



Seasonal Metal Distribution in Ondo Coastal Sediment, Nigeria

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ABSTRACT: The distribution of heavy metals in streambed sediment from an oil-producing region in Nigeria has been examined between the two distinct seasons (dry and wet). The highest mean concentration during the dry season (wet season in brackets) was 2083.37355.5 (2264.27347.3)mg/kg Cu and 0.1670.06 (0.1970.09)mg/kg Zn respectively. With similar patterns at both seasons, the order of increasing concentration was Zn < Cd < Ni < Pb < Cu. Apart from Pb, metal concentration occurred at greater concentrations during the wet season. Elevated concentration of Cu in the study was attributable to the nature of Nigerian soil. However, the impact of oil related activities within the study region may be contributing to the levels of other metals, particularly Pb. Significant correlations ($r = 0.05$; 0.01) were recorded between some of the metals, pH and %clay in the mud fraction. Cadmium vs Ni and Cu vs Ni were both significant at both seasons. The clay fraction of the mud were significantly correlated with Pb ($r = 0.949$), Cd ($r = 0.749$) and Ni ($r = 0.869$). The partition coefficient data showed that several factors controlled the adsorption of metals unto the sediment. Comparison of sediment with guideline values indicated anthropogenic enrichment but it was considered that only Cu, and possibly Pb pose potential threats to the ecology of the area. @ JASEM

In the recent years, there has been increasing concern by communities and concerned individual over the pollution of the marine environment, especially relating to the presence of anthropogenic contaminants and their possible biological effects. Not until 1996 when the first oil spill tagged 'YAYE' Oil Spill occurred within the coastal area of Ondo State, Nigeria, the ocean was considered generally free of contaminants. The delay in this study for metal input into the aquatic environment was born out of the fact that levels of metals in oil are considered very small. Thus, it is envisaged that possible and significant accumulation may have occurred over the years and which may now require urgent attention.

Heavy metals, such as cadmium, mercury, lead, copper nickel and zinc, are regarded as serious pollutants of aquatic ecosystems because of their environmental persistence, toxicity and ability to be incorporated into the food chains. Several investigations have been reported in the literatures on the concentration and partitioning of these metals in sediment. Some of these studies are based on the fact that the aquatic environment has been regarded as a dumping site especially in most developing countries. This indiscriminate dumping, in some cases, has led to serious health problems to animals and humans via ingestion of soil and/or sediment, seafood's and water. The toxicity of most of these metals has been attributed mainly to capability of the ions to form stable complexes with the active sites of protein. Factors such as pH, redox potential, and total organic carbon and cation exchange capacity (CEC) have been identified as some of the major factors controlling the levels of metals in the river system.

Little environmental data is available for the coastal region of Ondo State located within the southwestern region of Nigeria. The sampling sites are locations that are noted for large biological production and are especially important for commercial fish. The dominant potential source of contaminants is presumably the ongoing petroleum related activities. Consequently; the present report is on the analysis of a suite of trace metals (Cd, Cu, Pb, Ni and Zn). These along with Hg (not determined in this study) may be considered the most biological significant metals.

MATERIALS AND METHODS

Sample Collection and Preparation

Streambed sediments were sampled during the dry and wet seasons of 2005. Seven sampling sites were examined along with one reference location. The samples were collected at each site, one from midstream and one from each bank in a cross section fashion. About five locations were considered at each sampling site. Samples from each location were homogenized into a composite sample from which representative samples were taken. Details of the samples locations and site identification coordinates as revealed by global positioning system (GPS) are presented in Table 1. The mud fraction of the sediment, consisting of the silt plus clay sizes ($<63\mu\text{m}$) were used for metal analysis. With this fraction, the effect of varying granulometry on the trace metal contents between the samples was minimized¹³. Moreover, in this fraction which is generally enriched in clay minerals and organics, the particle-reactive metals are expected to be concentrated by ion exchange, adsorption and clay-metal-organic complex formation. In fact, this fraction remains the most

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desirable sediment component for monitoring metal pollution.

This fraction (mud) was obtained by suspending a 5g of a thawed grab subsample in deionized distilled water and homogenized. The suspension was sieved through a 230-mesh nylon screen, and the separated mud particles were then freeze-dried and powdered using an agate mortar and pestle. This process of mud separation by wet sieving may possibly results in hydrolysis of some metals or desorption from the sediment which may lead to loss of metal portions. This portion is considered negligible.

Chemical Analysis

A 0.5g aliquot of the dried powder was taken into a 140ml Teflon bomb and digested in 15ml of a high purity concentrated 7ml – HF + 5ml – HNO₃ + 3ml – HCl acid mixture on a hot plate at about 1100C for 6 hours within a fume cupboard. After cooling to room temperature, the digest was diluted to 100ml and dried and then again dissolved in 10% HNO₃ and made up to 20ml by adding deionized water. From the final solution, Cd, Cu, Pb, Ni and Zn were analysed using atomic absorption spectrophotometer (Alpha 4AAS, Chemical Tech. Analytical Euro). The pH (1:2.5 sediment: water) and electrical conductivity (EC) were measured using Hanna pH 211 microprocessor pH meter and EC meter (expressed in mS cm⁻¹ at 250C) respectively. Total organic carbon (TOC) and the CEC were analysed based on literature. Carbonate in the samples was measured by acid neutralization method as reported in literature.

Quality assurance (QA)/ control (QC) protocol prescribed by the U. S Environmental Protection Agency (EPA) for metal analysis was used. In this study, analytical precision through replicate runs and the use of certified standard reference material PACS-2 (heavily contaminated marine sediment available from the Natural Research Council, Canada) was employed. The results are shown in Table 2. The percent recoveries are quite reasonable.

Statistical Analysis

We performed statistical analysis by combining data from the two seasons. Statistical differences in seasonal metals level were determined by one-way ANOVA, followed by Duncan new multiple range test. Relationships between metals and other controlling factors were determined by bivariate correlation using the Pearson coefficient in a two-tailed test ($r = 0.01$ and 0.05). All analysis was performed using SPSS software (version 13.0).

RESULTS

Details of the pH, EC, TOC and CEC with percent clay in the individual sediment samples are included in Table 1. Table 3 shows the mean concentration (dry and wet seasons) of the trace metal in the mud fraction (<63 μ m size) of the sediments. The mean concentration of Cd at location S₆ was the highest (2.53mg/kg) and that from location S₄ during the dry season was the least (0.75mg/kg). The concentration of Cu at location S₂ was the highest during the wet season (2616.8mg/kg) while 1862.4mg/kg Cu was the least recorded at site S₃ during the dry season. Highest and least mean concentrations of 42.8mg/kg and 11.3mg/kg of Pb were recorded at S₆ and S₃ during the dry and wet season respectively. For Ni, highest and least values of 8.3mg/kg and 3.1mg/kg were recorded respectively at S₆ and S₃ sediments both during the wet season. Zinc, which was generally recorded at lowest concentration compared to other metals was at the highest and least concentrations (0.28mg/kg) and (0.02mg/kg) at S₆ and S₂ during the wet and dry seasons respectively. The results in Table 1 displayed significant seasonal variation in the metal levels which can be judged to be regular across the entire studied area. In fact, a similar pattern of increasing concentrations at both season was observed to follow the order Zn<Cd<Ni<Pb<<Cu and apart from Pb, higher concentrations of other metals were recorded during the wet season.

Table 1. Sample Locations and some Sediment Characterization[#]

Locations	Latitude(N)	Longitude(W)	pH	% Clay	OC	CEC	CaCO ₃ Equiv.
Ayetoro	06°06'12.4"	004°46'36.0"	6.6	15.4	9.34	96.15	18.6
Ilepete	06°02'10.0"	004°51'23.3"	6.3	15.2	7.86	98.81	16.4
Obe-Nla	06°00'51.9"	004°52'40.2"	6.3	15.9	9.95	124.15	16.1
Ikorigho	05°57'15.0"	004°53'59.6"	5.9	18.1	9.36	107.35	13.4
Ojumole	05°56'05.4"	004°53'10.2"	6.9	20.1	9.22	103.71	19.2
Otumara	05°56'42.8"	004°55'55.8"	6.1	22.4	9.66	115.91	14.9
Awoye	05°54'46.7"	004°57'56.2"	6.1	18.7	11.5	125.11	14.5
Igbokoda*	06°09'12.7"	004°44'32.5"	5.6	10.5	12.7	219.25	10.4

[#] Values are mean of the two seasons

- Reference location

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DISCUSSION

The results of sediment characterization test (Table 1) showed that the seasonal pH values ranges from 5.9 – 6.9. This is reflective of slightly acidic environment, though still quite tolerable to most aquatic organisms. The EC ranges between 0.826-0.880 mS cm⁻¹ while the TOC levels in the sediment were very high, ranging from 7% to 87% based on data on soil guidelines which are expected to be < 3.0%. This indicates large amount of detritus in the sediment which may be due to poor microbial degradation. The average CEC for both seasons are generally high ranging from 96.15 – 124.15 (meq/100g). This range is considered to be far above the EPA's guidelines for CEC. Moreover, the high CEC values indicate the presence of more clay and OC. Seasonal average values of CaCO₃ equivalent (in %) ranges from 13.34 -19.2. This range indicated the dominance of carbonate minerals in Ondo coastal sediment. Correlations among the metals concentrations, pH and OC content were determined. For both seasons, significant variability in both metal and OC concentration among individual sediment samples appears to be related to the portion of mud fraction found in each sample. Using the entire data set obtained during the study, significant correlations (= 0.05; 0.01) were recorded between some of the metals, pH and %clay in the mud fraction (Table 4). Cadmium vs Ni and Cu vs Ni were both significant at both seasons. pH only showed significant correlation with Cd (r = 0.813) while the clay fraction of the mud were significantly correlated with Pb (r = 0.949), Cd (r = 0.749) and Ni (r = 0.869). No significant correlations were found between Pb vs Cd and Cu and Pb. This lack of correlation showed that the metals are likely sourced differently. Most of the metals are negatively correlated with the CEC. This is of great concern as increased levels of these metals in the environment consequently results in decreased mineral element composition of the sediment. Thus, the nutritional value of sediment as food source to aquatic biota is reduced. It is interesting, moreover, to note that the metals are negatively correlated to percentage OC in the sediment. These negative correlations suggest that the metals are associated with a coarser type of particle.

Clearly, visible seasonal changes in the concentration of the metals were observed where, except for Pb, the concentrations of other metals

are higher during the wet season. The characteristic nature of the dry season sampling such as oil spillage which occurred few weeks before sample collection may be attributed to the level of lead obtained during this period. Comparing metal concentrations in the study with other related studies showed that except for Cu, levels of the metals are far less than those obtained in the Hecken Sack River and Newark Bay, which were 1076 mg/kg Cd; 2377222mg/kg Cu. 4217571mg/kg Pb, 39749mg/kg Ni and 395749mg/kg Zn⁴. Metals concentrations in the study were also compared with other studies considered to represent deposits influenced by petroleum related industrial activities. There are significantly higher (p<0.05) mean concentrations of Cd, Pb and Cu in mud samples of the sediments in the study than in mud of the near shore of the petroleum related industrial area of Colville Delta – Budhoe Bay region. The reason for these differences is uncertain. Some of the possible factors contributing to this disparity are relatively higher input of the metals into Ondo coastal area from confined terrestrial sources, anthropogenic input in the form of oil spill (oil contains some levels of metals) and this may further implicate, in particular that leaded gasoline has not totally been phased out in our petroleum products. In addition, the variation may result from regional differences in mass sediment accumulation rates. Alternatively, a relatively higher atmospheric deposition of anthropogenic metals may equally result in regional differences in sediment metal concentration. It has been shown that relatively higher concentrations of Ni and several other metals exist in freshly precipitated snow and that snow is a significant medium for sequestering and entraining atmospheric-borne metals with subsequent co-precipitation in the lagoon. It is therefore possible that over the year's higher metals fluxes tied to the depositional snow result in greater concentrations of metals in the mud of Ondo streambed sediment. Moreover, runoff activities and contaminants from land based sources introduced into the surface waters may rapidly become scavenged by suspended particles that tend to settle to the bottom where they become highly concentrated. This may be responsible for the increased level of some metals in this report. This is also in agreement with other study.

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Table 2. Results of QA/QC analysis (Trace Metals (mg/kg) dry weight basis)

Sample	Cd	Cu	Pb	Ni	Zn
Blank-1	-0.001	0.000	0.012	0.02	-0.11
Blank-2	0.001	0.001	0.017	0.05	-0.09
Blank-3	-0.001	0.000	0.015	0.04	-0.14
Mean	-0.001	<0.001	0.015	0.04	-0.11
Estimated MDL	0.002	0.001	0.004	0.05	0.006
SRM					
True value	NI	310	183	39.5	364
Recovery	-	317	163.4	31.4	379

MDL = Method Detection Limit SRM = Standard Reference Material. I = Not Indicated. a = Mean of Duplicate Analysis

Table 3. Trace Metals Concentration[#] (mg/kg dry weight) Sediments of Ondo Coastal River, Nigeria

Locations	Cd	Cu	Pb	Ni	Zn	
Ayetoro	1.92 ^b ±1.2 (2.14 ^a ±1.5)	2104.5 ^e ±2.1 (2199.2 ^e ±1.4)	11.9 ^c ±0.5 (9.3 ^b ±0.9)	4.9 ^d ±1.5 (5.7 ^b ±1.1)	0.28 ^a ±1.10 (0.34 ^a ±1.04)	
Ilepete	1.07 ^b ±0.75 (1.87 ^b ±1.05)	2566.7 ^c ±6.4 (2616.8 ^h ±1.9)	9.2 ^b ±0.1 (11.3 ^c ±2.3)	4.4 ^a ±2.1 (6.1 ^d ±2.3)	0.20 ^a ±0.02 (0.13 ^a ±0.14)	
Obe Nla	1.85 ^b ±0.13 (1.91 ^b ±2.09)	2004.2 ^h ±0.4 (2286.1 ^h ±2.1)	16.1 ^c ±0.1 (12.2 ^c ±2.1)	4.8 ^d ±1.5 (6.3 ^d ±1.9)	0.14 ^a ±0.01 (0.21 ^a ±0.09)	
Ikorigbo	0.75 ^a ±0.14 (1.12 ^b ±1.05)	2025.3 ^d ±1.5 (2341.3 ^h ±1.4)	19.9 ^c ±1.0 (13.4 ^c ±0.6)	3.1 ^a ±1.6 (5.1 ^d ±2.6)	0.12 ^a ±0.10 (0.19 ^a ±0.32)	
Ojumole	2.34 ^b ±0.38 (2.52 ^b ±0.14)	1862.4 ^g ±3.6 (1895.8 ^g ±6.1)	20.8 ^d ±0.4 (15.2 ^d ±0.3)	4.4 ^c ±0.3 (6.4 ^c ±0.3)	0.15 ^a ±0.10 (0.17 ^a ±0.36)	
Otumara	2.03 ^b ±1.10 (2.53 ^b ±0.81)	2499.3 ^h ±0.3 (2613.9 ⁱ ±3.6)	42.8 ^f ±0.1 (22.3 ^f ±0.9)	5.9 ^d ±1.3 (8.3 ^c ±1.4)	0.20 ^a ±1.23 (0.24 ^a ±0.24)	
Awoye	1.58 ^b ±0.61 (1.66 ^b ±1.04)	2162.5 ^f ±1.2 (2519.6 ^g ±1.9)	21.0 ^d ±0.3 (19.1 ^c ±1.8)	3.8 ^c ±1.2 (6.6 ^d ±1.3)	0.02 ^a ±0.01 (0.16 ^a ±0.50)	
Igbokoda*	1.27 ^b ±0.19 (0.82 ^b ±1.26)	1441.1 ^f ±1.15 (1643.3 ^g ±1.7)	14.3 ^a ±0.6 (9.2 ^c ±0.5)	1.3 ^b ±0.4 (2.5 ^d ±0.7)	0.27 ^a ±0.58 (0.04 ^a ±0.01)	
Mean±S.D	Dry Wet	1.60±0.67 1.75±0.75	2083.3±355.5 2264.4±347.1	18.3±11.7 13.2±5.9	4.7±1.4 5.8±1.9	0.16±0.06 0.19±0.09
C.V.	Dry Wet	1.5 9.6	65 270	75 218	21 52	200 110
CCME**	LEL SEL	0.60 10.00	16 110	31 250	16.0 75.0	120 820
C.B. PECs		4.98	149	128	48.6	459

Concentrations are mean of triplicate analysis. Values in parenthesis are results of the wet season

C.V: Coefficient of variation; *: Reference location;

C.B PEC: Consensus based probable effect concentrations (above which harmful effects are likely to be observed) (MacDonald et al., 2000).

** : Canadian Council of Ministers of the Environment Guidelines for the Protection of Aquatic Life, 2002

β: Recommended guidelines(µg/L) concentration for marine waters. This is the concentration which should not be exceeded for the protection of aquatic ecosystem, 1997

Means in the same column followed by the same superscript are not significantly different (α = 0.05) according to Duncan's New Multiple Range Test.

Table 4: Seasonal Correlation Matrix of Metals with some Controlling Factors

	Cd	Cu	Pb	Ni	Zn	pH	Clay	OC	CEC
Cd	1	.375	.630	.771*	.467	.725*	.821*	-.526	-.786*
Cu	.468	1	.499	.759	.616	.247	.553	-.696	-.720
Pb	.678	.687	1	.641	.182	.100	.905**	-.175	-.369
Ni	.896**	.760*	.890**	1	.742*	.630	.700	-.649	-.773
Zn	.661	.380	.358	.600	1	.597	.253	-.659	-.684
pH	.813*	.044	.249	.534	.536	1	.400	-.608	-.702
Clay	.749*	.539	.949**	.869**	.445	.400	1	-.394	-.641
OC	-.647	-.519	-.274	-.583	-.468	-.608	-.394	1	.859**
CEC	-.786*	-.643	-.561	-.795*	-.699	-.702	-.641	.859**	1

Significant /r/ *(P<0.05); ***(P<0.01.) Correlation data for the dry season are placed above the diagonal.

Wet and dry season Pearson coefficients are shown above and below the diagonal line respectively(correlated values are in bold form)

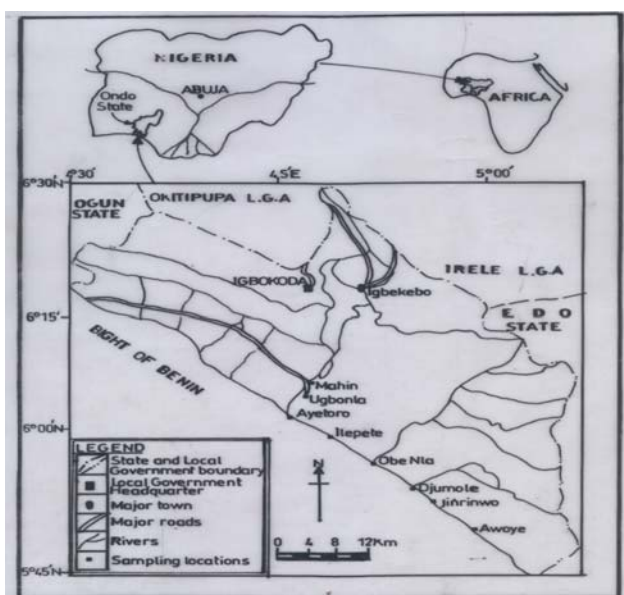


Fig.1. Map of the sampling locations (Inserted is the area map of Nigeria and Africa showing the geographical locations)

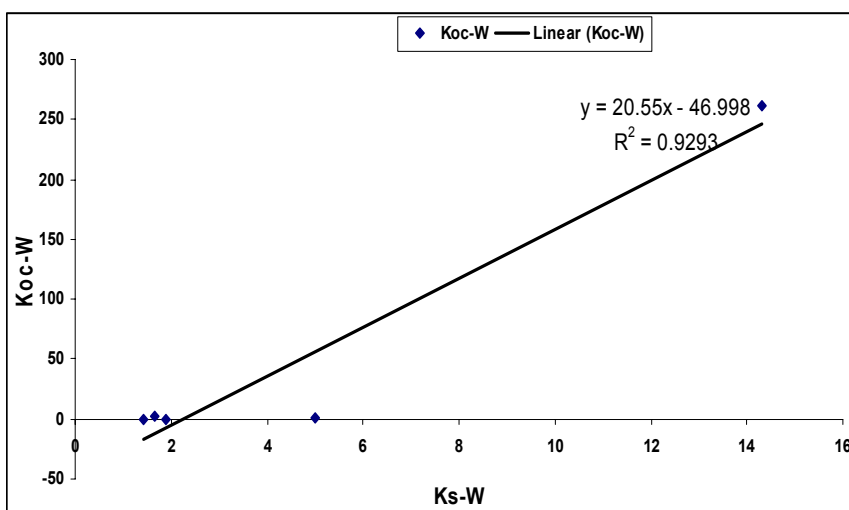


Fig.2-a: Variation of Equilibrium Coefficient during the Wet Season (W = Wet season)

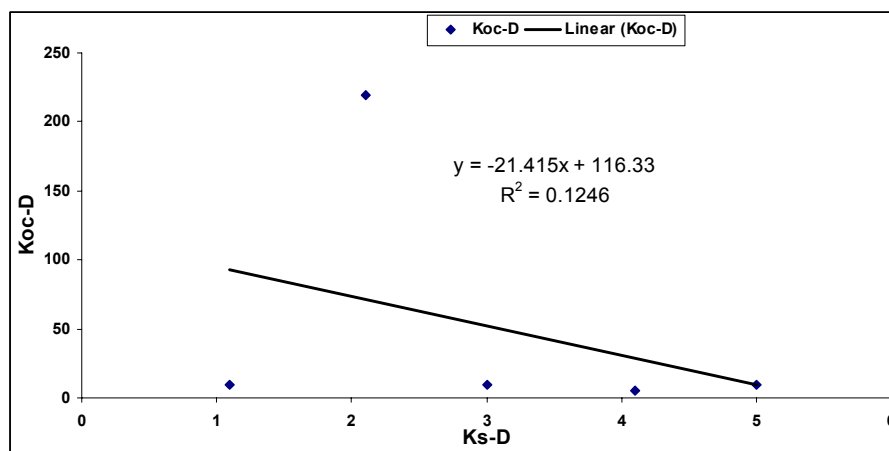


Fig.2-b: Variation of Equilibrium Coefficient during the Dry Season (D = dry season)

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The sediment water-partition coefficient, K_s , were observed to be greater than the organic carbon partition coefficient, K_{oc} , in three of the metals at both seasons with an order of decreasing adsorption as $Ni > Cd > Zn$. For Pb, the K_s was greater during the wet season. This again implicates the presence of more Pb in the aqueous media during the dry season, a factor that may be attributed to the oil spillage that occurred just before the dry season sampling. However, for Cu, K_{oc} were at higher level than K_s at both seasons. These finding imply that the tendency of the metals to be adsorbed unto the entire sediment particle is a function of several factors such as the characteristics of the metal, the physical and chemical nature of the sediment and possibly some molecular factors contributing to retention. Fig 2(a,b) are displays of the equilibrium partition coefficient variation at both seasons. In the wet season, significant positive correlation ($R^2 = 0.9624$) was observed between the two partition coefficient, K_s and K_{oc} , which can be interpreted to mean a balance flow of ions or particulates within the aqueous medium. The reverse is the case during the dry season ($R^2 = 0.1256$) and may be attributed to decreased movement and water wave during the period. The Cu as observed in this report must have been adsorbed unto the humic material (humus). In the hydrosphere, humic material typically makes up about 50% of the dissolved organic matter. From this limited information, it can be inferred that less fulvic acid and more of humic acid (solubility determinant) are present within the humic component of the sediment matrices. The humic material when bound to mineral phases usually forms coatings which prevent the release of metals into aqueous solution. The results in Table 3, where Cu was recorded at very high levels, when compared with K_s and K_{oc} values showed that their presence could probably be due to lithological source. This is because humic material is a naturally occurring organic matter of plants and microbial origin.

The concentrations of the metals in the sediment are compared with the consensus based probable effect concentrations and the Canadian Council of Minister of the Environment (CCME) for the protection of aquatic life. These guidelines relate to the potential impact of contaminant on biota, and are derived from analyses of relationship between benthic community health and sediment metal concentrations. Two guidelines are given; the lowest effect level, (LEL) or interim sediment quality guidelines (ISQG), which represent concentration contaminant below which there is a very low probability of effects on the biota and the

severe effect levels or probable effect level (PEL) which represent concentrations above which there is a high (>50%) probability of adverse effect on the biota.

Based on the limited available data (Table 3), all the sites had sediment concentrations of Cu far above SEL at both sapling seasons. This is a clear case of sediment heavily enriched with Cu and its associated toxic nature. However, it is unlikely that this is the result of pollution, as the concentrations of the other metal contaminants were relatively low. The excessively high level of Cu may be due to mineralogical occurrence. Cadmium did not exceed the SEL in any of the sediment but did exceed the LEL for all sites except for the reference location. The increased level of Cd in wet over the dry season couples with the concentration above the LEL calls for proper monitoring because of the possibility of greater concentration in the near future over the SEL. Lead exceeded the LEL at only one of the location (S_6). This may be due to the closeness of this location to oil wells.

Conclusion: It is to be noted that the coastal area of Ondo state is a representative of a typical oil-producing areas in Nigeria and its vicinity are a popular place for recreation (fishing, hunting and boating). The levels of the metals obtained showed that the area is heavily enriched with Cu, the occurrence of which was associated to lithological processes. Cadmium and lead levels in sediment may equally pose serious threat to the area in the near future based on the present concentrations. This region has also been imparted by oil and gas exploration. It is possible that any or all these activities could have contributed to contaminant input. We recommend that cautionary measure, such as prevention of oil spillages into the river, must be enforced to prevent any further increase in metals concentration in the environment. In addition, metals speciation should be carried out so that the form and extent of metal bioavailability can be evaluated further.

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assessment of heavy metal pollution in suspended solids and sediments of the river Danube. *Chemosphere* 51, 633 – 642.

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