

## Metal Pollution Indices of Surface Sediment and Water from the Upper Reaches of Sombriero River, Niger Delta, Nigeria

Ibigoni Clinton Howard<sup>1\*</sup> and Briggs Amonia Olulu<sup>2</sup>

<sup>1</sup>Department of Chemistry/Biochemistry Federal Polytechnic, Nekede, Owerri, Imo State, Nigeria

<sup>2</sup>Department of Chemistry, Rivers State University of Science and Technology Port Harcourt.

Rivers State Nigeria

\*E-mail: dromiete\_ib@yahoo.com

### Abstract

Metal pollution indices of the surface sediments and water of the upper reaches of Sombriero river was investigated using Absorption Spectrophotometry. The data obtained for the metals- Cd, Pb, V, Fe, Ni, Cu and Zn showed consistency in the metal pollution indices of the various stations of the study area. The stations with higher pollution indices were related to areas of intense activities. Several metal pair correlations were obtained in the surface sediments than in the surface water. Both media had Zn-Cd and Cu-Fe metal pair correlations. The pattern of the metals in the surface water at 95% significant level is Fe>Zn = Cu = Pb = N = Cd = V while that of the sediment is Fe>Zn = Cu = Ni = Pb = V = Cd. Each of the metals differed significantly between the media ( $P < 0.05$ ) sediment > water, indicating the former to be a better monitoring index of aquatic pollution by these metals. In comparison to other related work the degree of contamination of the upper reaches of the Sombriero River is low but a gradual enrichment of these pollutants could have a deleterious effect on the aquatic resources of the area and the consumers thereof.

**Key words:** Pollution indices, sediment, water, Sombriero river, Niger Delta

### Introduction

Heavy metals can be present in amounts several times higher than their natural background levels and pollute marine sediments and water in coastal regions near industries and urban areas (Andrade *et al.*, 2001; Masoud *et al.*, 2005). The aquatic ecosystem is frequently the ultimate recipient of heavy metal pollution from various sources-industrial wastewater, urban surface water runoff, accidental discharges into the aquatic environment through exploration and exploitation of natural resources, geological formation and weathering, agricultural practices etc (Biney

*et al.*, 1994; Masoud *et al.*, 2005; Gupta *et al.*, 2009). Heavy metal concentration in the water column can be relatively low in some cases, but the concentrations in the sediment may be elevated (Stanton *et al.*, 1983; Shukla and Sharma, 2009). Weis *et al.* (1992) have indicated that due to temporal and spatial variability in water column, it is always problematic to obtain representative samples to actually show the true concentration of contaminants in surface water. On the other hand sediments integrate contaminants over time and are in constant flux with the overlaying water

column, hence the analysis of heavy metals in sediments permits detection of contaminants that may be either absent or having low concentrations in the water column (Davies *et al.*, 1991; Shukla and Sharma, 2009).

Low level discharges of a contaminant may meet the water quality criteria, but long-term partitioning to the sediments could result in the accumulation of high loads of pollutants (Martine and Whitfield, 1983) thereby constituting environmental hazards to the urban and rural population that depend on these for various purposes. Once heavy metals are discharged into coastal waters, they rapidly become associated with particulates and are incorporated in the organic matter of the sediment which influence the adsorption of metallic elements (Jackson, 1998; Agirtas and Kilice, 1999; Goodwin *et al.*, 2003)

Aquatic microflora and microfauna, which constitute fish food, are capable of incorporating and accumulating heavy metals into their living cells from their environment. Consequently, small fish become enriched with the accumulated heavy metals. Predatory fish generally display higher levels of heavy metals than their prey and eventually man on consuming the predatory fish suffers from the results of an enrichment having taken place at each trophic level (Forstner and Wittman, 1983; Agah *et al.*, 2009).

River Sombrieo is one of the major rivers in the Niger delta that interconnects lots of communities and where major transportation, fishing, agricultural practices, exploration and exploitation of crude oil are being carried out. Besides, the economic life of the communities along the river depends mainly on the creeks and

mangrove mudflats of the river from where they fetch finfish, shellfish and wood.

### **Materials and methods**

Five sampling stations (SSA, SSB, SSC, SSD and SSE) hereafter referred to as A, B, C, D and E were chosen within the study area as indicated in figure 1. Sample station A lies within Longitude  $6^{\circ}45' 21.8''E$  and Latitude  $4^{\circ}45' 38.8''N$  which is the upper most part of Sombrieo River and towards the lower reaches of Orashi River. The major activity in this station is marine transport with outboard petrol engines and also the fermentation of cassava for the production of "fufu"-a familiar food in Southern Nigeria. Station B ( $6^{\circ}46' 21.1''E$  and  $4^{\circ}41' 32.7''N$ ) has a pipeline manifold that transports crude oil or condensate to Soku Gas Gathering Plant. This station receives the bulk of discharge of waste water runoff from domestic and municipal activities in the near by communities (Krakrama, Obonoma, Degema, Abonnema etc). Domestic and industrial wastes from Soku and the Gas Gathering Plant also release much waste to this station, in addition to the heavy marine transportation activities. Station C ( $6^{\circ}46' 51.5''E$  and  $4^{\circ}40' 29.6''N$ ) was at a fishing settlement, a fast growing settlement where several activities, such as crude oil, diesel and petrol bunkering take place. Station D ( $6^{\circ}48' 14.0''E$  and  $4^{\circ}38' 23.5''N$ ) was at the Idama oil Field, operated by one of the major oil companies in Nigeria. There is a flow station (wherein petroleum fluid is partially treated), wellheads and a manifold. There are dredge-spoils and waste pits with flare points, where hydrocarbons and associated emissions are discharged and waste fuels are burnt. Station E ( $6.49^{\circ} 10.0'E$  and  $4.38^{\circ}$



The  $K_d$  was transformed into natural logarithm form to ascertain the medium that concentrates the metal more.

$$K_d = \frac{[\text{Metal}]_{\text{sediment}}}{[\text{Metal}]_{\text{water}}}$$

### ***Correlation coefficient***

The correlation coefficients of the various metal pairs were calculated with the aid of Pearson product moment coefficient to show the association of the metal pairs in each medium.

### ***Coefficient determination***

The determination coefficient ( $r^2$ ) of each of the metal was carried out by regressing the values of one medium on the other to establish a functional relationship of how each of the metals will respond to a unit change in any of the medium.

### ***Statistical analysis***

All statistical analysis was carried out with the aid of Data Analysis Toolpak in Microsoft office Excell 2003<sup>®</sup> and SPSS. Differences in the levels of the metals within and between the media were separated by Duncan Multiple range test (DMRT) at 95% level of significance (Wahua, 1999).

### **Results**

The mean levels of the metals Cd, Pb, V, Fe, Ni, Cu and Zn in the surface sediments and water of the tidal flats of Sombriero river as presented in table 1 indicated Fe to be the highest in both media and Cd the least in the sediment, while V is the least in surface water. Each of the metal differed significantly between the media ( $P < 0.05$ ) sediment > water (Tab. 1). The pattern of the metals in the surface water at 95%

significant level is Fe > Zn = Cu = Pb = Ni = Cd = V while that of the sediment is Fe > Zn = Cu = Ni = Pb = V = Cd. Although there were no significant differences ( $P > 1$ ) of the metal pollution indices between the various stations the pattern of the metal levels in all the stations studied followed B > D > C > A > E for surface water (Fig. 2) and A > B > E > D > C for sediments (Fig. 3).

The regression analysis of the metals between both media showed some positive (Cd, V, Fe, Zn) and negative (Pb, Ni, Cu) linear relationships (Tab. 2). Zn had the strongest relationship between both media ( $r = 0.341$ ) and was closely followed by Pb ( $r = 0.335$ ) and Cd ( $r = 0.331$ ). The determination coefficient ( $r^2$ ) of the metals between the sediment and water indicated Zn (11.6%) and Cd (11.2%) to be more dependable to each of the medium than in the other metals. V had the highest log transformed partition coefficient and was followed by Fe while the least was Cd (Tab. 2). The Pearson product moment correlation coefficients of heavy metals in both media showed several metal pair correlations ( $P < 0.05$ ) (Tab. 3). Surface sediments had more correlations than the surface water. Both media have these metal Zn-Cd and Cu-Fe pair correlations.

### **Discussion**

Surface Sediment and water pollution is considered by many regulatory agencies to be one of the largest risks to the aquatic environment since many aquatic organisms spend the major portion of their lifecycle living on or in sediments. For the seven metals studied in the surface sediments and water (Cd, Pb, V, Fe, Ni, Cu and Zn), significant differences were not established among stations means. This may be due to the continuous dilution of the water body

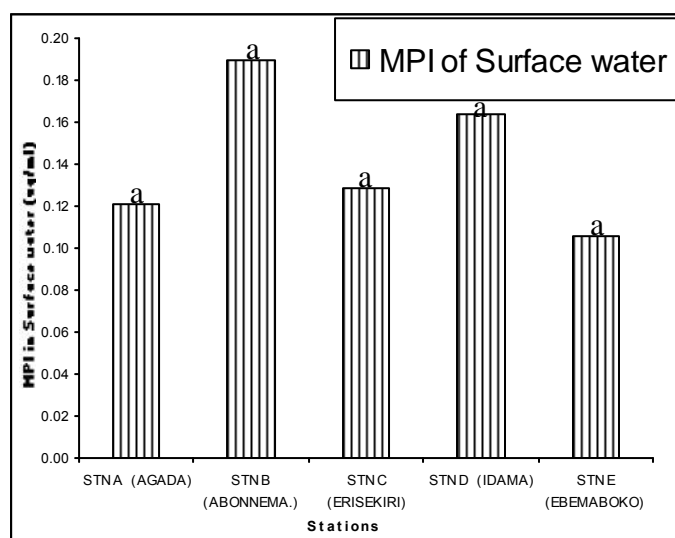
**Table 1.** Mean values of the metals form the various stations in the two media.

Media	Metals	Stations					Total Mean
		A	B	C	D	E	
Surface water (mg/l)	Cd	0.048 ± 0.011 <sup>a</sup>	0.061 ± 0.009 <sup>a</sup>	0.040 ± 0.008 <sup>a</sup>	0.040 ± 0.034 <sup>a</sup>	0.043 ± 0.013 <sup>a</sup>	0.043 ± 0.018 <sup>B,B*</sup>
	Pb	0.115 ± 0.056 <sup>a</sup>	0.242 ± 0.158 <sup>a</sup>	0.145 ± 0.113 <sup>a</sup>	0.221 ± 0.110 <sup>a</sup>	0.117 ± 0.114 <sup>a</sup>	0.168 ± 0.116 <sup>B,B*</sup>
	V	0.001 ± 0.001 <sup>b</sup>	0.004 ± 0.001 <sup>b</sup>	0.002 ± 0.001 <sup>b</sup>	0.004 ± 0.002 <sup>a</sup>	0.002 ± 0.000 <sup>ab</sup>	0.003 ± 0.001 <sup>B,B*</sup>
	Fe	1.778 ± 0.34 <sup>a</sup>	2.470 ± 1.12 <sup>a</sup>	2.067 ± 0.69 <sup>a</sup>	2.809 ± 0.81 <sup>a</sup>	1.601 ± 0.98 <sup>a</sup>	2.145 ± 0.867 <sup>A,B*</sup>
	Ni	0.115 ± 0.054 <sup>a</sup>	0.220 ± 0.142 <sup>a</sup>	0.168 ± 0.050	0.165 ± 0.094 <sup>a</sup>	0.094 ± 0.053 <sup>a</sup>	0.152 ± 0.089 <sup>B,B*</sup>
	Cu	0.377 ± 0.094 <sup>bc</sup>	0.591 ± 0.150 <sup>a</sup>	0.391 ± 0.075 <sup>ab</sup>	0.564 ± 0.082 <sup>ab</sup>	0.186 ± 0.193 <sup>c</sup>	0.422 ± 0.188 <sup>B,B*</sup>
	Zn	0.634 ± 0.218 <sup>a</sup>	0.535 ± 0.200 <sup>a</sup>	0.466 ± 0.165 <sup>a</sup>	0.373 ± 0.278 <sup>a</sup>	0.511 ± 0.183 <sup>a</sup>	0.504 ± 0.208 <sup>B,B*</sup>
Sediments (µg/g dry wt)	Cd	4.01 ± 2.75 <sup>a</sup>	3.50 ± 1.59 <sup>a</sup>	2.30 ± 2.45 <sup>a</sup>	3.17 ± 2.31 <sup>a</sup>	2.11 ± 1.75 <sup>a</sup>	3.018 ± 2.098 <sup>B,A*</sup>
	Pb	48.32 ± 28.64 <sup>a</sup>	31.81 ± 7.47 <sup>a</sup>	32.83 ± 26.23 <sup>a</sup>	18.73 ± 11.70 <sup>a</sup>	33.45 ± 14.39 <sup>a</sup>	33.453 ± 14.39 <sup>B,A*</sup>
	V	10.54 ± 3.82 <sup>b</sup>	11.79 ± 6.39 <sup>b</sup>	13.84 ± 11.39 <sup>ab</sup>	27.41 ± 14.20 <sup>a</sup>	16.14 ± 6.10 <sup>ab</sup>	16.141 ± 6.10 <sup>B,A*</sup>
	Fe	6914.0 ± 1071.2 <sup>a</sup>	6954.5 ± 1537.9 <sup>a</sup>	7543.0 ± 2138.7 <sup>a</sup>	7524.3 ± 1182.5 <sup>a</sup>	8495.3 ± 1877.2 <sup>a</sup>	8495.2 ± 1877 <sup>A,A*</sup>
	Ni	61.66 ± 40.06 <sup>a</sup>	69.45 ± 41.41 <sup>a</sup>	35.27 ± 37.58 <sup>a</sup>	41.18 ± 27.54 <sup>a</sup>	35.53 ± 32.09 <sup>a</sup>	48.617 ± 35.24 <sup>B,A*</sup>
	Cu	72.04 ± 45.39 <sup>a</sup>	77.60 ± 47.53 <sup>a</sup>	52.09 ± 49.35 <sup>a</sup>	46.13 ± 27.44 <sup>a</sup>	67.36 ± 33.52 <sup>a</sup>	63.042 ± 38.91 <sup>B,A*</sup>
	Zn	93.21 ± 52.92 <sup>a</sup>	97.67 ± 55.55 <sup>a</sup>	61.71 ± 47.10 <sup>a</sup>	66.57 ± 43.01 <sup>a</sup>	77.83 ± 25.11 <sup>a</sup>	79.398 ± 43.39 <sup>B,A*</sup>

-Within row (for each medium and metal), mean ± std with different superscript (lower case letters) are significantly different at P<0.05. (n= 20)

-Within column (Total mean metals within a medium), mean ± std with different superscript (upper case letters) are significantly different at P<0.05.(n =20)

-Within column (Total mean metals between media), mean ± std with different superscript (upper case letters\*) are significantly different at P<0.05.(n =20)



**Figure 2.** Surface water Metal pollution index (MPI) for each sampling station.

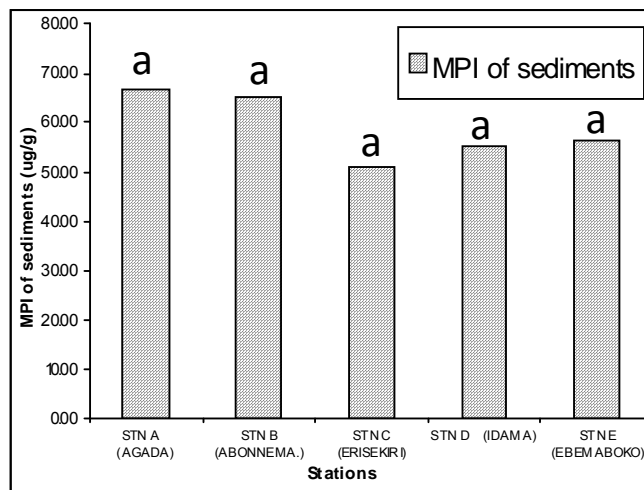


Figure 3. Sediment Metal pollution index (MPI) for each sampling station.

Table 2. Various relationships of the metals in the media.

Metals	Relationship [Sediment (y) and surface water (x)]	Determination coefficient (r <sup>2</sup> )	Correlation coefficient (r)	Partition coefficient (kd)	LogKd
Cd	Y = 3.904x + 2.8373	0.11%	0.331	65.067	1.813
Pb	Y = -57.345x + 42.664	11.22%	0.335	196.69	2.294
V	Y = 218.856x + 15.409	0.10%	0.032	6495.7	3.813
Fe	Y = 126.64x + 7214.6	0.50%	0.071	3490.3	3.543
Ni	Y = -19.054x + 51.52	0.23%	0.048	319.14	2.504
Cu	Y = -26.966x + 74.41	1.70%	0.130	149.53	2.175
Zn	Y = 71.056x + 43.602	11.60%	0.341	157.61	2.196

Table 3. Pearson product moment correlation coefficients between metal levels in the media

Metal pairs	Sediments	Surface water
Cd-Pb	0.602**	-
Fe-Cd	-0.485*	-
Ni-Cd	0.702**	-
Cu-Cd	0.515*	-
Zn-Cd	0.568**	0.601**
Ni-Pb	0.478*	-
Cu-V	-0.450*	-
Zn-V	-0.448*	-
Ni-Fe	-0.572**	-

Cu-Fe	-0.550*	0.540*
Zn-Fe	-0.498*	-
Cu-Ni	0.847**	-
Zn-Ni	0.873**	-
Zn-Cu	0.921**	-
Fe-Pb	-	0.582**
Cu-V	-	0.583**

\*\* Correlation is significant at the 0.01 level (n = 20) and  $r_{18} = 0.561$

\* Correlation is significant at the 0.05 level (n = 20) and  $r_{18} = 0.444$

from the lower and upper reaches of the river, similarity in physical conditions of the sediments, particle composition and organic matter of the sediments between the stations. The MPI of the surface water in stations B (Abonnema) and D (Idama flow station) was higher than that of the other stations while that of the sediments, stations A (Agada) and B (Abonnema) are higher than the other stations, although these difference were not significant. The high MPI in these stations could be due to domestic surface water runoff, Inland surface water runoff, waste water discharges, etc. Station A (Agada) has been noted earlier to be the receiving end of the Orashi River which houses a lot of crude oil industrial activities and the washings thereof empties into this station. The domestic runoff discharges and other farming activities from the adjoining lands also add to the sediment pollutant load of the station.

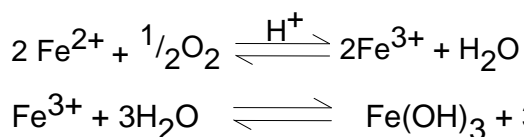
Cd levels obtained in this study in both media are higher than that reported by Masoud *et al.* (2005) in Lake Edku, Egypt, but similar to that reported by Okafor and Opuene (2007) from Taylor creek in the Niger Delta. Although Cd presented a low level in this study (when compared to similar studies in the region), it is very toxic to both aquatic and terrestrial organisms even at low concentrations. This is because dissolved Cd has acute LC<sub>50</sub> values as low

as 3.5mg/l in planktonic organisms. In addition, Cd is a sulphur seeking metal that tends to precipitate in anoxic sediments. Experiments carried out at concentrations lower than the values found in this study also show that Cd can be assimilated from anoxic sediments with high organic matter content, which generates the potential for bioaccumulation through dietary uptake.

The levels of Pb in the sediments were low when compared with Pb levels in the sediments of Taylor creek (Okafor and Opuene, 2007) and Antarctic sediments, but are higher than the sediments of Mombassa River, Kenya and Lake Edku, Egypt (Masoud *et al.*, 2005). The present result indicates that the maximum values are recorded at stations B and D, while the minimum was recorded at station A for surface water. Station A has the maximum value and station D the minimum for the sediments. The datum is of typical anthropogenic and urban activities (Maiti, 2003), and accumulation in plants and phytoplankton. Whether the levels found are a threat is dependent on a number of factors. For example, certain water chemistry parameters of the aquatic system, such as pH and oxygen levels, would control the rate of adsorption and desorption of Pb to and from the sediments. Lead in sediments is chemically precipitated from the surface water solution, and the remainder has been

transported in detrital particles. However, lead occurring in sediments has two distinct mineral associations, one with the clay minerals and the other with authigenic minerals and/or biogenous debris. When released into the environment lead has a long residence time compared with most other pollutants. It has low solubility and does not experience microbial degradation. For these two reasons, Pb has the potential to remain accessible within the sediments and consequently, aquatic food chains far into the future (Davies *et al.*, 1991).

Levels of Fe of the lower reaches of Sombriero river surface sediments and water exceeded those for the Taylor creek in the Niger Delta (Okafor and Opuene, 2007), Antarctic aquatic ecosystem (Andrade *et al.*, 2001) and Lake Edku, Egypt (Masoud *et al.*, 2005). This high levels of Fe especially in the sediments of this study could be due to high level of dissolved oxygen and pH that leads to precipitation of Fe(OH)<sub>3</sub>. High concentration of oxygen leads to iron oxidation and subsequent hydrolysis to form insoluble Fe(OH)<sub>3</sub> according to the following reactions: (Masoud *et al.*, 2005)



Apart from this the removal of iron and other trace elements from water systems by planktonic organisms may also take place through: 1) assimilation by organisms and subsequent transport as fecal material, and 2) body adsorption (Brewer, 1975).

For Zn metal, the highest levels were found at stations A and B, thus relating the likely source of this pollutant to surface water runoffs, waste water and domestic

discharges. Zn correlated with Cd in both surface water and the sediments indicating that both metals could be from the same sources and their partitioning between the two media could also be of the same mechanism. It is also noteworthy that Zn is an essential trace element for both flora and fauna and exposure to either deficient or high levels can have deleterious effects on an organism's health. It exists in sea water in submicromolar concentrations (Vasanti and Pillai, 1975). It has been reported that organic complexation controls the concentration of dissolved zinc in aquatic environment (Van Den Berg *et al.*, 1987). Zinc is essential for growth of marine organisms and its concentration affected by plankton communities (Masoud *et al.*, 2005). The kinetics of removal of Zinc in aquatic systems is strongly affected by the rates of biological processes. It is also a common pollutant found in several industrial effluents such as those produced by textile, basic chemicals, electroplating, motor and other industries. The level of Zn recorded in this study were higher than that reported in similar study in both surface water and sediment (Howard *et al.*, 2006, but lower than that of the Antarctic aquatic ecosystem (Andrade *et al.*, 2001) and the Taylor Creek (Okafor and Opuene, 2007).

The levels of Ni also showed a consistent distribution in the study area. The natural sources of this element are ferromanganese minerals and ferrous sulfides. Nickel may be present in some ground waters as a consequence of dissolution from nickel ore-bearing rocks. Nickel is used principally in its metallic form combined with other metals and nonmetals as alloys. This is corroborated by the significant correlation of Ni with Fe, and other metals such as Cu, Cd and Zn.



Average Ni concentrations are 94mg/g in igneous rocks and between 2.6 and 29 for different types of sedimentary rocks. The levels of Ni obtained were higher than the reported values for sediments in the Taylor creek (Okafor and Opuene, 2007) and Lake Edku, Egypt (Masoud *et al.*, 2005) but lower than those of the Marina area of Great Athens.

The level of Cu recorded in this study were higher than that reported in a similar study in both media ; they are however lower than that reported by Aboud *et al.* (2009) in the sediments of Bangalore Urban lakes and Lake Edku, Egypt (Masoud *et al.*, 2005). Cu correlated positively with Fe in both media signifying that the input sources into the river system might be the same and also both metals gets partitioned between both media the same way. Copper precipitation is influenced by biological and geological processes (Hasle and Abdullah, 1981). The data could be speculated that the source of the dissolved copper in water may be outlined to remobilization from sediments. However such approach could be subjected to further steps, mainly of adsorption and coprecipitation phenomenon of dissolved species on to suspended matter (Masoud *et al.*, 2005).

Vanadium levels in the sediments of the study area are lower than that reported by (EL-Moselhy, 2006) in the Marine coastal area of Egyptian seas, Mediterranean Sea and also below the range of typical background values (20 - 150 µg/g) that was recorded by Moore (1991). Vanadium levels in the surface waters of the study area are comparable to that obtained from Sea water and the Baltic sea (Soremark, 1967). Vanadium is a ubiquitous element in the earth's crust, and exist in divers' forms but the pentavalent form is the

most soluble, and is the primary agent of transport in surface water (Moore, 1991). Breslin and Duedall (1988) and FAO (1992) have stated earlier that the main source of vanadium is the petroleum activities and fuel burn. This is corroborated by the fact that Station D which is the Idama flow station had the highest V value of this study. Other significant sources include the dumping of sewage sludge, discharge of domestic wastewater and the industrial effluents specially fertilizers containing materials with high vanadium content. Vanadium is also solublized from stabilized oil ash waste in seawater (Breslin and Duedall, 1988).

### Conclusion

The data obtained in this study has showed consistency in the metal pollution indices of the various stations of the study area. This may be due to the continuous dilution of the water body from the lower and upper reaches of the river, similarity of the physical conditions of the sediments, particle composition and organic matter of the sediments may have also played major role. The stations with higher pollution indices are related to areas of intense activities such as the Idama flow station and Abonnema for the surface water and Agada and Abonnema for the sediments. Several metal pair correlations were obtained in the surface sediments than in the surface water. Both media had Zn-Cd and Cu-Fe metal pair correlations. The pattern of the metals in the surface water at 95% significant level is Fe>Zn=Cu=Pb=N=Cd=V while that of the sediment is Fe>Zn=Cu=Ni=Pb=V=Cd. This study revealed that the sediment from the upper reaches of Sombriero river contained very high significant amounts of heavy metals when compared with their

concentration in water. In comparison to other related work the degree of contamination of the upper reaches of the Sombriero River is low but a gradual enrichment of these pollutants could have a deleterious effect on the aquatic resources of the area and the consumers thereof.

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