Surveying of Heavy Metal Concentrations in Floodplain Sediments: A Case Study on the Nworie River, Southeast Nigeria

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Abstract
The underutilization of the floodplain sediment of Nworie River in Imo state for agricultural purposes has attracted great concern due to pollution along the floodplain from runoff into the River. To ascertain this, the selected physicochemical properties and heavy metals of the soil were sampled at the depths 0-15cm and 15-30cm to include sand, silk, clay, texture, moisture content, pH, Organic matter , Organic carbon , TN, CEC, Electrical conductivity, Exchangeable cations (Na, K and Mg) and heavy metal contents like lead , chromium , nickel and copper of the disturbed and undisturbed soils were analysed. The soil pH ranged between 5.9-6.2 indicating acidity with sandy Loam dominating the sampled sites. The soil parameters sampled varied between disturbed and undisturbed study area. Amongst the heavy metals analysed in the study area, Cu recorded the mean value of 13.85 ± 10.39 above the 1.00 mg/kg WHO/FEPA, Cr recorded 4.42 ± 1.56 above the 2.00 mg/kg WHO/FEPA and Pb 3.11 ± 0.43 above the 2.0 mg/kg WHO/FEPA standards at the disturbed site respectively. Data on heavy metals generated were subjected to ANOVA and differences in means were compared using statistical test and heavy metals were significantly ($P \leq 0.05$) in the disturbed site than undisturbed site. This then calls for change in the way solid wastes are dumped in drainages that runs down the river during rain events that leads to contamination of agricultural soils at Nworie River. There is need for proper land use planning for sustainable waste management in the area.

Keywords: *River, pollution, floodplain, sediment, physicochemical, heavy metals*

Introduction

The assessment of the pollution of river systems has been a part of many recent studies (Gao et al., 2014; Resongles et al, 2014; Xu et al., 2014;Tang et al., 2014; Xu et al., 2015; Dhivert et al., 2014) . The content of magnetic particles in soils and sediment is also often used for pollution mapping (Petrovský et al., 2001; Knab et al. ,2006).Studies of the geochemical of overbank sediment on a river floodplains are important due to the effect of contaminative land uses on the river floodplain from non-point sources. These contaminated floodplains form “chemical time bombs (CTB)” (Stigliani and Salomons, 1993; Ridgway et al., 1995). When a river breaks its banks and floods, it leaves behind layers of rock and mud, accumulations of sand, gravel, loam, silk and or clay and is often important aquifers, and gradually build up to create the floor of the floodplains (Ubuoh et al., 2016).

According to Karl (2012), soil is economically important, it support plant growth, reserve and purify water, function as nature’s recycling system, regulates the atmosphere, provides habitat for animals and insects, supply engineering materials and building foundations, it is used to filter waste and water, it produces and stores gases such as CO_2. Some of these essential contributions of soil to plant growth are hampered by the presence of contaminant, some of which are heavy metals such as Pb, Ni, Cr and Cu. According to Murray et al. (2009), heavy metals are metallic chemical elements that have a relative density of more than 5 g/l and are toxic or poisonous at high concentration.

Heavy metals gain access into the aquatic environment from both natural and anthropogenic sources and they become distributed in water bodies, suspended solids and sediments during the course of their transportation (Benn et al., 2003; Okoye et al., 2011; Yadar and Kumar, 2011). Heavy metal pollution of ecosystem is more in sediments (Luinnik and Zubenko, 2000; Olowu et al, 2010). The heavy metals can affect the aquatic biota, posing health hazards to fish consumers, such as humans and other wild life through food chain (Alinnor and Obiji , 2010; Singh and Kalamdhad,2011; Bhupander et al, 2011). It has also been reported that sediments serve as reservoirs and sinks for heavy metals and can cause the re-suspension of sediment-bound trace metals (Abida et al., 2009; Olowu et al., 2011). Re-suspension of sediments causes the oxidation of sediment leading to the mobilization of metals into the water body (Saulnier and Mucci, 2000). In unaffected condition, the natural means includes mineralogy and weathering, whereas the anthropogenic sources of heavy metal contamination includes disposal of untreated and partially treated effluents, runoffs carrying the indiscriminate use of heavy metals containing fertilizer and pesticides in farming, soil waste dumping, wet and dry fallout of atmospheric particulate matter (Macklin, et al., 2003), mine tailing leaded gasoline and pain animal manures sewage sludge, waste water irrigation, coal combustion residue, spillage of petrochemical and atmospheric deposition (Khan et al., 2008). The specific objective of this study is to evaluate heavy metals (Pb, Cu, Cr and Ni) deposit in Nworie river floodplain soil of Imo State and to suggest possible ways of soil management in the study area. There is need to extend such studies to the floodplain soil of major cities in the country in order to generate relevant information or data needed for the development of environmental policies since floodplains are present throughout the world and are the sites of significant agricultural, urban and industrial development.

This study was restricted to assessing the concentration of heavy metals in Nworie River floodplain sediments of Imo State for baseline information for policy makers.

Materials and Methods

Study Area

Nworie River in Owerri Municipal Council lies between longitude 7°00’E and 7°15’N and latitude 4°28’E and 4°40’N. It flows through the Federal medical Centre (FMC) Owerri, Alvan Ikoku College of Education (AIFCE) Owerri and Holy Ghost College Owerri (Fig. 1). The area is dominated by plains 200m above sea level except for elevation associated with Okigwe upland (ISEPA/ MPE, 2008). There are two major seasons: wet season which last from April to October and dry season from November to March. It has an annual rainfall of about 1700-2500mm which is concentrated almost entirely between the months of March and October. Average humidity of 80%-85% occurs during the rainy season. Temperature is similar all over the state, with maximum values ranging from 28-35^{0}C and minimum values from 19-24^{0}C (ISEPA/ MPE, 2008).). It covers a distance of about 7.5 Km across Owerri in South-eastern Nigeria (ISEPA/ MPE, 2008), with relative humidity of 70% in dry months and 90% in wet months. The study area is within the rain forest belt of Nigeria. The Nworie River is subject to intensive human and industrial activities and is used as a source of drinking water when the public water system fails (Udensi et al, 2014), it is where runoff from towns and villages emptied to cause siltation, sedimentation that lead to heavy water and soil pollutions (Ubuoh et al., 2014) (Fig. 2). Major lithological materials leading to the formation of soils of Imo state are coastal plain sands (Benin formation of the Oligocene – Miocene geologic era).

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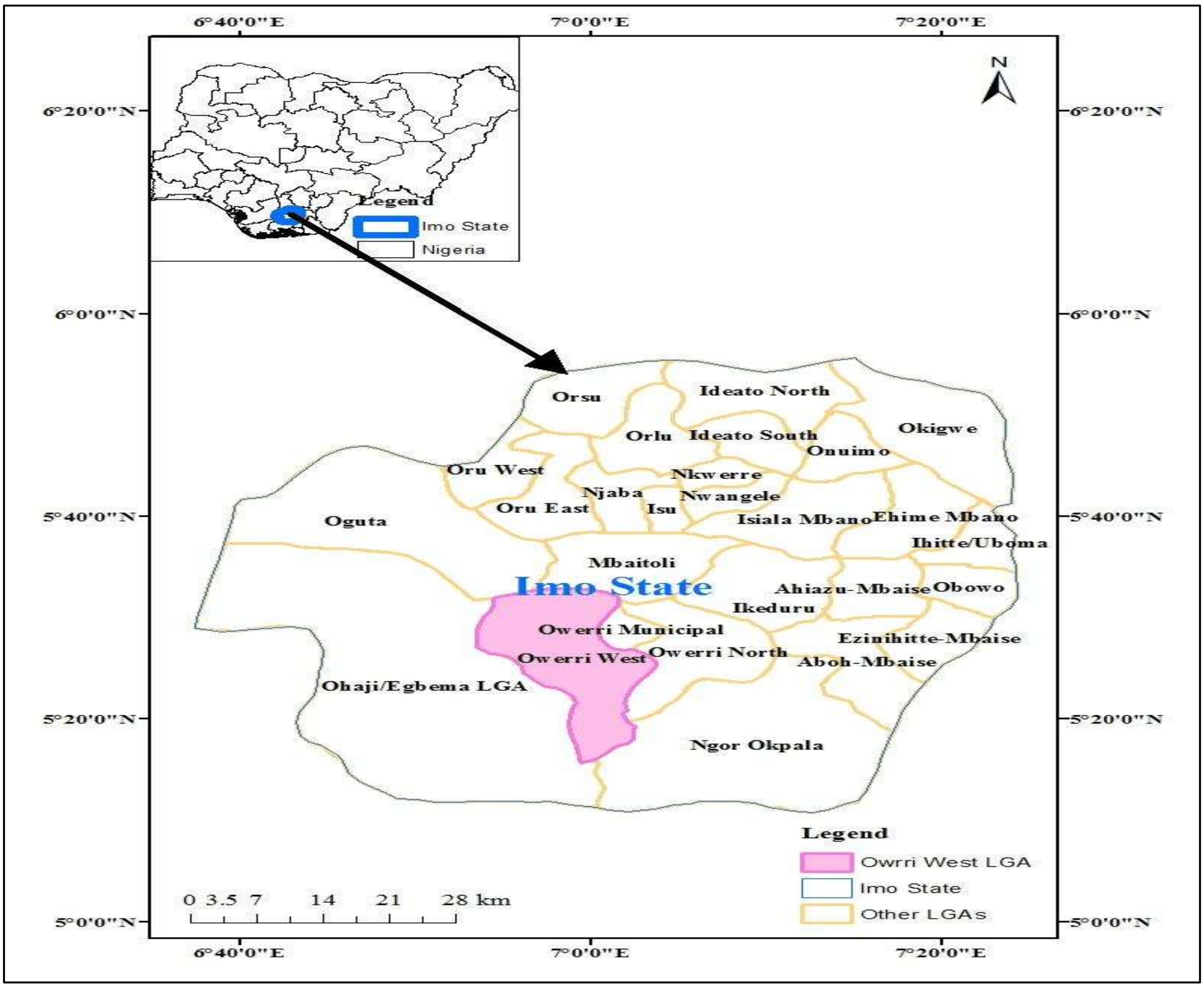


Fig. 1: Map of Imo State showing Owerri Municipal Council

Fig. 2: Danger looms in Imo over polluted Nworie River
source: www.vanguardngr.com

Experimental Design

Sampling design

This research work was designed using Completely Randomized Design (CRD) and the simple random sampling method was adopted in the sample collection. Soil samples were collected from various sites at various depths (0-15cm and 15-30cm) and sample points include viz: (A, B, C and D) from Nworie River floodplain where sediments were deposited (Fig 3):

i. Sample point **A**: St Micheal Catholic Church.

ii. Sample point **B**: Federal Medical Centre (FMC) Owerri.

iii. Sample point **C:** Umuzurike Hospital.

iv. Sample point **D:** an undisturbed site which serves as the control with vegetation and agricultural crops (Emmanuel College.)

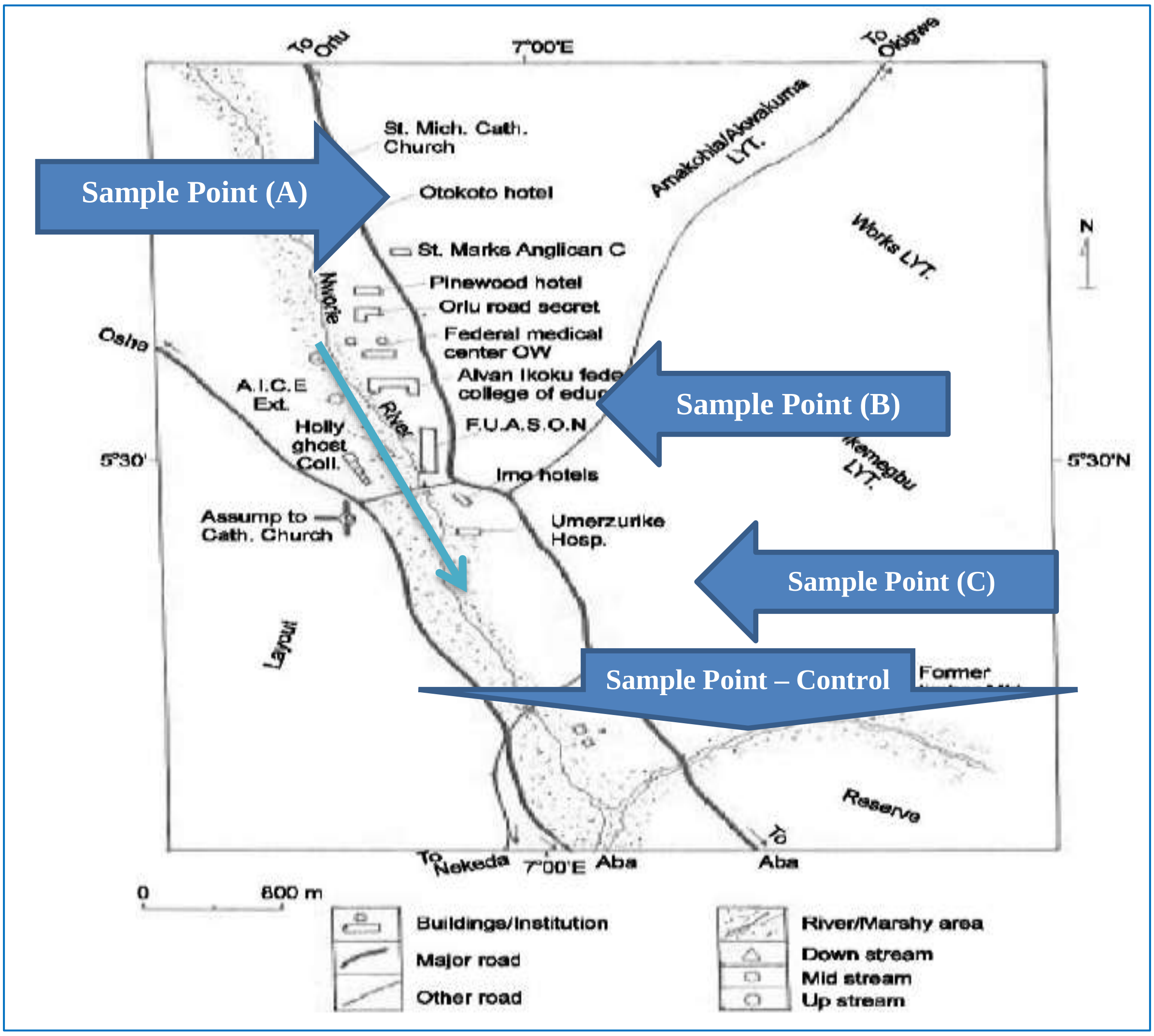


Fig.3: Map of Nworie River Showing Study Locations

Sample collection and preparation

Soil samples were collected during the month of October, 2015 during rain cessation at the interval of 200m between points A-C, along Nworie River in Imo State. Soil samples were equally collected from the control being point D where there was no sedimentation on the cultivated land away from the Nworie Riverside. A total of four sample points were sited that constituted six composite samples plus six replicate samples making 12 samples to form composite samples .Samples were collected using a soil auger, bagged and labelled appropriately and transported to the laboratory for analysis. Soil samples were subjected to pre-laboratory treatments: drying (at room temperature for few days), crushing, and sieving with a 2-mm sieve for metal analysis. The soil samples were then taken to Federal College of Land Resources Technology's Laboratory (FECOLART) Owerri. Particle size distribution (% sand, % silk and % clay) were determined by the hydrometer method, Soil pH was determined using the electrode pH meter, Percentage organic Carbon was determined using the Walkley-Black method, Electrical Conductivity was determined using a Conductivity meter, Exchangeable cations (K, Mg and Na) was determined using Ammonia acetate extraction and AAS for Mg, Flame Photometry for Na and K. Cation Exchange Capacity (CEC) was determined by titration, Total Nitrogen was determined by Regular Macro-Kjeldahl method. Heavy metals were determined by Dilute HCl Extraction (APHA, 1995). Atomic Absorption Spectrophotometers by Shimadzu (AAS- Model 6650) was used for the heavy metal analysis. World Health Organization (WHO) and Federal Environmental Protection Agency (FEPA) standards were used for comparison to heavy metals in floodplain sediment (Table 1).

Table 1: Standards of heavy metal concentrations in sediment

Rating	Lead (Pb)	Nickel (Ni)	Chromium (Cr)	Copper (Cu)
Low	<0.7	<0.002	<0.8	<0.01
Medium	0.7-2.0	0.002-0.02	0.08-2.0	0.01-1.0
High	>2.0	>0.02	>0.2	>1.0

Source: (FEPA, 1991).

Analysis of Variance (ANOVA): ANOVA was used to ascertain if the heavy metals increased significantly across the study area at ($P \leq 0.05$).

Results

The results of the findings are presented in Table 2 indicating the Physical and Chemical Properties in Sediment, Table 3 heavy metal concentration in sediments, The Mean Distribution of the physical and chemical properties in floodplain sediment and Control (Table 4), and Table 5 indicating the comparison of the mean and standard deviation of heavy metal Contents with standards in the study area.

Table 2: Results of the Physical and Chemical Properties in Sediment in the study area

S/N	Depth (cm)	% O.C	% O.M	pH	% Sand	% Silt	% Clay	Texture	% T.N	Na	Mg	K	CEC	Conductivity (µs/cm)
S/N:1	Depth (cm) :A1 (0 -15)	1.911	3.286	5.9	85.12	2.72	12.16	SL	0.455	3.7	0.7	0.5	8.5	100
S/N:2	Depth (cm) :A2 (15 -30)	2.847	4.896	6.2	84.12	3.72	12.16	SL	0.560	3.4	1.4	0.5	8.1	300
S/N:3	Depth (cm) :B1 (0 -15)	1.599	2.750	6.4	67.12	6.72	26.16	SCL	0.525	7.1	0.6	0.4	5.4	400
S/N:4	Depth (cm) :B2 (15- 30)	0.975	1.677	6.0	64.12	7.72	28.16	SCL	0.490	5.6	0.2	0.3	6.9	100
S/N:5	Depth (cm) :C1 (0 - 15)	4.602	7.915	5.0	81.12	4.72	14.16	SL	0.595	1.8	0.5	0.3	6.7	200
S/N:6	Depth (cm) :C2 (15 -30)	2.964	5.098	5.2	83.12	4.72	12.16	SL	0.490	4.7	0.3	0.3	7.9	100
S/N:7	Depth (cm) Ctrl 1 (0 -15)	3.432	5.903	6.4	85.12	6.72	8.16	SL	0.595	0.4	0.3	0.1	9.4	100
SN/:8	Depth (cm) Ctrl2 (15-30)	2.340	4.024	6.0	88.12	4.72	7.16	SL	0.315	0.3	0.1	0.1	8.8	100

Table 3: Concentration (µg/g dry wt) of heavy metals in floodplain sediment of Nworie River

Heavy Metals	A1 (0 - 15)	A2 (15 – 30)	B1 (0 - 15)	B2 (15 – 30)	C1 (0 - 15)	C2 (15 – 30)	Ctrl 1 (0 - 15)	Ctrl 2 (15–30)
Nickel *(mg/kg)*	6.2	7.7	2.9	0.6	3.0	1.3	0.8	1.6
Chromium *(mg/kg)*	3.6	6.0	5.5	1.8	4.2	5.4	4.0	5.1
Copper *(mg/kg)*	11.7	13.7	7.1	11.6	34.0	5.0	4.6	5.7
Lead *(mg/kg)*	3.341	2.949	3.248	2.346	3.168	3.589	0.012	0.478

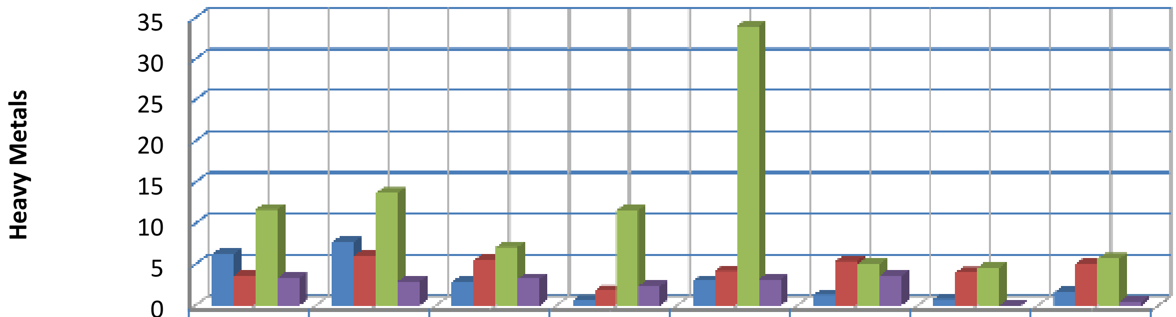
Ctrl: Control

Table 4: The mean distribution of the physical and chemical properties in floodplain sediment and Control in the study area

S/N	Parameters	Mean Distribution	
		Disturbed Site (Floodplain)	Undisturbed Site (Control)
1	% Sand	77.45	86.62
2	% Silk	5.05	5.72
3	% Clay	17.49	7.66
4	% Organic Carbon	2.483	2.886
5	% organic Matter	4.270	4.964
6	pH	5.9	6.2
7	CEC (cmol/kg)	7.4	8.7
8	Na (mg/kg)	4.4	0.4
9	Mg (mg/kg)	1.2	0.4
10	K (mg/kg)	0.4	0.1
11	Conductivity (ms/cm)	200	100
12	Texture	SL	SL
13	% Total Nitrogen	0.513	0.455

Table 5: Comparison of the Mean and Standard Deviation of Heavy Metal Contents with standards

Heavy Metal (mg/kg)	Mean and Standard deviation		WHO / FEPA Permissible Limit
	Disturbed Site	Undisturbed Site (Control)	
Nickel (Ni) *mg/kg*	3.62 ± 2.78	1.2 ± 0.57	0.002 / 0.02
Chromium (Cr) *mg/kg*	4.42 ± 1.56	4.55 ± 0.78	0.8 / 2.0
Copper (Cu) *mg/kg*	13.85 ± 10.39	5.15 ± 0.78	0.01 / 1.0
Lead (Pb) *mg/kg*	3.11 ± 0.43	0.25 ± 0.33	0.7 / 2.0



	A1 (0 - 15)	A2 (15 – 30)	B1 (0 - 15)	B2 (15 – 30)	C1 (0 - 15)	C2 (15 – 30)	Ctrl 1 (0 - 15)	Ctrl 2 (15– 30)
Nickel (Ni)	6.2	7.7	2.9	0.6	3	1.3	0.8	1.6
Chromium (Cr)	3.6	6	5.5	1.8	4.2	5.4	4	5.1
Copper (Cu)	11.7	13.7	7.1	11.6	34	5	4.6	5.7
Lead (Pb)	3.341	2.949	3.248	2.346	3.168	3.589	0.012	0.478

Fig.3: Showing Heavy Metal Concentrations in Sediments at different depths in the study Area

Discussion

From the result, heavy metal pollution of the study area has no effect on the soil textural class. The textural class is sandy loam for the disturbed and undisturbed site (control) (Table 4). The finding agrees with (Ogboghodo et al., 2000), who reported that heavy metal present in crude oil polluted soil has no effect on soil textural properties. Generally, the mean values sand in percentage ranges from 77.45-86.62%, silt from 5.05-5.72%, while clay varied between 7.66- 17.49% in both sites. The high content of sand in the study area suggests that intensity of chemical weathering and sedimentation are high. The result of pH values indicates that the soil is acidic. The value (pH5.9) can be attributed to the low leaching rate of the contaminated site. At this value, the formations of compounds like Al_3PO_4 and $FePO_4$ which are not readily made available for plants consumption are favoured. At a mean pH of 5.9, the exchangeable cations Na, K and Mg became displaced into soil solution and consequently leached. It also slows down microbial activities such as nitrification. There are significant effects of heavy metals on the Cations Exchange Capacity (CEC) of the heavy metal contaminated soil. As shown in the result, its mean value was observed to reduce by 1.6 relative to control. Since the CEC of a soil reveals the capacity of the soil to hold and release important cations, then a heavy metal contaminated soil suffers a significant reduction in cation conservation and release. The electrical conductivity of the study area is apparently low except for point A (0 – 15 cm) and point B (15 – 30 cm) that falls between the ideal conductivity brackets (200 - 1200). This implies that the fertility / nutrient level of the study area is very low, indicating little microbial activities. The mean total Nitrogen of the disturbed and undisturbed sites is 0.519 and 0.455 respectively. This suggests that nitrification reaction in the study area is very low. The mean value of percentage organic matter, carbon and clay ranges from 2.483, 4.270 and 17.490 respectively, where percentage clay falls below the standard (Not less than 50%). This indicates reduction in the fertility of the study area as percentage organic matter and percentage clay of a soil are the basis for soil fertility. The exchangeable cations of the study area are moderately concentrated except for Sodium (Na) that is above 2.0 indicating very high sodium content. Amongst the heavy metals analysed, Cu recorded high mean concentration in the study area with a mean value of 13.85 ± 10.39 for the disturbed site (Fig.3). This concentration surpassed the WHO and FEPA standards (1.00 mg/kg). Cu is negatively related with pH, % silt, % clay, Na, K, CEC and conductivity with a coefficient of (r = -0.53573, -0.16337, -0.22987, -0.77435, -0.22224, -0.00609) respectively. It is positively related with the other physicochemical parameters investigated in the study area. This increase can be attributed to the reduction in biomass, chlorophyll and catalase content of plants. At this concentration and a pH of 5.9, the solubility of Cu is increased which favours the vulnerability of plant root to absorb it and bio-accumulate in their system. Chromium (Cr) is the next most occurring heavy metal in the study area with concentration of 4.42 ± 1.56. This value exceeds the permissible limit (2.00 mg/kg) given by WHO and FEPA. There is a positive relationship of Cr with OC, OM, pH, % sand, % TN, Mg, K and conductivity with a coefficient of (r= 0.403439, 0.403403, 0.0598, 0.450498, 0.384048, 0.588079, 0.340641, 0.62736) respectively, whereas a negative correlation coefficient of (r= -0.38725, - 0.45973, -0.02552, -0.00056) were recorded against % silt, % clay, Na and CEC respectively. This implies that the fertility indices of the study area reduced with increase in Cr. This concentration makes Cr vulnerable to oxidize to Chromium IV, the most toxic form of Cr. This favours its solubility and distribution rate thereby affecting a larger range of plants in the disturbed area (Kalyanaraman and Sivagurunathan, 1993).

Although the concentration of Ni is not very high (3.62 ± 2.78), it exceeds the WHO and FEPA standards. A negative relationship was revealed with % silt, % clay and Na recording a coefficient of (r = -0.76183, -0.56648, -0.40999) respectively. The other physico-chemical properties of the study area increase with Ni (positively related). According to the result, its concentration increases with depth. This metal will pose much effect or threat to man, plants, animals and the environment on subsequent increase in the floodplain soil and would be hazardous as heavy metals deposit occurs in part of the soil where plant roots concentrates and in the form easily accessible by plants (Wagner, 1993).The least concentrated heavy metal in the study area as revealed by the result is Pb (3.11 ± 0.43) with a 2.86 ± 0.10 increase relative to the control. It invariably exceeds the WHO and FEPA standards. This result agrees with (Inuwa, et al, 2007), whose investigation on heavy metals in soil around the major industrial area in Nigeria, significantly exceeds the ideal concentration. Pb significantly ($P \leq 0.05$) increased after being subjected to ANOVA. Pb recorded a negative correlation coefficient of (r= -0.37187, -0.58028, -0.62359, -0.07153, -0.13978) with pH, % Silt, % Clay, % T.N and Na respectively. At this level, plants root readily take up this metal which accumulate in the leaves of leafy vegetables and at the surface of root crops (Ubuoh et al., 2014; Ubuoh et al., 2016). When these contaminated crops are consumed by man, they cause lower IQ, shortened attention span, hyperactivity and mental deterioration in children; it causes decrease reaction, loss of memory, nausea, insomnia, anorexia and weakness of the joints in adults. Although the control recorded slight increase in the heavy metal content relative to the standards used in this work, still it supports the growth of agricultural crops. According to Ciamporova and Mistrik (1993), these increases in the concentration of assessed heavy metals in the study area relative to the control, could be connected to the stunned growth, reduced Nitrogen in plant's tissue, reduced seed yield, lower protein content in seed, adverse effect on the growth and yield of maize plant. Higher photo toxicity, reduced shoots and root biomass was also attributed to increased concentration of heavy metals in soil (Verkleij and Prast, 1989). Reduced level of protein content in heavy metal exposed tissues has also been reported by (Satayakal and Jamil, 1997). Reduced enzyme activities, structural damage, reduced physiological and biological activities, reduced photosynthetic pigment and functional protein, could also be attributed to the increased heavy metal content in the study area (Wilcke et al., 1998). Table 4 shows an increased extractable concentration of heavy metals (Pb, Cu, Ni and Cr) in the disturbed soil relative to WHO and FEPA (1991) standards (Table 1).

Conclusion

This research laid its emphasis on analysing the heavy metal concentration of the study area

and also to suggest ways of managing the soil. A total of 8 soil samples were collected at varying depth in the study area and analysed for the presence of Pb, Cu, Ni and Cr. Although results from the control slightly exceed the standards used, the disturbed sites had a much higher concentration than the standards. Cu concentration at the study area was observed to be at a critical level (13.85 ± 10.39 mg/kg) which exceeds WHO standards. Other heavy metals recorded: Pb (3.11 ± 0.43), Cr (4.42 ± 1.56) and Ni (3.62 ± 2.78) all in mg/kg, while the control (undisturbed) site recorded Pb (0.25 ± 0.33), Cr (4.55 ± 0.78), Ni (1.20 ± 0.57) and Cu (5.15 ± 0.78). It is then concluded that sediment contamination by heavy metals is due to nonpoint source like runoff from roads, mechanic workshops etc. Based on the results, remediation measures are necessary to mitigate the heavy metal concentration in the study area in order to reduce the associated risks and make the soil suitable for agricultural purposes. This study recommends further research on the absorption, accumulation and consumption risk humans are exposed to when agricultural crops from the study area is consumed.

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