hazardous and can cause toxic effects on health of an ecosystem as well as humans (Balkhair & Ashraf, 2016; Alghobar & Suresha, 2017). Cadmium is intensively used in the industries in rechargeable batteries, paints, stabilization of plastic and in processing of Zn among others (Jaishankar, Tseten, Anbalagan, Mathew, & Beeregowda, 2014). Cadmium accumulates in the environment and gets to human diet through biomagnification (Jaishankar et al., 2014). If Cd gets into the human body, it causes reproductive disfunction, hepatic and renal toxicity as

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it possesses ability to bind cysteine, glutamate and histidine (Castagnetto et al., 2002; FDA [Food and Drug Administration]; Harmanescu, Alda, Bordean, Gogoasa, & Gergen, 2011; Jaishankar et al., 2014). Copper (Cu), Cr, Ni and Zn are essential for growth of existence of organisms (Jaishankar et al., 2014); (Rahman, Rahman, Reichman, Lim, & Naidu, 2014), but if excessively consumed they become hazardous and unsafe for human health.

Chromium occurs naturally in the environment but its high occurrence is influenced by burning coal, petroleum and oil, in the processing of fertilizers and pigments and in electroplating (Jaishankar et al., 2014).

Chromium occurs in several oxidation states in the environment from Cr_2^+ to Cr_6^+, where each oxidation state offers unique mechanisms of toxicity imposing damage to proteins including DNA (Jaishankar et al., 2014). Copper (Cu) is an essential nutrient, but excess intake of Cu causes hepatic damage, headache, acute esophageal aches, diarrhea and vomiting (Harmanescu et al., 2011); Jaishankar et al., 2014; Rahman et al., 2014).

Excessive intake of Manganese is associated with neurotoxicity as Manganese iron deposition in Parkinsonism (FDA; Harmanescu et al., 2011). Nickel contaminates soil through atmospheric deposition, mining of metallic materials, smelting, agricultural activities and industrial activities (Jaishankar et al., 2014). Nickel (Ni) is an essential nutrient, however if consumed excessively by human can be carcinogenic (Rahman et al., 2012a).

Lead (Pb) hardly provides for any biological roles if consumed. Lead (Pb) has carcinogenic effects (Jaishankar et al., 2014). Lead (Pb) damages chlorophyll where its toxicity arises from its ability to replace cations including Na+, Ca2+, Mg 2+ and Fe2+ (Harmanescu et al., 2011).

Lead (Pb) also induces cardiovascular diseases, reduces cognitive development, tumor induction and hypertension (Harmanescu *et al*., 2011). Contamination of soil by Zinc (Zn) is by mining and smelting of metal, atmospheric depositions and agricultural and industrial activities (Rahman et al., 2014).

Zinc (Zn) induces disruption of the immune system and consequently reduces immune function (Harmanescu et al., 2011).

MATERIALS AND METHODS

Description of the Study Site: This study was conducted in 9 selected areas of Port Harcourt, the Capital of Rivers State, Nigeria (Figure 1). The areas of interest were grouped into 3; urban, industrial and agricultural areas. The urban areas of interest included; GRA phase 2, Diobu- Mile 1 and Mguoba. Agricultural areas of interest included; Aluu, Eleme, Emuoha- Eu, while the industrialized areas were; Eleme which hosts the NNPC Refinery, Agbada-SPDC- flow station in a rural setting and Trans-Amadi. The characteristics and main activities (Table 1) conducted in the study areas include; drilling and mining, fishing, fish farming, horticulture, dairy farming and crop farming, industrial processing. The study areas were assigned codes as in Table 1.

Fig 1: Map of Nigeria showing Rivers state

Sampling: Composite samples were collected by random sampling from each of the three areas; urbanized, industrialized and agricultural in the wet season (April to October 2018). Five (5) individual samples were collected following a random pattern around each test field. The five individual samples were thoroughly mixed by coning and quartering in a sterile container to attain a homogenous composite mixture. A total of 12 composite samples; A1, A2, A3, I1, I2, I3 U1, U2 and U3 as test samples, and CA, CI and CU as control samples (Table 1), were collected from the topsoil within a depth of 0 to 15 cm using a standard auger 3 times in the rainy season. Homogenized composite samples (400 gm) were then packed in polyethylene bags using a sterile wooden shovel. Samples for microbial analysis were collected using pre-sterilized materials to prevent contamination of the samples. Locations of the sampling sites were identified using a GPS and the GPS readings recorded. Samples were transported to the laboratory for analysis.

Determination of levels of metals in soil: Concentration levels of Pb, Fe, Cu, Cd, Zn, Ca, Ni, Na, K, Cr, Mg, Mn, and S in soil were measured using Atomic Absorption Spectrophotometry [AAS] (APHA, 1995). The heavy metals were then measured at specified wavelengths; Lead: 283.2, Copper: 324.7, Cadmium: 228.9, Zinc: 213.9, Nickel: 341.5, Calcium: 422.7, Sodium: 589.00, Potassium: 766.5, Manganese: 279.5, Magnesium: 285.2, Chromium: 357.9 (APHA, 301A). Soil pH and conductivity was measured using the standard; electrical meter method (APHA, 1995).

Data Analysis: SPSS statistical software was used to analyse collected data. ANOVA was used to describe mean differences among the different sampling locations and the control samples. Means differences were described using Tukey HSD.

RESULTS AND DISCUSSION

Metals in soil: Lead: Heavy metals in agricultural soils are health risk. The mean levels of Pb in soil were within the WHO acceptable limit of ≤100 (ppm). There was significant difference in level of Pb among the test and control samples (p=.048). Levels of Pb demonstrated an increasing trend in I3 (Figure 2). The highest value of Pb was recorded in I3 (Trans-Amadi); 3.50±0.88 ppm (Table 2).

Copper: The mean levels of Cu in soil were within the WHO acceptable limit of ≤100 ppm. There was significant difference among the test and control samples (p=0.001). The levels of Cu demonstrated an upward trend in U2 (Diobu), with a mean of 1.07 ±0.12 (Figure 2). The highest values of Cu were recorded in I3; 0.35±0.01 ppm, CA; 0.29±0.12 ppm and U2; 0.73±0.25 ppm (Table 2).

Table 1: Characteristics and main activities in the selected study areas and assigned codes

No	Selected study areas	Study area coding (Locations)	Coordinates/ N Latitude E Longitude	Characteristic and main activities
Agricultural areas				
1	Aluu	A1	4° 56’ 11.160’ 6° 57’ 52.248’	Flow station
2	Eleme	A2	4° 44’ 09.874’ 7° 08’ 58.494’	Village close to refinery
3	Emuoha	A3	5° 00’ 00.018’ 6° 49’ 13.032’	Flow station
4	Control	CA	5° 00’ 21.384’ 6° 49’ 00.000’	>1 km away from suspected areas
Industrial areas				
1	Onne	I1	4° 46’ 00.402’ 7° 05’ 43.092’	Hosts the NNPC Refinery
2	Agbada	I2	4° 56’ 03.444’ 6° 58’ 42.060’	Hosts SPDC- flow station in a rural setting
3	Trans-Amadi	I3	4° 48’ 20.455’ 7° 02’ 17.646’	Schlumberger/, Hallburton
4	Control	CI	4° 47’ 13.788’ 7° 07’ 44.620’	>1 km away from suspected areas
Urban areas				
1	GRA phase 2	U1	4° 49’ 53.574’ 6° 59’ 45.552’	Inhabited areas Perecuma street
2	Diobu-Mile 1	U2	4° 47’ 20.382’ 7° 00’ 13.164’	Petroleum refinery
3	Mguoba	U3	4° 50’ 39.864’ 6° 58’ 20.232’	NTA
4	Control	CU	4° 49’ 17,040’ 6° 59’ 24.168’	>1 km away from suspected areas

Cadmium: The mean levels of Cd in soil were within the WHO acceptable limit of ≤3 ppm. There was no significant difference among the test and control samples (p=0.152). The levels of Cu demonstrated an upward trend in U2 (Diobu) [Figure 2]. The highest value was recorded in I1 (Onne); 0.06±0.01ppm while A2 (Eleme) recorded the least value of Cu; 0.02±0.02 ppm (Table 2).

Zinc: The mean levels of Zn in soil were within the WHO acceptable limit of ≤300 ppm. There was significant difference among the test and control samples (p=0.016). The levels of Zn demonstrated an increasing trend in I3 (Figure 2). The highest values of Zn were recorded in CI (Ogali); 5.42±2.85 ppm, and I3 (Trans-Amadi); 9.08±3.68 ppm while A1 recorded the least value; 0.94±0.35 ppm (Table 2).

Calcium: The mean levels of Ca in soil were within the WHO acceptable limit of ≤100 (ppm). There was no significant difference among the test and control samples (p=0.314). The levels of Ca demonstrated an increasing trend in CI and CA (Figure 2). The highest values of Ca were recorded in C1; 48.43±30.30, CA; 34.32±19.65 and U2; 43.41±41.79 (Table 2).

Nickel: The mean levels of Ni were within the WHO acceptable limit of ≤50 (ppm). There was no significant difference among the test and control samples (p=0.83). The levels of Ni demonstrated an upward trend in U2 (Figure 2). The highest value of Ni was recorded in U2; 1.11±0.37 (Table 2).

Sodium: The mean levels of Na in soil were within the WHO acceptable limit of ≤100 (ppm). There was no significant difference among the test and control samples (p=0.311). The levels of Na demonstrated an increasing trend in U2 (Diobu) [Figure 2]. The highest values of Na were recorded in I2 (Agbada); 454.13±299.01 ppm and CU; 443.67±253.26 (Table 3).

Potassium: The mean levels of K in soil were within the WHO acceptable limit of ≤100 (ppm). There was no significant difference among the test and control samples (p=0.401). The levels of K demonstrated an upward trend in CI and U2 (Figure 2). The highest values of K were recorded in CI; 13.21±6.29 and U3; 17.95±15.54 (Table 3).

Chromium: The mean level of Cr in soil were within the WHO acceptable limit of ≤100 (ppm). There was no significant difference among the test and control samples (p=0.769). The levels of Cr demonstrated an upward trend in U2 (Figure 2). The highest values of Cr were recorded in CA; 0.45±0.18 ppm and U2; 0.41±0.16 ppm (Table 3).

Magnesium: The mean level of Mg in soil were within the WHO acceptable limit of ≤100 (ppm). There was no significant difference among the test and control samples (p=0.286) (Figure 2). The highest mean values of Mg were recorded in CA; 23.45±12.17 ppm, CU; 22.85±14.00 ppm and U2; 23.04±7.22 ppm (Table 3).

Manganese: The mean levels of Mn in soils were within the WHO acceptable limit of ≤2,000 (ppm). There was no significant difference among the test and control samples (p=0.063). The levels of Mn demonstrated an increasing trend in U2 (Figure 2). The highest values of Mn were recorded in CA; 8.76±3.62, A3; 7.50±3.76 and U2; 7.50±3.28 (Table 3).

Table 2: Mean concentration (±SE) of heavy metals in soil

Study locations	Pb (ppm)	Cu (ppm)	Cd (ppm)	Zn (ppm)	Ca (ppm)	Ni (ppm)
CI	1.15±0.50	0.13±0.04	0.06±0.01	5.42±2.85	48.43±30.30	0.92±0.34
I1	1.27±0.28	0.13±0.03	0.04±0.01	1.57±0.43	7.55±5.23	0.84±0.33
I2	0.89±0.30	0.17±0.01	0.04±0.02	1.16±0.25	3.03±1.34	0.79±0.25
I3	3.50±0.88	0.35±0.01	0.05±0.02	9.08±3.68	2.13±0.61	0.92±0.33
CA	1.33±0.56	0.29±0.12	0.04±0.02	2.04±0.47	34.32±19.65	0.43±0.13
A1	1.04±0.36	0.17±0.00	0.03±0.01	0.94±0.35	0.860.31	0.74±0.29
A2	1.44±0.52	0.17±0.02	0.02±0.02	1.62±0.63	1.44±0.27	0.47±0.14
A3	1.37±0.48	0.19±0.02	0.04±0.01	1.91±0.44	1.69±0.25	0.99±0.33
CU	1.25±0.26	0.17±0.06	0.04±0.00	1.50±0.59	1.71±0.54	0.55±0.22
U1	1.52±0.44	0.13±0.01	0.04±0.01	2.04±0.45	4.06±1.14	0.65±0.26
U2	1.71±0.23	0.73±0.25	0.04±0.01	2.80±0.02	43.41±41.79	1.11±0.37
U3	0.92±0.33	0.02±0.01	0.03±0.01	1.22±0.15	7.20±4.38	0.63±0.27
Mean	1.45±0.16	0.22±0.04	0.04±0.01	2.61±0.51	12.99±4.81	0.75±0.08
P Value	0.048	0.001	0.152	0.016	0.314	0.828

SD: Standard deviation (Significant coefficients P=0.05)

The mean levels of Pb in soil were within the WHO acceptable limit of ≤100 (ppm). The highest value of Pb was recorded in I3 (Trans-Amadi) [3.50±0.88 ppm] (Table 2). Contamination of soil with Pb can be attributed to increased population, increased domestic wastes, chemical wastes from industries and transportation (Chen, Xia, Zhao, & Zhang, 2010). Contamination of soils by Pb can also be attributed to wash off from paints (Hunt, 2016). The mean level of Cr in soil was 0.27± 0.03 ppm which was within the WHO acceptable limit of ≤100 (ppm). The highest values of Cr were recorded in CA; 0.45±0.18 ppm and U2 (Diobu); 0.41±0.16 ppm (Table 3). The findings of Pb and Cr are in agreement with the findings of (Yang, Lu, Long, Bao, & Yang, 2011) where they described the top soil of the study areas as non-contaminated to moderately contaminated and therefore indicate moderate pollution. The mean levels of Cu in soil were within the WHO acceptable limit of ≤100 (ppm). The highest values of Cu were recorded in I3 (Trans-Amadi); 0.35±0.01 ppm, CA; 0.29±0.12 ppm and U2 (Mguoba); 0.73±0.25 ppm (Table 2).

Table 3: Mean concentration (±SE) of heavy metals in soil

Study locations	Na (ppm)	K (ppm)	Cr (ppm)	Mn (ppm)	Mg (ppm)
CI	140.30±20.06	13.21±6.29	0.26±0.12	2.74±0.05	2.46±0.45
I1	153.17±46.66	1.87±0.11	0.23±0.07	4.19±0.23	6.28±2.16
I2	454.13±299.01	2.52±0.23	0.39±0.15	5.90±0.60	13.64±7.60
I3	120.41±7.39	1.70±0.45	0.15±0.09	1.68±0.02	16.03±8.54
CA	96.08±8.39	8.50±5.26	0.45±0.18	8.76±3.62	23.45±12.17
A1	113.17±31.43	0.91±0.17	0.14±0.05	3.73±0.21	7.50±3.60
A2	70.48±18.83	2.54±0.25	0.30±0.11	4.03±0.51	2.05±0.35
A3	143.63±92.38	1.85±0.37	0.28±0.16	7.50±3.76	10.94±5.52
CU	443.67±253.26	9.66±3.76	0.23±0.06	1.54±0.67	22.85±14.00
U1	68.33±7.54	1.99±0.48	0.19±0.11	1.23±0.26	4.77±1.24
U2	138.01±3.12	10.08±4.81	0.41±0.16	7.50±3.28	23.04±7.22
U3	142.30±19.93	17.95±15.54	0.26±0.15	1.73±0.68	9.46±2.55
Mean	173.64±35.31	6.06±1.58	0.27±0.03	4.21±0.61	11.87±2.10
P Value	0.311	0.401	0.769	0.063	0.286

SD: Standard deviation (Significant coefficients P=0.05)

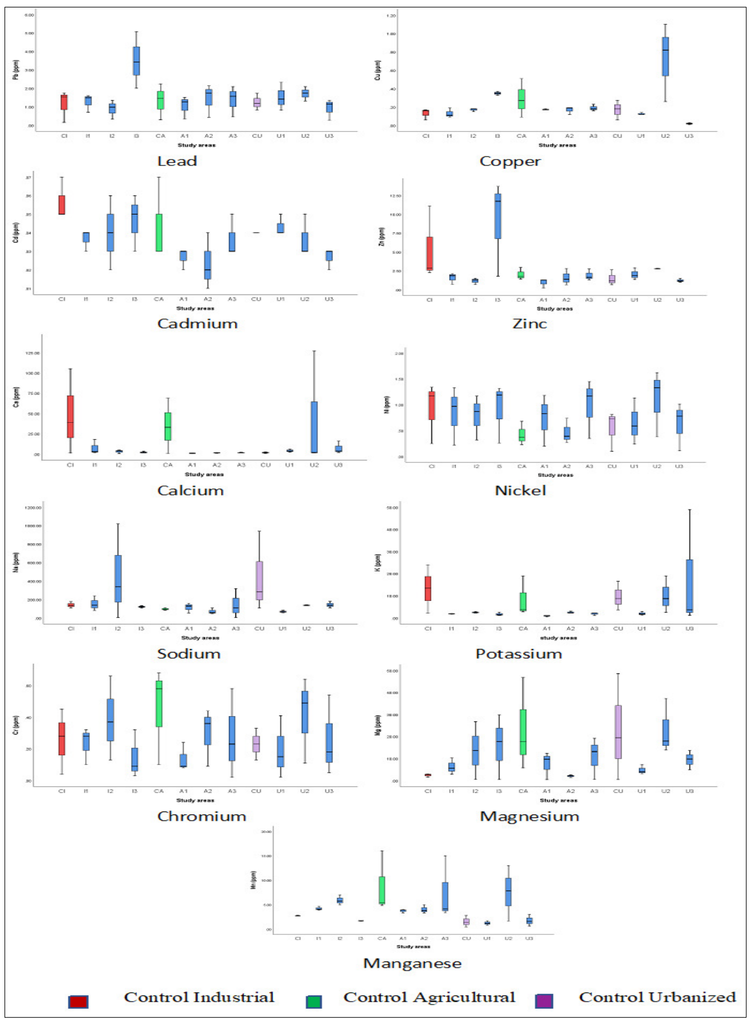

Fig 2: Variation in levels of metals

Copper is fungicidal and is often used in fungicides. The findings contradict findings by Adrees et al., 2015 and Ballabio et al., 2018, who linked distribution of copper in soil to agricultural activities. Levels of copper in soil can also be influenced by geological factors, climate, pedological, agricultural and industrial sources. Erosion plays a key role in transfer of Cu and can be a source of contamination of soil (Minkina et al., 2017; Ballabio et al., 2018). Copper can be found as insoluble complexes that lowers its motility in soil (Brazauskiene, Paulauskas, & Sabiene, 2008). The mean levels of Cd in soil were within the WHO acceptable limit of ≤3 (ppm). The highest value was recorded in I1 (Onne); 0.06±0.01 ppm while A2 (Eleme) recorded the least value of Cd; 0.02±0.02 ppm (Table 2). The findings can be related to findings of (Lu et al., 2010). Contamination of soils with cadmium is closely related to industrial activities in a particular area, for example metal processing industries. The mean level of Zn in soil were within the WHO acceptable limit of ≤300 (ppm). The highest values of Zn were recorded in CI; 5.42±2.85 ppm, and I3 (Trans-Amadi); 9.08±3.68 ppm while A1 (Aluu) recorded the least value; 0.94±0.35 ppm (Table 2). This can be attributed to heavy wash off from human settlements (Lu et al., 2010). The findings concur with findings of Lu, 2010 where industrial activity influences the levels and distribution of Pb and Zn (Lu et al., 2010). The mean levels of Na in soil were within the WHO acceptable limit of ≤100 (ppm). The highest values of Na were recorded in I2 (Agbada); 454.13±299.01 ppm and CU; 443.67±253.26 ppm (Table 3). The findings agree with those of Liu, Rong, and Zhao, 2017, where values of Na and EC were affected by land use practices (Liu et al., 2017). The mean level of K in soil were within the WHO acceptable limit of ≤100 (ppm). The highest values of K were recorded in CI; 13.21±6.29 ppm and U3 (Mguoba); 17.95±15.54 ppm (Table 3). There was insignificant variation in levels of K. This is in agreement with study by (Kihara et al., 2016). The variations can be attributed to land use practices, leaching and adsorption in soil (Kharal, Khanal, & Panday, 2018). The mean level of Ca in soil were within the WHO acceptable limit of ≤100 ppm. The highest values of Ca were recorded in C1; 48.43±30.30 ppm, CA; 34.32±19.65 ppm and U2; 43.41±41.79 ppm (Table 3). The mean level of Ni in soil was 0.7528± 0.07580 ppm which was within the WHO acceptable limit of ≤50 ppm. The highest value of Ni was recorded in U2 (Diobu); 1.11±0.37 ppm (Table 2). The mean level of Mg in soil was 11.87± 2.10 ppm which was within the WHO acceptable limit of ≤100 (ppm). The highest mean values of Mg were recorded in CA; 23.45±12.17 ppm, CU; 22.85±14.00 ppm and U2; 23.04±7.22 ppm (Table 3). The findings agree with findings of De Bauw et al., that Ca, Mg and Ni are varied in distribution and are affected by human and altitude differences (De Bauw, Van Asten, Jassogne, & Merckx, 2016). The mean level of Mn in soil was 4.21± 0.61 ppm which was within the WHO acceptable limit of ≤2,000 ppm. The highest values of Mn were recorded in CA; 8.76±3.62 ppm, A3; 7.50±3.76 ppm and U2; 7.50±3.28 ppm (Table 3). The findings are in agreement with findings of Hassan et al., 2017 which were within range. The findings can be attributed to land use practices as revealed with the current findings where urbanized, industrialized and agricultural areas recorded varied findings (Hassan et al., 2017).

Conclusion: This study examines the Human Influence on Soil Metals Status in parts of Rivers State, Nigeria. Levels of Pb, Fe, Cu, Cd, Zn, Ca, Ni, Na, K, Cr, Mg, Mn, and S were determined in soils. Some parameters; Pb, Cu, Cd, Zn, Ca, Ni, Na, K, Cr, Mg, Mn, and S recorded levels within permitted levels while some parameters; Zn and Pb recorded high levels above the permitted levels in I3 (Trans-Amadi). Cadmium (Cd) was recorded higher in industrialized areas as compared to urbanized and agricultural. Urban activities have highest influence in levels of Nickel in soil. The pollution of soils with metals in the studied sites is within permissible limits, however, levels of Zn, Cd and Ni should be on close monitoring to in the industrial areas and urbanized areas. The study establishes that petroleum activities variedly affect the levels of metal pollution in urbanized, industrialized and agricultural areas.

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