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Chemical Forms of Heavy Metals in Selected Wetland Soils of Akwa Ibom State, Nigeria

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ABSTRACT

Heavy metals normally occur in nature and are essential to life but can become toxic through accumulation in organisms. Against this background, a study was conducted to assess the chemical forms of heavy metals in two wetland soil types; the Inland Depression (IDP) and River Flood Plain (RFP). The objectives were to determine the total and chemical forms of copper and lead in the water soluble, exchangeable, organically bound, manganese oxide, amorphous iron oxide, crystalline iron oxide and the residual fractions and correlate the metal fractions with selected soil properties. Soil properties were determined from soils collected at depths of 0-45 cm. A total of forty-two soil samples (21 from each wetland soil types) were collected after the rainy season using soil auger. Data obtained were analyzed. Results indicated that total Cu and Pb obtained by soil digestion were higher than those obtained as sum of fractions in the two wetlands. Copper and lead fractions were predominant in the residual phase. The acidic nature of the soils restricted their association with the water soluble and exchangeable fractions. The correlations between physicochemical parameters and metals fractions of soils did not show a consistent relationship. It is concluded that the metals under study did not pose any environmental risks.

Keywords: Chemical forms, heavy metals, wetlands, soils.

INTRODUCTION

Akwa Ibom State is naturally endowed with both the coastal and inland wetlands ecosystem which constitutes a critical part of its environment. The total area occupied by wetlands in the state is about 31.6 % or 2219 km² of the entire land mass (DVH Consultant, 1995), while the total wetland area in Nigeria is estimated to be about 2,996,150 hectares or 7.6 % of its total landmass, out of which

858.00 hectares are mangrove swamps while flood plains occupy 2,138.150 hectares (Egbucha and Enejeke, 2013). Wetlands are often very difficult to define; it means different things to different people. However, depending on scientific discipline and ecosystems, soils saturated with water are often called flood, wetland, water logged, marsh or hydric soils (Ogban *et al.*, 2011).

Since wetlands are generally transitional zones between terrestrial landforms and water bodies, they have some of the features of both resembling aquatic ecosystem because of the dominant role of water in the system. Again, because of their relative position in the landscape, wetlands are usually the sink and recipient of nutrients and contaminants including heavy metals through surface or ground water flow (Udoh *et al.*, 2016) and industrial effluent. Heavy metals are elements that occur naturally in the earth's crust and required by plants in small amount for their bio-chemical activities. They are associated with various soil components in different ways and these associations determine their mobility and availability (Adam *et al.*, 2016). Exchangeable and water soluble are considered readily mobile and available to plants while metals bound to mineral matrix or incorporated into crystalline affixes of clays is mainly not available to plant or microorganisms (Alvarez *et al.*, 2006). Other forms like Mn-Fe oxide or organically bound may be potentially available. Knowledge of different fractions of heavy metal is necessary to understand the chemistry of heavy metals in soils as it enables us to know about plant availability, its binding forms, dynamics and impact on soil environment. Most of the researches on heavy metals in the studied area

remained confined to the determination of total heavy metals which may not provide information about the exact dimension of pollution. In view of the above, this research was conducted to assess the chemical forms of heavy metals and relate them with bio-availability.

MATERIALS AND METHOD

The Study Area

Akwa Ibom State is located in the South-Eastern Nigeria and lies between latitude 4.5° and 5.5°N and longitudes 7.5° and 8.7°E (SLUSS –AK, 1989). Soil samples at the depth of 0-45 cm were collected after the rainy season using soil auger at 7 locations per wetlands. In each location, soil samples were collected from three points and bulked to form a composite sample, making 21 samples per wetland soil type (Figure 1). The distance from one sampling point to another was approximately 80 meters long. A total of 42 soil samples were obtained for the study. The details about the sample locations, parent materials, vegetation and land use are given on Table 1. The soils were dried, grounded and passed through a 2 mm sieve and then stored in a prelabeled bag and used for the physicochemical and heavy metal determination.

Table 1: Summary of Study Location, Parent Materials and Land Use

Wetland Soil	Sample locations (Lat. and Long.)	Parent Materials	Vegetation/ Land Use
River Flood Plain	Idu – (5° 1' 38.408" N, 8° 1' 3.877" E)	Coastal plain sands	Farm land
	Adadia – (4° 58' 18.955" N, 8° 3' 32.561" E)	Coastal plain sands	Farm land
	Ayadehe – (5° 9' 58.677" N, 8° 2' 39.689" E)	Coastal plain sands	Farm land
	Oron – (4° 47' 27.547" N, 8° 14' 5.208" E)	Coastal plain sands	Fallow
	Ekeya – (4° 52' 59.740" N, 8° 8' 49.950" E)	Alluvial deposits	Farm land
	Nkara – (5° 22' 57.837" N, 7° 50' 15.130" E)	Sand stone	Farm land
	Ukat Aran – (4° 44' 12.520" N, 7° 58' 4.649" E)	Coastal plain sands	Farm land
Inland Depression	Akai – (4° 42' 17.220" N, 8° 0' 26.483" E)	Coastal plain sands	Farm land
	Nung Obong – (4° 41' 46.053" N, 7° 50' 15.130" E)	Alluvial deposits	Fallow
	Ukam – (4° 39' 55.778" N, 7° 46' 57.784" E)	Coastal plain sands	Farm land
	Obio Akpa – (4° 53' 24.327" N, 7° 42' 4.207" E)	Coastal plain sands	Farm land
	Edem Idim Okpot – (4° 42' 14.718" N, 7° 56' 3.709" E)	Coastal plain sands	Farm land
	Iwok – (4° 47' 4.183" N, 8° 2' 44.313" E)	Coastal plain sands	Farm land
	Ikot obio Inyang – (4° 45' 41.142" N, 7° 51' 39.469" E)	Coastal plain sands	Farm land

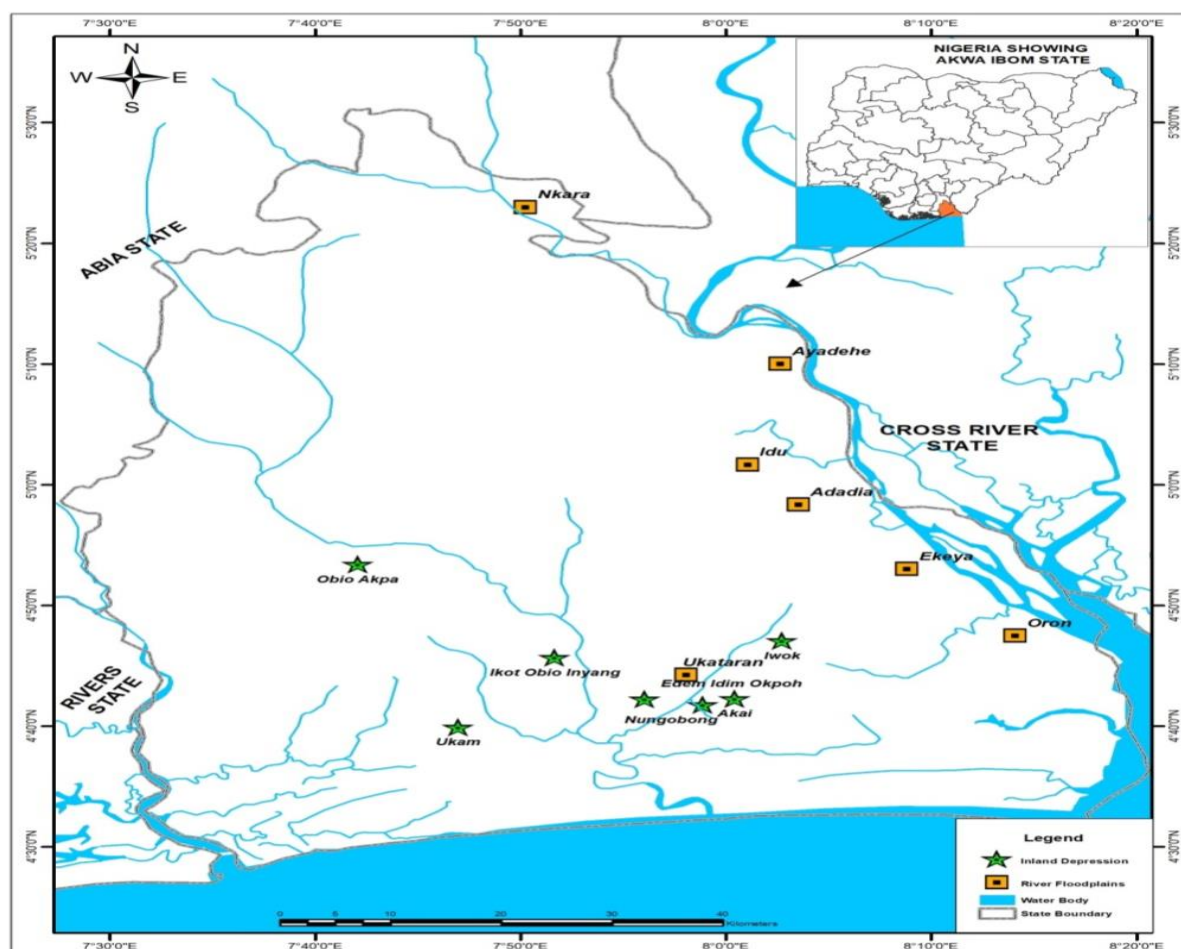


Figure 1: Map of the Study Area Showing Sampling Locations

Source: UNIUYO-GIS (2025).

Soil Analysis

The soils were analyzed for the physicochemical properties following a standard analytical method. Soil pH in H₂O was measured in a 1:2.5 soil to water ratio using a digital pH meter (Udo *et al.*, 2009). Electrical conductivity was measured using electrical conductivity bridge (Rhaodes, 1982). Organic carbon was measured by dichromate wet oxidation method of Walkey-Black (Nelson and Sommers, 1996). Available phosphorus (P) was extracted with Bray P-1 method as described by Udo *et al.*, (2009). Effective Cation Exchange Capacity (ECEC) and percentage base saturation were obtained by calculation (IITA, 1982).

Determination of Total Forms of Heavy Metals

Digestion of soil samples for total heavy metals was carried out with the mixture of concentrated HNO₃, HF and HCl at a ratio of 1:8:5 (Shuman, 1979).

Chemical Fractionation of Heavy Metals

Chemical fractionation of Cu and Pb in soil samples followed the procedures of Shuman (1979; 1983, 1985) to partition metals into the following geochemical phases:

F1. Water Soluble Fraction: Using deionized water at 1:5 soil/water ratios shaken for 2 hours, the process is repeated three times and combined (Shuman, 1985).

F2. Exchangeable Fraction: 1 MMg(NO₃)₂ solution adjusted to pH.7 was used for exchangeable ions. The solution was purified before use by passing it through a chelex 100 column (Shuman, 1983; 1985). Ten grams of the air-dried 2 mm soil was placed in a 250 ml polypropylene centrifuge bottles and 40 ml of a molar magnesium nitrate solution added and shaken for 2 hours.

F3. Organically Bound Fraction: The residues from F₂ were extracted with 0.7 MNaOCl adjusted to pH 8.5 (Shuman, 1985).

An aliquot was evaporated to dryness, and residues taken up to 1 M HNO_3 .

F4. Mn Oxide Fraction: One gram of soil was shaken for 30 min. in 50 ml of 0.1 M NH_2OH . HCl solution adjusted to pH.2 and placed on a reciprocating shaker (Shuman 1985).

F5. Amorphous Fe Oxides Fraction: One gram of soil was shaken for 4 hrs. in the dark in a mixture of 0.2 M $(\text{MH}_4)_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and 0.2 M $\text{H}_2\text{C}_2\text{O}_4$, adjusted to pH.3. It was then centrifuged and supernatant filtered, a 5 ml aliquot was evaporated to dryness on a steam bath and ignited in a muffle furnace for 4 hrs. at 450°C . The residues were dissolved in 1 M HNO_3 and taken to volume, after being transferred quantitatively to a 25 ml volumetric flask (Shuman 1985).

F6. Crystalline Fe Oxides Fraction: One gram of soil in 50 ml solution (as for step F₅) plus 0.1 M ascorbic acid was stirred occasionally on a boiling water bath for 30 mins. Aliquots of extracts from steps F₄, F₅ and F₆ were evaporated, ignited and taken up in 1 M HNO_3 for analysis (Shuman, 1979).

F7. Residual Fraction: Eight grams of the residues from F₃ were digested with a mixture of concentrated hydro fluoric, nitric and perchloric acids (Shuman, 1979; 1985).

Instrumentation

All extracts and digestion solutions were analyzed for Cu and Pb by Atomic Absorption Spectrophotometer (AAS); UNICAM 939 model.

Statistical Analysis

The data obtained were summarized and interpreted using simple descriptive statistical methods to obtain minimum, maximum, mean, range, standard deviation and coefficient of variation (Ndem, 2005). Pearson's correlation coefficient was also used to assess the relationship between heavy metals fractions and some soil properties.

RESULTS AND DISCUSSION

Physicochemical Properties of the Studied Soils

Results of the physicochemical properties of soils are presented on Table 2. The proportion of sand, silt and clay in the soil

ranged from 696.30 – 889.50; 725.60 – 931.4 gkg^{-1} with mean values of 794.50 and 819.70 sand, 26.03 – 198.10 and 23.50 – 120.00 gkg^{-1} with mean values of 74.85 and 60.40 silt and 65.00 – 193.00 and 42.30 – 141.30 gkg^{-1} with mean values of 130.62 and 180.50 gkg^{-1} clay for the river flood plain and the inland depression soils respectively. Texturally, the soils were on the average sandy loam in texture. The high proportion of sand in the inland depression was due to low gradient which allows tidal waters to remain in the soil for long periods. The values of pH of the studied soil were low and varied from moderately to slightly acidic with pH in water ranging from 4.8 – 6.3 and 4.5 – 6.6 with mean values of 5.21 and 5.79 for the river flood plain and inland depression respectively. Also, the pH in 1M KCl were very acidic and ranged from 4.1 – 5.0 to 4.6 – 5.0 with means of 4.96 and 4.61 for the RFP and IDP respectively lower than those measured in water suspension, indicating that all soils at their natural pH are negatively charged. However, the overall pH of the soil is within the normal soil pH of the region. Exchange acidity values were moderate to high for the RFP (0.01-5.1 cmolkg^{-1}) and IDP (0.08 – 2.26 cmolkg^{-1}) with means of 2.21 and 1.13 cmolkg^{-1} respectively. The high exchange acidity found in the river flood plain could be attributed to the flood water; this is because flooding affect exchange acidity and reflects low pH of the soil which may have indirect negative effects on the soil fertility. The electrical conductivity recorded in this study was generally low and ranged from 0.02 to 0.04 and 0.001 to 0.110 with mean values of 0.026 and 0.014 dSm^{-1} respectively, for the RFP and IDP. High rainfall distribution may likely contribute to these low values. The two wetland soils had substantial amount of organic carbon and ranged from 4.22 to 10.6 and 5.13 to 18.52 with mean values of 16.24 and 16.86 gkg^{-1} for the RFP and IDP respectively. Total nitrogen content of the soil was very low and ranged from 0.06 to 0.80 with a mean values of 0.33 gkg^{-1} for the RFP and 0.25 gkg^{-1} for the IDP. Nitrogen is lost from water logged

soils by leaching and denitrification. Available phosphorus in the studied soils was high and varied widely in the two wetland soils ranging from 18.23 to 32.5 and 8.12 to 21.0 with mean values of 27.36 and 28.91 mgkg^{-1} for the RFP and IDP respectively. The relatively high available phosphorus in these soils could be attributed to the variation in biotic and abiotic factors such as pH and organic matter content of the soils responsible for the retention and release of P among the two wetland types. The mean values of total exchangeable bases ranged from 0.04 to 2.29 cmolkg^{-1} with Ca constituting 1.30 and 2.29; Mg 1.16 and 1.60; K 0.06 and 0.10 and Na 0.04 and 0.04 for the RFP and IDP respectively. The findings agreed with the reports of Essoka and Esu

(2004) who observed a high Mg content in soils of inland depressions of Central Cross River State, Nigeria. The ECEC values were rated low and ranged from 1.94 to 8.09 with a mean of 4.81 for the RFP and IDP ranging from 1.82 to 13.76 with a mean of 5.84 cmolkg^{-1} . The low CEC in the soil indicates the low nutrient reserve due to their low clay content and coarse textured nature of the soil. The degree of base saturation varied among the studied soil with values ranging from 22.02 to 99.63 and 52.01 to 98.99 with mean values of 55.1 and 77.80 % for the RFP and IDP respectively. According to Tabi *et al.*, (2012), the high base saturation of the studied soils could be attributed to the recent alluvium deposits that enriched the soil with exchangeable bases.

Table 2: Summary of the Physicochemical Properties of the Stud Area

Variables	River Flood Plain (RFP)		Inland Depression (IDP)	
	Range	Mean	Range	Mean
pH (H_2O)	4.8-6.3	5.21	4.5-6.6	5.79
pH (KCl)	4.1-5.0	4.96	4.6-5.0	4.61
EC_{20} (dSM^{-1})	0.02-0.04	0.026	0.001-0.110	0.014
Organic C (gkg^{-1})	4.22-10.6	16.24	5.13-18.52	16.86
Total N (gkg^{-1})	0.06-0.8	0.33	0.01-0.73	0.25
Available P (mgkg^{-1})	18.23-32.5	27.36	8.12-21.0	28.91
Exchangeable Bases:				
Ca (cmolkg^{-1})	0.2-3.10	1.30	0.46-11.51	2.98
Mg (cmolkg^{-1})	0.21-4.00	1.16	0.4-4.13	1.60
K (cmolkg^{-1})	0.05-0.08	0.06	0.02-0.9	0.10
Na (cmolkg^{-1})	0.04-0.06	0.04	0.02-0.07	0.04
Exchange acidity (cmolkg^{-1})	0.01-5.10	2.21	0.08-2.26	1.13
ECEC (cmolkg^{-1})	1.94-8.09	4.81	1.82-13.76	5.84
Percent base saturation (%)	22.02-99.63	55.1	52.01-98.99	77.86
Particle Size Distribution (gkg^{-1})				
Sand	696.30-889.50	794.50	725.60-931.40	819.70
Silt	26.03-198.10	74.85	23.50-120.00	60.40
Clay	65.00-193.00	130.62	42.30-141.30	180.50
Texture	Sandy loam		Sandy loam	

Total Forms of Heavy Metals in Soils of the Study Area

The result of soil total heavy metals is given on Table 3. The order of total metal content in the soil by the soil digestion method was

as follows: $\text{Cu} > \text{Pb}$ in both soils. The reverse was the case for the total metal obtained as sum of fractions where Cu was found to be higher than Pb only in the river flood plain. However, less Cu was obtained than Pb in the inland depressions. The low values

obtained by fractionation could indicate that losses during the process, e. g. in the washing were very high. It also indicates reabsorption problem that minimizes the results in the first steps of the fractionation procedure and

possibly over estimates them in the last (Shuman, 1985). This problem may be responsible for the high contents of elements in the residual fraction.

Table 3: Total Copper (Cu) and Lead (Pb) as Sum of Fractions (Sof) and Soil Digestion (Sod) of the Sampled Soils

Cu		River Flood Plain		Pb	
	SO _F	SOD	SO _F	SOD	
Range	15.72 – 32.26	31.41 – 68.89	16.75 – 30.49	21.43 – 43.55	
x±std	24.70±4.20	47.76±13.18	24.61±3.52	32.67±5.11	
CV (%)	17.03	27.6	14.34	15.63	
		Inland Depression			
Range	17.37 – 41.54	32.70 – 69.63	23.61 – 35.14	21.05 – 48.01	
x±std	28.43±6.37	50.33±10.50	28.56±3.21	35.76±6.98	
CV (%)	22.42	20.86	11.25	19.51	

Key: CV = Coefficient of variation, <15% = least varied, 15 – 35% = moderately varied, >35 = highly varied.

Copper Fractions

Results of copper fractionation are presented on Table 4. Copper was predominantly associated with the residual fraction in the RFP and IDP and ranged from 10.26 to 21.24 mgkg⁻¹ and 11.84 to 22.48 mgkg⁻¹ with mean values of 15.72 and 17.13 mgkg⁻¹ respectively. Cu were also found to be higher in the organically bound, Mn oxide, amorphous Fe oxide and crystalline Fe oxide fractions and ranged from 0.01 to 6.52 mgkg⁻¹, 0.26 to 11.56 mgkg⁻¹, 0.20 to 6.42 mgkg⁻¹ and 0.80 to 11.16 mgkg⁻¹ with mean values of 1.93, 3.52, 2.44 and 3.30 mgkg⁻¹ for the IDP than the RFP ranging from 0.03 to 3.10 mgkg⁻¹, 0.78 to 11.41 mgkg⁻¹, 0.22 to 10.31 mgkg⁻¹ and 0.19 to 6.06 mgkg⁻¹ with means of 1.40, 3.44, 2.34 and 2.03 mgkg⁻¹. Water soluble fraction was low in the studied soil and ranged from 0.01 to 0.02 mgkg⁻¹ and 0.01 to 0.03 mgkg⁻¹ with mean values of 0.03 and 0.01 mgkg⁻¹ for the RFP and IDP respectively. Similarly, exchangeable fraction was also low and ranged from 0.01 to 0.41 and 0.01 to 0.26 with mean values of 0.02 and 0.07 for the RFP and IDP respectively. The mean values in all fractions were above the critical available levels of 0.2 mgkg⁻¹ Cu for DTPA (Lindsay and Norvell, 1978) with the exception of water soluble and exchangeable Cu fractions that falls

within the critical range. The soils could therefore be regarded as being low in available Cu. The values of Cu fractions in this study disagreed with those of Udo *et al.*, (1979) on soils developed on sedimentary rocks (0.32 – 1.06 mgkg⁻¹) and Cu in Nigerian soils in general (Osiname *et al.*, 1973). Copper is reported to possess low mobility in the weathering zone due to low solubility (Chesworth, 1991). Patrick and Pardue (1997) found a very small amount of Cu under acid reducing conditions that are water soluble. They explain this to be very likely tied up with soluble organic matter that is present under anaerobic and not present in aerobic conditions. Shuman (1985) observed low Cu in exchangeable and Mn oxide fractions. The very low Cu found in water soluble form suggests that the metal may occur in chelated form (Stevenson and Cole, 1999) and this could signify a low availability of the metal to crop plant. Alva *et al.*, (2000) extracted the highest Cu level from precipitate forms. Parkpian (2012) found Cu predominantly in crystalline fractions which are not different from the findings in this study. Other studies have indicated Copper as being associated with organic fraction (Miller and Mcfee, 1998 and Shuman, 1985). Shuman (1985) reported 1.6 – 68.6 % Cu in organically bound form in 10

representative soils in the South Eastern United States. In this study, the major Cu content was found in the residual fraction in the studied soils as opposed to organically bound. The association of copper in the organically bound fraction may undoubtedly reflect the greater mineralization and younger geological age of the area. After the decomposition of organic residue, the soil Cu levels tend to decrease. On the average, the

orders of magnitude for copper fractions were as follows: residual > Mn oxide > amorphous Fe oxide > Crystalline Fe oxide > organically bound > exchangeable > water soluble for the IDP and Residual > Mn oxide > amorphous Fe oxide > crystalline Fe oxide > organically bound > water soluble > exchangeable for the RFP.

Table 4: Mean Values (Mgkg⁻¹) of Copper in the Various Soil Fractions of the Two Wetland Soil Types

Soil	Water Soluble	Exchangeable	Organically Bound	Mn oxide	Amorphous Fe oxide	Crystalline Fe oxide	Residual
River Flood Plain							
Range	0.01-0.02	0.01-0.41	0.03-3.10	0.78-11.41	0.22-10.31	0.19-6.06	10.26-21.24
Mean	0.03±0.05	0.02±0.08	1.40±0.90	3.44±2.26	2.34±2.14	2.03±1.43	15.72±2.86
Inland Depression							
Range	0.01-0.03	0.01-0.26	0.01-6.52	0.26-11.56	0.20-6.42	0.80-11.16	11.84-22.48
Mean	0.01±0.00	0.07±0.09	1.93±1.36	3.52±2.35	2.44±1.88	3.30±2.34	17.13±3.09

Results of lead fractionation are presented on Table 5. Lead was also predominant in the residual fraction of the two wetland soils, and ranged from 12.54 to 21.46 mgkg⁻¹ and 15.17 to 24.04 mgkg⁻¹ with means of 18.33 and 20.21 mgkg⁻¹ for the RFP and IDP respectively, thus the residual fraction has been shown to be an important phase in regulating Pb availability. Water soluble and exchangeable Pb levels were typically low ranging from 0.01 to 0.10 mgkg⁻¹, 0.02 to 2.16 mgkg⁻¹, 0.01 to 4.35 mgkg⁻¹ and 0.35 to 4.90 mgkg⁻¹ with means of 0.07, 0.75, 1.32 and 1.83 respectively in both soils and only traces amount was associated with all other fractions. Exchangeable fractions are released into soil solution of low pH. This fraction represents heavy metal soluble in water as well as those held by electrostatic adsorption (Baranowski *et al*, 2002), the low levels of lead in this fraction further suggest low contaminations risk and low bioaccumulation in the study areas. This finding disagreed with the results of Jin *et al.*, (2005) who pointed to Pb as being associated with the exchangeable fraction.

Lead bound to the organic matter was low in the two wetland soils and ranged from 0.01 to 1.31 mgkg⁻¹, 0.02 to 1.80 mgkg⁻¹ with mean values of 0.08 and 0.15 mgkg⁻¹ respectively for the RFP and IDP. Similar results were reported by Feng *et al.*, (2009) who observed that the high levels of lead in soil samples could be as a result of regular use of antifungal fumigation over crops and acid rain, hence available for plant uptake, thus, the metal is bio available and mobile in the soil. Considerable amount of Pb was found in the Mn oxide, amorphous Fe oxide and crystalline Fe oxide. The proportion of Pb in the Mn oxide ranged from 0.41 to 4.21 mgkg⁻¹, 0.05 to 4.67 mgkg⁻¹ with means of 1.62 and 2.00 mgkg⁻¹ in the RFP and IDP respectively.

Amorphous Fe oxide and crystalline Fe oxide ranged from 0.01 to 4.21 mgkg⁻¹, 0.02 to 5.09 mgkg⁻¹, 0.15 to 3.10 mgkg⁻¹, 0.07 to 4.64 mgkg⁻¹ and had the means of 1.55, 2.29 and 1.34, 1.67 mgkg⁻¹ for the RFP and IDP respectively Gambrel (1994) reported about a half of total indigenous Pb in coastal sediment was recovered in potentially

available forms. According to Baranowski *et al.*, (2002), the acidity of the soils increases

the solubility of Pb and increases its availability for plants uptake.

Table 5: Mean Values (Mgkg⁻¹) of Lead in the Various Soil Fractions of the Two Wetland Soil Types

Soil	Water Soluble	Exchangeable	Organically Bound	Mn Oxide	Amorphous Fe Oxide	Crystalline Fe Oxide	Residual
River Flood Plain							
Range	0.01-0.10	0.02-2.16	0.01-1.31	0.41-4.21	0.01-4.21	0.02-5.09	12.54-21.46
Mean	0.07±0.02	0.75±0.70	0.08±0.29	1.62±1.22	1.55±1.19	2.29±1.32	18.33±2.51
Inland Depression							
Range	0.01-4.35	0.35-4.90	0.02-1.80	0.05-4.67	0.15-3.10	0.07-4.64	15.17-24.04
Mean	1.32±0.97	1.83±1.04	0.15±0.44	2.00±1.18	1.34±0.85	1.67±1.14	20.21±2.19

Correlation Between the Different Fractions of Copper and Lead with Soil Properties

Correlation analysis between copper and lead fractions and some physicochemical properties in the studied soils are presented on Tables 6 and 7. In the river flood plain soils; exchangeable Cu had a significant but positive correlation with pH ($r = 0.576^{**}$; $P < 0.01$). Organically bound copper correlates positively with available phosphorus ($r = 0.424^{**}$; $P < 0.01$). Sand and clay fractions also followed the same pattern as that of soil pH and organically bound copper fraction and possessed significantly positive correlation with water soluble sand fraction ($r = 0.549^{**}$; $P < 0.01$) and clay ($r = 0.435^{**}$; $P < 0.01$). Studies by Shuman (1985) indicated that only clay fractions correlated with exchangeable Cu. In another study by Kotoky *et al.*, (2003), available Cu did not correlate with soil pH. Still in the river flood plain soils, Pb fractions had no significant relationship with another soil property except water soluble and pH ($r = 0.436^{**}$; $P < 0.01$), ECEC ($r = 0.472^{**}$; $P < 0.01$) and clay ($r = 0.475^{**}$; $P < 0.01$).

The significant relationship between water soluble Pb and pH indicates that the strongly acid condition kept some of the Pb in readily

soluble form. However, there was a negative correlation with the MnO Pb fraction with total nitrogen, ECEC, sand, silt and clay fractions, Vi_3 ; TN ($r = -0.425^{*}$; $P < 0.05$), Av.P ($r = -0.429^{*}$; $P < 0.05$), sand ($r = -0.581^{*}$; $P < 0.05$), silt ($r = -0.529^{*}$; $P < 0.05$) and clay ($r = -0.430^{*}$; $P < 0.05$) (Table 6). These findings disagreed with the conclusion of Jerzy *et al.*, (2018) who obtained a strong positive correlation between fractions of Cu and Pb in the soil. In the inland depression, organic carbon correlated positively with the exchangeable Cu fraction ($r = 0.471^{**}$; $P < 0.01$), OB ($r = 0.533^{**}$; $P < 0.01$), AFeO ($r = 0.505^{**}$; $P < 0.01$), CFEO ($r = 0.454^{**}$; $P < 0.01$) with the residual fraction recording the highest correlation ($r = 0.651^{**}$; $P < 0.01$). However, in the case of clay, it showed a negative correlation with water soluble Cu ($r = -0.459^{*}$; $P < 0.05$) (Table 7). The highest correlation of Cu with the residual fraction is suggestive to non-availability to biotic environment. Pb fractions has no significant relationship with any other soil property except water soluble and pH ($r = 0.429^{*}$; $P < 0.01$), ECEC ($r = 0.489^{*}$; $P < 0.01$), sand ($r = 0.549^{**}$; $P < 0.01$) and clay ($r = 0.440^{**}$; $P < 0.01$). The significant relationship between water soluble Pb and pH indicates that the strongly acid condition kept some of the Pb in readily mobile form.

Table 6: Correlation Coefficient for Heavy Metals of Soil Fractions and Soil Properties for River Flood Plain

	pH (H ₂ O)	OC	TN	Av. P	ECEC	Sand	Silt	Clay
Copper								
Water Soluble (WS)	0.012	0.031	0.231	0.129	-0.101	0.549**	-0.168	-0.435**
Exchangeable (Exch)	0.576**	-0.057	-0.110	0.312	-0.188	-0.209	0.112	0.144
Organically Bound (OB)	0.108	0.033	-0.118	0.424**	-0.058	0.146	-0.215	0.214
Mn Oxide (MnO)	0.374	0.271	0.217	0.286	-0.100	-0.173	0.206	0.061
Amorph. Fe Oxide (AFeO)	0.191	-0.242	0.012	-0.287	-0.055	0.008	0.078	-0.095
Cryst. Fe Oxide (Cryst. FeO)	-0.074	-0.046	0.297	0.051	-0.051	-0.193	0.192	-0.031
Residual (Res)	-0.058	-0.398	-0.259	0.217	-0.198	0.089	0.005	-0.110
Lead								
WS	0.436*	0.236	0.203	0.324	0.472*	0.181	0.052	0.475*
Exch.	-0.279	0.200	0.059	-0.034	0.128	-0.172	0.146	-0.213
OB	0.211	-0.125	-0.302	-0.228	-0.183	-0.123	-0.033	0.225
MnO	-0.141	-0.297	-0.425**	-0.429*	-0.370	-0.581*	-0.529*	-0.430*
AFeO	0.062	-0.354	-0.094	-0.025	-0.310	0.083	-0.135	-0.004
CFeO	0.052	0.052	0.069	-0.179	0.362	-0.260	0.282	-0.083
Res	-0.300	-0.327	-0.394	-0.222	0.121	-0.119	-0.081	0.014

Table 7: Correlation Coefficient for Heavy Metals of Soil Fractions and Soil Properties for Inland Depression

	pH (H ₂ O)	OC	TN	Av. P	ECEC	Sand	Silt	Clay
Copper								
WS	-0.361	-0.085	-0.356	0.105	0.217	0.227	-0.118	-0.459*
Exch	0.132	0.471**	0.092	0.222	-0.083	-0.177	0.217	0.124
OB	0.160	0.533**	0.057	0.325	-0.330	-0.057	0.238	-0.146
Mn O	0.182	0.228	-0.175	-0.031	-0.332	-0.377	0.183	0.291
AF _e O	-0.271	0.505**	0.170	-0.110	0.125	0.360	-0.432	-0.462
CF _e O	0.073	0.454**	0.126	-0.290	0.000	-0.126	0.044	-0.031
Res.	-0.072	0.651**	0.137	-0.055	-0.023	-0.100	0.085	-0.095
Lead								
WS	0.429	-0.351	0.055	0.273	0.489**	0.549**	-0.228	0.440**
Exch	0.055	-0.155	0.057	0.026	0.008	-0.074	-0.055	0.070
OB	0.218	-0.044	-0.164	0.200	-0.049	0.015	-0.036	0.039
Mn O	-0.125	0.191	0.012	0.332	0.214	-0.194	0.282	0.014
AF _e O	0.132	-0.219	0.117	-0.075	0.304	0.164	-0.212	-0.104
CF _e O	-0.317	0.127	0.025	0.212	0.088	-0.027	-0.074	-0.068
Res.	-0.384	-0.046	0.255	0.136	0.288	-0.240	0.271	0.129

CONCLUSION AND RECOMMENDATIONS

This research was undertaken to assess the chemical fractionation of heavy metals and their association with different chemical forms in selected wetland soils of Akwa Ibom State. The results from this study showed that the concentrations of all the fractions of heavy metals in different soil types under study were found variable. The heavy metals were mainly associated with the residual fraction. The acidic nature of the soils restricted the association with the water soluble and exchangeable fractions. It is evident from the study that soil properties played a significant role in defining the chemical forms of heavy metals in the soil. The present study indicates that the metals under study do not pose any environmental risks. However, regular soil monitoring of heavy metal levels in both soils is necessary since the system is dynamic, this will provide a comprehensive and up-to-date information for better soil management, soil remediation and soil contamination control.

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