Geochemical Assessment of Heavy Metal Contamination in rural and urban wetlands in Akwa Ibom State, Nigeria

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Abstract: Nutrient and waste inputs into wetlands have dire consequences on both soil and water quality and by extension dependent aquatic flora and fauna. Within this purview, heavy metal contamination was assessed in a rural and urban wetland in Akwa Ibom State, Nigeria. Soil samples were analyzed for Pb, Zn, Fe, Ni and Cd using AAS. Results show marked variations of heavy metal concentrations within study area. Mean values of Fe (713.22 ± 59.39), Pb (5.95 ± 0.42), Zn (88.54 ± 8.03) and Cd (1.53 ± 0.65) were higher in the urban site while Ni (9.45 ± 1.56) was higher in the rural area. Heavy metal contamination status was assessed using four indices; enrichment factor, geo-accumulation index, contamination factor and degree of contamination. The calculated enrichment factor values for the studied metals in both wetland areas were significant for Zn and Pb. The same trend was also true for Geo-accumulation index values and contamination factor in the two wetland sites. Additionally, result for degree of contamination was high for both wetlands; urban (39.08) rural (33.71). Cluster analysis was employed to show the heavy metals source apportionment in the wetlands. The results of this study clearly show that presently, these wetlands are contaminated due to increased anthropogenic activities and as such, adequate measures should be put in place by relevant authorities to checkmate and regulate human activities around wetlands in order to protect them from further deterioration and contamination.

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1. Introduction

Heavy metal deposition and enrichment is of increasing global concern due to the awareness surrounding their detrimental effects on humans and the environment. Heavy metals according to Nies (1999) are elements with specific gravity greater than 5 g/cm^3. They are recognized as toxic pollutants all over the world from natural and anthropogenic sources. Due to increased population pressure, urbanization and industrialization, the emission and deposition of wastes rich in heavy metals have been on a geometric increase in our diverse ecosystems, particularly wetlands; which act as sinks for these metals. Currently, studies have shown that the anthropogenic inputs of heavy metals in our environment exceed the natural inputs and these sources include burning of fossil fuels, mining and smelting of metalliferous ores, municipal wastes, sewage, pesticides and fertilizers (Kabata-Pendias and Pendias, 1989).

Heavy metals accumulate more easily in wetlands as a result of changes in natural environment and dominating influence of anthropogenic activities (Mitsch and Gosselink, 2000). In wetlands, heavy metals exist mainly in water, in sediment and in plants. Their distribution cause changes among the different compartments of each system. The accumulations of heavy metals in wetlands have deleterious effect on human health, as wetlands are the important sources of food and water for human beings. Plants are essential components of wetland ecosystems and are sensitive to varying degrees of disturbances and alteration in their natural habitats. One of such is the influx of heavy metal pollutants generated and deposited directly or indirectly into ponds which pose a severe threat on species with no tolerance to heavy metal infiltrations. Also, their growth in terms of distribution may be affected at high toxicity levels. Plants respond differently to increasing concentrations of toxic metals in soil, depending on the sensitivity of plants' exposure intensity. Some species of plants may become extinct in such wetlands, some may show poor growth with low density and frequency while others, on the contrary, may be stimulated by these elements. In wetlands with high heavy metal infiltrations, most plant species (metalophytes) have developed tolerance towards metals, and others (hyperaccumulators) are characterized by the capacity to accumulate high quantities of metals in their tissues.

Waste discharge either from point or non-point sources is a menace associated with anthropogenic activities leading to the degradation and deterioration of wetlands. This by extension may affect the growth and diversity of plant species inhabiting such wetlands. Consequently, this study is designed to test the effects of anthropogeneity on contamination status of the ponds using certified ecological indices and to assess the influence of these contaminants (heavy metals) on plant distribution.

2. Materials and Methods

2.1. Study Area

This study was carried out in Mbak Akpan Ekpenyong (7º 59’ 9” E; 5º 0’ 7” N) and Udo Udoma (7° 55’ 19” E; 5° 0’ 35” N) wetlands in Uyo, Local Government Area of Akwa Ibom State, Nigeria (Figure 1). The topography of the rural wetland (Mbak Akpan Ekpenyong) is undulating with sparsely distributed homesteads and farmlands. In contrast, the topography of the urban wetland at Udo Udoma is sloppy with several infrastructural architecture and residential buildings that dominate the surrounding landscape. Akwa Ibom State is located in Southern Nigeria and is characterized by two distinct climate; dry and wet seasons. The annual rainfall varies from 4000mm along the coast to 2000mm inland. The average humidity is about 75% to 95%. Temperature values are relatively high in Akwa Ibom State throughout the year, with the mean annual temperatures varying between 26°C to 36°C (Akwa Ibom State Government, AKSG, 2008).

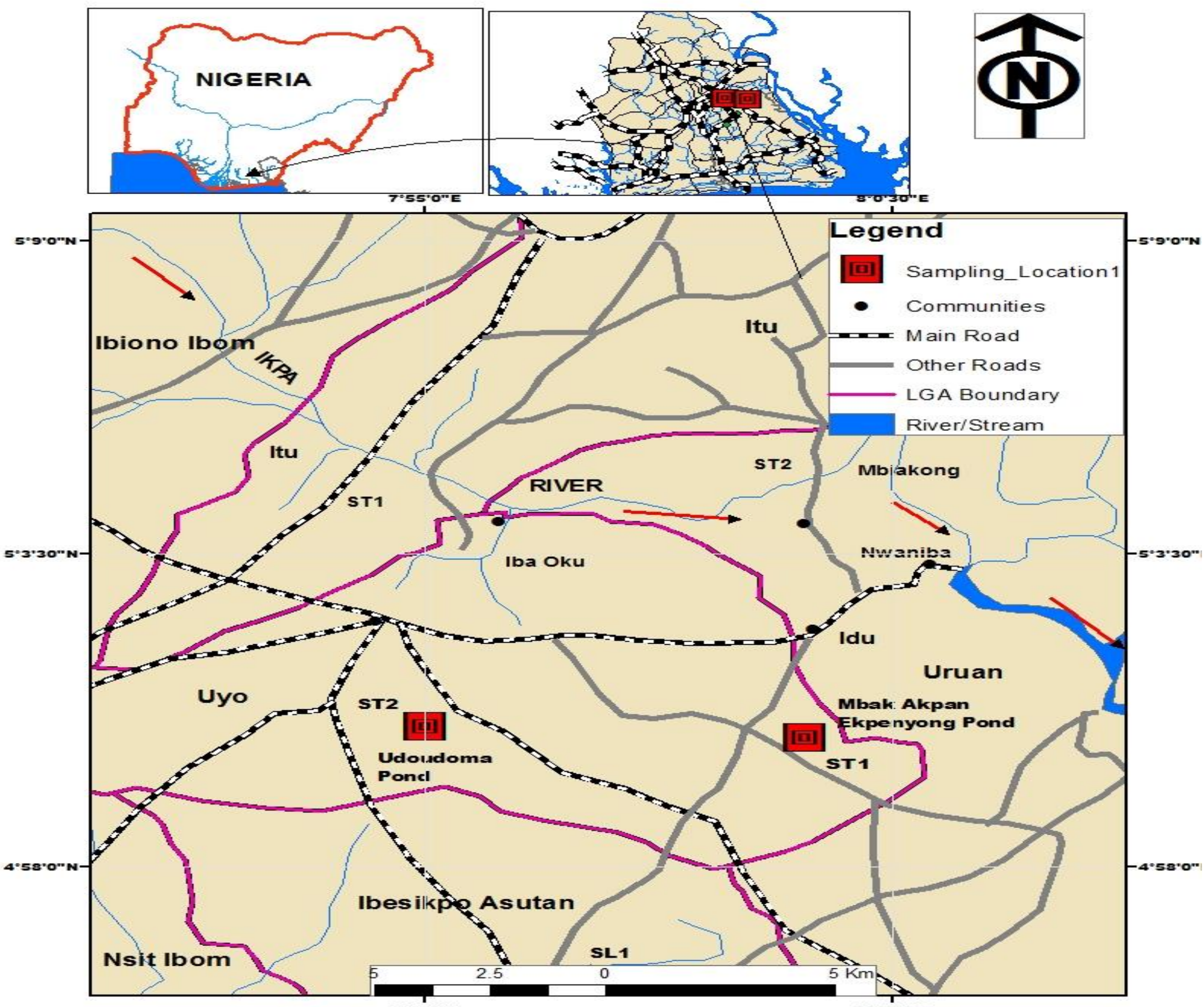

Figure 1: Map of the Study Area

2.2 Soil Sampling

Soil samples were collected from the study sites using a soil auger at two different depths (0 – 15 cm and 15 – 30 cm), stored and preserved in well labeled Ziploc bags for laboratory analyses.

2.3 Physicochemical Analysis of Heavy metals in Soil Samples

Samples were ground, mixed, and sieved using a 0.5mm sieve. Subsequently, soil samples were digested using 15 ml of concentrated nitric acid and perchloric acid at a ratio 1:1 to 2 g of soil and allowed to stand for 135 minutes until the mixture became colourless. The samples were filtered and washed with 15 ml of deionized water, and filtrate made up to 100 ml in a standard flask. Five heavy metals (Pb, Fe, Zn, Cd and Ni) were determined from the filtrate at their respective wavelengths using Unicam 939 Atomic Absorption Spectrophotometer (AAS).

2.4 Statistical Data Analysis

Mean and standard error were computed from triplicates of soil physico-chemical parameters using Statistical Package for Social Sciences (SPSS 20.0). Paleontological Statistics (PAST 3.0) was also employed for cluster multivariate analysis to show the heavy metals source apportionment in the wetlands.

2.4.1. Ecological Risk Assessments

2.4.1.1 Determination of Crustal Enrichment factors

To evaluate the magnitude of contaminants in the environment, the enrichment factors (EFs) were computed relative to the abundance of species in source material to that found in the Earth's crust and following equation was used to calculate the EFs as proposed by Sinex and Helz (1981).

$$EFs = (C_M/C_{X\ sample})/(C_M/C_{\times\ Earth's\ crust})$$

Where C_M is the content of metal studied and C_X is the content of immobile element. Immobile elements may be Al or Fe (Chatterjee *et al*., 2007). The choice of iron is due to the fact that it is an immobile element due to its natural sources (1.5% vastly dominate its input) (Tippie, 1984). In this study, iron was used as a conservative tracer to differentiate natural from anthropogenic components. Also, the background concentrations (the reference Earth's crust values) of Fe, Ni, Pb, Zn and Cd were taken from a control site situated 30m away from the study sites. The average reference values of Fe, Ni, Pb, Zn and Cd were 216.3 mg/kg, 3.1 mg/kg, 0.32 mg/kg, 6.8 mg/kg and 1.04 mg/kg respectively.

Five contamination categories are recognized on the basis of the enrichment factor (Sutherland, 2000) namely; EF (<2: deficiency to minimal enrichment; 2 – 5: moderate enrichment; 5 -20: significant enrichment; 20 – 40: very high enrichment; > 40: extremely high enrichment).

2.4.1.2 Determination of Geo-accumulation Index

The geo-accumulation index (Igeo) formula calculated for different metals as introduced by Muller (1969) is as follows:

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5 \times B_n}\right)$$

Where, Cn is the measured concentration of element n in the sediment and Bn is the geochemical background for the element n which was taken from a controlled site. The factor 1.5 is introduced to include possible variations of the background matrix correction factor due to lithogenic variations. Muller (1969) proposed seven grades or classes of the geo-accumulation index as follows: I_{geo} (0: unpolluted; 0 – 1: Unpolluted to moderately polluted; 1 – 2: Moderately polluted; 2 – 3: moderately polluted to highly polluted; 3 – 4: highly polluted; 4 – 5: highly to very highly polluted; > 5: very highly polluted).

2.4.1.3 Determination of Contamination factor and Degree of Contamination

The assessment of soil contamination was also carried out using the contamination factor and degree of contamination. The contamination factor was calculated using the formula provided by Hakanson (1980) as follows:

$$CF = \frac{Cmetal}{Cbackground\ value}$$

Where Cmetal is the total metal concentration and Cbackground represent the average reference value of the element in sediment. The values obtained in the control site were used as background values (Fe = 216.3mg/kg, Ni =3.1 mg/kg, Pb = 0.32 mg/kg, Zn = 6.8 mg/kg and Cd = 1.04 mg/kg).

Hakanson, (1980) classified the degree of soil contamination as indicated by contamination factor (CF) as follows: CF (< 1: low contamination; 1 ≥ CF ≥ 3: moderate contamination; 3 ≥ CF ≥ 6: considerable contamination; CF > 6: Very high contamination).

The sum of the contamination factors of all elements examined represents the contamination degree of the environment. Four classes are recognized according to Hakanson (1980) as follows C_d<6: low contamination degree, 6≤ C_d <12: moderate contamination degree; 12≤C_d<24: considerable contamination degree; C_d ≥ 24: very high contamination degree.

3. Results

3.1 Soil Heavy Metal Contents in Rural and Urban wetlands

The heavy metal contents in soils of the two wetlands as shown in Table 1 reveals that Fe (713.22 ± 59.39), Pb (5.95 ± 0.42), Zn (88.54 ± 8.03) and Cd (1.53 ± 0.65) were higher in values in the urban wetland while Ni (9.45 ± 1.56) value was higher in the rural wetland.

Table 1: Mean (±S.E) Heavy metal contents of soil in rural and urban wetlands

Heavy metals	Rural wetland	Urban wetland	WHO, 2008	*FME LIMIT, 1998
Fe (mg/kg)	663.65 ± 69.81	713.22 ± 59.39	0.3	20
Ni (mg/kg)	9.45 ± 1.56	8.41 ± 1.57	0.5	0.1
Pb (mg/kg)	4.73 ± 0.20	5.95 ± 0.42	0.05	0.05
Zn (mg/kg)	80.23 ± 3.57	88.54 ± 8.03	5.0	< 1
Cd (mg/kg)	1.06 ± 0.16	1.53 ± 0.65	0.005	0.01

***** FME (Federal Ministry of Environment)

3.2 Heavy Metals Contamination Factors

a) Enrichment Factors

The enrichment values of the study areas are shown in Table 2. The enrichment factors in the rural wetland followed this order: Pb (4.82) > Zn (3.85) > Ni (0.99) > Cd (0.33). In the urban wetland, the enrichment factor values followed this sequence: Pb (5.64) > Zn (3.95) > Ni (0.82) > Cd (0.45). Pb and Cd had the highest and lowest enrichment factors respectively in the two sites. On the basis of enrichment factor, the wetland soils is classified as being minimally enriched with Ni and Cd and moderately enriched with Zn. The soil was moderately enriched and significantly enriched with Pb in the rural and urban wetlands, respectively.

Table 2: Soil enrichment factors in the study wetlands

Heavy metals	Rural wetland	Urban wetland
Ni	0.99	0.82
Pb	4.82	5.64
Zn	3.85	3.95
Cd	0.33	0.45

b) Geo-accumulation Index (I-geo)

The calculated I-geo values for toxic metals of soils collected from the rural and urban wetlands are illustrated in Table 3. In the rural wetland, the I_{geo} values followed this order: Pb (3.30) > Zn (2.98) > Fe (1.04) > Ni (1.02) > Cd (-0.56) while in the urban wetland the sequence of accumulation were as follows: Pb (3.63) > Zn (3.12) > Fe (1.14) > Ni (0.86) > Cd (-0.03). Generally, Pb and Cd had the highest and lowest I-geo index values for both rural and urban wetlands. Based on the geo-accumulation index, the wetland soil is classified to be moderately polluted with Fe, unpolluted to moderately polluted with Ni, highly polluted with Pb and moderately polluted to highly polluted with Zn. Negative values observed for Cd is a result of deficient to minimal enrichment and/or relatively low levels of contamination.

Table 3: Soil Geo-accumulation indices of heavy metals in rural and urban wetlands

Heavy metals	Rural wetland	Urban wetland
Fe	1.04	1.14
Ni	1.02	0.86
Pb	3.30	3.63
Zn	2.98	3.12
Cd	-0.56	-0.03

c) Contamination Factor and Degree of Contamination

From Table 4, Pb had high contamination values of 18.59 and 14.78 in urban and rural wetlands. This was closely followed by Zn with values ranging from 11.79 to 13.02. Cadmium had the least contamination factor values of 1.02 in the rural wetland and 1.47 in the urban wetland. The contamination factors in the study sites in decreasing order followed a similar trend; Pb> Zn >Fe >Ni > Cd. Based on the rating of the contamination intensity, these wetland soils are classified as being considerably contaminated with Fe and Ni, moderately contaminated with Cd and highly contaminated with Pb and Zn. From the degree of contamination, urban wetland had a higher value (39.08) than the rural wetland (33.71). Based on the classification, the values obtained for the degree of contamination in both wetlands were greater than 24 (>24) and this is a reflection of a very high contamination degree.

Table 4: Contamination factors and degree of contamination of heavy metals in the study wetlands

Heavy metals	Rural wetland	Urban wetland
Fe	3.07	3.29
Ni	3.05	2.71
Pb	14.78	18.59
Zn	11.79	13.02
Cd	1.02	1.47
Contamination degree (C_d)	33.71	39.08

3.3 Cluster Analysis

Cluster multivariate analysis shows the heavy metal source apportionments in the rural and urban wetlands, respectively (Figures 2 and 3). From the dendrograms, three cluster groups were identified based on the various sources of heavy metals in both wetlands. They were; crustal or geogenic source (Fe), anthropogenic sources (Zn) and intermediate or combined sources (Cd, Pb and Ni).

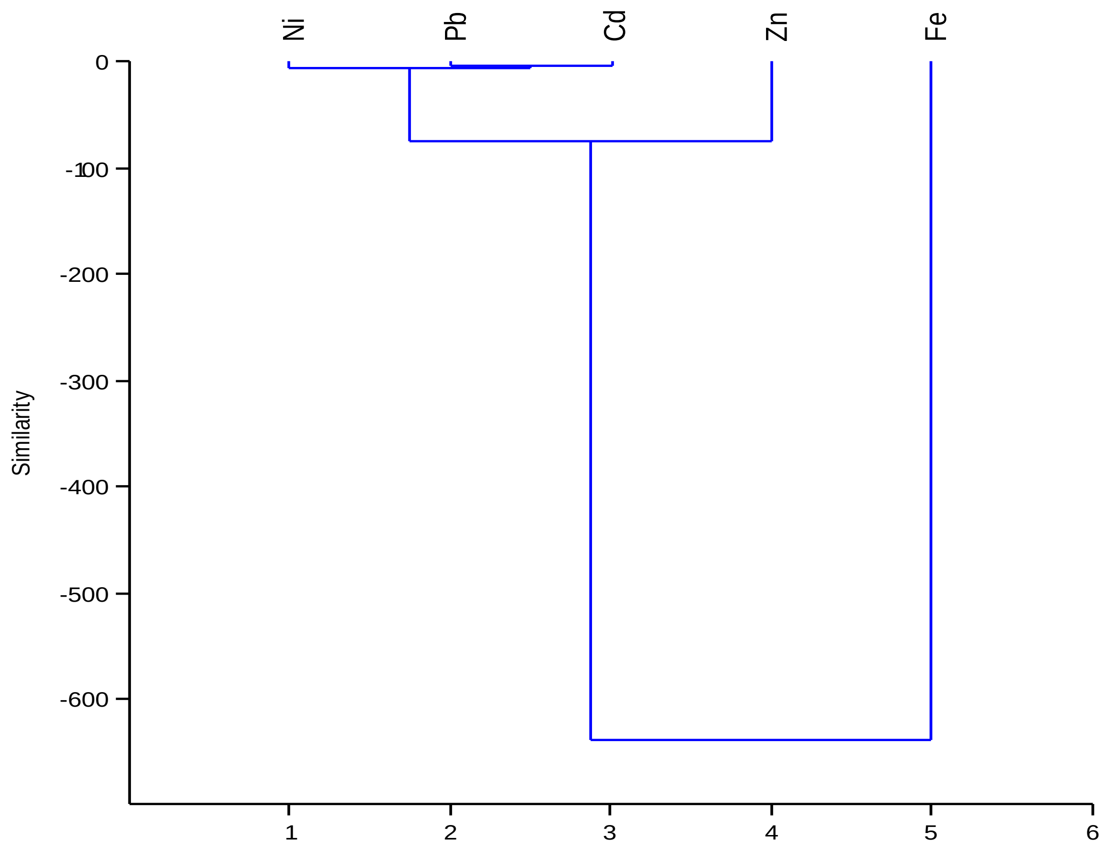

Figure 2: Cluster dendrogram showing heavy metal source apportionment in the rural wetland

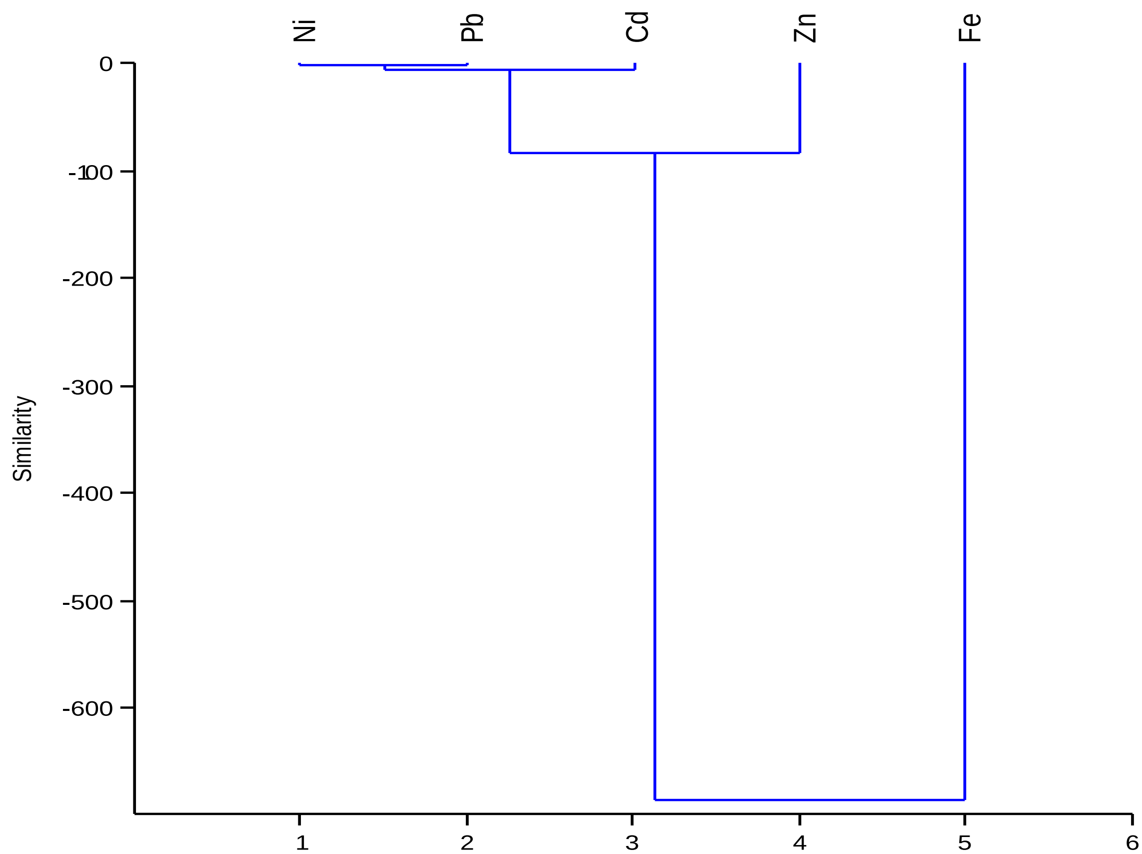

Figure 3: Cluster dendrogram showing heavy metal source apportionment in the urban wetland

4. Discussion

Variations were observed in the levels of heavy metal accumulation in both wetlands. The urban wetland had high levels of heavy metal contaminants such as Fe, Pb, Zn and Cd while the rural wetland recorded a high value for Ni only. The high levels of these contaminants in the urban wetland may be attributed to the severity of anthropogenic perturbations including; deposition of household and municipal wastes, infrastructural encroachment, construction and demolition activities, runoff of road salts and dust and emissions from automobile exhaust fumes, industrial plants and power generation plants mostly prevalent in urban and satellite towns (Udueze, 2004; Al-Khashman, 2007; Thorpe and Harrison, 2008). These scholars recognized improper and indiscriminate waste disposal practices as one of the major sources of anthropogenic pollution/contamination in wetland ecosystems. Also, Ihenyen and Aghimien (2002) enunciated on the effect of human and land use wastes on both urban and rural wetlands. They highlighted the issue of heavy metal contamination and loss in natural ecosystem.

From the calculated indices, the wetland soils tested were mostly enriched and contaminated with Pb, Zn, Ni and Fe. The high enrichment of heavy metals may be a possible indication of human-induced contamination in this wetlands as indicated by the cluster dendrogram, which grouped these metal into same source apportionment (anthropogenic sources). In addition, the low levels of these contaminants in the rural wetland when compared with the urban wetland may be a possible reflection of less anthropogenic incursions within the area. High levels of iron (Fe) in the study area soils may be attributed to its lithogenic or geogenic origin rather than of anthropogenic source (Kumar *et al*., 2017). Cd showed relatively low levels of contamination which may be allied to less human activities emitting and depositing this biological nuisance into the wetlands (Ita, 2017; Mbong *et al*., 2013). Pb and Zn were the most abundant and dominant contaminants in the both wetlands. This portends serious health dangers both for humans and other aquatic organisms dependent on these wetlands. High levels of Pb within any ecosystems predisposes humans to cancers and other related genetic deformation (Baldwin and Marshall, 1999). The high levels of Ni observed in the rural wetland may be attributed to high deposition of solid wastes and domestic cleaning products in the area. This corroborates with the findings of Alloway (1995) where the scholar reported that domestic cleaning products ranging from soap (100 – 700 mg/kg), powdered detergents (400 – 700 mg/kg) and powdered bleach (800 mg/kg) may prove to be important sources of Ni in soils. A very high degree of contamination observed in both wetland soils with the urban wetland recording higher values than the rural wetland may be a function of intense environmental stress and other human-related activities in these wetlands. This further highlights that these ecosystems currently, is devoid of good management and conservational practices from humans.

5 Conclusion

The study shows that human activities around wetlands pose a serious threat to their sustenance and conservation. Apart from destroying and utilizing them for infrastructural development, they are also used as dumpsites for wastes of various forms which leads to the release and accumulation of toxic metals in the soil. Investigation of the soil heavy metal contents showed variations in both wetlands due to different intensities of anthropogenic activities. From this study, high values of Pb, Zn, Fe, and Cd were recorded in the urban wetland except Ni which was high in the rural wetland. Indices such as enrichment factor, geo-accumulation index and contamination factor revealed widespread pollution by Pb and Zn. These were followed by Fe, Ni and Cd. The urban wetland had a higher degree of contamination than the rural wetland. Generally, the degree of contamination of these metals in both wetlands showed a very high contamination. Conclusively, the information obtained shows that the distribution of metal concentrations in the study areas emanate mostly from anthropogenic perturbations and proper environmental monitoring should be put in place by government and other environmental protection agencies to safeguard the integrity of wetlands within the state.

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