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Enrichment of Heavy Metals in Sediments as Pollution Indicators of the Aquatic Ecosystem

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Abstract. The sediment pollutant status of twenty three communities (villages) within the Ilaje local government area of Ondo state, Nigeria, was examined. These are communities, where oil spillage had occurred. Three other locations at Igbokoda were equally considered as a reference point. Nine heavy metals; copper (Cu),cadmium (Cd),cobalt (Co),iron (Fe),chromium (Cr),nickel (Ni),lead (Pb), zinc (Zn) and manganese (Mn) were determined in the sediments collected from the various communities. The lowest concentrations were observed with Co and Zn ranging from 0.11 to 0.82 mg/kg and 0.02 to 0.29 mg/kg respectively, while Co and Fe were at the highest concentrations ranging from 1004 to 2879 mg/kg and 806 to 3809 mg/kg respectively. Most of the metals in this study occur at concentration that calls for serious environmental concern especially for the water and its resources. Local differences were equally observed in relation to the depth of the ocean. Some of the metal controlling factors such as pH, organic carbon, and cations exchange capacity were implicitly considered and each was found to correlate respectively, with the metals examined. The results provided relevant benchmarks for addressing the protection of benthic organisms and for assessing the potential impact of sediment-associated chemical (heavy metals) on aquatic biota. The positive correlations as being displayed by some of the metals are indicative of similar source of pollutants.

Keywords: heavy metals, oil spillage, sediments, pollution, toxicity

Introduction

Sediments are essential component of aquatic ecosystem acting as carriers, sink and potential sources of contaminants (Adriano *et al.*, 2005; Kretzschmar and Schafer, 2005; Adriano, 2001; Kuang-Chung *et al.*, 2001). They provide habitat for a wide variety of benthic organism as well as juvenile forms of pelagic organisms. Most of the near shore sediments are brought to the sea by the action of rivers. Thus, their composition is determined largely by the lithology of the contributing catchments area (Karageorgis *et al.*, 2005). The organisms in sediment are in constant contact with the sediment, and therefore, constant contact with any contaminant that may be adsorbed to the sediment particles. Potential impacts to benthic organisms include both acute and chronic toxicity with individual populations and community,the level effects, bio-accumulation of contaminants and the potential to pass contaminants along the predators of benthic species reported by (Adams *et al.*, 1992; Marcus, 1991).

Though metals occur naturally in sediment, it does not necessarily follow that it would not cause adverse ecological effect. The presence of one metal can significantly affect the impact that another metal may have on an organism. The effect can be synergistic, additive or antagonistic (Eisler, 1993). In-depth assessments of several studies show that the metal concentrations in suspended and streambed sediments are useful in understanding processes that affect metal contaminants in rivers and estuaries. Analysis of streambed sediments for trace element concentrations is one aspect of the integrated assessment of water quality in the Natural Water Quality Assessment (NAWQA) programme (Gurtz, 1994).

Sediments as a time integrative medium of particulate matter transported by streams, when analysed can provide a better assessment of conditions in a stream for water quality assessment purposes than analysis of discrete water samples, which can provide a snapshot of conditions at the time of sampling. The present work describe the analysis of trace metals in streambed sediments collected in February, 2005, four months after a major oil spillage into some communities within Ilaje, local government area of Ondo state, Nigeria.

Study area. The aim of the present work was to document, for the first time, as an independent, and unbiased research on the sediment metal concentrations for twenty three (23) communities within Ilaje, local government area of Ondo state, Nigeria. These are the riverine villages, where dramatic and impactive oil spillages have occurred due to oil operations. The same sea that linked all the communities is equally to the Atlantic Ocean. A lot of investigations have been conducted by government and even Ministry of Environment but with

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amazing report inspite of the observed adverse ecological effect on the entire communities. The implication of these effects on the entire food chain compele the present study. The area map of the sampling zone is shown in Fig.1.

Materials and Methods

Sediment samples were collected in February, 2005 during the dry season. For each community, four strategic sampling points were considered. After collection, they were mixed, stirred in labeled polythene bags and preserved in cooler in the field. Control samples were collected from three other locations within the same geographical region in Igbokoda, where both the industrial and anthropogenic activities were minimized. Sampling locations and depth were equally recorded using the global positional system (GPS) to serve as a reference for future evaluation. Table 1 summarizes the sampling site characteristics.

Sediment samples were air-dried in a relatively contaminant free air environment before digestion. An air-dried sample (0.250 g) was loaded into a Pyrex test tube and then digested

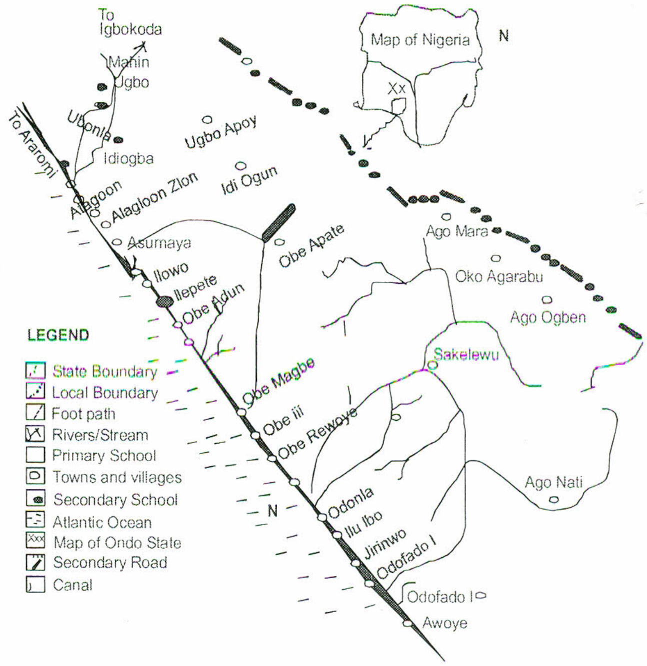

Fig. 1. Map of the study area

Table 1. Site identification and coordination

Abbreviation	Names of communities	pH (sediment)	Latitude (degree)	Longitude (degree)	Altitude (meters)
A	Ayetoro (town)	7.9 - 8.4	06°06' 12.4''	004°46' 36.0''	12
B	Idi ogba	6.5 - 6.6	06°05' 56.1''	004°47' 13.2''	14
C	Alagbin zion	5.9 - 6.1	06°04' 48.8''	004°47' 14.9''	14
D	Oroto	5.7 - 5.8	06°04' 22.3''	004°48' 53.7''	14
E	Asumaga	6.0 - 6.1	06°03' 20.9''	004°39' 58.9''	12
F	Ilowo	6.3 - 7.00	06°03' 15.6''	004°50' 10.1''	11
G	Ilepete	7.5 - 7.6	06°02' 10.0''	004°51' 23.3''	14
H	Obeadun	7.0 - 7.1	06°01' 35.5''	004°51' 57.5''	16
I	Obe Nla	6.9 - 7.0	06°00' 51.9''	004°52' 40.2''	16
J	Erebino	6.5 - 6.7	05°59' 51.3''	004°53' 37.1''	15
K	Ikorigbo	6.6 - 6.7	05°57' 15.0''	004°53' 59.6''	10
L	Obe iji	6.7 - 6.8	05°59' 16.9''	004°54' 09.8''	9
M	Obereweje	6.7 - 6.8	05°58' 55.6''	004°54' 27.2''	13
N	Obebowoto	6.6 - 6.7	05°56' 52.4''	004° 54' 34.4''	13
O	Ojumole	6.6 - 7.4	05°56' 05.4''	004°53' 10.2''	15
P	Atlantic ocean	7.7 - 7.8	05°57' 00.4''	004°55' 34.7''	16
Q	Atlantic (inside)	7.9 - 8.2	05°56' 59.8''	004°53' 52.2''	16
R	Otumara	6.9 - 7.5	05°56' 42.8''	004°55' 55.8''	14
S	Odonla	6.3 - 7.3	05°56' 24.5''	004°56' 56.7''	13
T	Ilu abo	7.5 - 7.6	05°55' 38.5''	004°56' 44.7''	13
U	Jinrinwo	7.5 - 8.0	05°55' 55.1''	004°57' 28.7''	10
V	Odofado	6.9 - 7.1	05°55' 18.3''	004°58' 03.7''	12
W	Awoye	6.8 - 7.8	05°54' 46.7''	004°57' 56.2''	10
X	Igbokoda 1	6.8 - 7.2	06°09' 12.3''	004°44' 32.4''	10
Z_1	Igbokoda 2	6.4 - 6.9	06°09' 12.4''	004°43' 33.7''	13
Z_2	Igbokoda 3	6.6 - 6.8	06°09' 12.7''	004°44' 32.5''	11

by using 4.0 ml of perchloric acid (60% by weight) (USEPA, 1986). After digestion, the solution was diluted to 30 ml with distilled water and then centrifuged for 20 mins and separate the supernatant from solids. The obtained supernatant was used for determining the concentration of Pb, Cd, Zn, Co, Fe, Cr and Ni by the atomic absorption spectrophotometer (Alpha 4AAS, Chemical Tech. Analytical, Euro).The pH (1:2.5, sediment: water) was measured using Hanna pH 211 microprocessor pH meter. Organic carbon was determined using the Walkley and Black method wet combustion method (Nelson and Sommers, 1982), and the cation exchange capacity (CEC) was analysed using the method of Polemio and Rhoades (1977).

In order to avoid contamination, all glassware were soaked in 10% HNO_3. Analytical grade reagents were used for the digestion. Standard solutions of each metal were equally analysed to correct for instrument accuracy as described by Abachi and Douabal (1985).

Statistical analysis. Means, maximum values, minimum values and standard deviations of the nine heavy metals were determined. The statistical relationship between the individual elements across the twenty three communities (excluding three control sites at Igbokoda) was determined by bivariate correlation using the Pearson and Spearman coefficient in a two-tailed test, $p<0.05$. All data analysis was carried out by using of SPSS for windows 12.0 version.

Results and Discussion

Total metal concentrations of the streamed sediment show a wide range of values from background to a level considered to reflect gross contamination. A descriptive statistics is shown in Table 2. For Cd, the range is 0.012-2.997 mg/kg; Cu, 1004 - 2879 mg/kg; Co, 0.11-0.82 mg/kg; Cr, 2.01-44.09 mg/kg; Fe, 806.30-3809.00 mg/kg; Ni, 3.40-5.90 mg/kg; Pb, 10.00-32.06 mg/kg; Zn, 0.02- 0.29 mg/kg and Mn, 16.24 - 73.52 mg/kg. The general pattern of distribution is shown in Fig.2 (a-c) and 3. The value of Fe and Cu was of several orders of magnitude higher than those of other metals whereas, Zn and Co remained within a relatively narrow range. The concentration of Fe in the sediment from the Atlantic Ocean beside Ayetoro town was the highest (3809 ± 5.2 mg/kg) and those of Cd at Obe, Iji was the least (0.012 ± 0.255 mg/kg).The results of some metal controlling factors examined in this report are shown in Fig. 3, with marked differences across the entire sampling locations.

Local differences in heavy metal concentration were evident in the results. This can be attributed to the changes in the velocity within the ocean. Although particle size distribution

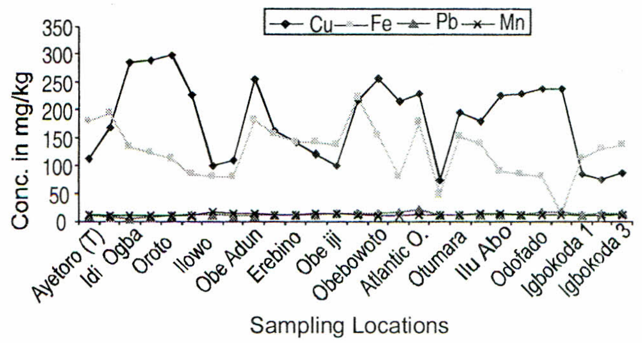

Fig. 2a. Copper and Fe variations across the sampling location.

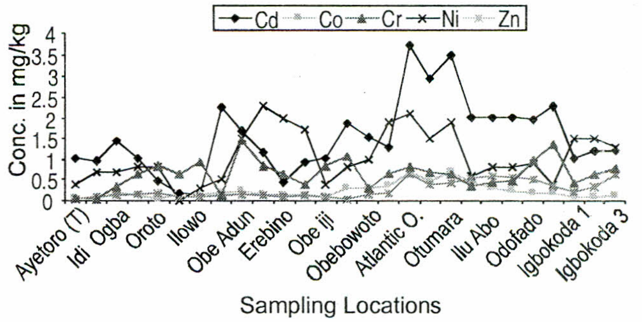

Fig. 2b. Cobalt, Cr, Ni, Zn and Cd variations across the sampling location.

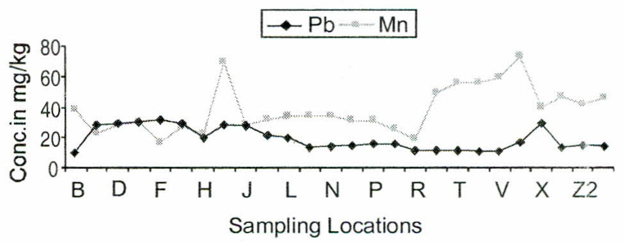

Fig. 2c. Lead and Mn variations across the sampling locations.

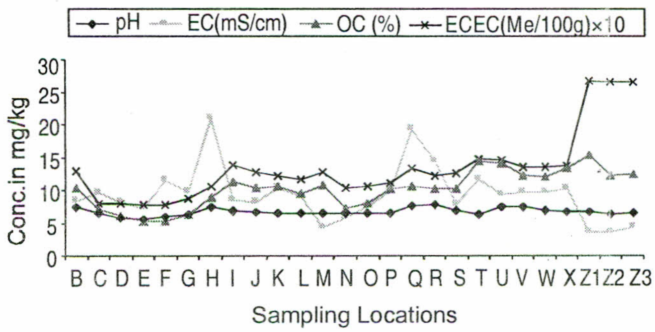

Fig. 3. Distribution pattern of some metal controlling factors.

Table 2. Descriptive basic statistics of the heavy metals (mg/kg) in the studied sediments[b]

Parameters		Cd	Cu	Co	Cr	Fe	Ni	Pb	Zn	Mn
Mean		1.449	2249	0.4109	2.984	1591	4.548	19.77	0.1722	38.35
Std. error of mean		0.1402	104.0	0.0339	0.1162	134.6	0.2346	1.661	0.0122	2.936
Median		1.278	2275	0.4100	3.010	1483	4.700	16.16	0.1900	34.23
Mode		0.012[a]	1004[a]	0.360[a]	2.920	806.3[a]	4.400	10.00[a]	0.20	16.24[a]
Std. deviation		0.6728	498.9	0.1623	0.5575	645.5	1.125	7.968	0.0586	14.97
Variance		0.4527	248966.9	0.0264	0.3108	416653	1.265	63.49	0.0034	224.2
Range		2.985	1874.8	0.710	2.080	3003	5.200	22.06	0.23	57.28
Minimum		0.012	1004	0.110	2.010	806.3	0.700	10.00	0.02	16.24
Maximum		2.997	2879	0.820	4.090	3809	5.900	32.06	0.25	73.52
Sum		33.34	51718	9.450	68.63	36602	104.6	454.7	3.96	997.0
Percentage	25%	1.009	2004	0.300	2.550	1192	4.200	11.80	0.1300	28.23
	50%	1.278	2275	0.410	3.010	1483	4.700	16.16	0.1900	34.23
	75%	2.001	2713	0.500	3.340	1890	5.100	29.14	0.2200	47.74

[a] = multiple modes exist; the smallest value is shown, [b] = limited to first 100 cases; n = 23

was not carried out in the present work, it is known to be current velocity dependent (Rzoska, 1980).The results of the pH ranges from 5.7 at Oroto community to 8.4 at Ayetoro i.e. from weekly acidic (5.0 - 6.5) via neutral (6.5 -7.5) to basic (7.5-8.7) values (Denis, 1993). The results are not surprising because, it is a salt water zone and thus reflects the equilibrium partitioning of irons and other substances between water and sediment. Increase in metal level will raise the potential for water contamination. This could have serious implications for human health and environmental quality.

Sediment as heavy metal accumulators. The use of sediments as heavy metal sinks and consequently indicators of ore bodies or pollution is important. The metal concentration of sediment has been found to reflect the degree of pollution in an area.The present study has revealed to a very large extent, the significance of sediments as a good indicator of metal pollution. However, the constituents of sediments dictate their ability to concentrate heavy metals. Some sediments, such as clays, have an ability to concentrate most heavy metals while other, like carbonates are more selective, especially in marine system (Talbot and Chegwidden, 1983) which represent the present work. The result indicates that a lot of metals are accumulated in the sediment of each site due to the high pH of the river so that low concentrations are in the water column in comparison to the sediment.

Metals level across sampling locations. The concentration of heavy metals in the present study brings for serious concern. This is important because the quality of water and aquatic lives such as fishs, crabs, periwinkles and some sea birds depend on the quality of sediment. De Carlo *et al.* (2005) carried out a study on the trace elements in streambed sediments of O'ahu, Hawai, United States. Concentrations of Zn (160-640 mg/kg); Ni (150-430 mg/kg); Co (33-120 mg/kg); Cr (270-660 mg/kg), were far above those reported in this study. However, those of Cd (0.1-1.4 mg/kg) were found to be generally lower while most of the Pb concentrations fall within those reported here.

Metals, like Co and Zn were found to be generally low across all the sampling locations with cobalt recording 0.82 mg/kg, while zinc recorded 0.25 mg/kg as their highest concentrations. Ni, Cr and Cd were found to shared a pattern or trend in their level at almost all sampling points with arithmetic increase from Cd via Cr to Ni. An average of 2.4 mg/kg (S.D=1.8) Cd concentration in river sediment from Belgium and Luxembourg has been reported (Swennen *et al.*, 1998), a value considerably similar to those reported here. The range of 0.1 and 0.4 mg kg^{-1} of Cd as reported by De Carlo and Anthony (2002), are quite in agreement, about 58% of the sediment of Cd concentration in this report. Overall concentration of Cd in streambed sediments from Ilaje communities appear to be higher than the mean concentration of soils around the world (0.48 mg/kg, n=38, mean values) reported by Kabata-Pendias (2001). In Europe, during the late 1990s, the studies of the average concentration of Cr in river sediments that was ranged from 47.7 mg/kg

(S.D=24.7) for Croatia (Peh and Miku,2001) to 126 mg/kg (S.D=150) for Belgium and Luxemburg(Swennery *et al.*, 1998).These values are several order of magnitude higher than those reported in this study.

Pb concentrations in the sediment were unique in that the values obtained were not associated with other metals. Several factors favour the accumulation of heavy metals in sediment. These included the following:

(i) incorporation into the shell material during and after growth.
(ii) adsorption into the shell material during and after growth.
(iii) isomorphic replacement of Ca^{2+} by elements of a similar ionic radius and charge i.e. Pb^{2+}.

These three processes favours the accumulation of Pb over many of the other heavy metals as it, like Ca is divalent, has a similar ionic radius, is not a transitional metal and unlike most heavy metals, lead is thought to form $PbCO_3$ as its major species in seawater (Zirino and Yamamito, 1972).

In the report, the streambed sediments are heavily enriched with Cu and Fe relative to the other metals. Cu displayed a lower variability 1004-2879 mg/kg (S.D=98.75, n=23) with a geometric mean of 2184.1mg/kg, while Fe ranges from 806.3 - 3809 mg/kg (S.D=672.82, n=23) with a much lower geometric mean of 1526.5 mg/kg.Apart from three communities; Obe-Iji; Obereweje and Obebowoto where less than 1500 mg/kg of Cu were recorded in their metal sediments level, the other twenty communities have their levels higher than 1895.8 mg/kg of Cu with Odofado community recording the highest concentration. Considering the percentage of metals was in oil, the concentrations of Cu and Fe recorded in this report cannot actually be related to oil pollution. The higher values across the entire sampling zone are indicative, probably of the presence of their ore bodies within the area. However, the unusually high values obtained at location such as Odonla, Ilu Abo, Jirinwo, Odofado and Awoye in spite of the depth of the ocean can be associated with the closeness to the Atlantics Ocean from which oil spillage occurs. The downward flow of water through Otumara to Awoye and Ojumole towards Ikorigbo may be responsible for the trend in metal levels. This however, needs further confirmation.

The results of the present study were found to correlate, to a very large extent with the depth of the sea (Table 1). Highest values of metals were recorded at greater depth of the sea. Though this is not totally true for all the metals as they are generally present at very low concentrations. The metal levels obtained at Obe Adun, Obenla, Erebinwo, Atlantic Ocean shore, Ojumole and Otumara were all found to be generally higher than those from other communities. In addition, there are, generally decrease in metal levels as the sea depth decreased. This can be associated with the prevention of sedimentation process by water currents. It also indicates the significance of suspended matter in the transportation of local heavy metals in such environments thus, the concentrating the metals at region of greater depth.

Trace element concentrations in sediments are controlled not only by contribution from anthropogenic activities but also from geochemical process (De Carlo *et al.*, 2005). Correlation analysis is one of the possible approaches that can be employed to elucidate sources of heavy metals, and as observed in the present work (Table 3), a positive correlation ($p<0.01$ and 0.05) of Cu with Ni and Zn indicate a similar source. The same can be said of Zn with Co and Ni. Elements such as Pb and Fe that correlates negatively, perhaps display different sources of metals.

Correlation between metals level and controlling factors. A critical factor for sediment toxicity is contaminant bioavailability. A correlation matrix of some of the metal controlling parameters in sediments as observed in this study is shown in Fig. 3 The results agreed to a very great extent with

Table 3. Correlation between heavy metal contents (mg/kg) in the studied sediments

Elements	Cd	Cu	Co	Cr	Fe	Ni	Pb	Zn	Mn
Cd	1.000	-0.146	0.237	0.293	0.329	0.083	-0.136	-0.066	-0.136
Cu	0.027	1.000	0.291	0.597**	0.004	0.465*	0.268	0.521*	0.032
Co	0.091	0.318	1.000	0.397	-0.142	-0.047	0.371	0.567**	-0.246
Cr	0.324	0.570**	0.381	1.000	0.150	0.333	0.278	0.310	-0.113
Fe	0.298	-0.028	0.014	0.084	1.000	0.514*	-0.810**	0.046	0.443*
Ni	0.185	0.295	-0.216	0.218	0.373	1.000	-0.391	0.246	0.248
Pb	-0.201	0.315	.0.414*	0.409	-0.673**	-0.395	1.000	0.117	-0.450*
Zn	-0.115	0.555**	0.474*	0.173	0.206	0.122	0.087	1.000	-0.179
Mn	-0.143	0.243	-0.123	0.100	0.254	0.429*	-0.316	0.047	1.000

* = significant at the 0.05 level (2-tailed); N = 23 in each case, ** = significant at the 0.01 level (2-tailed); Spearman and Pearson coefficients are shown above and below the diagonal line respectively

the findings of Boulding (1994) that the lower the pH of a zone, the lower the base saturation, though there is no strict proportionality. The deviations from this findings especially at Otumara and other communities downstream could be explained due to the fact that for a given base saturation value, the adsorbent complex of a sediment having a high cation exchange capacity (CEC) could release many more H^+ ion into the solution than the sediments with a low CEC.

Apart from yielding valuble information about the availability of exchangeable cations in sediments, it has been established that certain elements such as Zn, Cu, Mn, Fe, and Al are more available in very acid environment (Boulding, 1994). Consequently, it is not surprising the high levels of Cu, Fe, and Mn were recorded in this study. The results of the conductivity shows that sediment falls between moderately saline (4-8 mS/cm) through to very saline (8-16 mS/cm) to extremely saline (> 16m S/cm), according to environmental sampling protection ageny's environmental export system (EPA's ESES) (Russell, 1994). The organic carbon (OC) content can be said to be very high, being greater than 3.0 % as recommended by Loring and Raintala (1992). The high level of OC across the sampling locations must have been due to the anoxic state of the water. Anoxia has been identified as an enrichment factor for OC (Karageorgis *et al*., 2005).

Heavy metal toxicology. Trace element are intrinsic in nature, in fact, many are essential micronutrients (copper, iron, selenium, zinc etc) and thus are important for functioning of plants and animals (Leland and Kuwubara, 1985). Above certain levels, however, these trace elements can have toxic effects when ingested. In general heavy metals produce their toxicity by forming complexes or 'ligands' with organic compounds. These modified biological molecules lose their ability to function properly and result in malfunction or death of the affected cells. The most common groups involved in ligands formation are oxygen, sulphur and nitrogen. When metals bind to these groups they may inactivate important enzyme systems or affect protein structure. The metal levels recorded in the recent work, call for serious environmental concern. Heavy metals are dangerous because they tend to bioaccumulate (and increase in the concentration of a chemical in a biological organism over time, compared to the chemicals concentration in the environment). The impact of metals are generally made manifest in the quality of fish and other aquatic organisms and the water within the sediment zone. Values of metals in this study were quite above their tolerable levels in water and fish in particular. This posses serious environmental threat to the inhabitants who depend solely on this water and its resources for their livelihood (USEPA,2004; DWAF,1996).

Apart from Idi-Ogba, Ikorigbo and Obe, Iji communities where least values were recorded, other communities are prone to cadmium-toxicity as long as they depend on the water and its resources for living. The values of Cu and Fe recorded in the recent study calls for concern and further investigation. They were recorded at highly elevated levels across all the sampling points. These perhaps could be an indication of copper and iron ore deposits within these locations. This is of great economic value. However, it must be noted that high doses of copper in particular can cause anaemia, liver and kidney damage and stomach and intestinal irritation (Ansari *et al*., 2004). Ingestion accounts for most of the toxic effects of iron because iron is absorbed rapidly in the gastrointestinal tracts (Roberts, 1999). Hemochromatosis, an iron overload disease may result in a situation under this present study.

Levels of Cr were found to be high but are generally lower than that of nickel across the sampling locations with average values of 2.74 mg/kg and 4.41mg/kg respectively. These are very high values for drinking water and aquatic biota's. Possible sources of Ni in the present sites include deposition of particulate nickel in fossil fuels (from oil spill) and other industrial operations such as dredging; a regular exercise being carried out within some of the communities examined in this report. Apart from the control sites at Igbokoda, where less than 1.0 mg/kg and slightly above 1.0 mg/kg of Cr and Ni were recovered respectively, all the communities considered in the study recorded Cr and Ni at levels of serious environmental risk.

Zinc and Co recorded the least of concentrations in the sediment as shown in Table 3. Zinc at sufficient concentrations can result in lethal or sub lethal effects. Marine fish and oysters have been noted for accumulating higher levels relative to freshwater organisms (Philips and Russo, 1998; Duke, 1967).

Data relative to aquatic sediment quality and general comparative assessment. The concentration of trace elements were compared to consensus-based interim sediments quality guidelines, ISQGs (MacDonald *et al*., 2000, CCME, 1999) and those of Persaud *et al*. (1992). Both guidelines identify a concentration below which aquatic invertebrates are unlikely to be adversely affected, designated as lowest effect level (LEL) and a severe effect level (SEL) above which toxicity is likely. Virtually all the communities recorded sediments concentration of Cu and Fe exceeding the SEL. Therefore, based on the metal concentration, sediments can serve as a source of heavy metals for the aquatic system. Similarly, twenty two communities recorded Cd exceeding the LEL but none exceeded SEL.Two communities (Asumaga and Awoye) recorded Pb concentrations in the sediment at a level exceeding LEL. Other metals determined in this study were

Table 4. Comparative assessment of mean metal concentrations (mg/kg dry weight) with selected data in other part of the world

	Cd	Cu	C	Cr	Fe	Ni	Pb	Zn	Mn
Present study n = 27	1.45	2248.2	0.40	2.96	1634.9	4.73	19.82	0.18	38.34
Oceanic crust (MORB)[a]	0.14	74	47	300	-	150	0.49	79	-
Kahili stream[b]	14	240	47	380.8	10%	200	200	640	-
World soils[c]	1.0	5.20	10	100	-	30-40	2-200	10-300	-
World average river SP[d]	1.0	100	20	100	-	90	100	350	-
CCME EQG FW and MW SQG[a]									
Fresh water ISQG	0.60	35.7	NS	37.3	-	-	35.0	123	-
Fresh water PEL	3.5	197	NS	90.0	-	-	91.3	315	-
Marine ISQG	0.70	16.0	NS	26.0	(2%)	16	31.0	120	460
Marine PEL	4.2	110	NS	110.2	(4%)	50	110	270	1100

n = number of samples; MORB = mid-ocean ridge basalts; SP = suspended particles; Avg = average; EQG = environmental quality guideline; ISQG = interim sediment quality guideline; PEL = probable effect level; NS = no sediment criterion; CCME = Canadian Council of Ministers of the Environment (2002). [a] = Rice (1999); [b] = De Carlo *et al*., (2005); [c] = Pais and Jones (1997); [d] = Li (2000)

found to fall below the LEL, though some were recorded at a value very close.

A comparative assessment of the present study with other parts of the world, as shown in Table 4. Cd, Cu and Fe were found to be higher than reported data's while those of Co, Cr, Ni and Zn were observed to fall far below most reported cases. Lead concentrations fall generally within most of the reported data's, while information on manganese was very scarce for comparative assessment.

Conclusion

This study is of particular interest in that it serves to increase the knowledge on the sediment metal quality status within the studied area. Concentration of trace elements displayed large variations and reflect a combination of anthropogenic and natural sources. Based on the concentration of some metals observed in this report a flexible, sites-pecific bioaccumulation models are probably necessary to provide the information about the dose of contaminants that animals can experience in the environment. Knowledge of dose is important in understanding contaminant effects from sediments. Thus a tissue-base interpretation of metals effect (predicting effect of metals from bioaccumulation) could be a viable approach to further advancing a field relevant understanding of adverse effects of sediment-bound contaminants such as heavy metals. no with standing, the data in this report will be of use for further detailed studies in the region as well as to complement other geochemical databases.

Recommendations. In order to enhance sustainable development, especially within the riverine areas of Ondo state, the following are the recommendations.

- Education and awareness campaign on the environmental impacts of metal pollution.
- A proper monitoring strategy for the sediments and water resources, within the riverine zone.
- A proper legislation on compensations to communities where oil spillages had occurred.

Finally, analysis of all environmental media (sediments, water and air) should be carried out in order to be able to qualitate and quantitate the pollutional status of the communities.

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