Assessment of Sediment Contamination by Heavy Metals in River Orogodo (Agbor, Delta State, Nigeria)

B.R. ISSA[1]*, F.O. ARIMORO[2], M. IBRAHIM[3] G.J. BIRMA[1] and E.A. FADAIRO[1]

[1]Petroleum Training Institute, Effurun, Delta State (Nigeria).
[2]Delta State University, Abraka, Delta State (Nigeria).
[3]Niger State Ministry of Education, Minna (Nigeria).

ABSTRACT

Sediment samples from the coast of River Orogodo in Agbor, Delta State, Nigeria were sampled over four months (May to August) and analysed for heavy metals (Cd, Mn, Fe, Cu, Ni, Pb, Zn, Cr) using Atomic absorption spectroscopic method. Some specific physico-chemical characteristics, such as organic matter, pH and conductivity which are known to influence the interactions and dynamics of metals within the sediment matrix were also determined. The result of the analysis indicates significant difference ($p < 0.05$) in pH, organic matters, Mn, Zn and Cr levels for the four month variation.

The concentration ranges of metals (in mg/kg of dry sediment) measured were in order of Fe (339-925) > Mn (4.02 -0.50) > Zn (1.91 -1.11) > Cu (1.04-0.10) > Pb (0.96-0.30) > Ni (0.75-0.57) >Cd (0.43-0.09) > Cr(0.30-0.10). The significant correlation ($p < 0.05$) however exists between some of the metals and some also show high correlations at $p < 0.01$. The concentrations of most heavy metals are low, but iron content is higher than the background value and DPR standard for soil/sediment which indicates significant contamination by iron in the water body.

Key words: Sediment, Contamination, Heavy metals and Pollution.

INTRODUCTION

The most often polluted phases of the environmental are the aquatic system, especially the surface water. This is because contaminants in air, soil or on land ultimately end up in the aquatic systems via local precipitation, water surface run-off and leaching of rocks and solid wastes (Forstner and Wiltman, 1983). Sewage, industrial wastes and agricultural chemicals such as fertilizers and pesticides, mineral and petroleum exploration and exploitation are however, the main causes of surface water pollution (Yong, 1999).

The activity of trace metals in aquatic systems and their impact on life vary depending upon the metal species. Of major importance in this regard is the ability of metals to associate with other dissolved and suspended components. Most significant among these associations is the interaction between metals and organic compounds in water and sediment. These organic species, which may originate naturally from process such as vegetative decay or result from pollution through organic discharge from municipal and industrial sources, have a remarkable affinity and capacity to bind metals (Signer, 1974).

It is widely recognized that marine ecosystems can become contaminated by trace of metals from numerous and diverse sources. However, anthropogenic activities, such as mining and industrial processing of ores and metals, still remain the principal cause of the increase amount of heavy metals which have been dumped in to the oceans (DeGregori *et al.,* 1996).

According to Mateu et al (1996), trace metal levels can be indicators of concentration of other pollutants to which they are potentially related.

There is now considerable evidence in the scientific literature that contaminants such as trace metals, phosphorous, pesticides, PCBs and polycyclic aromatic hydrocarbons, can be taken up and concentrated by sediments and suspended matter in aquatic systems. Transportation of these contaminants associated with particulate matter represents a major pathway in the biogeochemical cycling of trace contaminants (Allen, 1982).

Heavy metals belong to the group of elements whose hydro-geochemistry cycles have been greatly accelerated by man. Anthropogenic metals emission into the atmosphere such as Pb, Hg, Zn, Cd and Cu are 1:3 orders of magnitude higher than natural fluxes. As a consequence these elements are expected to become increasingly accumulated in natural reservoirs.

Protecting sediment quality is an important part of restoring and monitoring the biological integrity of our Nation's water as well as protecting aquatic life, wild life and human health. Sediment is an integral component of aquatic ecosystem providing habitat, feeding, spawning and rearing areas for many aquatic organisms.

Sediment also serves as reservoir for pollutants and therefore a potential source of pollutants to the water column, organisms, and ultimately human consumers of those organisms.

Contaminated sediment can cause lethal and sub-lethal effect in benthic and other sediment associated organisms (US EPA 2001). Also natural and human disturbances can release pollutants to the overlying water, where pelagic (water column) organisms can be exposed. Sediment pollutants can reduce or eliminate species of recreational, commercial or ecological importance, either through direct effects or by affecting the food supply which the sustainable population requires. The extent and severity of sediment contamination in U.S has been documented in the National Sediment Inventory (NSI). The evaluation of sediment contamination data indicates that thousands of locations have been affected through out the country (US EPA2001).

Orogodo River is one of the numerous freshwater bodies that abound in the Niger Delta area of southern Nigeria. It is a typical municipal stream flowing through Agbor town with a pollution of over 100,000 people (Arimoro et al, 2008). The river is subjected to organic pollution load arising from the effluent discharge from the abattoirs stations along the river bank, which comprises of stomach and intestinal contents of slaughtered animals, ashes of burnt animals materials that are slaughtered daily that makes up an enormous volume of waste discharge regularly into the stream without treatment. Furthermore, the river is influenced by frequent disturbance from human and animal activities which if not properly managed can pose severe health risk to the populace. There is need to assess the level of heavy metal contamination in Nigeria water sediments and also see the effect of these contamination to the aquatic life and ecosystem in general.

This work covers sampling of whole sediment and analysis to ascertain the level of contamination of heavy metals in River Orogodo.

The consistent sediment collection, holding time consideration, sediment manipulation and storage methods were used to help provide high quality samples with which accurate data can be obtained for the national inventory and for other programs to prevent, remediate, and manage contaminated sediment and this work would also attempt to make some recommendations.

MATERIAL AND METHOEDS

Description of the study area

River Orogodo lies between latitude 5°.10'-6°.20' N and longitude 6°.10'—6°.21'E (fig. 1) The River is fed principally by ground seepage from an aquifer in the thick rainforest of Mbiri and secondarily by precipitation, municipal effluence and surface run off from the riparian communities. The River flows through the major town of Agbor in Southern-Nigeria. The river substratum consists mainly of fine sand mixed with mud and occasionally with coarse sand and pebbles. Decaying macrophytes and debris also form part of the substratum. The climate

of Agbor town and its environs, although comparatively stable, is not uniform. A rhythm of rainfall occurs in conjunction with movements of the southwest Monsoon winds across the Atlantic Ocean and the timing of these movements varies from year to year.

Site I

The station is located at the point of discharge of effluents from the Agbor Abattoir. The abattoir effluent is mainly organic, made up of faeces, blood and ashes produced during the slaughter, roasting and burning of animals (donkeys and cows). This station is exposed to direct heat of the sun and has heavy algal growth in some areas but, with very few macrophyes (*Nymphae lotus, Azolla spp, utricularia sp and Salvinia sp.*) and duckweeds (*Lemna*) closed to the banks. The

steambed is covered by coarse sand. The current velocity is relatively fast (mean value = 0.58 ms⁻¹). Average depth is about 0.5 m and width 5.8 m/ Rubbish and domestic waste from the town are emptied into the river few kilometers from this station during heavy down pour (Arimoro et al, 2008).

Station II

The sampling station is located within the main town at Agbor, about 500m from site I and has a depth range of 0.38 m – 0.50 m. The current velocity ranges from $0.58 – 0.68 ms^{-1}$. This site is heavily perturbed by various human activities including laundering, car washing, dumping of refuse and defecation by both humans and livestock. During the early hours of the day, nomadic cattle herders take their animals to this site to drink and feed on grasses by the side of the river,

Table 1: Some physico-chemical characteristics and heavy metals of river sediment within River Orogodo from May to August 2008

S. No	Parameter	Station I	Station II	T-test	Probability
1	pH	5.81±0.10 (5.58-6.04)	5.95±0.14 (5.67-6.34)	2.58*	0.04
2	Conductivity (µS/cm)	2074±106.4 (1912-2387)	1967.8±313.92 (1143-2669)	0.46	0.34
3	Organic matter (%wt)	0.103±0.07 (0.09-0.12)	0.125±0.01 (0.11-0.16)	3.57*	0.02
4	Cadmium (mg/kg)	0.185±0.04 (0.10-0.27)	0.247±0.07 (0.09-0.43)	1.77	0.08
5	Manganese (mg/kg)	1.92±0.75 (0.50-3.68)	3.07±0.41 (2.19-4.02)	3.05*	0.03
6	Iron (mg/kg)	583.3±55.0 (450-715)	619±128.6 (339-925)	0.47	0.33
7.	Copper (mg/kg)	0.49±0.13 (0.20-0.84)	0.36±0.23 (0.1-1.04)	0.99	0.19
8	Nickel (mg/kg)	0.62±0.01 (0.60-0.65)	0.67±0.04 (0.57-0.75)	1.60	0.10
9	Lead (mg/kg)	0.59±0.11 (0.30-0.84)	0.63±0.13 (0.34-0.96)	1.21	0.16
10	Zinc (mg/kg)	1.63±0.17 (1.20-1.91)	1.17±0.02 (1.11-1.20)	2.72*	0.04
11	Chromium (mg/kg)	0.31±0.0001 (0.30-0.32)	0.18±0.03 (0.10-0.25)	4.74*	0.009

Note *indicate significant paired t-Test at 0.05 level (one tail)

Values are mean ± standard error and minimum and maximum values in parenthesis

 Table 1 above shows that pH, organic matter, Zinc and Chromium have significant different at 0.05 level.

Table 2a. Correlation matrix between some physico-chemical parameters and heavy metals in Station I of River orogodo study area

	pH	Conductivity	organic matter	Cd	Mn	Fe	Cu	Ni	Pb	Zn	Cr
pH	1										
Conductivity	0.865852	1									
Organic matter	-0.90641	-0.79276	1								
Cd	0.998664	0.89042	-0.9081	1							
Mn	0.983248	0.868935	-0.8162	0.982839	1						
Fe	0.981249	0.901724	-0.9595	0.986113	0.939466	1					
Cu	0.976517	0.95131	0.90589	0.986293	0.960212	0.986921	1				
Ni	0.678554	0.920542	-0.7567	0.713442	0.635026	0.785538	0.816187	1			
Pb	0.990941	0.851131	-0.9543	0.989585	0.949964	0.992594	0.970276	0.704757	1		
Zn	0.125267	0.482481	-0.4007	0.166833	0.032794	0.306561	0.307318	0.785235	0.200989	1	
Cr	0.916157	0.678092	-0.6882	0.901441	0.951404	0.821788	0.832429	0.366508	0.867187	-0.2713	1

coincidentally voiding their excreta into the water. The sparse vegetation in this site consists mainly of *commelina, Nymphaea sp., Pancium repens, Pistia stratiotes and Vossia Cuspidata.*

Sample collection

High density polyethylene container was chosen because its relatively inert nature and generally unbreakable. All the sample containers were soaked for seven days in hydrochloric acid (HCl), followed by seven days in nitric acid (HNO_3) and finally Seven days in deionized water. The cleaned containers were labeled, (US EPA, 2001).

The bed sediments were collected in each station using 20cm Birge-Eckman grab sampler and transferred into the cleaned containers.

Sample transport and storage

The transport and storage method was designed to maintain structural and chemical quality of the sediment. The sediment collected was transferred from the sampler to the sample container where it was temporarily stored and transported immediately to the laboratory for the next stage.

Sample preparation

In the laboratory, samples were air dried for two weeks before grounded into fine particles using pistil and mortar and sieved through a 2mm sieve.

About 200g of the sieved samples were sub sampled by quartering for analysis. Extraction of metals from sediment, using mixed acid digestion method was done. 20ml of a mixture of concentrated $HClO_4$ and HNO_3 at a 2:1 ratio (v/v) on a hot plate and the mixture was heated to almost dryness. 20ml of HNO_3 was added to the solution and filtered in to 50ml volumetric flask through whatman 42 filter paper. The filtrate obtained was made-up to 50ml mark with distilled water.

Laboratory Analysis

The pH of sediment samples were determined using Jenway pH meter (model 3520) following the procedure described by Hender short et al (1993). Total organic matter and conductivity were analysed following the procedure described

by Radojavic and Bashkin, (1999). The total concentration of heavy metals was determined using Atomic Absorption Spectrophotometer (Unicam, model 969). All acid used were analytical grade and Quality Control was assured by the use of procedural blank.

DISCUSSION

The mean of four (4) month variation results of specific physicochemical characteristics and some heavy metals analysed in River Orogodo sediments within the study area are presented in table two (1). The pH was slightly acidic in a range 5.58- 6.34, which is peculiar to Nigerian soil/ sediment (Odu, 1996). The low pH condition affects metal speciation and may enhance metals' solubility and possible leaching into the water column.

High acidity of sediment has been attributed to a combination of possible oxidation of pyrity (FeS_2) in the sediment to produce sulfuric acid, depleted calcium level or increased aluminum concentration in sediment (Odu, 1996).

The result of the total organic matter lies in the range of 0.09- 0.19 (%wt). Total organic matter influenced the other physical and chemical sediment characteristics including reserve of exchanged bases and interaction and dynamics of trace metal, hence maximum soil/sediment capacity for heavy metals are adjusted according to these macro-nutrients DPR (2002). Organically bound metals may dissociate as free ions and participate in cation exchange reactions with various minerals and leaving organisms, depending on ambient pH, ionic strength and temperature. Hence the organic matter

Table 2b: Correlation matrix between some physico-chemical parameters and heavy metals in Station I of River orogodo study area

Correlations

		pH	Conductivity	organicmatter	Cd	Mn	Fe	Cu	Ni	Pb	Zn	Cr
pH	Pearson Correlation	1	.934*	-.881	.985**	.865	.971*	.908*	.923*	.970*	.863	.933*
	Sig. (1-tailed)		.033	.060	.007	.068	.015	.046	.038	.015	.069	.033
	N	4	4	4	4	4	4	4	4	4	4	4
Conductivity	Pearson Correlation	.934*	1	-.992**	.944*	.689	.935*	.768	.963*	.922*	.950*	.996**
	Sig. (1-tailed)	.033		.004	.028	.155	.033	.116	.018	.039	.025	.002
	N	4	4	4	4	4	4	4	4	4	4	4
organicmatte	Pearson Correlation	-.881	-.992**	1	-.899	-.605	-.892	-.694	-.947*	-.875	-.950*	-.987**
	Sig. (1-tailed)	.060	.004		.051	.197	.054	.153	.026	.062	.025	.006
	N	4	4	4	4	4	4	4	4	4	4	4
Cd	Pearson Correlation	.985**	.944*	-.899	1	.890	.998**	.823	.970*	.996**	.925*	.956*
	Sig. (1-tailed)	.007	.028	.051		.055	.001	.088	.015	.002	.037	.022
	N	4	4	4	4	4	4	4	4	4	4	4
Mn	Pearson Correlation	.865	.689	-.605	.890	1	.899	.724	.804	.915*	.730	.724
	Sig. (1-tailed)	.068	.155	.197	.055		.050	.138	.098	.043	.135	.138
	N	4	4	4	4	4	4	4	4	4	4	4
Fe	Pearson Correlation	.971*	.935*	-.892	.998**	.899	1	.784	.978*	.999**	.939*	.953*
	Sig. (1-tailed)	.015	.033	.054	.001	.050		.108	.011	.000	.031	.024
	N	4	4	4	4	4	4	4	4	4	4	4
Cu	Pearson Correlation	.908*	.768	-.694	.823	.724	.784	1	.684	.786	.586	.739
	Sig. (1-tailed)	.046	.116	.153	.088	.138	.108		.158	.107	.207	.130
	N	4	4	4	4	4	4	4	4	4	4	4
Ni	Pearson Correlation	.923*	.963*	-.947*	.970*	.804	.978*	.684	1	.970*	.990**	.982**
	Sig. (1-tailed)	.038	.018	.026	.015	.098	.011	.158		.015	.005	.009
	N	4	4	4	4	4	4	4	4	4	4	4
Pb	Pearson Correlation	.970*	.922*	-.875	.996**	.915*	.999**	.786	.970*	1	.928*	.941*
	Sig. (1-tailed)	.015	.039	.062	.002	.043	.000	.107	.015		.036	.030
	N	4	4	4	4	4	4	4	4	4	4	4
Zn	Pearson Correlation	.863	.950*	-.950*	.925*	.730	.939*	.586	.990**	.928*	1	.972*
	Sig. (1-tailed)	.069	.025	.025	.037	.135	.031	.207	.005	.036		.014
	N	4	4	4	4	4	4	4	4	4	4	4
Cr	Pearson Correlation	.933*	.996**	-.987**	.956*	.724	.953*	.739	.982**	.941*	.972*	1
	Sig. (1-tailed)	.033	.002	.006	.022	.138	.024	.130	.009	.030	.014	
	N	4	4	4	4	4	4	4	4	4	4	4

*. Correlation is significant at the 0.05 level (1-tailed).

**. Correlation is significant at the 0.01 level (1-tailed).

Table 3(a): Correlation matrix between some physico-chemical parameters and heavy metals in Station II of River orogodo study area

	pH	Conductivity	Organic .m	Cd	Mn	Fe	Cu	Ni	Pb	Zn	Cr
pH	1										
Conductivity	0.933802	1									
oranic matter	-0.88063	-0.99186	1								
Cd	0.985013	0.943657	-0.8989	1							
Mn	0.86452	0.689485	-0.6052	0.890023	1						
Fe	0.970682	0.934656	-0.8921	0.997512	0.89941	1					
Cu	0.908178	0.768271	-0.6941	0.823351	0.724047	0.783527	1				
Ni	0.923421	0.963464	-0.9471	0.96971	0.803748	0.977577	0.683652	1			
Pb	0.969765	0.921614	-0.8752	0.996381	0.914706	0.999337	0.785741	0.970431	1		
Zn	0.862959	0.949729	-0.9504	0.925491	0.729771	0.938839	0.585686	0.989967	0.928277	1	
Cr	0.933016	0.996359	-0.9873	0.955854	0.723737	0.952539	0.739279	0.982483	0.940865	0.971764	1

of sediments is known to play a major role in determining the bioavailability of heavy metals (Adams et al, 2002).

It is observed from table 2 that the concentration of each metal in the sediments increases from station I to II. The colour of the sediment which varies from brown to reddish brown could have been impacted by the presence of high iron content in the sediment.

It is difficult to make an overall assessment of the degree of the contamination of sediments by heavy metals because of the variations in the concentration of heavy metals within locations.

As can be seen from table (2) above, metal levels in the two stations exist in the order Fe >Mn >Zn >Cu >Pb > Ni >Cd > Cr, most of which were generally lower than those reported for Lagos lagoon (Okoye, 1991) and Niger Delta coastal waters (Kakulu et al, 1988). However, similar trend in some heavy metals distribution was obtained in other similar studies. The high concentrations of Fe in the sediment have no identifiable point source discharge rather than lithological or crustal origin (Asaolu, 1998). There is no doubt that wastes generated due to human activities are discharged on land or stream in and around the study area were transported by surface run-off to the water body by rain. Thus, contribution from run-off in this regard may be significant as evident in the concentration distribution of these metals in river Orogodo sediment (Table1). On the other hand, the relatively low metal level recorded in the study which is also exposed to municipal run-off may be attributed to the resent dragging of the river.

Matrices of correlation coefficient between the metal levels in the sediment for the four (4) month variation (Table 3a and 3b respectively) show high significant ($p < 0.05$) which is the direct correlation between some of the metals. The high correlation between metals indicates common lithological or crustal sources for the metals rather than the anthropogenic sources (Turekian, 1977).
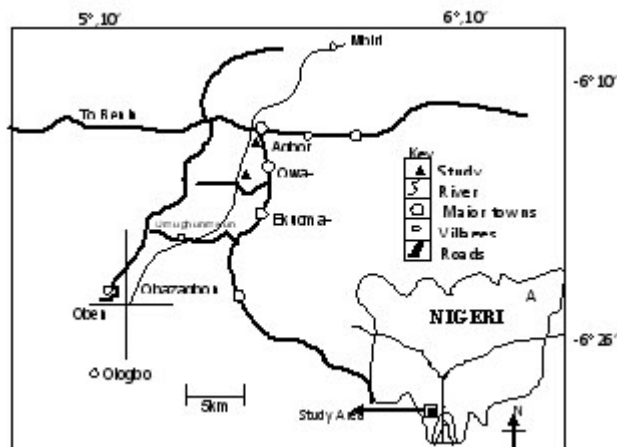
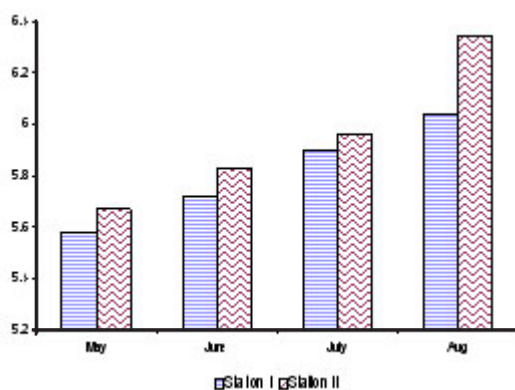**Fig.1: Map of the study area showing the sampling sites**

Fig. 2: Monthly variation in pH in the sampling sampling stations of River Orogodo (May to Aug 2008)
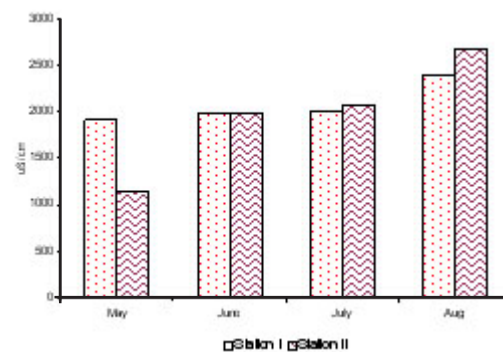

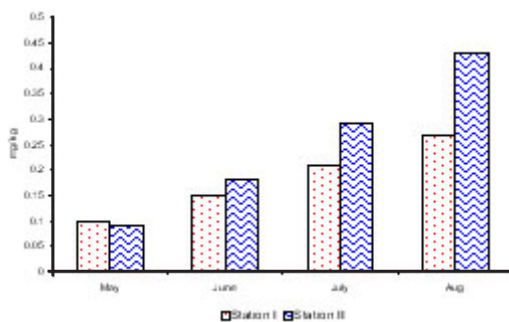**Fig. 3: Monthly variation in conductivity in the stations of River Orogodo (May to Aug 2008)**

Fig. 4: Monthly variation in organic matter in the sampling stations of River Orogodo (May to Aug 2008)
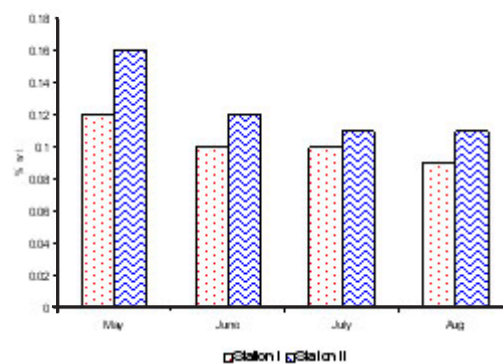

Fig. 5: Monthly variation in cadmium in the sampling stations of River Orogodo (May to Aug 2008)
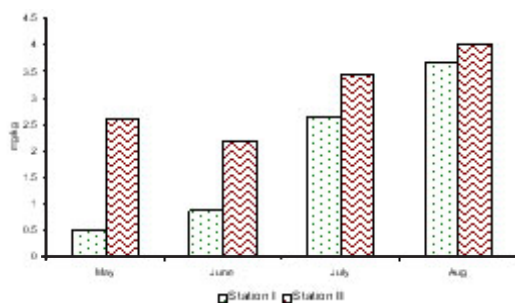
Fig. 6: Monthly variation in manganese in the sampling stations of River Orogodo (May to Aug 2008)
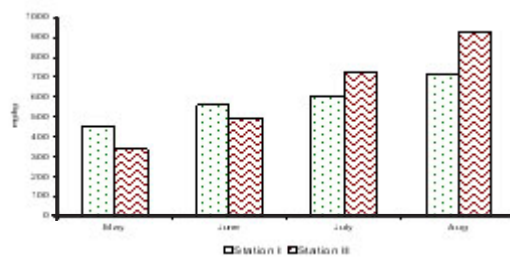

Fig. 7: Monthly variation in iron in the sampling stations of River Orogodo (May to Aug 2008)
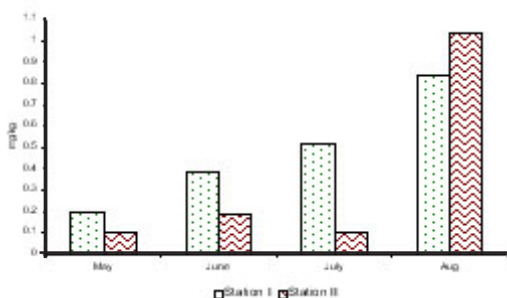

Fig. 8: Monthly variation in copper in the sampling stations of River Orogodo (May to Aug 2008)
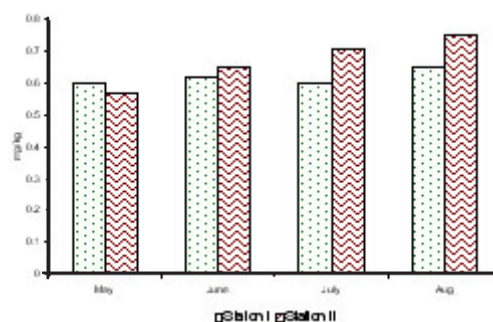

Fig. 9: Monthly variation in nickel in the sampling stations of River Orogodo (May to Aug 2008)
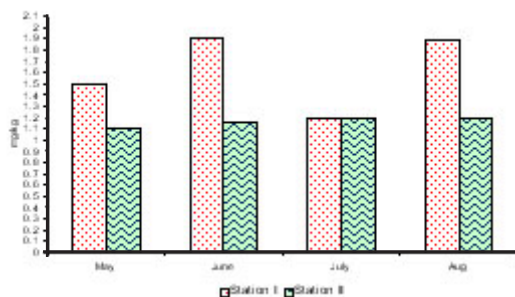

Fig. 10: Monthly variation in lead in the sampling stations of River Orogodo (May to Aug 2008)
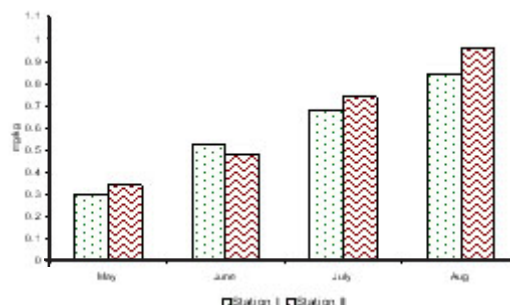

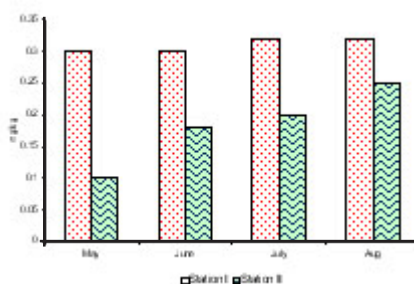**Fig. 11: Monthly variation in zinc in the sampling stations of River Orogodo (May to Aug 2008)**

Fig. 12. Monthly variation in chromium in the sampling stations of River Orogodo (May to Aug 2008)

Table 3(b): Correlation matrix between some physico-chemical parameters and heavy metals in Station II of River orogodo study area

Correlations

		pH	Conductivity	organicmatter	Cd	Mn	Fe	Cu	Ni	Pb	Zn	Cr
pH	Pearson Correlation	1	.866	-.906*	.999**	.983**	.981**	.977*	.679	.991**	.125	.916*
	Sig. (1-tailed)		.067	.047	.001	.008	.009	.012	.161	.005	.437	.042
	N	4	4	4	4	4	4	4	4	4	4	4
Conductivity	Pearson Correlation	.866	1	-.793	.890	.869	.902*	.951*	.921*	.851	.482	.678
	Sig. (1-tailed)	.067		.104	.055	.066	.049	.024	.040	.074	.259	.161
	N	4	4	4	4	4	4	4	4	4	4	4
organicmatter	Pearson Correlation	-.906*	-.793	1	-.908*	-.816	-.960*	-.906*	-.757	-.954*	-.401	-.688
	Sig. (1-tailed)	.047	.104		.046	.092	.020	.047	.122	.023	.300	.156
	N	4	4	4	4	4	4	4	4	4	4	4
Cd	Pearson Correlation	.999**	.890	-.908*	1	.983**	.986**	.986**	.713	.990**	.167	.901*
	Sig. (1-tailed)	.001	.055	.046		.009	.007	.007	.143	.005	.417	.049
	N	4	4	4	4	4	4	4	4	4	4	4
Mn	Pearson Correlation	.983**	.869	-.816	.983**	1	.939*	.960*	.635	.950*	.033	.951*
	Sig. (1-tailed)	.008	.066	.092	.009		.030	.020	.182	.025	.484	.024
	N	4	4	4	4	4	4	4	4	4	4	4
Fe	Pearson Correlation	.981**	.902*	-.960*	.986**	.939*	1	.987**	.786	.993**	.307	.822
	Sig. (1-tailed)	.009	.049	.020	.007	.030		.007	.107	.004	.347	.089
	N	4	4	4	4	4	4	4	4	4	4	4
Cu	Pearson Correlation	.977*	.951*	-.906*	.986**	.960*	.987**	1	.816	.970*	.307	.832
	Sig. (1-tailed)	.012	.024	.047	.007	.020	.007		.092	.015	.346	.084
	N	4	4	4	4	4	4	4	4	4	4	4
Ni	Pearson Correlation	.679	.921*	-.757	.713	.635	.786	.816	1	.705	.785	.367
	Sig. (1-tailed)	.161	.040	.122	.143	.182	.107	.092		.148	.107	.317
	N	4	4	4	4	4	4	4	4	4	4	4
Pb	Pearson Correlation	.991**	.851	-.954*	.990**	.950*	.993**	.970*	.705	1	.201	.867
	Sig. (1-tailed)	.005	.074	.023	.005	.025	.004	.015	.148		.400	.066
	N	4	4	4	4	4	4	4	4	4	4	4
Zn	Pearson Correlation	.125	.482	-.401	.167	.033	.307	.307	.785	.201	1	-.271
	Sig. (1-tailed)	.437	.259	.300	.417	.484	.347	.346	.107	.400		.364
	N	4	4	4	4	4	4	4	4	4	4	4
Cr	Pearson Correlation	.916*	.678	-.688	.901*	.951*	.822	.832	.367	.867	-.271	1
	Sig. (1-tailed)	.042	.161	.156	.049	.024	.089	.084	.317	.066	.364	
	N	4	4	4	4	4	4	4	4	4	4	4

*. Correlation is significant at the 0.05 level (1-tailed).

**. Correlation is significant at the 0.01 level (1-tailed).

CONCLUSION

This study presented data on the baseline pollution of bottom sediment of River Orogodo by heavy metals. It is shown that the concentrations of heavy metals like Zn, Pb Cr, Mn, Ni, C u, and Cd in the sediment are low, but require monitoring to prevent an increase. The concentration of Fe is higher when compared with the background value and target/ intervention values for micropollutant of a standard soil which may constitute risk to the environment. The concentration of heavy metals in the sediment increased from station I to station II.

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