DISTRIBUTION OF METALS IN SEDIMENT CORE OF OROGODO RIVER, SOUTHERN NIGERIA

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Abstract: The concentrations of heavy metals such as Cu, Ni, Pb, Mn, Fe, Cr and Zn were studied in core sediments of Orogodo River, Nigeria to understand heavy metal contaminations of core sediments as a result of urban sprawl and agricultural practices. The core sediment samples were collected from 0 to 60 cm depths using a corers, digested with a mixture of acids and the metal concentrations were quantified using atomic absorption spectrophotometry. The assessment of contamination of the core sediment was based on the enrichment factor and geoaccumulation index. The mean concentrations of metals in the core sediment were 0.5-5.0 mg kg^{-1} and 0.9 – 8.8 mg kg^{-1} for Cu; 0.8- 12.9 mg kg^{-1} and 0.6-6.5 mg kg^{-1} for Pb; 42.8 -42.1 and 21.8-46.4 mg kg^{-1} for Mn; 291-713 and 159-704 mg kg^{-1} for Fe, 0.6-1.1 and 0.3-2.0 mg kg^{-1} for Cr ; 14.9 -85.9 and 16.3-94.8 mg kg^{-1} for Zn in dry and wet seasons, respectively. The geoaccumulation index and enrichment factors indicate that the top sections of sediment cores were significantly polluted with Cu, Ni, Pb and Zn in comparison with pre-industrial and urbanization concentrations.The principal components analysis (PCA) results indicated that metals in the sediments originated from myriad of sources which include those associated with traffic, burning of fuel, industrial and as well as municipal wastewater.

Keywords: Core sediment, heavy metals, urbanization, Orogodo River

Introduction

Sediments have the ability to faithfully record environmental impacts on fluvial systems over time. The marked tendency of heavy metals towards solid phase partitioning and the ability of sediments to integrate long term information makes the sediment attractive for assessing the impact of mining, industry and urban development on the fluvial environment (Birch *et al*., 2001). In aquatic system, these pollutants are rapidly removed from the water body and settle with particulate matter to form bottom sediments. Although some of these contaminants can be mobilized via bio-activity from sediment sink, an intact column of the sediment will remain undisturbed by human activities, providing a record to indicate the levels of pollutants over a long period of time. Plotting the contaminant concentration against the depth of successive thin-layers of sediment provides time-based information that is used for assessing the extent of contamination in different periods of urban development (Fung & Lo, 1991).

Orogodo River is a shallow municipal river in Agbor, Delta State, Nigeria. The river was once a valuable recreational resource for the Agbor community and its environment. In recent years, increasing soil erosion in the catchment area, triggered by deforestation and uncontrolled urban sprawl has caused massive influx of sediments. The influx of sediments has substantially reduced the depth of the Orogodo River. The middle reaches of the river are subjected to pollution arising from effluents from the abattoir (slaughter house), paint and foam industries, run off from automobile workshops, gasoline filling station and as well as municipal wastewater. The lower and upper reaches of the Orogodo are also subjected to surface run off from agricultural farms. Agricultural and urban runoffs from the riparian communities are also discharged into the river. Limited information are currently available, most of these studies were restricted to effect of water quality to changes in macro invertebrate assemblage (Arimoro *et al.*, 2007a,b; 2008). Recently, the speciation patterns of metals in the core sediments (Iwegbue, 2011) and the seasonal and spatial changes in the characteristic of metals in the streambed and surface water have been documented (Iwegbue *et al.*, 2012). In view of these facts, it becomes necessary that study of metals in core sediments of the river be presented. Information from such study provides records of environmental impacts on fluvial systems over time. The objective of the study is to determine the distribution of some metals in the core sediment of Orogodo River.

Materials and Methods

Description of the study area

The Orogodo River is about 50 km long and located in the Delta State, Nigeria. It lies between latitude $5^0 0^1$- $6^0.2^1$N and longitude $6^0\ 10^1$ - $6^0 26^1$ E (Fig. 1). The stream is fed principally by ground seepage from an aquifer in the thick rainforest zone of Mbiri and also by precipitation, municipal effluents and surface runoff from the riparian communities. It flows through the main towns of Agbor, Owa-Ofie, Ekuma-Abavo, Oyoko in Delta State and ends up in the River Ethiope, southern Nigeria (Arimoro *et al.,* 2007a, b, 2008).

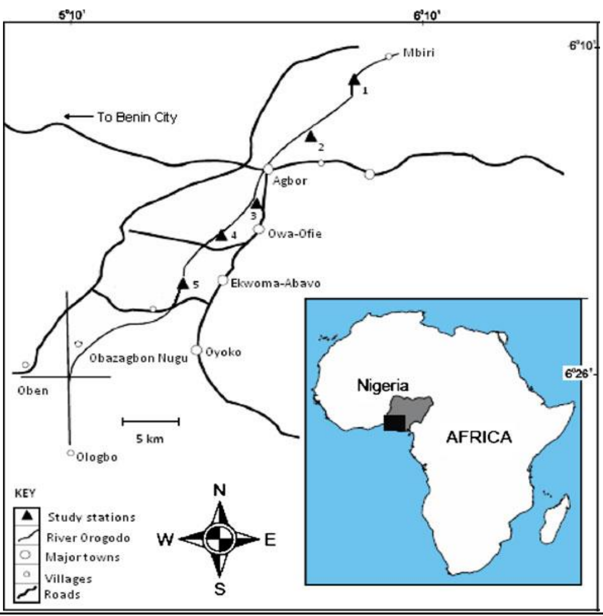

Fig. 1: Map of the study area

The study area is underlain by the Miocene-Recent Benin Formation. This formation, previously recognized as the Coastal Plain Sands, stretches over a considerable portion of Nigeria, adjacent to Deltaic Plain Sediments. The formation generally consists of unconsolidated and friable sandy beds, with intercalations of gravely units and lenses. Within the area, the Benin Formation is capped by lateritic soil in the first few metres followed by fine grained sands that vary in thickness from 9 to 58 metre. Underlying these, is a sequence of medium to coarse grained sands with several horizons of intercalated discontinuous lenses of clay (Olobaniyi *et al.*, 2007).

Sampling collection and analysis

A total number of twenty five (25) core sediments were collected at five different locations in the river by inserting a 1 m – long stainless steel corer with an internal diameter of about 6 cm. At each location, five samples taken within 5 m^2 at each location, were combined into a composite for 0-5, 5-10, 10-15, 15-25, 25-30, 30-35, 35-40, 40-45, 45-50, 50-55 and 55-60 cm depths from which a subsample was taken for analysis in order to reduce variance due to heterogeneity (Birch *et al.*, 1998; 2001). The corer was pushed manually as far as possible. The sediment core was sliced into thin horizontal sections of 5 cm each and packed in a polyethylene bag and transported to the laboratory. The entire samples were sieved to pass through less than 850 µm mesh and stored in a cold room (4^0C) until the analysis was completed. One gram (1.0 g) of the core sediment sample was weighed into a 50 mL Teflon beaker and 9 mL of HNO_3, 4 mL of HF, 1 mL of concentrated HCl, and 2 mL of $HClO_4$ were then added and left overnight. The next day, samples were digested at 120 ^{0}C for 2 h. The digest was slowly evaporated until fumes of $HClO_4$ appeared. The digested sample was filtered through a 0.45 µm filter and made up to 25 ml mark with 1 mol L^{-1} nitric acid. The sample solution was analyzed for Cu, Ni, Cr, Zn Fe, Pb and Mn using flame atomic absorption spectrophotometry (SENS AA, Melbourne, Australia).

Quality assurance and quality control

Glassware was cleaned with Suprapur (Merck) HNO_3 1:1 (overnight at room temperature) and rinsed thoroughly with deionized Milli Q water. Suprapur (Merck) HCl, HNO_3, $HClO_4$ and HF were used for acid digestion.

Quality control of the results was performed by analysis of the Estuarine sediment reference certified material BCR – CRM 277 issued by the Commission of European Communities. The percentage recovery with respect to certified values was 89% for Fe, 94% for Mn, 97% for Cu, 101% for Ni, 96% for Cr and 93.2% for Zn.

Computation of enrichment factor (EF) and geoaccumulation index (Igeo)

In order to assess the extent of the impact of heavy metals on Orogodo River, it is necessary to establish pre-anthropogenic (background) concentrations in the sediment. Background concentration can be determined by analyzing core data (Loring & Rantala, 1992; Birch *et al.*, 1998; Birch *et al.*, 2001), using the mean metal concentrations of textural equivalent sediment reported in the literature (Turekian & Wedepohl, 1961) and by analyzing pristine regions of the catchment (Murray, 1996). As has been show in other studies, average crustal abundance of trace metals is inappropriate for estimating local background levels (Birch *et al.*, 1998; Birch *et al.*, 2001). Background concentration was therefore estimated by calculating the mean concentration of trace metals in the bottom two layers (Fung &Lo, 1997).

Enrichment factor can give an insight into differentiating an anthropogenic source from a natural origin. EF values close to 1 are considered to have a natural source (Nolting *et al.*, 1999). Further, EFs can also assist the determination of the degree of metal contamination. Five contamination categories are recognized on the basis of enrichment factor (Sutherland, 2000; Loska & Wiechula, 2003) (Table 3).

$$EF = \frac{C_n}{B_n} \qquad \text{.........................(1)}$$

Where *Cn* is the measured concentration of the element and *Bn* is the background concentration. In this case, the background concentration was estimated by calculating the mean concentration of trace metals in the bottom layer (Fung & Lo, 1997).

The index of geoaccumulation enables the assessment of contamination by comparing the current and pre-industrial concentration used with bottom sediment (Miller, 1969). The geoaccumulation index is given by the equation.

$$Igeo = \text{Log } 2 \frac{Cn}{1.5Bn} \qquad \text{....................(2)}$$

The factor 1.5 is applied because of the possible variations in the background values due to lithological variations (Rogan *et al.*, 2010). *Cn* and *Bn* retains the usual meaning as in equation 1.

Under the Miller Index of Geoaccumulation, *Igeo* is divided into seven grades ranging from unpolluted to very seriously polluted (Table 2)

Table 1: Contamination categories based on EF values

EF < 2	Deficiency to minimal enrichment
EF = 2 – 5	Moderate enrichment
EF = 5 – 20	Significant enrichment
EF = 20 – 40	Very high enrichment
EF > 40	Extremely high enrichment

Table 2: Index of geoaccumulation (*Igeo*) and contamination level

Igeo	*Igeo* class	Contamination level
<0	1	Uncontaminated
0-1	2	Uncontaminated to moderately
1-2	3	contamination
2-3	4	Moderately polluted
3-4	5	Moderately polluted to highly polluted
4-5	6	Highly polluted
>5	7	Highly to very highly polluted
		Very seriously polluted.

Source (Rogan *et al.*, 2010)

Statistical analysis of results

Analysis of variance and Tukey multiple-comparison test were used to determine whether the concentrations of the metals varied significantly within the core and between sites and seasons respectively with values less than 0.05 ($p<0.05$) considered to be statistically significant. The statistical calculations were performed with SPSS version 11.5. Relationship between metals in the first four layers of the core was established using principal component analysis and cluster analysis.

Results and Discussion

The results for spatial and seasonal distribution of Cu, Ni, Pb, Mn, Fe,Cr and Zn in the core sediments of the Orogodo River are presented in Table 3. The mean concentrations and range covering the five sampling stations are also presented in Table 3. The mineralogy, physical and chemical characteristics of the sediments are found elsewhere (Iwegbue *et al.*, 2012). Briefly, the pH of the sediment ranged between 5.1 and 7.3 for both seasons. The pH of the river sediment were slightly lower in the wet season than the dry season. The total organic matter expressed as total organic carbon was highly variable. The percent total organic carbon showed a decline with depth. The conductivity of the sediment ranged between 34.5-369 µS cm^{-1} and 38.9 – 400 µS cm^{-1} for dry and wet seasons, respectively. The sand fraction is the predominant fraction in the Orogodo river sediments. The percent fraction of sand in the sediment ranged from 87-95%. The silt content was extremely low ranging from 0-2%, while the clay content ranged from 4-13% at 0-20 cm depth. The results indicated a significant decrease ($p<0.05$) in metal concentrations with depths. The results were compared with universal guidelines on sediment toxicity limits by different international environmental authorities and the Department of Petroleum Resources of Nigeria limits for metals in sediments (Table 4). The concentrations of metals found in the core sediments were below these guidelines and standards established by these international agencies.

The concentrations of Cd, Pb, Cu, Cr, Ni, Pb, Mn, Fe and Zn in the top layers (0 – 20 cm) are typical of those normally encountered in surface sediments in Nigeria (Ihenyen, 2001; Iwegbue *et al*., 2006; Iwegbue 2007; Iwegbue *et al.*, 2007a, b) and Swartkpos River estuary South Africa (Binning & Baird, 2001).

The highest concentration of Cu (25.8 mg kg^{-1}) was observed at 0-5 cm depth in site III in wet season. However, the concentration in the rest of the sediment profile remained similar during wet and dry season. This indicates that seasonal changes have little influence on the distribution of Cu in deeper sections of the sediment core. In the dry season, the highest level of Cu was observed at 0-5 cm depth at site IV (9.0 mg kg^{-1}). This could be due to input from the abattoir waste being discharged into the river at this point. The elevated levels of Cu at sites II and III during wet season could be explained by the fact that these sampling locations are the major points where municipal wastewater is discharged into the Orogodo River. The concentrations of Cu in the core sediment ranged from 0.3 – 25.8 mg kg^{-1} in all seasons and depths.

The concentrations of Ni in the sediment samples ranged between 0.5-8.5 mg kg^{-1} and 0.8-37.5 mg kg^{-1} in all sites and depths in wet and dry seasons, respectively. Elevated levels of Ni were observed within 0-10 cm sections of the sediment core at site V in dry season. Generally high levels of Ni could be due to increased discharge of municipal wastewater during the wet season.

The levels of Pb showed a decline with depth in all sites except for site II and III that had constant values of Pb throughout the profile. The concentrations of Pb in sediment range between 0.01 and 25.7 mg kg^{-1} at all sites, depths and seasons. Elevated levels of Pb were observed at site III throughout the sediment compared to any other site investigated. The elevated level of Pb at site III was due to the fact that this site receives the greatest influx of sediment, urban wastewater, run-off from automobile mechanic workshops and gasoline filling station.

The concentrations of Mn in the sediment ranged between 0.01-78.8 mg kg^{-1} and 0.01-67.3 mg kg^{-1} at all sites and depths for dry and wet seasons, respectively. The highest level of Mn was observed at site V in both seasons. Significant seasonal changes ($p<0.05$) were observed in the concentrations of Mn in the core layers (0-15 cm) in sites I and II. However, no seasonal variation was observed at sites III, IV and V and at the deeper sections of the core. The concentrations of Mn decreased with increasing depths and remained constant at 20-35 cm depths and above. The lowest level of Mn in the core sediment was in site III.

Iron concentrations spanned between 27.8-1078 mg kg^{-1} and 27.6-1164 mg kg^{-1} at all sites and depths for wet and dry seasons, respectively. Significant spatial variations were observed in the concentrations of Fe in the sediment core. No significant temporal variability was observed in the concentrations of Fe in the sediment core at all sites. The concentrations of Fe in the sediment were observed to follow the order III>I>V>II>IV. Higher levels of Fe were observed in the core sediments of the river's upper reaches (site I) as compared to the Fe concentrations in the sediment core of the downstream reaches of the river (site V).

The concentrations of Cr in sediment core ranged between 0.3-2.5 mg kg^{-1} and 0.3-2.0 mg kg^{-1} for wet and dry seasons, respectively. The concentrations of Cr in the core sediment showed significant seasonal and spatial variations. The highest concentration of Cr was observed in the core of site V during the wet season. The concentrations of Cr appeared to be nearly constant at the bottom layers at all sites. The levels of Cr recorded in the present study were similar to chromium levels found in sediments of Ase river, Nigeria (Iwegbue *et al*., 2007a,b).

Zinc is the second most abundant metal in the sediment core in terms of concentration. The concentrations of Zn ranged between 10.8-336.5 mg kg^{-1} and 1.3-115 mg kg^{-1} for dry and wet seasons, respectively. Significant temporal variance was observed in the concentrations of zinc in the first three sections of the core. Elevated levels of zinc were observed in the first section (0-5 cm) of the core at site I (upstream), III (mid stream) and IV (downstream reaches) of the river. High levels of zinc in the sediment are largely due to discharges of agricultural wastes and run off from the nearby farms.

Table 3: Mean concentrations of metals (mg kg^{-1}) in core sediments of Orogodo River

Depth (cm)	Cu		Ni		Pb		Mn		Fe		Cr		Zn	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
0-5	5.0±2.7	8.8±9.9	12.9±14.0	6.7±1.0	6.5±11.0	6.9±11.0	42.1±21.1	46.4±18.2	713±358.	704±309	1.1±0.6	2.0±0.4	185.9±119.7	94.8±16.0
	(2.5-9.0)	(2.8-25.8)	(3.3-37.5)	(5.8-8.5)	(0.01-25.7)	(0.01-25.9)	(25.1-78.8)	(25.4-67.3)	(308-1164)	(391-1078)	(0.5-2.0)	(1.8-2.5)	(87.3-336.5)	(77.0-115.0)
5-10	3.3±1.1	3.3±0.8	10.0±12.4	5.8±0.3	6.5±11.0	6.3±10.3	35.4±19.3	40.3±18.3	552±372	618±280.	0.8±0.2	1.8±0.3	138.2±102.5	66.4±14.1
	(2.5-5.0)	(2.8-4.5)	(2.8-32.0)	(5.5-6.3)	(0.01-25.7)	(0.01-24.2)	(11.9-65.4)	(15.1-60.6)	(56-1036)	(342-1033)	(0.5-1.0)	(1.5-2.3)	(86.0-321.5)	(52.3-84.8)
10-15	2.6±0.7	2.9±0.9	4.1±2.1	5.8±0.4	5.6±9.6	5.9±10.0	30.4±19.3	35.2±17.8	435±286	488±206	0.7±0.1	1.7±0.4	65.2±16.3	63.4±13.2
	(2.0-3.0)	(2.3-4.5)	(2.8-7.5)	(5.5-6.3)	(0.01-22.3)	(0.0-23.1)	(10.6-61.2)	(12.8-60.0)	(50-804)	(313-802)	(0.5-0.8)	(1.3-2.3)	(49.8-86.3)	(52.0-83.3)
15-20	1.9±0.9	2.8±0.8	2.9±1.0	5.4±0.4	5.6±9.6	5.5±9.6	27.0±21.0	30.1±21.3	378±242.	463±175	0.6±0.1	1.5±0.4	55.8±13.6	54.2±12.0
	(1.0-3.0)	(2.0-4.0)	(2.0-4.3)	(5.0-6.0)	(0.01-22.2)	(0.01-22.1)	(1.9-59.5)	(2.1-59.9)	(48-655)	(311-719)	(0.5-0.8)	(1.0-2.0)	(38.5-70.8)	(42.8-71.0)
20-25	1.8±0.9	2.5±0.7	2.1±1.0	5.2±0.3	5.4±9.3	5.3±9.4	25.3±21.3	27.5±20.9	352±228	386±236	0.6±0.1	1.4±0.4	47.8±9.2	48.7±7.8
	(0.8-3.0)	(2.0-3.5)	(1.0-3.5)	(4.8-5.5)	(0.01-21.5)	(0.01-21.7)	(0.6-59.0)	(0.5-56.5)	(38-648)	(66-713)	(0.5-0.8)	(1.0-2.0)	(37.5-57.75)	(39.5-61.0)
25-30	1.7±0.8	2.1±0.4	2.1±0.8	4.8±0.5	5.3±9.1	5.2±9.2	24.9±21.6	25.1±21.0	334±219	359±224	0.5±0.0	1.2±0.3	42.7±8.4	42.0±12.3
	(0.8-3.0)	(1.8-2.5)	(1.5-3.3)	(4.0-5.3)	(0.01-21.1)	(0.01-21.2)	(0.01-58.6)	(0.01-55.8)	(35-625.)	(50-660)	(0.0-0.5)	(0.8-1.5)	(35.5-51.8)	(21.5-53.8)
30-35	1.4±0.7	1.9±0.4	1.8±0.6	4.3±0.9	5.2±9.1	5.0±9.0	22.6±21.5	23.4±20.9	324±219	333±210	0.50±0.0	1.1±0.2	36.8±8.8)	37.1±12.8
	(0.8-2.5)	(1.5-2.5)	(1.0-2.3)	(2.8-5.0)	(0.01-21.0)	(0.01-20.7)	(0.01-57.4)	(0.01-55.4)	(29-623)	(48-610)	(0.0-0.5)	(0.8-1.3)	(24.0-46.0)	(17.8-51.8)
35-40	1.3±0.6	1.9±0.4	1.6±0.5	2.5±0.7	5.0±9.1	4.9±9.0	20.3±21.7	21.2±21.8	281±239.	310±201	0.4±0.1	0.7±0.2	32.6±10.4	23.6±13.1
	(0.8-2.3)	(1.5-2.5)	(1.0-2.0)	(2.5-4.0)	(0.01-20.9)	(0.01-20.7)	(0.01-56.4)	(0.01-55.4)	(28-616)	(41-595)	(0.3-0.5)	(0.5-1.0)	(18.8-45.0)	(7.0-30.8)
40-45	1.1±0.7	1.7±0.5	1.3±0.7	2.1±0.3	4.8±8.6	4.6±8.3	18.8±21.8	19.6±21.6	269±241	265±221	0.4±0.1	0.6±0.2	25.7±7.0	17.5±14.9
	(0.5-2.3)	(1.0-2.3)	(0.5-1.8)	(1.8-2.5)	(0.01-19.9)	(0.01-19.1)	(0.01-54.9)	(0.01-53.8)	(28-614)	(34-587)	(0.3-0.5)	(0.3-0.8)	(15.3-33.0)	(6.5-27.3)
45-50	1.0±0.7	1.3±0.4	1..3±0.0	1.5±0.5	7.9±10.5	4.4±8.1	25.2±27.1	20.5±23.8	400±184	251±212	0.4±0.1	0.4±0.2	20.1±10.4	13.9±13.7
	(0.3-2.0)	(0.8-1.5)	(1.3-1.3)	(1.0-2.0)	(0.01-19.8)	(0.01-18.7)	(0.01-53.9)	(0.01-52.7)	(263-609)	(29-569)	(0.3-0.5)	(0.3-0.8)	(5.3-28.5)	(3.3-33.5)
50-55	0.7±0.1	1.0±0.5	1.3±0.0	0.9±0.6	11.2±10.9	5.1±8.0	26.4±37.4	19.7±23.3	451±223	276±210	0.3±0.0	0.3±0.0	14.9±5.8	7.6±8.3
	(0.5-0.8)	(0.3-1.5)	(0.0-1.3)	(0.3-1.3)	(3.5-18.9)	(0.01-16.8)	(0.01-52.9)	(0.01-51.6)	(293-608)	(29-537)	(0.0-0.3)	(0.0-0.3)	(10.8-19.0)	(1.3-17.0)
55-60	0.5±0.0	0.9±0.2	0.8±0.0	0.6±0.2	3.2±0.0	1.0±1.7	42.8±0.0	21.8±17.2	291±0.0	160±120	0.3±0.0	-	-	16.3±0.0
	(0.0-0.5)	(0.8-1.0)	(0.0-1.3)	(0.5-0.8)	(0.0-3.2)	(0.01-2.9)	(0.00-42.8)	(5.1-39.3)	(0.0-291)	(28-260)	(0.0-0.3)	-	-	(0.0-16.3)

Wet= wet season; Dry = dry season

Table 4: Some International Guidelines for metals in sediments*

Metal	Crustal abundance value	Shale	Screening lead guideline of Ontorio Ministry of Environment		NOAA Sediment quality guidelines		FDEP Sediment guidelines		The CCME interim sediment quality		Sediment quality objecties in guideline Netherland	
			Low	Severe	ERL	ERM	TEL	PEL	IGM	PEL	TV	MPC
Cd	0.11	0.3	0.6	10	1.20	9.6	0.68	4.21	0.6	3.5	0.8	12
Co	20	19	-	-	-	-	-	-	-	-	-	-
Cr	100	90	26.0	110	81.0	160.06	52.30	160.00	37.3	90.0	-	-
Cu	50	45	16.0	110	34.0	270.0	18.70	108.00	35.7	197.0	36.0	73
Mn	950	850	460.0	1110	-	-	-	-	-	-	-	-
Fe	4.1	4.7	-	-	-	-	-	-	-	-	-	-
Ni	80	68	16.0	75	20.9	51.6	15.90	42.80	-	-	-	-
Pb	14	20	31.0	250	46.7	218.0	30.20	112.00	35.0	91.3	85.0	530
Zn	75	95	120.0	820	150.0	410.0	124.00	271.00	123.0	315.0	140.0	620

*All concentrations in μg g^{-1}, except iron (Fe) in %

Table 5: Enrichment factor of heavy metals in core sediment of Orogodo River

Depth(cm)	Cu		Ni		Pb		Mn		Fe		Cr		Zn	
	Dry	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**
0 – 5	10.1 ± 4.6 (6.50– 18.0)	10.9± 7.7 (2.8 – 20.6)	13.6 ± 10.7 (3.3 – 30.0)	11.3 ± 7.3 (3.7 – 23.0)	15.6 ± 32.1 (1.0 – 73.0)	26.8 ± 56.6 (1.0 – 128.0)	504 ± 1120 (1.8 – 2508)	511±1134 (1.7-2540)	5.3± 3.9 (1.9-11.1)	5.8 ± 4.9 (2.0-14.1)	4.2±2.3 (2.0-8.0)	5.47±2.10 (3.00-7.00)	17.7±21.6 (6.0-56.1)	24.5±27.6 (2.9-71.2)
5 – 10	6.8 ± 2.0 (5.0 – 10.0)	5.2 ± 3.5 (2.8 – 11.0)	10.4 ± 9.6 (2.8 – 25.6)	10.1 ± 7.3 (3.4 – 22.0)	13.0 ± 26.3 (1.0 – 60.0)	21.7 ± 45.4 (1.0 – 103.0)	240 ± 530 (1.5 – 1188)	304 ± 671) (1.5 – 1505)	2.8 ± 1.5 (1.70-5.43)	5.2 ± 5.0 (1.9-13.9)	3.2±0.8 (2.0-4.0)	5.07±2.24 (2.33-7.00)	9.7±5.4 (5.0-18.3)	18.6±22.9 2.1-57.8)
10 – 15	5.5 ± 1.9 (4.0– 8.0)	4.7 ± 3.3 (2.3 – 10.0)	4.8 ± 2.0 (2.5 – 6.5)	10.0 ± 7.2 (3.4 – 22.0)	1.2 ± 0.3 (1.0 – 1.7)	1.3 ± 0.5 (1.0 – 2.2)	215 ± 474 (1.4– 1063)	258± 571 (1.5 – 1280)	2.4 ± 1.6 (1.3 - 5.2)	4.2 ± 4.03 (1.5 - 11.3)	2.8±0.5 (2.0-3.0)	4.5±1.7 (2.3-6.0)	6.1±5.8 (2.6-16.4)	17.7±21.5 (1.8-54.2)
15 – 20	3.8 ± 1.4 (2.5 – 6.0)	4.6 ± 3.3 (2.0 – 10.0)	3.5 ± 1.6 (2.3 – 5.7)	9.3 ± 6.5 (3.1 – 20.0)	1.18 ± 0.31 (1.00 – 1.71)	1.2 ± 0.4 (1.0 – 1.8)	39.5 ± 83.1 (1.4 – 188)	44.7 ± 94.1 (15.2 – 213)	2.2 ± 1.6 (1.1 - 4.9)	4.1 ± 4.1 (1.3 - 11.2)	2.2±0.5 (2.0-3.0)	4.1±1.9 (2.0-6.0)	5.1±4.7 (2.4-13.5)	15.8±19.9 (1.5-50.0)
20 – 25	3.6 ± 1.4 (2.5 – 6.0)	3.9 ± 2.5 (2.0 – 8.0)	2.4 ± 1.1 (1.0 – 3.5)	8.96 ± 6.21 (3.1 – 19.0)	1.16 ± 0.29 (1.00 – 1.66)	1.2 ± 0.3 (1.0 – 1.7)	12.7 ± 23.7 (1.2 – 55.0)	12.5 ± 22.7 (1.4 – 53.0)	2.0 ± 1.6 (1.1 - 4.8)	2.1 ± 0.8) (1.3 - 3.5)	2.0±0.0 (2.0-2.0)	3.9±1.7 (1.7-6.0)	4.3±3.7 (2.0-10.8)	13.2±15.6 (1.4-39.6)
25 – 30	3.4 ± 1.5 (2.5 – 6.0)	3.3 ± 2.1 (2.0 – 7.0)	2.5 ± 0.7 (1.5 – 3.0)	8.0 ± 5.2 (3.0 – 16.0)	1.2 ± 0.3 (1.0 – 1.6)	1.2 ± 0.3 (1.0 – 1.6)	1.7 ± 1.2 (1.2 – 3.8)	1.9 ± 1.3 (1.0 – 4.1)	1.9 ± 1.4 (1.0 - 4.4)	2.0 ± 0.8 (1.2 - 3.4)	2.0±0.0 (2.0-2.0)	3.3±1.8 (1.3-6.0)	3.9± 3.4 (1.8 – 9.9)	11.7±15.3 (1.2-38.0)
30 – 35	2.9 ± 1.2 (2.0 – 5.0)	3.0 ± 1.9 (1.4 – 6.0)	2.2 ± 0.98 (1.0 – 3.0)	6.8 ± 3.6 (2.9 – 11.0)	1.1 ± 0.2 (1.0 – 1.5)	1.13± 0.2 (1.0 – 1.4)	1.6 ± 1.0 (1.0 – 3.4)	1.7 ± 1.1 (1.0 – 3.7	1.8 ± 1.4 (1.0 - 4.3)	1.8 ± 0.8 (1.1 - 3.2)	2.0±0.0 (2.0-0.0)	3.0±1.6 (1.3-5.0)	3.3 ± 2.9 (1.6 – 8.4)	10.5±13.8 (1.2-34.2)
35 – 40	2.6 ± 1.2 (1.5 – 4.5)	3.0 ± 1.9 (1.4 – 6.0)	1.9 ± 0.8 (1.0 – 2.7)	5.0 ± 3.2 (1.4 – 10.0)	1.1 ± 0.1 (1.0 – 1.3)	1.1 ± 0.2 (1.0 – 1.3)	1.3 ± 0.4 (1.0– 1.9)	1.4 ± 0.4 (1.0 – 2.0)	1.2 ± 0.2 (1.0 - 1.4)	1.7 ± 0.8 (1.1 - 3.1)	1.6±0.6 (1.0-2.0)	1.87±0.8 (1.0-3.0)	3.0 ± 2.6 (1.2 – 7.4)	4.2±3.9 (1.1-10.0)
40 – 45	2.3 ± 1.4 (1.0 – 4.5)	2.4 ± 1.1 (1.4 – 4.0)	1.5 ± 0.7 (1.0 – 2.3)	3.7 ± 2.6 (1.0 – 8.0)	1.1 ± 0.1 (1.0 – 1.2)	1.1 ± 0.1 (1.0 – 1.3)	1.1 ± 0.1 (1.0 – 1.3)	1.2 ± 0.2 (1.0 – 0.4)	1.1 ± 0.1 (1.0 - 1.3)	1.6 ± 0.8 (1.1 - 3.1)	1.8±0.5 (1.0-2.0)	1.6±1.0 (1.0-3.0)	2.2±2.6 (1.0-4.8)	2.2±1.9 (1.1-5.6)
45 – 50	2.0 ± 1.4 (1.0 – 4.0)	1.9 ± 1.2 (1.0 – 4.0)	1.3 ± 0.5 (1.0 – 1.7)	3.0 ± 1.7 (1.00 – 5.00)	1.1 ± 0.1 (1.0 – 1.2)	1.1 ± 0.1 (1.0 – 1.2)	1.1 ± 0.2 (1.0 – 1.2)	1.1 ± 0.1 (1.0 – 1.3)	1.0 ± 0.1 (1.0 - 1.1)	1.1 ± 0.2 (1.0 - 1.4)	1.7±0.6 (1.0-2.0)	1.3±0.5 (1.0-2.0)	1.4±0.7 (1.0-2.4)	1.4±0.7 (1.0-2.6)
50 – 55	1.2 ± 0.3 (1.0\ – 1.5)	1.2 ± 0.2 (1.0 – 1.5)	1.3 ± 0.5 (1.0 – 1.7)	1.7 ± 0.8 (1.0 – 2.5)	1.0 ± 0.1 (1.0 – 1.1)	1.0 ± 0.1 (1.0 – 1.2)	1.1 ± 0.2 (1.0 – 1.2)	1.1 ± 0.2 (1.0 – 1.3)	1.0 ± 0.0 (0.0 - 1.0)	1.1 ± 0.1 (1.0 - 1.2)	1.0±0.0 (0.0-1.0)	1.0±0.0 (0.0-1.0)	1.0±0.0 (0.0-1.0)	1.0±0.0 (0.0-1.0)
55 – 60	1.0± 0.0 (0.0 – 1.0)	1.0 ± 0.0 (0.0 – 1.0)	1.0 ± 0.0 (0.0 – 1.0)	1.0 ± 0.0 (0.0– 1.0)	1.0 ± 0.0 (0.00– 1.0)	1.0 ± 0.0 (0.0 – 1.0)	1.0 ± 0.0 (0.0 – 1.0)	1.0 ± 0.0 (0.0 – 1.0)	1.0± 0.0 (0.0 - 1.0)	1.0 ± 0.0 (0.0 - 1.0)	1.0±0.0 (0.0-1.0)	0.0±0.0 (0.0-0.0)	0.0±0.0 (0.0-0.0)	1.0±0.0 (0.0-1.0)

Enrichment factors and geoaccumulation index in core sediment

Table 5 displays the mean and range of metal enrichment factors of the sediment profile. Computed enrichment factors showed significant enrichment with Cu at the surface while Ni showed moderate enrichment to very high enrichment at some sites. For Pb, only the first two sections of site II showed extremely high enrichment. However, at other sites and depths, they were minimally enriched with Pb. Manganese in site III showed extremely high enrichment factors in the first four sections, while site V showed significant enrichment and other sites showed minimal to moderate enrichment factor with Mn. For Zn, only sites I, II and III had enrichment factors greater than 10 indicating non crustal sources (Nolting *et al.*, 1999), at the deeper sections, the enrichment factor decreased to unity indicating crustal sources. The enrichment factors of Fe and Cr ranged from 1.00-14.08 and 1.0-8.0, respectively in all sites depths and seasons. The top sections of Orogodo river sediment could be categorized as "moderate to significant enrichment" with Fe and Cr since the enrichment factors are within the values 2-20.

The average *Igeo* values of Cu, Ni, Pb, Mn, Fe, Cr and Zn in core sediment of Orogodo River are shown in Table 6. According to the defined *Igeo* classes, the top section of core (0-10 cm) fit into moderately polluted and highly polluted range with Cu, Ni, Pb, Fe and Zn. However, the *Igeo* index values for Pb, Fe (in dry season) and Mn (in dry and wet seasons) indicate that top section was uncontaminated with Pb, Fe and Mn. *Igeo* value for Mn indicate that the entire sediment column were uncontaminated with Mn. *Igeo* values of the studied metals showed a decline with depth. Beyond 30 cm depths, the *Igeo* values indicate that deeper sections of the sediment column were uncontaminated with the study metals except Pb in the wet seasons.

Table 6 : Igeo value for metals in core sediments of Orogodo River

	Cu		Ni		Pb		Mn		Fe		Cr		Zn	
Depth (cm)	**Dry**	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**
0-5	2.74	2.73	3.51	2.82	0.43	2.23	-0.61	0.51	0.71	1.55	1.47	2.40	3.06	1.96
5-10	2.12	1.30	3.14	2.61	0.41	2.11	-0.86	0.30	0.34	1.36	1.07	2.24	2.63	1.45
10-15	1.77	1.14	1.86	2.60	0.20	2.00	-1.08	0.11	-0.01	1.02	0.88	2.12	1.55	1.38
15-20	1.34	1.06	1.36	2.51	0.19	1.91	-1.25	-0.12	-0.21	0.95	0.53	1.98	1.32	1.15
20-25	1.26	0.89	0.86	2.45	0.15	1.87	-1.34	-0.25	-0.31	0.68	0.53	1.88	1.10	1.00
25-30	1.14	0.67	0.91	2.32	0.13	1.83	-1.42	-0.38	-0.39	0.58	0.40	1.60	0.94	0.78
30-35	0.90	0.49	0.63	2.16	1.06	1.77	-1.50	-0.48	-0.43	0.47	0.40	1.47	0.72	0.61
35-40	0.74	0.49	0.47	1.40	0.05	1.75	-1.66	-0.62	-0.64	0.37	0.07	0.88	0.54	-0.05
40-45	0.55	0.32	0.15	1.14	-0.02	1.64	-1.77	-0.72	-0.70	0.15	0.21	0.66	0.20	-0.48
45-50	0.42	-0.08	0.15	0.66	0.70	1.60	-1.35	-0.67	-0.13	0.06	0.14	0.21	-0.15	-0.82
50-55	-0.16	-0.47	0.15	-0.05	1.21	1.79	-1.28	-0.73	-0.05	0.20	-0.60	-0.60	-0.58	-1.69
55-60	-0.58	-0.58	-0.59	-0.59	-0.59	-0.59	-0.58	-0.59	-0.58	-0.58	-0.60	-	-	-0.59

Principal component analysis (PCA)

PCA is a multivariate analytical method that is used to reduce a set of original variable and to extract a small number of latent factors (principal components PCs) for analyzing relationship among observed variables (Golobocanin *et al.*, 2004). Three components of group of metals were extracted at the various depths (0-20 cm) (Tables 7 – 11) for dry and wet seasons. The components or compositions of these factors were different in the dry season, group 1(or factor 1) expressing about 43.0% of the total variance including metals mainly from anthropogenic (Cu and Cr) (Yongming *et al.*, 2006); group 2 expressing about 35.7% of the total variance including Pb, Fe and Zn which are associated with traffic activities. Zinc compounds have been used as antioxidants (e.g. zinc carboxylate complexes and zinc sulphonates) and as dispersant improvers for lubricating oil (Yongming *et al.*, 2006). It has been reported that tire wire contribute significant amount of zinc to the urban environment (Shah & Shaheen, 2008; Shah *et al.*, 2008; Iwegbue *et al.*, 2012); group 3 (explaining 17.6% of the total variance) includes Ni and Mn. Nickel and Mn are fuel additives particularly in burning fuels (diesel), which are used in operating residential electricity systems (Sheppard *et al*., 2000; El-Hassan *et al.*, 2006; Iwegbue *et al*., 2012). In the wet season, group 1 (or factor 1expressing about 55.4% of the total variance which include metals such as Mn and Zn; group 2 explaining about 28.2% of the variance and include metals such as Cu, Pb and Fe; group 3 (explaining about 15.6% of the total variance and includes metals such as Cr and Ni. Similarly, at the 10-15 cm depth, three components were also extracted in both seasons. For instance, in the dry season, group 1 (expressing about 47.0% of the total variance) include metals such as Cu, Pb and Fe; group 2 (explaining 26.1% of the total variance) include Cr and group 3 (explaining about 23.86% of the total variance) include Ni and Mn. In the wet season, three group were identified based on the PCA, group 1 consisting of about Pb and Fe expressing about 41.2% of the total variance; group 2 consisting of Cr, Ni, and Mn expressing 33.9% of the variance and group 3 consisting only Cr explaining about 17.7% of the total variance. The PCA results indicates that certain metals are cluster together in the same group. The presence of metal in the same group reflects similar behaviors and common source. However, the grouping of these metals showed variations with respect to depths and seasons which indicates myriad of sources and seasonal influence on the sources.

Conclusion

The concentrations of metal ions in core sediment of Orogodo River showed a decline with an increase in the depth. The concentrations of metals found in the core sediments were below international guidelines and standards for metals in sediments. However, the geoaccumulation index and enrichment factors indicate that the top sections of sediment core were significantly polluted in comparison with pre-industrial concentrations. Following from the above, three main sources of metals in the core sediments of Orogodo River can be identified; which include those mainly derived from industrial activities, traffic and those associated with burning of fuel (diesel). Metals in the sediments of Orogodo River are in part related to discharges from automobile mechanic workshops, abbatoir, paint industry, agricultural farms and as well as urban wastewater.

Conflict of Interest
Authors declare that there are no conflicts of interest.

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