Research Paper

Speciation, bioavailability and ecological health riskof sometransition metals in wetland soils at Oguta lake, Nigeria.

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ABSTRACT
In line with 2021 world environment day theme, restoration of ecosystem, the current research sought to establish the need to protect Oguta lake ecosystem. Spatial distribution, total metal concetrations,speciation, bioavailability, contamination factors, ecological health risk and potential ecological health risk were assessed. After characterization of the fifteen soil samples, four first row transition metals were in wetland soils analyzed by standard sequential extraction methods and metal concentrations quantified with aid of A Analyst 400 Perkin Elmer AAS techniques. Total metal concentrations revealed that Cu was hihgest metals at all sites as well as hihest cocentration recorded (115.5mg/kg). Comparing total extraction with sequential extractions, recovery values showed good aggreement,Metals species were grouped into available, non-bioavailable residual fractions. The Mean concentrations of species revealed the following ranges: F1: (1.00-13.89); F2: (3.24-21.04); F3: (1.00-13.89); F4: (2.60-25.31); F5: (2.13-24.00); F6: (1.00-18.83). The decreasing order of speciation was Cu> Zn> Mn> Fe. While copper was most affected by physicochemical properties, iron showed least affected. Association with fractions showed that Zn, Cu and Mn with exception of Fe, were extremely connected with the immovable fraction. In conclusion this investigation shows that the metals mostly occurred in the most available forms, therefore, it is likely that the metals were derived from anthropogenic sources. Hence, soils could posse toxicity problem to aquatic lives.
KEYWORDS: *Contamination factors, MetalFractions, Specie, Ecotoxicity, Sequential extraction*

I. INTRODUCTION

Metal speciation in wetland soils can be employed to identifyand quantifydifferent species, forms and phases of metals that are existingin wetland soils. This preferred for the characterization and ecotoxicological status of the wetland (Verla et al, 2018; Cai et al., 2019).Soil may likely become pollutedby the building upof heavy metals and metalloids through constant dischargefrom the rapid expansion of industries, mine tailings, dumping of high metal wastes, leakage fromgasoline and paints products, pesticides, sewage irrigation, residues from coal combustion, the use of fertilizers on land, animal dungs sewage slurry, crude oil spillage, and deposits from the atmosphere (Khan et al., 2008; Zang et al., 2010; Zakrzewska and Klimek, 2018).Soils are the mainbasinfor heavy metals dischargedinto the environment by abovementionedhuman activities and unlike organic chemicalswhich are oxidizedby action of micro-organism into carbon (IV) oxide, most metal do not undergo bio or chemical degradation(Kirpichtchikova et al., 2006), and their overallabsorptionin soils continues over a long period of time after being introduced(Adriano, 2003). Metalcould experience changes in their chemical forms (speciation) and bioavailability(Horsfall and Spiff 2005). The existenceof heavy metals in soil can strictly preventthe microbial degradation of organic pollutants (Maslin and Maier 2000). Heavy metal pollutionof soil may position to high risks which may eventually become at threats to human and the ecosystem through direct assimilationor closeinteractionwith pollutedsoil, the food cycle (soil-plant-human or soil-plant-animal-human), intakeof contaminated ground water, reduction in the quality of food (securityand sales) via phyto-toxicity, devaluation in land usage for agricultural processes. These challenges lead tofood insecurity, and land tenancyproblems. (McLaughlin et al., 2000; McLaughlin et al., 2000; Ling, Shen, Gao, Gu, and Yang 2007).

There is substantial protection and refurbishmentof the soil biotathat is contaminated by heavy metals. By characterizing an eco-friendly environment and public health, at both national and globallevels, can be advocated, based on sound scientific data. Characterizing thechemical properties of environmental conditions, particularly those found within our food web is very necessary (Zhang, Liu and Wang(2010). While characterizing the soil would provide an understanding about heavy metal speciation and bioavailability, an attempt to remediate soils polluted with heavy metal would require knowledge of the contamination source, chemical properties of the heavy metals, and other environmental and health effects associated with the uptake of these heavy metals into the human body. Risk assessment is an efficient scientific method which permits decision makers to manage polluted sites in low-cost manner while preserving public human health and the ecosystem at large (Zhao and Kaluarachchi, 2002).

Immobilization, cleansing of soil and phytoremediation tools are the most frequently utilized among the list of best demonstrated available technologies (BDATs) for removal of heavy metal from polluted sites. But however, despite the low-cost and eco-friendly nature, field utilizations of these techniques have only been reported in developed countries. In most developing countries, like Nigeria, these techniques are yet to be employed commercially reasons may possibly be due to lack of awareness of their inherent advantages and principles on how it works.

The evaluation of heavy metals contamination of soil as a means of monitoring the status of the environment for the good of the ecosystem is crucial because of the increasing domestic and industrial activities of man (Wu et al., 2018). Previously, it was assumed that the basic component of soils could only be explained on the basis of local geology, but in recent studies, it became clear that the surface layers of soils are significantly affected by natural supply of elementsdirectly from the atmosphere as well man-made sources(Steinnes et al., 1997). In a developing country like Nigeria where the discharge and disposal of all sorts of waste into the environment by anthropogenic sources is overwhelming, hence, repeated evaluation of the pollution status of the environment especially the soil is imperative (Levy et al., 1992).Some of these heavy metals are of utmost importance to life in minute quantities and are described as micronutrients; essential and required for the body build-up, to enhance proper growth and developmentin living organism, but when theseconcentrations exceed the maximum limits in the ecosystem, they become very harmful to the human health and the ecosystem, thus leading to destructions of structures or interruption with incumbent uses of the environment (Alloway and Ayres 1997).

As earlier stated, soils are sinks of heavy metals are strongly retained and highly persistent in soils for a very period of time without been degraded phytolytically, biochemically which is critical. Heavy metals can pile-up and be divided in the environment based on the biochemical and geological cycle. Whenheavy metals enter the environment and find their way eventually into the soil, there is an occurrence of soil-metalinterchange during which different conditions willdepict their level of bioavailability, movement, and toxic effect. The bioavailability, movement, and toxic effect of heavy metals in the environment depends greatly on their specific chemical forms. (Pierzynski, Sims and Vance2000; Basta, Ryan and Chaney 2005)

Heavy metals in the soil generated due to human activities tends to be more mobile, hence bioavailable than edaphic, or lithogenic soils. Metal-bearing solids at polluted sites can emanate from a several range of anthropogenic activities in the form of metal tailings, improper disposal of high metal wastes in landfills, leaded gasoline and paints, land application of fertilizer, animal dungs, biosolids (sewage sludge), compost, pesticide, coal combustion residues, petrochemicals, and atmospheric deposition [D'Amore et al., 2005].

Many materials generated by various industries are extremely dangerous due to their content heavy metals. Others may pose low plant nutrients or may eventually contain no soil properties (DeVolder et al., 2008). Once made available in the soil, heavy metals are adsorbed by the pre-existing rapid reactions (minutes, hours), accompanied by slow rate of adsorption reactions of days or maybe years and are, therefore, divided into several chemical forms of varying bioavailability, movement, and toxic level.(Levy et al., 1992; Kang et al.,2017). Theredistribution is assumed to be influenced greatly by reactions of heavy metals in soils such as mineral precipitation and dissolution, exchange of ions, adsorption, and desorption, aqueous complexation, biological immobilization and mobilization, andPlant uptake(Manahan, 2003; Greany, 2005). Copper and Zn metals are one of the topmost essential elements needed by plants, microorganisms, animals, and human beings. However, the relationship between water-soil pollution, the uptake of metals by plants is solely dependent by various physiochemical soil factors as well as the physiological characterization of the crops. Soils polluted with trace metals may stir upboth direct and indirect hazard, by direct, harmful effects of metals on the rate of crop growth and efficiency, and indirect, by entrance into the food cycle with a potential harmful effect on human health. Even a decrease on the yield of crops by a small percentage could cause a feasible long-term loss in manufacturing and profits. Recently, food importers are now specific about maximum permissible limits of metals in food, which might reduce the chances of the farmers to export their infected crops(Pourbaix, 1974; Khodadoust, Reddy and Maturi 2004).

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The aim and objective of this research work is to determine the speciation of selected first row transition metals in wetland soil from the soil of Ogutalake as a way of understanding the heavy metal contamination of soils and its ecological risk at the banks of the lake. This could inform agriculturists undertaking activities at the banks of the lake and give policy makers data to make more useful policies for our environment.

II. MATERIALS AND METHODS

2.1 STUDY AREA

The study area for this research is Oguta Lake in Oguta Imo State, Nigeria.The lake is located inOguta and it is approximately thirtymiles that is a distance of 48.27 km from the junction of the Ndoniand Orashi River. It is a unique nature's endowment,and it is about five miles (8.05 km) in length from east to west and a width of one-half mile (2.41 km). Water-flow from NjabaRiver is the main tributary to Oguta Lake. The remaining three tributaries are Awbana, Utu and Orashirivers, respectively. The OrashiRiver flows across Oguta Lake through the south-west area and these two rivers remain unmixed, showing a clear demarcation of the different waters.

Oguta Lake is located between latitude 5°41' and 5°44' North of equator and longitude 6°56' and 6°45' East of Greenwich. It is a natural lake with surface area of 1.80 km^2 at climax flood anddepth of 7.00 m during dry seasons, average depth of 5.50 m. the Njaba and Obana rivers are the two major river that contributes water for the lake, the lake empties itself into the River Niger drainage system through River Orashi. It has a minimum and maximum surface area of 1.80 and 2.48 km^2, respectively. Surface temperature of the lake is 24.31°C. The lake has wetlands closed to it to the south and west sides.

Sampling and sample pre-treatment

Soil samples were taken in containers at 5cm depth using mechanical digger (auger) from soils around the banks of the lake Samples were taken randomly round the lake starting from a point and proceeding away from the bank. To actualize the aim of this study, five (5) composite soil samples were collected at five different locations and brought to the IMSU University laboratory for analysis.The five soil samples collected from the field were pre-treated by sun-drying them and then sievedwith2 mm meshto remove large undesired particle size.

Physicochemical analysis of the soil

The physicochemical characterizations of the soil were determined in triplicates using standard methods. pH was determined from 1:2:5 2 mm soil to water ratio in a 100 ml beaker agitated for 5 minutes (Favar et. al., 2011). EC was determined with use of EC meter in a supernatant passed through Whatman filter paper number 1. Temperature was measured by use of a gardeners' thermometer inserted into the soil sample onsite for 2 mins. Organic matter was determined by use of high temperature furnace at 550 °C for 4 hours followed by 2 hours at 950 °C. This method is called Loss in ignition (Heiri et. al., 2001). Using method USEPA, test 9081 A, the cation exchange capacity was determined in soil sampler (USEPA, 1986).

Preparation of some reagents

1M of Ammonium acetate (NH_4COOCH_3): This was prepared by diluting 7.7g of ammonium acetate in 100ml of distilled water.

3 M Sodium acetate (CH_3COONa^+): This was prepared by diluting 24.6g of sodium acetate in 100ml of distilled water.

0.025 M Hydrochloric acid (HCl): This was prepared by diluting 85.5ml of hydrochloric acid in 100ml of distilled water.

0.05 M Sulphuric acid (H_2SO_4): This was prepared by reacting 2.77ml of sulphuric acid in 100ml of distilled water.

0.2 M $(NH_4)_2C_2O_4$: This was prepared by mixing 2.48g of $(NH_4)_2C_2O_4$ in 100ml distilled water.

25% CH_3COOH: This was prepared by mixing 25ml of CH_3COOH in 100ml distilled water (Verla et al 2017).

Sequential extraction

The metal species were extracted into six fractions according to the following method: water soluble (F_1), exchangeable (F_2), bound to carbonate (F_3), plant available (F_4), bound to Mn (F_5), bound to amorphous Fe oxide (F_6). One gram of mass of the individual soil samples were measured and extractions were carried out through steps (F) and using centrifugation and filtration at 10,000 rpm sampling was made up in 100ml conical flask. The residue was washed with distilled water after subsequent extractions so as to dissolve selectively and prevent possible inter-phase interference between the extracted solutions.

Metals which are soluble in water were extracted using a solution of 50 ml distilled water at pH7.0 and at 28°C for 30 min. The Exchangeable metals were determined in the residue from fraction 1 which was

extracted with 25 ml of 1.0 M NH_4COOCH_3. The suspension was shaken for 30 min at 28°C. Metals bound to carbonate were determined in the residue from fraction 2 which was extracted with 3 M sodium acetate (CH_3COONa^+) adjusted to pH 5.0 with acetic acid (CH_3COOH). The suspension was shaken for 30 min. Plant available metals were determined in the residue from fraction 3 which was extracted by shaking with a solution mixture of 50 ml of 0.025 M HCl + 0.05 M H_2SO_4 for 30 min at 28°C. Metal fraction bound to Mn-oxide were determined from residue from fraction 4 was shaken for 30 min at 28°C with a solution of 25 ml 0.1 M $NH_2OH.HCl$ in 25% CH_3COOH (pH 2 to 3). Fraction bound to amorphous Fe-oxide were determined from the residue from fraction 5 was extracted with 25 ml of 0.2 M $(NH_4)_2C_2O_4$ (pH 3.0) for 30 min at 50°C using a water bath with occasional stirring (Ramos, Hermandez, Gonazales 1994; Verla, 2016; Sun et al., 2019).

Determining Heavy Metal Content Soil Samples
1 g of soil sample was placed in a Pyrex glassware and I0ml concentrated nitric acid added and was mixture heated to 90°C for 6hrs before allowing to dry. The mixture was left to cool at room temperature and procedure repeated, this time with 10ml conc. HNO_3 and 10ml of 2M HCl. The digests was warmed to redissolve the metal salts with 20 ml of 2 M HC1, then centrifuged 30000 rpm for 15 mins and the clear volume made up to the mark in a 25 ml volumetric flask (Adekunle et al., 2003). Using AAS, A ANALYST Perkin Elmer 400 metals concentrations were quantified for all 15 samples (Shu et al., 2008).

Quality control
Standard procedures, best laboratory practices and replicate sample collection and analysis were applied to generate quality analytical data. Reagents blanks were also examined as used by Nematollahi et. al., (2018). To ensure that contaminants were excluded, laboratory wares were washed first with phosphate free soap and rinsed twice with distilled water before leaving in a 10 % HNO_3 acid solution for 24 hours. Before use, the glass wares were rinsed twice again with double-distilled water and were allowed to dry at room temperature in a semi-closed mode (Moore et. al., 2015). Using the recovery percentages as applied by Verla et. al., (2016) i.e equation (1), accuracy and reproducibility of results by sequential extraction method were evaluated.

$$\% \ Recovery = \frac{c_{TOT}}{\sum c_{(F_1+F_2+F_3+F_4+F_5+F6)}} \ x \ 100 \ .... \ (1)$$

Calculated % recovery values of selected metals in Oguta lake wetlands soil samples ranged between 82.04 and 97.44 %. These values represent good analysis and accuracy for both total metal extractions using HNO_3: HCl and the sequential extraction method in which fractions where finally summed up. However, there could have been some error in analysis of Mn (64.4%) at site C and Fe (110.2%) at site B.

Data Analysis
Statistical data analysis was performed with SPSS software, version 18. Only mean of triplicate analysis was recorded were appropriate and standard deviation determined. Statistical significance was described at 0.05 and 0.01 probability. Levels of contaminations of heavy metals in site was assessed by contamination indices: Contamination factors (C_f) and the degree of contamination (C_d).

III. RESULTS AND DISCUSSION
Table 1: The physicochemical properties of the soil samples at various sampling points

Properties	A	B	C	D	E	Mean	SDV
pH	4.06	4.24	7.36	4.35	4.60	4.92	1.38
Temp (^{o}C)	28.3	28.1	28.0	28.2	28.2	28.16	0.11
EC (µS/cm)	104.0	111	110	106	114.6	109.12	4.19
Moisture (%)	18.14	12.6	20.2	17.2	21	22.29	3.30
OM	1.47	1.7	0.8	1.6	1.2	1.35	0.36

Physicochemical properties: Physicochemical characteristics of the investigated soils are shown on table 3.0. The pH of soils from the soil samples in this study ranged from 4.06 to 7.36. With exception of C, the children park soils were acidic pH < 7. This agrees with reported pH values of soils within Imo State (Verla et al.,2015). Generally, pH values of soil divided into five degrees, strong acidic Ph<5.0, acid pH 5.0-6.5, neutral pH 6.5-7.5, alkaline pH 7.5-8.5, strong alkaline pH>8.5, As can be seen from results the soils from C were alkaline. However, at lower pH metals solubility tends to decrease and absorption reactions become more important than precipitation and complexation reactions. This encourages percolation of metals into deeper soil horizon.The soils showed temperatures ranging from 28.0 ^{o}C to 28.3 ^{o}C with site A having highest value (28.3±0.11^{o}C). Soil temperatures are significant in their influence on soil characteristics. High temperature reduces growth of microorganism, and has been associated with soil acidity.The soil electrical conductivities (EC) also differed significantly among the soil samples (p < 0.05). EC varied widely ranging from 104.0 uS/cm at A to 114.6 uS/cm at E. EC values indicate ionic concentration of soils. The EC level is a good indication of the amount of

nutrient available in the soil. It is observed that sample E showed an out layer with EC of 114.6 uS/cm. The moisture percentage in the soils ranged from B (12.6 %) to C (20.2 %). High soil moisture content has been linked to larger soil particles and leaching processes. While moisture reduces dust, organic matter is effective in trapping moisture [Ogundiran and Afolabi 2008]. Soil organic matter (SOM) content did not only ascertain the nutritional position, but invariably had an effect on the movement of heavy metals. Organic matter controls both the physical and health properties of the soil. The percent organic matter for the five sites ranged from 1.2 at E and D to (1.7 ±0.36 %) at B. Organic matter is known to form complex with heavy metals.

Table 2: Metals fractions determined by sequential extraction (mg/kg) of the soil samples

Sample Sites	Metal Species in various Samples																			
	A				B				C				D				E			
Specie	Cu	Mn	Zn	Fe	Cu	Mn	Zn	Fe	Cu	Mn	Zn	Fe	Cu	Mn	Zn	Fe	Cu	Mn	Zn	Fe
F1	6.44	4.78	13.89	2.44	6.00	2.78	11.00	1.00	2.11	8.00	10.00	2.44	9.01	3.78	12.91	2.44	6.44	4.78	11.00	4.22
F2	21.04	15.78	15.33	7.00	20.41	16.7	12.21	3.24	21.00	10.20	12.20	8.00	19.11	16.78	17.20	7.99	21.00	15.78	12.21	8.12
F3	25.31	3.67	15.01	12.22	21.00	5.27	16.01	11.22	22.11	2.60	12.00	13.11	22.00	6.67	11.00	12.10	25.33	3.67	16.01	13.10
F4	22.10	5.77	15.77	5.99	22.00	7.17	13.53	8.96	22.10	7.00	18.00	5.01	13.10	9.77	12.61	5.68	22.10	5.77	13.53	5.13
F5	24.00	9.32	12.79	4.00	15.00	5.21	11.00	3.91	21.00	10.21	5.76	2.11	16.00	8.32	12.72	4.00	24.00	9.32	11.01	2.13
F6	16.84	11.56	11.23	2.51	14.84	12.6	10.24	1.51	14.00	12.53	10.23	3.51	10.81	1.00	9.68	4.51	18.83	14.51	13.22	3.51
Sum	115.73	50.88	84.01	34.16	99.25	49.73	73.99	29.84	102.32	50.54	68.19	34.18	90.03	46.32	76.12	36.72	117.7	53.83	76.98	36.21
C_{TOT}	98.5	48.2	78.5	42.05	102.4	40.8	67.00	30.90	109.7	32.4	60.9	31.08	78.62	43.80	70.34	32.6	115.5	50.3	70.65	32.00
% Rev	85.11	94.7	93.44	110.2	88.06	82.04	90.55	90.14	97.43	64.1	89.30	90.93	87.32	94.47	92.41	8878	98.13	93.44	91.77	83.37
RAC	27.48	20.56	39.22	9.44	26.41	19.48	23.21	4.24	23.11	18.20	12.20	10.44	28.12	20.56	30.11	10.43	27.44	20.56	23.21	12.34

Table 3: Bioavailable, non-bioavailable, residual fractions, Contamination factors (CF) and ecological risk Index (ERI) of soil.

Metal	Fraction	Values of Bio, NBio and Res fraction					Contamination factors					Ecological risk index				
		A	B	C	D	E	A	B	C	D	E	A	B	C	D	E
Cu	Bio	52.74	47.41	45.22	50.12	52.77	3.9	3.5	3.35	3.71	3.9	19.5	17.50	16.75	18.55	19.50
5;	NBio	46.1	37	43.10	29.1	46.10	3.41	2.74	3.19	1.16	3.41	17.05	13.70	15.95	10.80	17.05
13.5	Res	16.84	14.84	14	10.81	18.83	1.25	1.10	1.04	0.80	1.39	6.25	5.50	5.20	4.00	6.95
Mn	Bio	24.23	24.77	20.8	27.23	24.23	26.0	26.99	22.67	29.68	26.41	26.00	26.99	22.67	29.68	26.41
1,	NBio	15.09	12.38	17.21	18.09	15.09	16.58	13.60	18.91	19.88	16.58	16.58	13.60	18.91	19.58	16.58
0.91	Res	11.56	12.56	12.53	1.00	14.51	12.70	13.80	13.77	1.10	15.95	12.70	13.80	13.77	1.00	15.95
Zn	Bio	44.22	39.22	34.2	41.11	39.22	44.22	39.22	34.2	41.11	39.22	44.22	39.22	34.20	41.11	39.22
1,1	NBio	28.56	24.53	23.76	25.33	24.54	25.56	24.53	23.76	25.33	24.54	28.56	24.53	23.76	25.53	24.54
	Res	11.23	10.24	10.23	9.63	13.22	11.23	10.24	10.23	9.63	13.22	11.23	10.24	10.23	9.63	13.22
Fe	Bio	21.66	15.46	23.55	32.53	25.44	0.08	0.061	0.094	0.13	0.10	0.06	0.04	0.07	0.09	0.07
0.7,	NBio	9.99	12.87	7.12	9.68	7.26	0.04	0.05	0.03	0.04	0.03	0.03	0.04	0.02	0.03	0.02
261.2	Res	2.51	1.51	3.51	4.51	3.51	0.01	0.01	0.01	0.02	0.01	0.07	0.07	0.07	0.01	0.01

Metal Speciation

Succeeding the subsequent extraction proceedings outlined above, the percentages of heavy metals analogous to individual fractions were calculated. The heavy metals take separate speciation patterns and some show notable spatial variations. The first step of serial extraction generates the acid-soluble fraction (F_1) of metals that are not strongly linked to carbonates. Heavy metals links to acid-soluble fractions in the F1 are soluble in water and in a carbonate, they bind state that is subject to ion exchange. The metals were absorbed in clay and humus, which is subtle to changes occurring in the environment and enables easy movement and modifications under acidic conditions. The results of this investigation have shown that the order of association with F_1 was observed for the selected metals: Zn 58.8 >Mn 37.03 > Cu 30 > Fe 12.54. Zn and Mn were highly linked with the mobile fraction with 39% and 18%, respectively, which raises concerns, regarding its common toxicity on lives. These results agree with previous studies that have highlighted the potential threats caused when other metals are highly associated with F_1 (Okoye and Ibeto 2008; Verla et al., 2020).

The second fraction of reducible metals (F_2) indicates the metals usually associated with Fe and Mn oxy/hydroxides that are difficult to release due to strong ionic wrapping. However, if oxidation-reduction potential (Ev) and oxygen levels in seawater decrease, these may deoxidize and cause secondary pollution, which can be seen in the environmental pollution associated with extensive human activities. It was observed that the order of association between F_2 and the selected metals was 50% > Zn > Cu > 25% > Cd > 15% > Fe were mainly associated with the reducible fraction with an average of 39%, 31% and 26% of their total contents, respectively.

A high % of associations of Zn and Cu to the reducible fraction in contaminated sediments of estuaries, bays and riverbeds has been reported. The large number of metals associated with the reducible fraction raises concerns their potential mobility in the water phase and subsequent bioavailability as shown in table 3.2. Despite their low percent association in F_1, the risk of environmental and ecological damage from heavy metals cannot be ruled out.

The sequential fractionation is an oxidizable fraction (F_3) that is bound to organic matter and sulfides. Under oxidizing conditions, organic matter degradation can lead to the release of the metals bound to this

fraction. The organic fraction released during the extraction process is not bioavailable, since it exists in stable humic substances that release small amounts of metals slowly (Chaudhary, Saika and Owen 2008). Research results have shown a % of association as low as 6%, 12% and 14% for Fe, Cu and Zn, respectively. The low content of metals associated with F_3 might be due to the small amount of organic matter.

The fourth step in the sequential extraction shows that a fraction of metals is associated with alumino-silicate minerals, the so-called residual fraction (Res). The R behavior is the most stable because it is bound primarily to the crystal lattices of silicate, and it can only be released over time as a function of the weathering process. It has no bioavailability, because its life is shorter than the period of time it takes for the natural weathering process to occur (Duan et al., 2018). Results show the average % association with the Res fraction in the following decreasing order: Cu>Mn> Zn > Fe > 15%.

Bioavailability

The most mobile fractions in a speciation analysis are usually assumed to be the most bioavailable fractions(Antoniadis et al., 2017). Bioavailability generally refers to the total metal fractional concentration that can easily be bioaccumulated or taken up in a living organism. Many researchers have shown that total metal concentration in a sample cannot be bioavailable. In terms of relative mobility, the water soluble and exchangeable metals F_1 and F_2 are the most mobile fractions and are here assumed to constitute the risk to both plants and animals. Since these fractions can be easily biosorped (Duan et al., 2018; Verla et al 2019).

Therefore, summing up the F_1, F_2 and expressing as a percentage of the total fractions gives the bioavailability. This is also the value for mobility. The non-bioavailable fraction is F4 and F5 while F_6 was referred to as the residual fraction table 3. Cupper showed the highest bioavailability in all five sites ranging from 45.22 at site c to 52.77 at site e. metal bioavailability followed the trend Cu: E>A>D>B>C; Mn: D>B>C>E>A; Zn: A>D>C>E>A and Fe: D>E.C>A>B.

Plots of Bio, Nbio and Res metals fractions were plotted with physicochemical properties to obtain a general relationship.
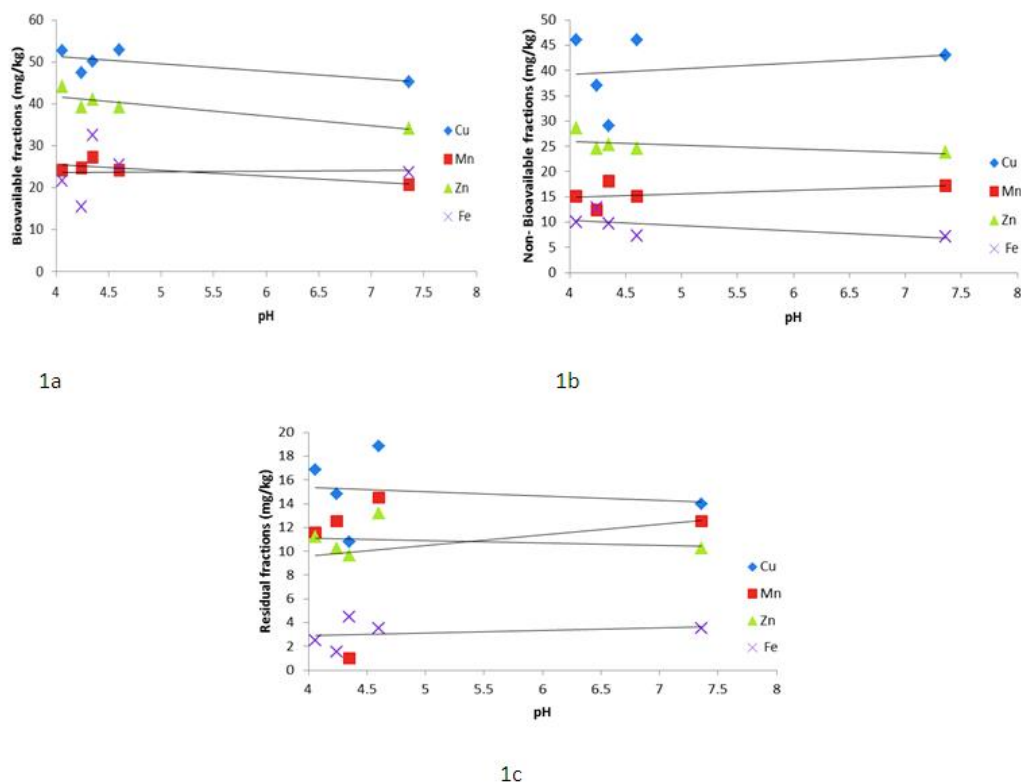

1a

1b

1c

Figure 1a, b, c: Plot of Bio, NBio and residual fraction in the soil against pH

2a

2b

2c
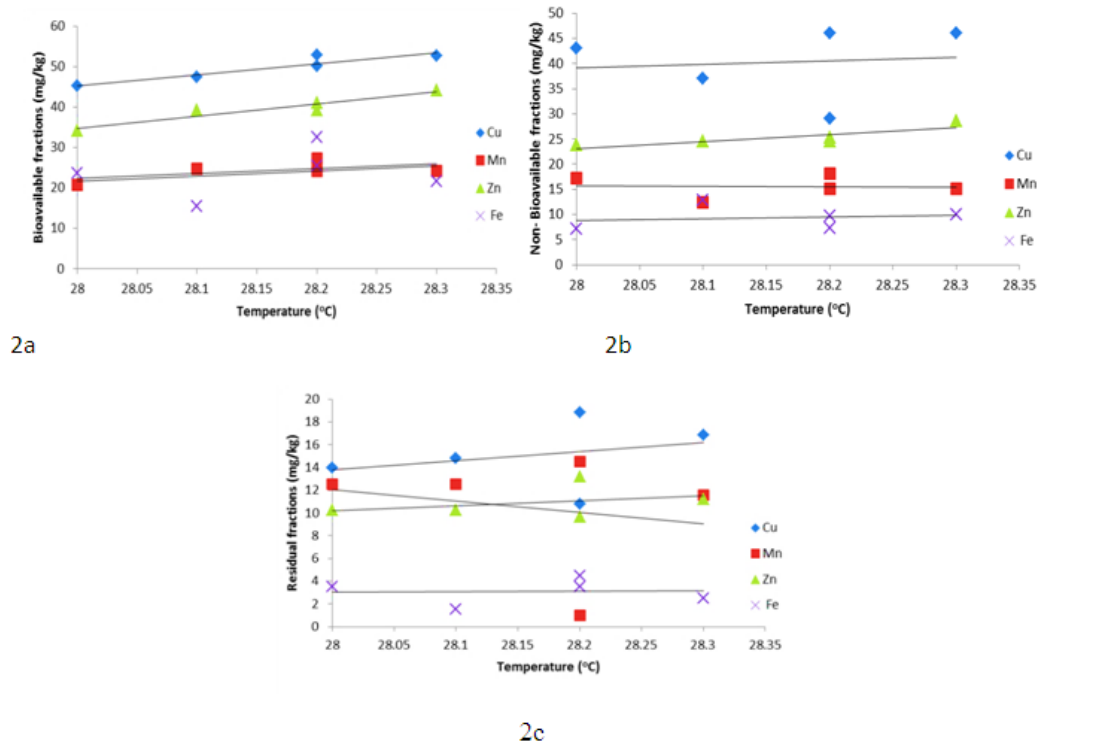
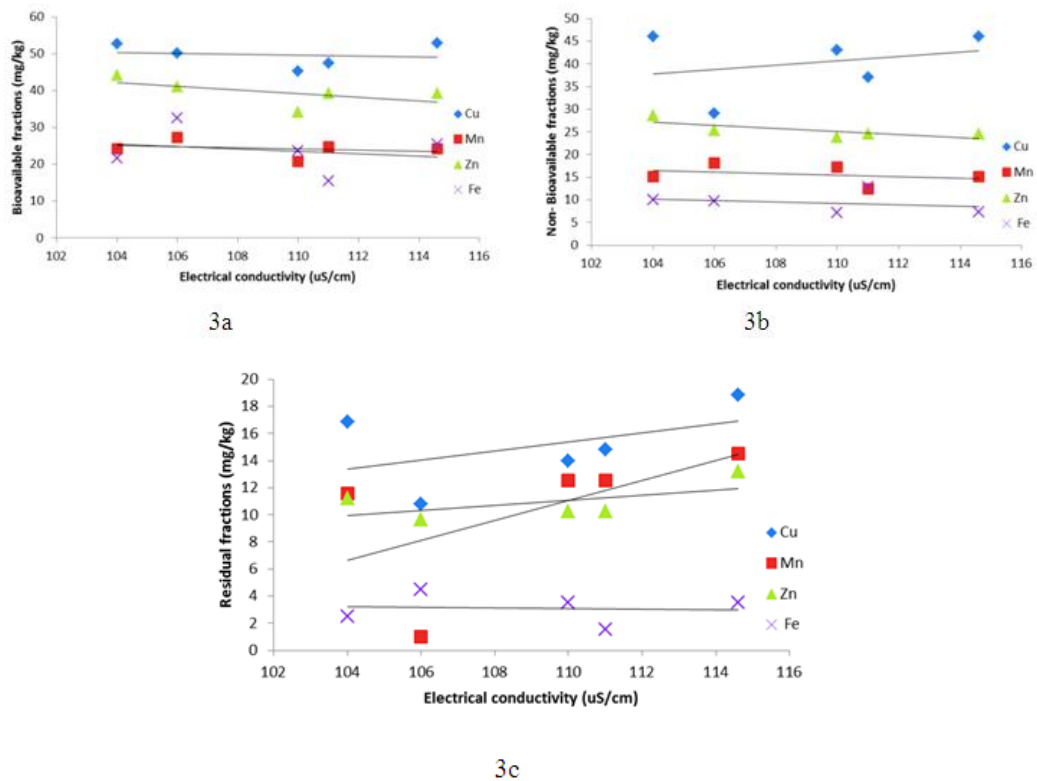Figure 2 a,b,c: Plot of Bio, NBio and Res metals in the soil against temperature
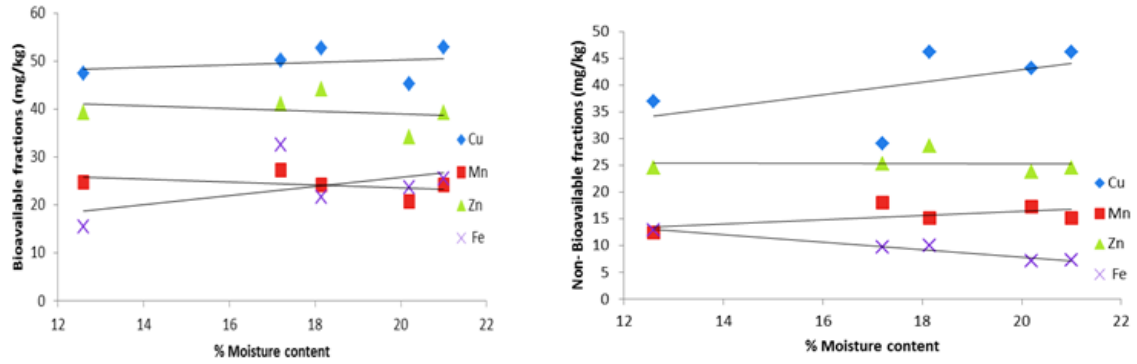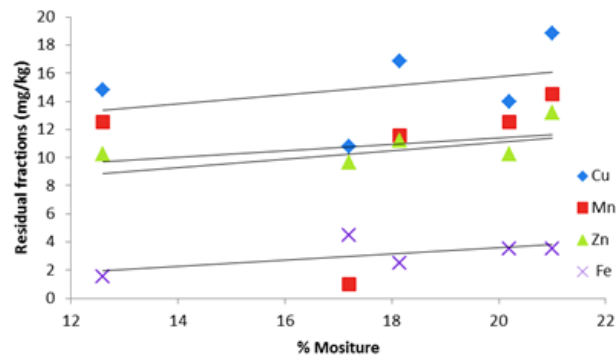

3a

3b

3c

Figure 3 a,b,c: Plot of Bio, NBio and Res metals in the soil against electrical conductivity.
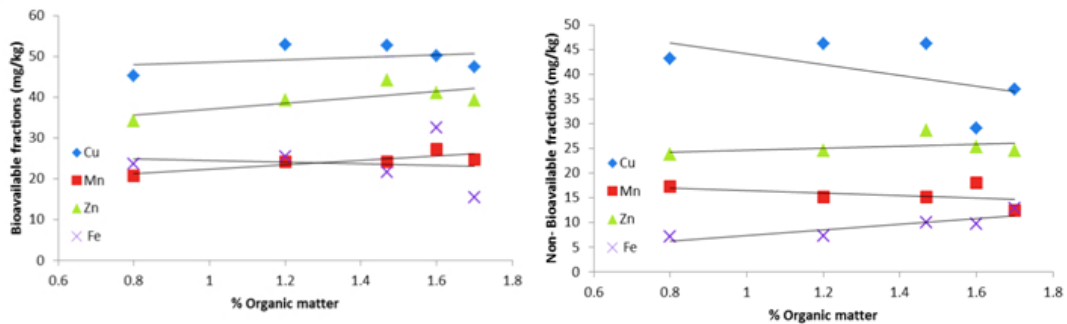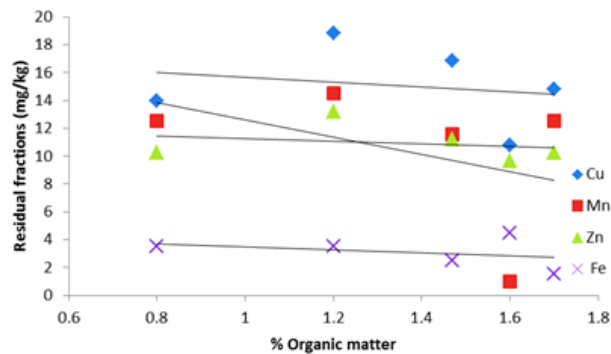
4a

4b

4c

Figure 4 a,b,c: Plot of Bio, NBio and Res metals in the soil against soil against moisture

5a

5b

5c

Figure 5 a,b,c: Plot of Bio, NBio and Res metals in soil against % organic matter content

Bioavailability and Physicochemical properties

Plot of bioavailable fractions against physicochemical properties (Fig 1a, b,c to 5 a,b,c) revealed the behavior of Bio fractions of various metals with physicochemical properties. The Bio against pH (Fig 1a) shows that there is general decrees in the Bio fraction increasing pH while the Nbio fraction for Cu slightly increase with pH the Nbio fraction if Fe showed a slight decree with increasing pH. The residual fraction of Mn revealed an increase with pH for whereas the res fraction for Fe was constant with increasing pH.

Fig 2 a and b revealed a general trend for both Bio and Nbio in which both increase with slight temperature for all four metals. Except for Res of Fe that was constant Cu and Zn revealed increasing trend. (Fig 2c) showed a general decrease with EC for Bio and Nbio fractions of all metals was observed. While the Res fractions for Mn increased rapidly with EC, that of Zn and Cu increased slowly but Res fractions for Fe was constant with increasing EC (Fig 3). Fig 4 revealed another interesting trend in which all fractions Bio, Nbio and Res showed a general slow increase with increasing % of moisture content of soil. Fig5 equally revealed an increasing trend for Bio, Nbio fractions with increasing organic matter. The Res fraction appears to remain unaffected by OM except for cupper that a slight decrease was observed.

These variation in behavior of metal Bio, Nbio and Res, fractions with physicochemical properties is possible the effects of chemical processes and reactions such as ionization, salvation, hydrolysis, and other reactions capable of influencing metal species behavior in wetland soil (Osakwe, 2010).

Risk assessment code (RAC)

Fe constituted the convert risk in almost 50% of the sites. However (1<RAC<10) was considered low risk assessment code [Chen et al., 2015]. Therefore, Fe was not a threat in the near future. Other metals exhibited 10<RAC <30, values considered medium risk except for Zn (RAC 39.22) that was adjudged the highest at site A and the highest of all sites.

Ecological risk assessment

PERI, the potential ecological risk index is a fast and simplified quantity that defines the risk to the ecology arising from a contaminant. In term of PTMs, the PERI is calculated using equations 2 and 3.

$$C_f = \frac{C_s}{C_{Bg}}....2$$

$$ERI = T_r x C_f \ldots\ldots..3$$

$$PERI = \sum T_r x C_f \ldots\ldots..4$$

where Cf is the monometal contamination factor; Cs is the metal concentration as determined in the sample; C_{Bg} is the background concentration, Tr defines the toxic response factor of eachparticular metal. In the current work Tr for metals and background values respectively are found in table 2 after the metals symbol separated by a comma:Cu = 5, 13.5; Mn=1,0.91; Zn=1,1 and Fe =0.07, 261.35(Liu et al., 2018; Sun et al., 2019).
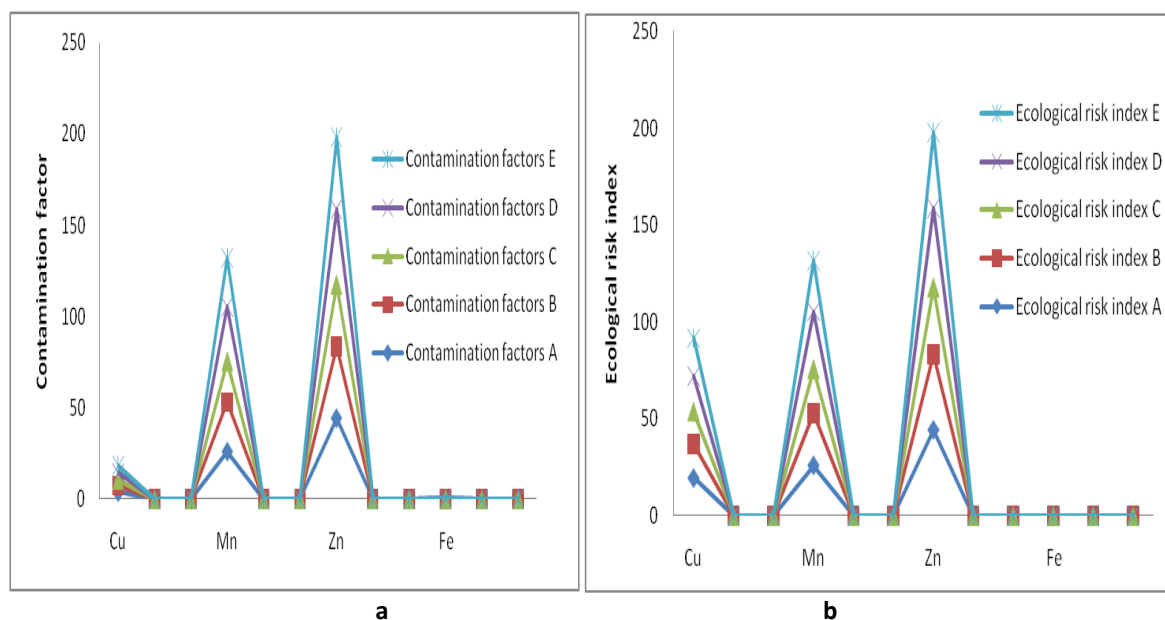

Figure 6 a,b: Bar Plot of contamination factors and ecological risk index of metals at various sites

Fig 6 (a) shows that contamination factors of Fe and Cu were generally low at all sampling sites, whereas Zn had the highest contamination factors, summing up to 200 at site E. in order of decreasing contamination factors for Zn the sites followed the order E > D > C > B > A. though this order was observed for Mn, all sites showed lower contamination factors of Mn compared to Zn.

It was no surprise that Ecological Risk Index (ERI) followed similar trend as contamination factor. In order of decreasing metals in the current assessment are Zn >Mn> Cu while Fe showed no risk at all. Therefore, Zn and Mn could constitute a potential ecological risk index (PERI) of concern (Figure 6b). PERI< 40 is considered low potential ecological risk (Cai et al., 2019; Enyoh et. al., 2020), only Zn showed high ecological risks (160 < PERI < 320) at site D and E respectively. They are locals at site D and E, who involved in various activities that are likely the source of heavy metals. In addition, these are the points close to loading and offloading of a small vessel that facilitates movement between the two villages separated by the lake.

Table 4: Correlation metals species and soil physicochemical parameters at Point A and B

Metals	Parameter	R^2 value	Linear equation	Metals	Parameter	R^2 value	Linear equation
		Sample point A				Sample point B	
Copper	pH	0.259	Y= 2.826x + 5.864	Copper	pH	0.160	Y=1.937x+7.345
	Temperature	0.542	Y= -49.35x +14.09		Temperature	0.555	-43.55x+1243
	EC	0.509	Y= 1.300x – 122.1		EC	0.126	0.564x-44.73
	Moisture	0.020	Y= 0.328x +13.92		Moisture	0.058	-0.488x+25.59
	Organic matter	0.264	Y= -10.92x +33.25		Organic matter	0.161	-7.435x+26.05
Manganese	pH	0.205	Y=-1.613x + 15.80	Manganese	pH	0.050	Y=-0.887x+11.79
	Temperature	0.013	Y= -5.023x +149.3		Temperature	0.151	-18.5x+528.3
	EC	0.254	Y = 0.590x – 56.55		EC	0.058	-0.488x+25.59
	Moisture	0.513	Y= -1.065x + 26.56		Moisture	0.751	-1.425x+32.84
	Organic matter	0.547	Y= 10.09x -45.96		Organic matter	0.304	8.325x-2.844
Zinc	pH	0.022	Y= 0.132x + 13.90	Zinc	pH	0.738	Y=1.311x+6.296
	Temperature	0.178	Y= -4.476x +14.09		Temperature	0.650	-14.86x+431.3
	EC	0.164	Y= -0116x + 27.30		EC	0.001	-0.017x+14.62
	Moisture	0.360	Y = -0.219x +18.47		Moisture	0.020	-0.091x+11.12
	Organic matter	0.015	Y= -0.412x + 15.06		Organic matter	0.531	-4.259x+18.00
Iron	pH	0.782	Y=2.400x – 5.484	Iron	pH	0.583	Y=2.360x-5.951
	Temperature	0.909	Y=31.42x-891.2		Temperature	0.473	-25.66x+728.5
	EC	0.054	Y=0.208x-16.41		EC	0.003	0.061x-1.035
	Moisture	0.001	Y=0.047x+5.478		Moisture	0.089	0.385x-1.202
	Organic matter	0.312	Y=-5.807x+13.49		Organic matter	0.765	-10.35x+18.44

Table 5: Correlation of metals species and soil physicochemical parameters at Point C and D

Metals	Parameter	R^2 value	Linear equation	Metals	Parameter	R^2 value	Linear equation
		Sample point C				Sample point D	
Copper	pH	0.146	2.421x+5.746	Copper	pH	0.522	2.662x+2.738
	Temperature	0.438	-53.42x+1522		Temperature	0.939	-43.1x+1229
	EC	0.416	1.341x-1286		EC	0.433	0.796x-71.03
	Moisture	0.001	-0.090x+19.28		Moisture	0.001	-0.054x+16.82
	Organic matter	0.172	-10.05x+30.06		Organic matter	0.085	-4.110x+20.91
Manganese	Ph	0.739	-1.952x+17.21	Manganese	pH	0.063	-0.884x+13.41
	Temperature	0.299	15x-415		Temperature	0.137	-15.79x+453.7
	EC	0.077	0.207x-15.08		EC	0.166	0.472x-42.43
	Moisture	0.163	-0.383x+14.43		Moisture	0.621	-1.159x+27.74
	Organic matter	0.615	6.821x-0.816		Organic matter	0.127	-10x+31.2
Zinc	pH	5E-5	0.021x+11.48	Zinc	pH	0.331	-0.969x+18.05
	Temperature	0.022	-5.814x+174.9		Temperature	0.000	0.55x-2.2
	EC	0.325	-0.601x+77.26		EC	0.001	-0.017x+14.62
	Moisture	0.187	-0.579x+21.93		Moisture	0.802	-0.629x+24.50
	Organic matter	0.061	-3.037x+15.34		Organic matter	0.216	6.280x+1.314
Iron	pH	0.689	2.750x-7.404	Iron	pH	0.701	2.296x-4.859
	Temperature	0.879	-37.52x+106.2		Temperature	0.950	-32.43x+919.8
	EC	0.017	0.142x-9.414		EC	0.075	0.247x-20.53
	Moisture	0.011	-0.147x+8.764		Moisture	0.004	-0.073x+7.748
	Organic matter	0.160	-5.085x+12.41		Organic matter	0.198	-4.674x+12.21

Table 6: Correlation of metals species and soil physicochemical parameters at Point E

Metals	Parameter	R^2 value	Linear equation
Copper	pH	0261	2.836x+5.810
	Temperature	0.542	-49.36x+1410
	EC	0.508	1.1299x-122.0

	Moisture	0.020	0.334x+13.81
	Organic matter	0.266	-10.97x+38.31
Manganese	pH	0.205	-1.1613x+15.80
	Temperature	0.013	-5.023x+149.3
	EC	0.254	0.590x-56.55
	Moisture	0.513	-1.065x+26.86
	Organic matter	0.547	10.09x-4.596
Zinc	pH	0.739	1.310x+6.300
	Temperature	0.651	-14.85x+431.1
	EC	0.001	-0.016x+14.54
	Moisture	0.020	0.091x+11.11
	Organic matter	0.532	-4.259x+18.00
Iron	pH	0.667	2.524x-5.885
	Temperature	0.770	-32.73x+928.2
	EC	0.000	0.012x+5.214
	Moisture	0.013	-0.15x+9.214
	Organic matter	0.126	-4.212x+11.73

Limitations of study: This study assessed the distribution of Cu, Mn, Zn and Fe in six species by sequential extraction and by total metal concentration using HNO_3 and HCC. Data was limited to dry season cause of time and finances. However, it could be more information to have the rainy season for comparison. Soil is a complex mixture, and few physicochemical properties may not define. Therefore, the influence of microorganisms such as bacteria and other soil fauna may limit the detection of actual concentration of metals. In this case more accurate and method is required data here was interpreted using existing chemo metric models reported elsewhere. Real time assessment is therefore suggested to circumvent such discrepancies.

IV. CONCLUSION

The results show that the content of selected metals was distributed as bends, with varying degrees. With the exception of Fe, the amount of all metal contents in soil is considerable high, due to pollution. From speciation analysis, Cu, Mn, Zn and Fe exist mainly in the residual fraction and, thus, are of low bioavailability. Zn and Cu were found to be abundant in the non-residual fraction and, thus, of high potential mobility, which is an indication of significant anthropogenic sources. RAC and ecological risk revealedthat site E could develop into a dangerous health hazard with Zn as the metal with overall concern at all sites while Fe and Zn in almost all sites showed significant influence by pH and Temperature.In the near futureif current activities continue, Oguta lake may become a danger to the people.

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