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Study on the physicochemical properties and heavy metal status of sediment samples from Ohii Miri river in Abia State, Nigeria

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Abstract

The physicochemical properties and heavy metal status of sediment samples from Ohii Miri River in Abia State, Nigeria were studied. The section of the river studied (from Ahia-Eke to Amaoba-Ime) was divided into three segments designated as Stations A, B, and C. Five sediment samples were collected at each location. Values obtained from the five sampling points were averaged. The sediment samples were analyzed for pH, electrical conductivity, % organic carbon, % organic matter, % ammonium nitrogen, % nitrate nitrogen, % nitrogen, % sand, % silt, % clay, and heavy metals (Fe, Pb, Zn, Mn, Ni, Cd, and Cr) in the rainy and dry seasons respectively using standard procedures. Correlation analysis was also employed to examine the relationship between the various parameters in the sediment samples. The results obtained for heavy metals were compared with USEPA standard. The results showed that the sediment was acidic and the heavy metals concentrations exceeded the USEPA standard. Positive correlations were found to exist between Pb with Zn, Ni; Fe with Ni as well as Ni with Cd in the rainy season. In the dry season, Ni correlated positively with Pb, Zn; Cd with Pb, Ni. Positive correlations existed between Cr in dry season with Cr in rainy season and Pb in dry season with Cr in rainy season. PER indices (contamination factor, degree of contamination, ecological risk factor, sum of the individual potential risk, and geo-accumulation factor) have been calculated. Values of geo-accumulation factor showed that the sediment is not polluted with the studied heavy metals.

Keywords: Ohii Miri River; Physicochemical parameters; heavy metals; Concentration; Permissible limit; Correlation; Potential ecological risk.

Introduction

There have been serious concerns, in recent times, on the indiscriminate waste disposal which most often, end up in the water bodies (Omole and Isiorho, 2011; Gani *et al.*, 2013). Before now, water bodies, especially running waters were thought to be the safest means of

disposing waste materials. As people become aware of the implication of water pollution on health, several laws prohibiting water pollution have been enacted (Federal Water Pollution Control Act, 2002; Water Pollutant Discharge

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Permit System, 2008). However, in developing countries, such law is either not in place or not effective and as such direct waste dumping into water bodies are still in practice. According to Eugene and Busch (2011), 30 to 50% of wastes generated in the sub Saharan Africa (Nigeria inclusive) are disposed in a way that is detrimental to the environment and public health. Of all the sources of water, surface water is the major recipient of pollutants. Effluents from industries, wastes from agricultural institutions and lands as well as domestic wastes are either directly discharged into surface waters or find their way into it through erosion. Influent seepage of urine and leachate from polluted surroundings such as pit latrine (which are very common in developing countries) or soak-away sited upstream could also enrich surface waters with contaminants (Okoye, 1991). Effluent discharged into water bodies leads to accumulation of contaminants such as heavy metals, organometallic or persistent organic pollutants (Ridgwa and Simmiel, 2002). These contaminants become distributed between the aqueous and solid phases of the water bodies. According to Point *et al.* (2007), the sediment is well recognized as an important sink for the compounds present in the upper water column, through the deposition and the burial of suspended particles. On the other hand, the occurrence of bio-turbation and re-suspension processes, currents and waves, dredging and other anthropogenic activities may enhance the remobilization of these compounds at the sediment-water interface, thus resulting in bio-accumulation and bio magnification processes along the whole tropic chain. These contaminants may adversely affect the physical, chemical, and biological characteristics of water (David and Johanna, 2000). However, many aquatic animals of which man directly or indirectly rely upon for survival live in the sediment and several reports have shown that they are capable of accumulating high concentrations of heavy metals (Tole and Shitsama, 2003; Kumar and Achyuthan, 2007; Soegianto *et al.*, 2008). Several researches have

been undertaken to assess the accumulation of contaminants particularly, heavy metals in the water sediment. Addo *et al.* (2011) studied the water quality and levels of some trace metals in water and sediments of the Kpeshie Lagoon located in Accra, Ghana. The result obtained showed that heavy metals in the sediment especially nickel, lead, and chromium were adjudged a potential health risk to humans and the aquatic life of the lagoon's ecosystem. The contamination status of the heavy metals was confirmed on the basis of enrichment factor and geoaccumulation index. Saeed and Shaker (2008) also reported that Mn in Lake Edku sediment and Cd in Lake Manzala sediment, Egypt were higher than the sediment quality guidelines. Ohii Miri River passes through several communities; Ahia-eke, Ibeku, Umudike and Ama-obaIme, etc in Ikwuano Local Government Area of Abia State. The river passes through so many agricultural establishments; some of them were established more than 20 years ago. These agricultural establishments over the years have been using fertilizers and other agro- chemicals which directly or indirectly end up in Ohii Miri River. Meanwhile, this river is the main source of water for drinking and other household's activities for the communities along its course. Moreover, aquatic animals from this river form a greater percentage of the aquatic animals consumed in Abia State and its environs. This report focuses on the physicochemical properties and the heavy metal status of the sediment samples from Ohii Miri River in Abia State, Nigeria which the findings would be informative for future scientific studies.

Materials and Methods

Sampling Area/Collection of Samples

Ohii Miri River studied originate from Ahia-eke and runs through Federal Department of Agricultural Land Resources, Abia State University, National Root Crops Research Institute, Michael Okpara University of Agriculture and Amaoba - Ime. The portion of the river studied was between Ahia-eke and Amaoba-

Ime (Figure 1). This portion was divided into three segments referred to in the work as stations A, B and C. Station A is the portion of the river from Ahia-eke to Abia State University (ABSU), Umuhia Campus. From ABSU, Umuhia Campus to Michael Okpara University of Agriculture, (MOUAU) is Station B while station C stretches from MOUAU to Amaoba-ime. Each of the stations was divided into five sampling site. Sediment samples collected from station A were labeled S1, S2, S3, S4, S5, station B were labeled S6, S7, S8, S9, S10, and station C were labeled S11, S12, S13, S14, S15. Samples were collected in rain and dry seasons respectively.

Sample Preparation/Treatment

The sediment samples were dried and crushed with a wooden roller, sieved with a 2 mm sieve, labeled and stored in soil bags for chemical and physical parameters determination. The actual method used for the determination of physicochemical properties of the sediment samples was as described by AOAC (2005) and reported elsewhere (Olubunmi and Olorunsola, 2010). Samples for determination of heavy metal was weighed (2g) and digested with concentrated HNO₃ and HClO₄ in the ratio of 4:1 as described by Vowotor *et al.* (2014). The digest was allowed

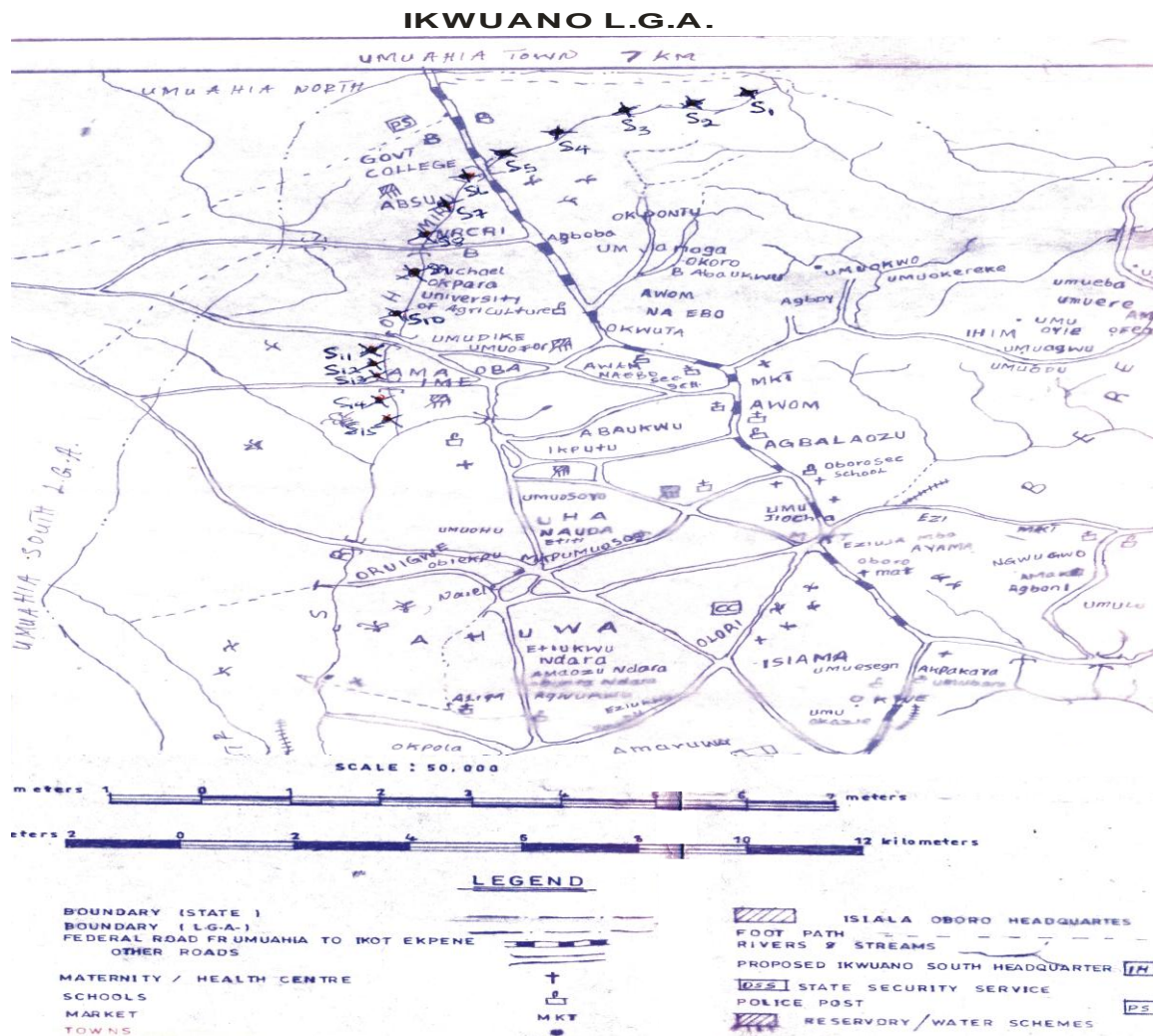


Figure 1: Map of Ikwuano L.G.A. showing the sampling sites

to cool and transferred into polyethylene bottles, labeled and preserved in the refrigerator prior to metallic elements (Fe, Pb, Zn, Mn, Ni, Cd, and Cr) determination using Unicam939/959 atomic absorption spectrophotometer (AAS).

Statistical Analysis

The data obtained were subjected to analysis of variance. Experimental means were compared using the Duncan new multiple range test (DNMR). Relationships between parameters were examined using correlation analysis (SPSS 17.0 version).

The contamination factor (C_F^i) was calculated using equation 1 (Qingjie *et al.*, 2008):

$$C_F^i = \frac{C_{0-1}^i}{C_n^i} \quad (1)$$

where C_{0-1}^i is the concentration of the examined element in the examined environment, C_n^i is concentration of the examined element in the reference environment (Table 10). The degree of contamination (C_d), ecological risk factor (E_r^i), the sum of the individual potential risk (RI), and the geo-accumulation factor (I_{geo}) were calculated using expressions 2, 3, 4, and 5 (Wang *et al.*, 2013) respectively.

$$C_d = \sum C_F^i \quad (2)$$

$$E_r^i = T_r^i \times C_F^i \quad (3)$$

$$RI = \sum E_r^i \quad (4)$$

$$I_{geo} = \log_2 \left[\frac{C_{0-1}^i}{1.5 \times C_n^i} \right] \quad (5)$$

where T_r^i is the metal toxic response factor for a given substance (Cu = Pb = Ni = 5, Zn = 1, Cd = 30, Cr = 2) and the numerical factor '1.5' account for possible variation in background data due to lithogenic effect.

Results and Discussions

Physicochemical Parameters

The mean values of physical and chemical properties obtained for the sediment from Ohii Miri River in Abia State, Nigeria in the rainy and dry seasons respectively, are presented in Tables 1 and 2. The gross mean of the parameters [(Station A + Station B + Station C)/3] is given in Table 3. It is clear from Table 1 that mean values of 4.85 ± 0.45 , 5.13 ± 0.53 and 4.54 ± 0.18 obtained in station A, B and C, respectively in rainy season falls within the acid range. A similar trend is observed for pH in the dry season (Table 2). Close inspection of Table 3 revealed that the water was more acidic in the rainy season (4.84 ± 0.46) than the dry season (5.05 ± 0.30). It could be that more acid forming materials such as fertilizer and agro-chemicals were being washed into the river by erosion during rainy season. These materials may get settle down in the sediment thus increasing the acidity of the sediment during rainy season (Moore *et al.*, 2009). Meanwhile, this value was not within the maximum permissible limit of WHO (6.50-7.50) which according to Abulude and Lawal (2002) is an indicator of a good fish population. As could be seen from Table 1, the electrical conductivity of the sediment samples in the rainy season was not significantly different from one another in all the stations. In the dry, season, higher electrical conductivity value of 9.45 ± 4.16 $\mu\text{S}/\text{cm}$ was obtained in station A which decreased to 9.21 ± 2.22 $\mu\text{S}/\text{cm}$ in station B and to 6.22 ± 2.51 $\mu\text{S}/\text{cm}$ in station C. The mean seasonal electrical conductivity in the dry season (8.29 ± 3.23 $\mu\text{S}/\text{cm}$) was higher than the value of 1.58 ± 1.26 $\mu\text{S}/\text{cm}$ in rainy season (Table 3). There is currently no official guideline as to what is considered safe level for conductivity (Karikari, 2007). However, the conductivity of most freshwaters ranged from 10 to 1000 $\mu\text{S}/\text{cm}$, but many exceed 1000 $\mu\text{S}/\text{cm}$ especially in polluted waters, or those receiving large quantities of land run-off (Chapman, 1992).

Table 1: Mean concentrations of physicochemical parameter of sediment samples in rainy season for each station

PARAMETER	STATION A	STATION B	STATION C
pH	4.85 ^b ± 0.45	5.13 ^a ± 0.53	4.54 ^c ± 0.18
Conductivity $\mu\text{S}/\text{cm}$	1.52 ^a ± 0.94	1.72 ^a ± 1.96	1.51 ^a ± 0.90
% Organic Carbon	3.97 ^a ± 1.93	7.09 ^a ± 2.10	7.04 ^a ± 3.91
% Organic Matter	6.84 ^a ± 3.33	12.22 ^a ± 3.62	12.15 ^a ± 6.73
% NH ₄ -N	0.07 ^a ± 0.04	0.09 ^a ± 0.07	0.09 ^a ± 0.06
% NO ₃	0.02 ^a ± 0.01	0.03 ^a ± 0.01	0.04 ^a ± 0.03
% N	0.07 ^a ± 0.03	0.10 ^a ± 0.03	0.80 ^a ± 0.05
% Sand	79.60 ^a ± 6.07	65.60 ^b ± 14.24	60.40 ^b ± 10.35
% Silt	11.80 ^a ± 4.77	14.20 ^a ± 6.72	15.60 ^a ± 8.67
% Clay	8.60 ^a ± 1.79	20.2 ^b ± 9.65	24.40 ^b ± 7.80

Mean values of the same row with the same superscript are not significantly different at 5% level of probability using DMRT. Station A = Ahia-eke, Station B = Umudike, Station C = Amoeba Ime.

Table 2: Mean concentrations of physicochemical parameter of sediment samples in dry season for each station

PARAMETER	STATION A	STATION B	STATION C
pH	4.82 ^a ± 0.21	5.11 ^a ± 0.21	5.22 ^a ± 0.34
Conductivity $\mu\text{S}/\text{cm}$	9.45 ^a ± 4.16	9.21 ^a ± 2.22	6.22 ^a ± 2.51
% Organic C	2.10 ^a ± 0.54	2.46 ^a ± 1.12	1.55 ^a ± 0.96
% Organic Matter	3.52 ^a ± 0.88	4.25 ^a ± 1.93	2.68 ^a ± 1.65
% NH ₄ -N	0.07 ^a ± 0.03	0.07 ^a ± 0.03	0.08 ^a ± 0.05
% NO ₃	0.03 ^a ± 0.01	0.03 ^a ± 0.01	0.04 ^a ± 0.03
% N	0.18 ^a ± 0.07	0.23 ^a ± 0.11	0.13 ^a ± 0.09
% Sand	67.40 ^a ± 9.53	64.20 ^a ± 14.93	64.00 ^a ± 9.76
% Silt	17.80 ^a ± 12.60	24.20 ^a ± 18.09	20.20 ^a ± 10.73
% Clay	14.80 ^a ± 7.07	11.60 ^a ± 5.01	16.40 ^a ± 10.62

Mean values of the same row with the same superscript are not significantly different at 5% level of probability using DMRT. Station A = Ahia-eke, Station B = Umudike, Station C = Amoeba Ime.

Table 3: Gross mean seasonal concentrations of parameters in sediment samples

PARAMETERS	RAINY SEASON		DRY SEASON	
	MEAN \pm SD	RANGE	MEAN \pm SD	RANGE
pH	4.84 ^b \pm 0.46	(4.25-5.82)	5.05 ^a \pm 0.30	(4.64-5.60)
Conductivity μ S/cm	1.58 ^b \pm 1.26	(0.56-5.22)	8.29 ^a \pm 3.23	(4.06-15.45)
% Organic C	6.03 ^b \pm 3.00	(0.55-10.75)	2.04 ^a \pm 0.93	(0.97-3.68)
% Organic M	10.40 ^a \pm 5.16	(0.95-18.53)	3.48 ^b \pm 1.58	(1.68-6.34)
% NH ₄ -N	0.08 ^a \pm 0.06	(0.012-0.211)	0.07 ^a \pm 0.04	(0.035- 0.155)
% NO ₃ -N	0.03 ^a \pm 0.02	(0.011-0.078)	0.03 ^a \pm 0.02	(0.020-0.084)
% Nitrogen	0.09 ^b \pm 0.04	(0.035-0.155)	0.18 ^a \pm 0.09	(0.07-0.35)
% Sand	68.53 ^a \pm 13.02	(45.2-85.2)	65.20 ^a \pm 10.93	(41.8-83.8)
% Silt	13.87 ^a \pm 6.60	(5.40-29.40)	20.73 ^a \pm 13.39	(1.40-51.4)
% Clay	17.6 ^a \pm 9.53	(7.40-33.4)	14.26 ^a \pm 7.61	(6.8-30.8)

Mean values of the same row with the same superscript are not significantly different at 5% level of probability using DMRT. Station A = Ahia-eke, Station B = Umudike, Station C = Amoeba Ime.

The higher value of conductivity obtained in the dry season is indicative of high concentration of inorganic Dissolved solid (chloride, nitrate, sulphate, phosphates and calcium) in the water since conductivity is related to the concentration of Total Dissolved Solids (TDS) (Addo *et al.*, 2011). It is very clear from Tables 1 and 2 that there were no significant differences ($p > 0.05$) between the values of % organic carbon, % organic matter, % ammonium nitrogen, % nitrate nitrogen and % nitrogen obtained in each of the stations in the rainy season and dry seasons. However, the gross mean seasonal values (Table 3) of % nitrogen were higher in dry season than the rainy season and differed significantly at $p < 0.05$. The mean concentration of organic carbon was also significantly higher in the dry season than the rainy season in the sediment samples. This is indicative of pollution of the water probably by decaying natural organic matter and synthetic sources; detergents, pesticides, fertilizers

herbicides and chlorinated organic compounds from the agricultural institutions located along the course of the river (Davis *et al.*, 2006). The percentage sand, silt and clay in the sediment samples in rainy and dry seasons are also given in Tables 1 and 2. In the rainy season, the upper segment of the river (Station A) had significantly the highest mean percentage of sand ($79.6 \pm 6.07\%$) and there was no significant difference between the percentages of sand (65.6 ± 14.24) and (60.4 ± 10.35) obtained for stations B and C. The highest percentage of clay were obtained at the lower segment of the river station C with the value of $24.40 \pm 7.80\%$ which decreased in the middle segment (Station B) to $20.2 \pm 9.65\%$ and the upper segment (Station A) to $8.6 \pm 1.79\%$. However, there were no significant differences ($p > 0.05$) between the value of % sand, silt and clay obtained in all the stations in the dry season

Table 4: Mean concentrations of heavy metal concentrations of sediment samples in rainy season for each station

PARAMETER	STATION A	STATION B	STATION C
Fe(Mg/Kg)	21.43 ^a ± 2.98	16.35 ^b ± 1.90	13.17 ^c ± 2.40
Pb(Mg/Kg)	49.16 ^a ± 14.47	44.72 ^a ± 22.96	25.70 ^b ± 0.23
Zn(Mg/Kg)	26.01 ^a ± 14.53	37.80 ^a ± 33.77	9.15 ^a ± 3.60
Mn(Mg/Kg)	4.74 ^a ± 1.17	4.13 ^a ± 2.15	4.88 ^a ± 2.31
Ni(Mg/Kg)	2.01 ^a ± 0.31	0.85 ^b ± 0.38	0.43 ^b ± 0.26
Cd(Mg/Kg)	0.87 ^a ± 0.12	0.34 ^b ± 0.14	0.58 ^b ± 0.29
Cr(Mg/Kg)	0.33 ^b ± 0.08	0.51 ^a ± 0.18	0.21 ^b ± 0.08

Mean values of the same row with the same superscript are not significantly different at 5% level of probability using DMRT. Station A = Ahia-eke, Station B = Umudike, Station C = Amoeba Ime.

(Table 2). These values obtained for % sand, silt, and clay are in the range reported by Allesandro (2009). The even distribution of sand, salt, and clay in all the stations (A, B and C) particularly in the dry season could be attributed to topography and land forms of the area. The low clay content in some stations suggest that the sediment undergone high degree of weathering and leaching (McLennan, 1995).

Heavy metals status of Ohii Miri River

Sediment is very important tracer of metal in aquatic system (Abeh *et al.*, 2007). The concentration of heavy metals in sediment gives an idea of possible pollution status of the water body and also enable protective measures to be taken against excessive exposure either directly or indirectly. According to Davis *et al.* (2006), sediment is the major depositories of heavy metals holding over 99% of the total amount of heavy metals in aquatic environment. Tables 4 and 5 present the mean seasonal variation of the heavy metal concentrations of sediment samples from Ohii Miri River in Abia State, Nigeria in the rainy and dry seasons respectively, and the gross average of the seasonal variation of heavy metal

concentrations in the sediment [(Station A+ Station B + Station C)/3] is given in Table 6. From Table 4, it is observed that the concentrations of Fe in the lower segment (station C) had the highest significant value of 26.77 ± 0.45 mg/kg.

The gross mean seasonal concentration of Fe in the dry season differs significantly ($p < 0.05$) from the value in the rainy season while there was no significant difference ($p > 0.05$) between the values of Pb in the rainy and dry season. Comparing the values of Fe and Pb obtained for the two seasons with the permissible limit (USEPA, 1986), it is very clear that the values were far above the permissible values. For instance, 16.98 ± 4.20 mg/kg (rainy season) and 26.55 ± 0.83 mg/kg (dry season) for Fe against 1.0 mg/L permissible limit and 39.68 ± 17.93 mg/kg (rainy season) and 43.40 ± 15.08 mg/kg (dry season) for Pb against 0.05 mg/L permissible limit. This suggests that Ohii River which is the major source of drinking water for people living along the course is heavily polluted with Fe and Pb. The result obtained for Fe is in strong agreement with other reports (Asaolu *et al.*, 1997; Asaolu and Olaafe, 2004; Nwajei and Gagophien, 2000; Adefemi and Awokunmi, 2010) that iron occurs at high concentration in Nigeria soil. As warned by

Table 5: Mean concentrations of heavy metal concentrations of sediment samples in dry season for each station

PARAMETER	STATION A	STATION B	STATION C
Fe (Mg/Kg)	26.47 ^b ± 1.04	24.43 ^a ± 1.01	26.77 ^b ± 0.45
Pb (Mg/Kg)	40.05 ^a ± 8.00	53.20 ^a ± 19.85	36.95 ^a ± 12.35
Zn (Mg/Kg)	158.28 ^b ± 42.61	158.41 ^b ± 32.55	115.53 ^a ± 17.75
Mn (Mg/Kg)	19.93 ^a ± 5.56	28.93 ^a ± 10.50	22.22 ^a ± 12.52
Ni (Mg/Kg)	9.24 ^a ± 1.47	10.93 ^a ± 4.68	8.77 ^a ± 1.71
Cd (Mg/Kg)	2.00 ^a ± 0.53	2.22 ^a ± 0.63	2.18 ^a ± 0.39
Cr (Mg/Kg)	1.15 ^a ± 0.21	1.47 ^a ± 0.34	0.76 ^b ± 0.25

Mean values of the same row with the same superscript are not significantly different at 5% level of probability using DMRT. Station A = Ahia-eke, Station B = Umudike, Station C = Amoeba Ime.

Table 6: Mean seasonal concentrations of parameters in sediment samples

PARAMETERS	RAINY SEASON		DRY SEASON	
	MEAN ±SD	RANGE	MEAN ±SD	RANGE
Fe(mg/kg)	16.98 ^b ± 4.20	(10.53-26.33)	26.55 ^a ± 0.83	(24.64-27.29)
Pb(mg/kg)	39.68 ^a ± 17.93	(25.38-81.85)	43.40 ^a ± 15.08	(26-25-87.5)
Zn (mg/kg)	24.32 ^b ± 23.91	(4.03-88.83)	44.08 ^a ± 36.71	(89.84-198.92)
Mn(mg/kg)	4.58 ^b ± 1.83	(2.61. - 7.93)	23.69 ^a ± 10.03	(12.16-44.1)
Ni(mg/kg)	1.10 ^b ± 0.75	(0.23. -2.45)	9.65 ^a ± 2.94	(6.68-18.65)
Cd(mg/kg)	0.60 ^b ± 0.29	(0.18. -1.03)	2.13 ^a ± 0.50	(1.21-2.97)
Cr (mg/kg)	0.35 ^a ± 0.17	(0.13. -0.78)	1.12 ^a ± 0.39	(0.44-1.87)

Mean values of the same row with the same superscript are not significantly different at 5% level of probability using DMRT. Station A = Ahia-eke, Station B = Umudike, Station C = Amoeba Ime.

the Centers for Disease Control and Prevention (2003), iron overload can lead to hemochromatosis, a disease characterized by fatigue, weakness, joint pain, abdominal pain, or organ damage. Pb in the other hand is known for its poisonous nature and USGAO (2000) has reported that Pb poisoning can cause stunted growth and learning disabilities in children as well as enhance crime and anti-social behavior in children. Also, as documented by WHO (1996), high concentrations of Pb in the body can cause permanent damage to the central nervous system, the brain, and kidney.

There were no significance differences ($p > 0.05$) between the values of Zn and Mn in all the stations in the rainy season (Table 4) but in the dry season, the middle segment of the river (station B) had highest significant values of 158.41 ± 32.55 mg/kg and 28.93 ± 4.68 mg/kg for Zn and Mn respectively (Table 5). However the mean seasonal concentrations of Zn and Mn in dry season were higher than the values in the rainy season (Table 6). A comparison of the gross mean seasonal values of Zn and Mn (Table 6) with the USEPA (1986) standard (1.0 mg/L for Zn and 0.05 mg/L for Mn) clearly shows that the

the concentrations reported that accumulation of manganese in the kidney, liver and bones causes manganese psychosis. High level of Zn has been associated with disruption in the homeostasis of other essential elements (Anadu *et al.*, 1989). It could be seen also from Table 4 that the upper segment of the river (Station A) had significantly the highest values of 2.01 ± 0.31 mg/kg and 0.87 ± 0.12 mg/kg for Ni and Cd respectively, in the rainy season while significant higher value of 0.51 ± 0.18 mg/kg for Cr was obtained in Station B. There were no significant difference ($p > 0.05$) between the concentration of Ni and Cd in Station B and C respectively in the rainy season. In dry season (Table 5), there were no significant difference between the values of Ni and Cd obtained in all the stations. The middle segment of the river (Station B) had significantly the highest Cr value of 1.47 ± 0.38 mg/kg. There was significant difference between the Cr values of 1.15 ± 0.21 and 0.76 ± 0.25 mg/kg obtained in Station A and C (Table 5). The mean seasonal concentration of Ni and Cd in the dry season was significantly higher than the values in the rainy season (Table 6). Comparing the mean seasonal values (Table 6) of Ni, Cd, and Cr with the USEPA

(1986) permissible limits (Ni = 0.5 mg/L; Cd = 0.01 mg/L; Cr = 0.05 mg/L), it is seen that the concentrations of the three metals are only slightly higher than the standard. Generally, the concentrations of Fe, Pb, Zn, Mn, Ni, Cd, and Cr in sediment samples were significantly higher in the dry season than the rainy season. The high concentrations of these heavy metals in the sediment may be due to accumulated effect of continuous release and deposition of wastes containing these metals in the river through erosion, indirect disposal of domestic and agricultural wastes, spilling of loaded crude etc. into the water body. In the dry season, evaporation decreases the volume of the water and hence these metals become more concentrated. These heavy metals, if gain excess into human system through either direct consumption of the water or food chain is capable of posing health problems.

Correlation Analysis

Correlation analysis was used to examine the relationship between the various parameters in the water samples. Table 7 shows the correlation matrix of the relationship between

Table 7: Correlation matrix for heavy metals concentration in sediment in rainy season

Heavy metals in sediment in rainy season	Heavy metals in sediment in rainy season						
	Fe	Pb	Zn	Mn	Ni	Cd	Cr
Fe	1						
Pb	0.530*	1					
Zn	0.272	0.589*	1				
Mn	0.035	-0.241	-0.225	1			
Ni	0.868**	0.518*	0.252	-0.116	1		
Cd	0.514	0.201	-0.095	0.119	0.556*	1	
Cr	0.090	0.199	0.461	-0.106	-0.021	-0.319	1

*Correlation is significant at the 0.05 level (2-tailed).

**Correlation is significant at the 0.01 level (2-tailed).

heavy metals concentration of sediment in dry season. As could be seen from the table, Ni correlated positively with Pb ($r = 0.565$, $P < 0.01$). Zn ($r = 0.565$, $P < 0.05$) and Cd correlated significantly with Pb ($r = 0.623$, $P < 0.05$), Zn ($r = 0.570$, $P < 0.05$) and Ni ($r = 0.750$, $P < 0.01$). This also suggests that they are related and may be from the same source. Table 9 shows the correlation matrix of the relationship between the various

concentration of heavy metals in sediment in dry and rainy season. Fe in rainy season correlated positively and significantly with Zn in dry season ($r = 0.648$, $P < 0.01$). Cr in dry season correlated positively and significantly with Cr in rainy season ($r = 0.912$, $P < 0.01$) and Pb in dry season correlated positively and significantly with Cr in rainy season ($r = 0.617$, $P < 0.05$).

Table 8: Correlation matrix for heavy metals concentration in sediment in dry season

Heavy metal in sediment in dry season	Heavy metal in sediment in dry season						
	Fe	Pb	Zn	Mn	Ni	Cd	Cr
Fe	1						
Pb	0.002	1					
Zn	0.066	0.408	1				
Mn	-0.157	-0.019	0.188	1			
Ni	0.009	0.865 ^{**}	0.565 [*]	-0.027	1		
Cd	0.287	0.623 [*]	0.570 [*]	0.130	0.750 ^{**}	1	
Cr	-0.143	0.427	0.201	0.160	0.258	-0.207	1

*Correlation is significant at the 0.05 level (2-tailed).

**Correlation is significant at the 0.01 level (2-tailed).

Table 9: Correlation matrix for heavy metals concentration in sediment in rainy and dry seasons

Heavy metal levels in dry season	Heavy metal levels in rainy season						
	Fe	Pb	Zn	Mn	Ni	Cd	Cr
Fe	0.040	0.316	-0.103	-0.248	-0.183	-0.020	-0.022
Pb	-0.091	-0.040	0.330	-0.315	-0.037	-0.345	0.617 [*]
Zn	0.648 ^{**}	0.354	0.207	-0.095	0.495	0.233	0.172
Mn	0.162	0.220	0.514	0.161	-0.041	-0.103	0.250
Ni	0.068	-0.107	0.247	-0.368	0.071	-0.170	0.421
Cd	0.062	0.000	0.263	-0.380	-0.015	-0.050	0.016
Cr	0.169	0.245	0.357	0.168	0.061	-0.215	0.912 ^{**}

*Correlation is significant at the 0.05 level (2-tailed).

**Correlation is significant at the 0.01 level (2-tailed).

Sediment Contamination Assessment

The Hakanson potential ecological risk (PER) method was employed in assessing the level of pollution of the studied sediment. The PER method was originally developed by Hakanson to assess the characteristics and environmental behavior of heavy metal contaminants in soil sediments (Hakanson, 1980). This assessment which is performed using parallel and equivalent index classification, gives a quantitative approach of predicting the level and extent of potential hazards. The PER technique is based on element abundance and several preconditions (Dumcius *et al.*, 2011; Liu *et al.*, 2009). These preconditions include: concentration (increase in heavy metal concentration increases PER); species number (multiple metals in sediment tend to synergistically increase PER); toxic response (heavy biological toxic metals have high tendency of potential risk); and sensitivity. The contamination factor (C_F) which is usually employed to assess possible anthropogenic input of metals to sediment (Vowotor *et al.*, 2014) was calculated using equation 1. The results obtained are presented in Table 11. According to the Håkanson (1980) classification, $C_F < 1$ points to low contamination factor, $1 \leq C_F < 3$ indicates moderate contamination factor, $3 \leq C_F < 6$ points to considerable contamination, and $C_F \geq 6$ suggests very high contamination factor. It is clear from Table 11 that the C_F values are less than unity for all the studied heavy metals in both

rainy and dry seasons except for Pb. It can be infer that the sediment from Ohii Miri river is low in Fe, Zn, Mn, Ni, Cd, and Cr but moderately enriched with Pb in both rainy and dry seasons. However, the low values of contamination factor (0.001 to 1.102 in rainy season and 0.001 to 2.152 in dry season) in the sediment show that the slight heavy metal pollution of Ohii Miri river was not likely to originate from anthropogenic activities. The heavy metals probably originated from natural processes. Similar observation has been reported by Olubunmi and Olorunsola (2010) on the heavy metal contamination of Agbabu bitumen deposit area of Ondo State, Nigeria.

The degree of contamination (C_d) which has been used recently by Vowotor *et al.* (2014) to assess the excessive values of monitored elements in soil sediment samples, was deployed as indicator of the extent of the sediment contamination. This was evaluated using equation 2 and the values obtained for rainy and dry seasons are presented in Table 11. The classification of level of contamination with respect to C_d value is that $C_d < 8$ is indicative of low contamination, $C_d \geq 8, < 16$ points to moderate contamination, $C_d \geq 16, < 32$ suggests relatively contamination whereas $C_d \geq 32$ indicates very high contamination (Qingjie *et al.*, 2008). It is obvious from Table 11 that the values of C_d in both rainy and dry seasons fall under the first class of the C_d classification.

Table 10: Consensus-Based Sediment Quality Guidelines of Wisconsin (CBSQG)

Metal	Consensus Based Sediment Value (mg/kg dry wt)
Cadmium	0.99
Chromium	43
Iron	20,000
Lead	32
Manganese	460
Mercury	0.18
Nickel	23
Zinc	120

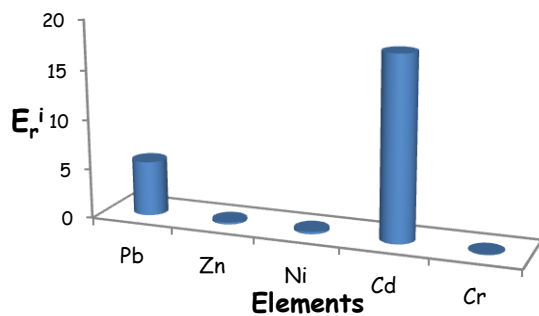
Wisconsin Departmental of Natural Resources (2003)

The values of the ecological risk factor (E_r^i) and the sum of the individual potential risk (RI) obtained by using equations 3 and 4 respectively are also presented in Table 11. According to Qinglie et al. (2008), the classification of these indices is as follow: $E_r^i < 40$ is indicative of low contamination; $E_r^i \geq 40 < 80$ suggests moderate contamination; $E_r^i \geq 80 < 100$ points to strong contamination; $E_r^i \geq 100 < 320$ indicates very strong contamination; while $E_r^i \geq 320$ suggests extremely strong contamination. Similarly, $RI < 150$ is indicative of low contamination. $RI \geq 150 < 300$

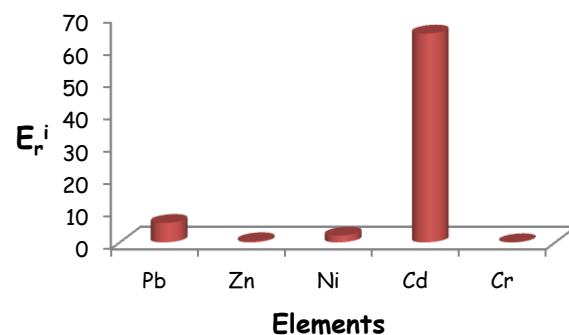
points to moderate contamination, $RI \geq 300 < 600$ suggests strong contamination, while $RI \geq 600$ signifies very strong contamination. Judging from the E_r^i and RI values shown in Table 11, it can be concluded that the sediments from Ohii Miri river are low in heavy metal contaminants in both rainy and dry seasons. Meanwhile, it is obvious from the table that Cd (18.3 in rainy season and 64.58 in dry season) is the most contributing factor to the RI values obtained. This seems to agree with the findings of Ogunkunle and Fatoba (2013) that Nigeria soil is gradually being enriched with Cd. However, to assess the level of individual heavy metal enrichment in the sediments, chart of E_r^i

Table 11: PER values of heavy metals in Ohii Miri river in the rainy and dry seasons

Element	Parameter									
	Rainy season					Dry season				
	C_F^i	C_d	E_r^i	RI	I_{geo}	C_F^i	C_d	E_r^i	RI	I_{geo}
Fe	0.001	-	-	-	-5.880	0.001	-	-	-	-10.143
Pb	1.102	-	5.51	-	-0.445	1.203	-	6.015	-	-0.319
Zn	0.203	2.071	0.203	24.269	-2.888	0.367	4.221	0.367	73.094	-2.030
Mn	0.100		-		-7.236	0.052		-		-4.865
Ni	0.048		0.240		-4.972	0.420		2.100		-1.838
Cd	0.610	-	18.300	-	-1.308	2.152	-	64.560	-	0.520
Cr	0.008	-	0.016	-	-7.527	0.052	-	0.052	-	-5.848



(a)



(b)

Figure 2: Ecological risk factor (a) during rainy season (b) during dry season

versus individual element was plotted for rainy and dry seasons (Figures 2a and b). The plots show that the level of heavy metal enrichment in the sediment is in the order: $Cd > Pb > Ni > Zn > Cr$. A comparison of Figure 2a with 2b reveals that the heavy metal accumulation in the sediment is higher in the dry season than in the rainy season. This might be due to the reduction in the water volume during the dry season due to evaporation.

The degree of contamination of the sediment was also evaluated by calculating the geo-accumulation parameter (I_{geo}) (equation 5) and the results obtained are given in Table 11. Muller (1969) classification of I_{geo} grouped it into seven grades: $I_{geo} \leq 0$ (grade 0), unpolluted; $0 < I_{geo} \leq 1$ (grade 1), slightly polluted; $1 < I_{geo} \leq 2$ (grade 2), moderately polluted; $2 < I_{geo} \leq 3$ (grade 3), moderately severely polluted; $3 < I_{geo} \leq 4$ (grade 4), severely polluted; $4 < I_{geo} \leq 5$ (grade 5), severely extremely polluted; and $I_{geo} > 5$ (grade 6), extremely polluted. It can be clearly seen from Table 11 that the I_{geo} values of all the studied metals were lower than unity and negative in both seasons except Cd in the dry season. It can be concluded based the Muller's grading that the metals were grade 0 and the sediments were not polluted in both seasons. However, Olubunmi and Olorunsola (2010) have noted that the I_{geo} factor is not readily comparable with enrichment factor due to the nature of I_{geo} calculation which involves a logarithm function and a background multiplication factor of 1.5.

Conclusion

This study has established that Ohii Miri River is acidic and hard hence might not be very good for direct consumption. The sediment is highly enriched with inorganic dissolved solid such as chloride, nitrate, sulphate, phosphates and calcium. Positive correlations exist between Pb with Zn and Ni, Fe with Ni, and Ni with Cd in the

rainy season; Ni with Pb, Zn and Cd with Pb and Ni in the dry season. Also, Positive correlations exist between Cr in dry season with Cr in rainy season and Pb in dry season with Cr in rainy season. More so, PER indices revealed that the river is not highly contaminated with heavy metals.

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