Sciencia Acta Xaveriana
An International Science Journal
ISSN. 0976-1152

Volume 3
No. 2
pp. 51-64
Sep 2012

A study of the Trends in the Physico- Chemical Properties of the Surface Water and the Heavy Metals Composition of the Bottom Sediments of Ijana River, Warri, Delta State, Nigeria.

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Abstract : A study was carried out to investigate the concentrations, distribution and speciation of some heavy metals such as Cd, Cu, Pb, and Cr in the bottom sediments of Ijana River which has been contaminated by effluent from petroleum exploitation activities. The total concentration levels of Cd, Pb, Cu, and Cr were determined specifically at upstream, effluent zone, downstream and recipient of storm water of the river. Pb, Cu, and Cr were found to be the most abundant metals in the river. The distribution pattern of the river indicates the source of pollution to be land-based. Sequential extraction showed that 30 -60% of Cd, were exchangeable fraction, indicating that Cd in the sediments posed a high risk to local environments while Cu, Pb and Cr were at moderate risk levels. From the relationship between percentage fraction of metal speciation and total metal concentration, it was found that the distribution of Cd, Cu, and Pb in some fractions were dynamic in the process of pollutants migration and the stability of metals in sediment of the Ijana River decreased in the order Cr > Pb > Cd > Cu. The correlation analysis suggest that some of the metals are strongly associated, indicating a common source or chemical similarity. The pollution load index (PLI) of the studied area ranged from 0.10 to 50.78 which indicated the sediments were polluted while the index of geoaccumulation showed that all the sampling points may face a severe metal pollution/contamination problem in the future.

Keywords : Pollution Load Index (PLI) , Index of Geoaccumulation, Speciation, Sediment Pollution, Heavy metals, Correlation analysis.

(Received April 2012, Accepted August 2012)

1. INTRODUCTION

According to Mason (1991), heavy metal pollution is one of the five major types of toxic pollutants commonly present in surface and ground waters. The pollutants tend to accumulate in organisms, and become persistent because of their chemical stability or poor biodegradability, they are readily soluble and therefore environmentally mobile. Heavy metals form one of the major contributors to the pollution of natural aquatic ecosystems (Purves, 1985; Sanders, 1997). The elevated levels of heavy metals in the Niger Delta aquatic environment as a result of industrial discharges from refining operations have been reported by Atuma and Egborge, (1986); Ikomi and Owabor (1997); Ikomi and Emuh (2000); Spiff and Horsfall, (2004); Brades, et al, (2004). The unregulated discharge of untreated effluents into natural receptors by industries in Nigeria has also been reported by Egborge, (1994, 2000). Warri refinery and Petrochemical Company limited Ekpan Warri, generate effluent and discharge it into a natural receptor – River Ijana. Therefore, it is important to monitor pollution limits of heavy metals in the aquatic ecosystem, so that approximate measure of the potential hazards can be attained. These measures should give an estimation of the type of effects that could be expected after exposure to heavy metals.

The toxicity of metals in solutions depends on the degree of oxidation of a given metal ion and the form in which it exists. For example, the maximum allowable concentration of Cr (IV) the USSR was 0.001mg/l whereas it was 0.5mg/l for Cr (III). As a rule however, the ionic form of a metal is the most toxic form (Bestemyanov and Krotov, 1985), the toxicity is reduced if the ions are bound into complexes with natural organic matter such as fulvic and humic acids. Various environmental factors such as temperature, pH, water hardness, dissolved oxygen, light, salinity and organic matter can influence the toxicity of metals in solutions (DWAF, 1996). Also, the lack of natural elimination processes for metals aggravates the situation. As a result, metals shift from one compartment within the aquatic environment to another including the biota often detrimental effects through sufficient bioaccumulation. Food chain transfer also increases toxicological risk in humans (Rainbow, 1985; Mason. 1991). As a result of adsorption and accumulation, the concentration of metals in bottom sediments is expected to be higher than in the water body and this sometimes can cause secondary pollution problems; therefore, bottom sediments are repository of heavy metals. Metals in natural waters can exist in truly dissolved colloidal and suspended forms. The proportion of these forms varies with metals and for different water bodies. Consequently, the toxicity and sedimentation potential of metals change depending on their forms (Bestemyanor and Krotov, 1985). Non–essential metals often exert their action through their chemical similarity to essential elements for Cd, with Cu and Zn (George, 1982). However, the effects of toxicity are usually additive or synergistic (Depledge, 1987).

Warri Refinery and Petrochemicals Company Limited generate effluents and discharge it into River Ijana. Therefore, it is important to monitor pollution limits of heavy metals in the aquatic ecosystem carefully, so that approximate measures of the potential hazards can be attained. These measures should give an estimation of the type of effects that could be expected after exposure to heavy metals.

Thus, the objective of this research is to have a comprehensive study analysis of the physico-chemical parameters of the water as well as the concentration, chemical forms and distribution of heavy metals in the bottom sediment of River Ijana.

2. STUDY AREA

River Ijana is located within longitude 5.540E and 5.70W and latitude 5.310N and 5.60S as shown in the Figure 1. It stretches from low population density of Ubeji and Ughuotor that generate rural/urban waste that are discharged into the river untreated. It meanders through its course and empties into the Tobi creek. The activities along the river course include auto-mechanic workshops, petroleum refinery and services, bathing, fishing, and swimming.

The river is unidirectional in the upper reach and tidal in the lower reach. Its upstream reach is fresh water with dense forest vegetation. The downstream reach is however brackish and consist of mangrove. The area experiences tropical humidity of the semi-hot equatorial type with a mean annual rainfall of about 3000mm (Alakprodia, 2001). The wet season period stretches from April to October each year. With occasional precipitation in the dry season month of November – March.

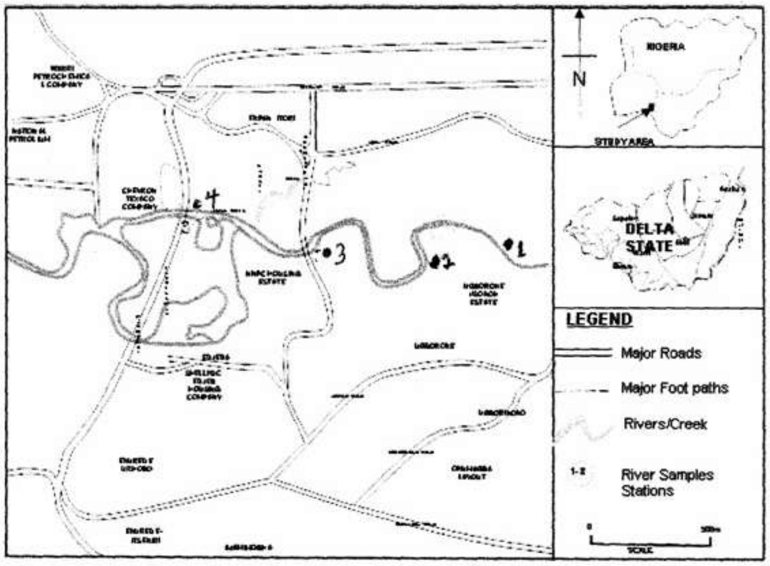

Figure 1. The Map of Warri Showing the Study Area

3. EXPERIMENTAL

Four sampling points were identified and they were established to cover possible impacted areas zone 1; about 100 metres upstream along the river course from the point of discharge of Warri refinery effluents. Zone 2: This is the point of unimpacted area along the river course.

Zone 3: This is the point of discharge of Warri refinery effluent and zone 4 about 100 metres downstream of the Ijana river from the point of discharge of Warri refinery effluent.

Sample collection and analysis: This composite water sampling method was used in collection of sample in each sampling point. A 2-litre plastic polyethylene container thoroughly cleaned was used. The sediment samples were obtained by using grab sampler (Auckman grab). Each grab content was immediately emptied into the polythene bag and stirred in an ice-chilled 50ml capacity cooler and taken to the laboratory for analysis. Air dried sample were finally homogenized by grinding using agate mortar (Adekota et al, 2003).

The analysis of physic-chemical parameters were based on the principles and procedures outlined in standard methods for the examination of heavy metals in water and sediments (APHA, 1995) while the speciation analysis was done following the procedure of Tessier's, 1995. The concentrations of heavy metals in the samples were analysed using Pye-unicam atomic absorption spectrophotometer.

4. RESULTS AND DISCUSSION

Table1 : Physico-chemical properties of surface water of Ijana River

Parameter	Zone I	Zone 2	Zone 3	Zone 4
	WS1	WS2	WS3	WS4
pH	6.68	6.74	6.70	6.69
TDS (mg/l)	70.6	71.66	6.43	58.19
TSS (mg/l)	32.00	39.00	43.00	50.00
Salinity(mg/l)	16.66	16.66	16.66	15.00
DO (mg/l)	4.73	6.56	4.57	4.83
BOD (mg/l)	9.54	8.24	8.29	8.99
COD (mg/l)	7.82	6.64	7.52	6.86
Bicarbonate (mg/l)	34.16	31.72	39.04	31.72
Sulphate (mg/l)	10.91	13.99	9.07	8.46
PO_4 – P (mg/l)	0.14	0.16	0.16	0.19
N (mg/l)	0.46	0.62	0.38	0.48
Cd (mg/l)	0.021	0.011	0.038	0.037
Pb (mg/l)	0.038	0.031	0.044	0.046
Cr (mg/l)	0.002	0.001	0.009	0.179
Zn (mg/l)	0.108	0.002	0.004	0.009

The measured physico – chemical characteristics of the surface water samples of Ijana River are presented in table 1. The DO values ranged from 4.57 to 6.56 mg/l in the different sampling points which compares favourably with the values of 6.2 mg/l obtained for Owena River. The values of DO were higher in zone 2, the unimpacted area than the other values as a result of dilution.

The low values of DO in the effluent zone can be accounted for by the fact that oxygen is being utilized for plant growth and other photosynthetic activity. By chlorophyll carrying organisms in the water.

The COD of the river ranged from 6.64 to 7.82 mg/l. The highest COD content was recorded upstream from the point of discharge of effluent carrying oxygen demanding substances into the rivers.

The nitrate levels obtained for the rivers were relatively low when compared with the levels reported for some Nigerian rivers. The phosphate levels ranged from 0.14 to 0.19 mg/l. The highest values were obtained in the river downstream from the point of discharge of Warri refinery effluent. The high values obtained here is attributed to the fact that laundry operations are often carried out here and so another major source of phosphate might be from detergents and soaps, in which polyphosphates can stimulate the growth of aquatic plants, which can impair the quality of water. It could also be due to run-offs containing nutrients from the adjoining farms since the rivers flow through predominantly agricultural areas.

The sulphate levels was between 8.46 and 13.99 mg/l. These levels are high when compared to other rivers. This is likely to be due to increased use of the river for laundry purposes with detergents.

The pH varied from slightly acidic to almost neutral. The concentration levels of the metals measured are also presented in table I. The values of the trace metals from the surface water were found to be lower than the maximum allowable levels in marine waters set by the World Health Organisation (WHO). They were comparable to the values obtained by Okoye et al for Lagos Lagoon.

Table2 : Distribution Patterns of Heavy Metals in Zone I

Form	**Zone I**			
	Pb	**Cu**	**Cd**	**Cr**
Water Soluble	2.81	0.80	2.75	3.07
Exchangeable	10.73	3.60	2.40	15.63
Carbonate	6.40	5.64	4.53	11.67
Fe–Mn Oxide Reducible	4.43	4.38	1.90	23.08
Organic	3.75	0.12	1.34	11.51
Residual	12.80	3.37	0.42	7.52
Total fraction	40.92	17.91	13.34	72.48
Potentially available	28.10	14.54	12.92	64.92
Total metal (acid digestion)	42.55	18.37	12.99	70.24

The distribution and the chemical species of the heavy metal polluted in the bottom sediment of Ijana river is shown in table 2 and Figure 1. From the table, Cr has the highest concentration level, of the water soluble forms with 3.07µg/g, followed by Pb with 2.81µg/g, Cd with 2.75µg/g, and Cu with 0.80µg/g. The trend of the bio-available form was Cr > Pb > Cd > Cu. This could be as a result of considerable high solubility of Cr.

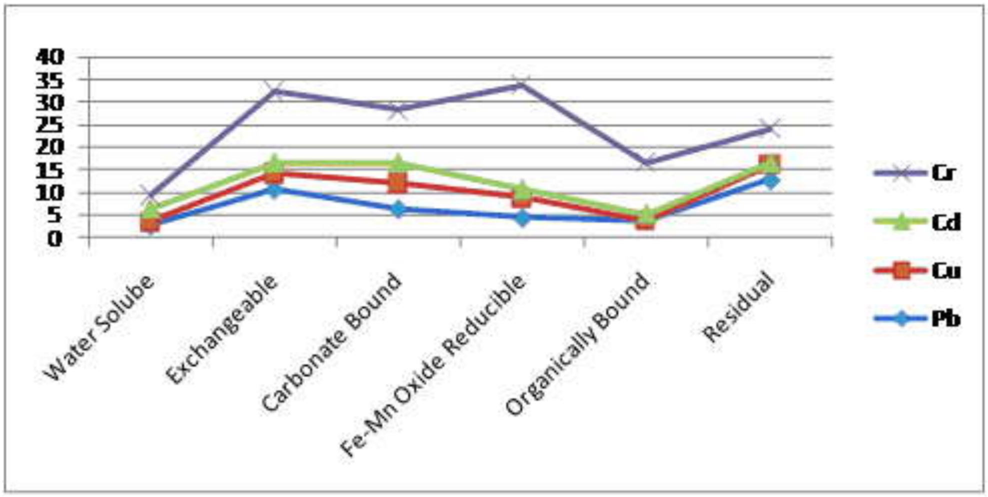

Figure 2 . Distribution Pattern for Zone 1

Table 3 : Distribution Patterns of Heavy Metals in Zone 2

Form	Zone 2			
	Pb	Cu	Cd	Cr
Water Soluble	4.83	0.24	0.291	2.87
Exchangeable	5.78	3.41	2.88	13.42
Carbonate	6.48	5.64	3.61	9.89
Fe–Mn Oxide Reducible	5.25	5.75	2.23	23.65
Organic	5.95	8.53	2.97	16.22
Residual	10.40	2.51	1.45	5.45
Total fraction	38.69	26.08	16.05	71.50
Potentially available	28.29	23.57	14.60	66.05
Total metal (acid digestion)	36.81	27.02	17.11	69.99

Table 3 presents the various forms of metals and their concentration levels in the unimpacted areas along the river course. The distribution pattern is Pb > Cd > Cr > cu while the potentially available forms follow the order Cr > Pb > Cu > Cd. The exchangaeable, reducible,and residual forms are depicted in Figure 2.

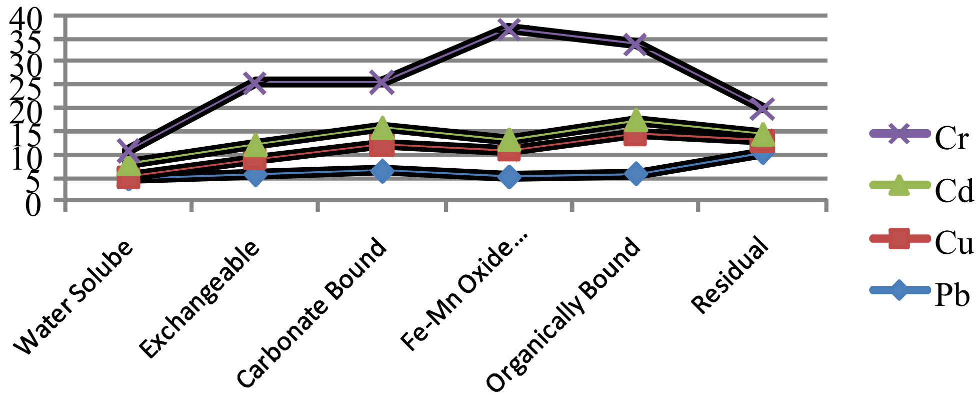

Figure 3 . Distribution Pattern for Zone 2

Table 4 : Distribution Patterns of Heavy Metals in Zone 3

Form	Zone 3			
	Pb	**Cu**	**Cd**	**Cr**
Water Soluble	4.43	0.31	2.85	5.94
Exchangeable	3.70	2.15	3.09	15.35
Carbonate	8.25	8.41	3.54	11.33
Fe–Mn Oxide Reducible	7.75	6.81	2.46	11.47
Organic	6.28	3.75	3.59	16.22
Residual	12.23	1.61	2.29	5.29
Total fraction	42.64	23.04	17.82	65.60
Potentially available	30.41	21.43	15.53	60.31
Total metal (acid digestion)	40.28	24.88	18.07	63.10

In table 4, the water soluble and exchangeable fractions follow the order Cr > Pb > Cd > Cu while the organic and reducible fractions follow the order Cr > Pb > Cu > Cd.

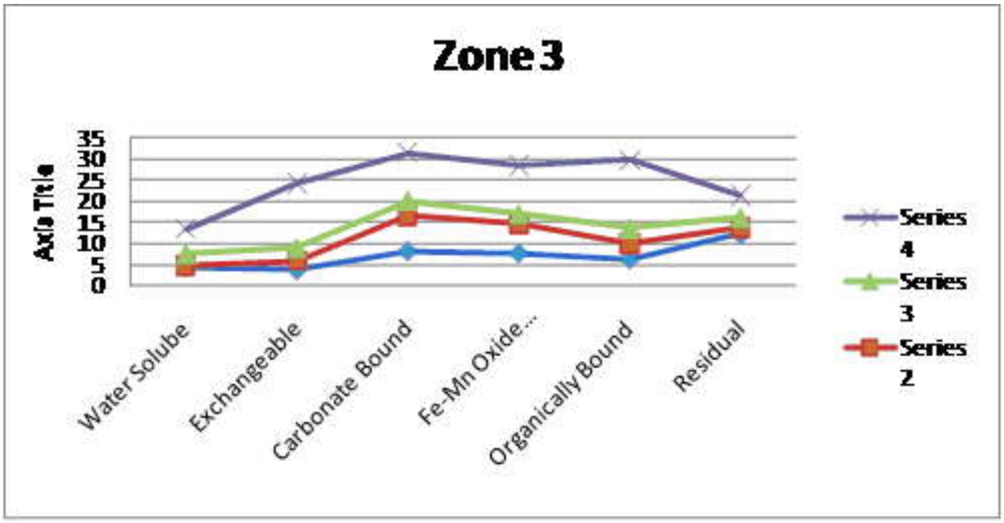

Figure 4 . Distribution Pattern for Zone 3

Table 5 : Distribution Patterns of Heavy Metals in Zone 4

Form	Zone 4			
	Pb	Cu	Cd	Cr
Water Soluble	2.25	0.35	3.19	5.12
Exchangeable	5.18	5.05	3.69	14.74
Carbonate	7.73	4.43	3.45	11.33
Fe–Mn Oxide Reducible	6.93	6.33	1.46	9.53
Organic	6.38	1.10	2.50	17.20
Residual	12.78	3.88	1.62	5.90
Total fraction	41.55	21.14	15.91	63.83
Potentially available	28.77	17.26	14.29	57.93
Total metal (acid digestion)	43.09	19.88	17.04	64.15

Table 5 presents the concentration pattern of the various phases and the distribution of the heavy metals in the phases are shown in the Figure 4 and Figure 5. Chromium tends to be more released in the sediments and is thus more available.

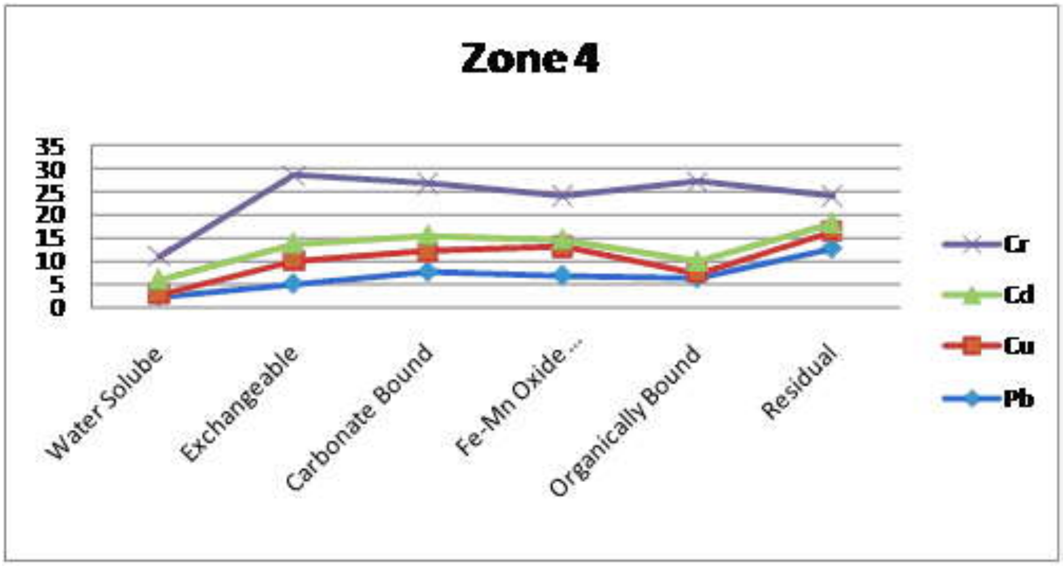

Figure 5. Distribution Pattern for Zone 4

Cd mean concentration level of 12.99mg/l at zone I could be attributed to rural and urban effluents along the river course. However, higher value zone 3 of 18.07 is a pointer to the fact that leachate from the refinery sludge lagoon containing Nickel-Cd batteries and Cd plate items along the jetty and the refinery effluent at zone 3 empties into the natural receptor. Cd presence in the study area was a result of industrial discharges, resulting from refinery operations, and household wastes; which support the earlier findings of DWAF (1996), Merian (1991).

In view of the fact that the major use of water in the study area is fishing and domestic, the concentration levels of Cd recorded exceeded that recommended by WHO, for aquatic ecosystem, it is therefore of great concern since Cd is extremely toxic and the consumption of water high in Cd could cause adverse health effects to end users. Since Cd has been found to be toxic to fish and other aquatic organisms, which conforms to similar reports of DWAF (1998). The high concentration of Cr and Cu in the study area could be attributed to the dumping of wood treated with chemicals made from salts of Arsenic, Chromium, and Copper in mixed soluble formulae (as Copper- chrome arsenate preservatives) being used to prevent fungi and pest attack which provide a potential source of chemical spills and drainage from the treated wood within and around the river course, which support the earlier findings of Ndiokwere, (2004).

Similarly, effluent from photographic colour laboratory around the study area could also be a source of Cr in the river as reported by Brades et al (2004).

Lead and Cu high concentration within the study area is a pointer to the fact that naturally, Lead and Cu are distributed in surface water due to weathering of minerals and atmospheric deposition (Merian, 1991; Robinson, 1996). Also, lead and Cu presence at high concentration in the study area could be related to industrial and other technical uses most of which are; electric storage batteries, petroleum refinery catalyst, chemical pigment and alloy production, leachate from refining sludge lagoon containing Nickel – Cd batteries and Nickel plate items, emissions from burning of fossil fuels and gasoline which contain high levels of tetraethyl lead (TEL) which support the earlier findings of Horsfall, (2001) and Stoeppler, (1991). Cu levels in the study area could be attributed to the high concentration of Cd and Iron in that Zn occurs in nature with other metals of which iron and Cd are the most common which supports the work of Dallas and Day, (1993).

From the distribution pattern of the individual parameters, the downstream point is more contaminated than the upstream point. This is a pointer to the fact that there is unregulated discharge of contaminated effluent into the natural receptor – River Ijana without prior treatment by industries and communities within the study area.

5. Conclusion

In the bottom deposit from River Ijana, the total concentration of metal determined was between 38.81µg/g for Pb, 18.37 – 27.02 for Cu, 12.99 – 18.07µg/g for Cd, and 63.10 – 70.24µg/g for Cu.

Taking into account the fact that an earlier investigation into the River Ijana did not show the presence of point sources of heavy metals contamination. Therefore, the results of the speciation analysis can be used as a reference for investigating heavy metal concentration and speciation of sediments of other water bodies. Moreover, they provide a reference for monitoring the anthropogenic effects in natural water bodies and for the assessment of the actual hazards coming from heavy metals penetrating the environment as a result of human activities. The study apart from augmenting the present knowledge of water pollution studies also embodies baseline information and trends on the distribution, chemical forms and bioavailability of selected heavy metals in the Ijana River surface water and bottom sediments. This river provides water for drinking, fishing and other purposes for communities living around it hence the need to monitor periodically these parameters because of the possibility of their accumulation especially the heavy metals.

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