

LEVELS OF TRACE METALS IN SEDIMENTS FROM QUA IBOE RIVER AND ITS TRIBUTARY

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ABSTRACT

The levels of five trace metals (Pb, Sb, Cd, Co and Cu) in the sediments collected from Qua Iboe River and those of one of its tributaries which received a battery effluent were determined using atomic absorption spectrophotometer. Levels of all the metals downstream of both Qua Iboe River (QIR¹) and its tributary (ATS¹) were higher than those upstream (QIR² and ATS²) except Cd which showed an almost constant concentration in all the sites (0.44 - 0.49 $\mu\text{g g}^{-2}$). The degrees of accumulation of these metals in the main Qua Iboe River and its tributary were computed.

INTRODUCTION

As many different types of industries are being established in Nigeria, there is a growing concern over the possible ecological disturbances the wastes from these industries are likely to create. Since majority of these industries are located near natural water bodies, their wastes containing metals and non metals are often directly or indirectly discharged into them. The introduction of metals into the environment by anthropogenic activities is well documented (1 and 2). The fate of trace metals such as Pb, Sb, Cd, Co and Cu in the aquatic environment is of great concern owing to their impact on the entire ecosystem. This is particularly true of slow-running streams which receive non-point municipal and industrial discharges from cities and towns.

Usually, the metals in aquatic environment can be accommodated in three basic reservoirs: water, sediment and biota (3). The biota reservoir is particularly important as organisms adversely affected by water pollution in turn adversely affect their consumers. Accordingly since the biota reservoir is small compared to the water which in turn is smaller than the sediment reservoir, it follows that most of the metals in a stream or river at any point in time reside in the sediment. Stream and river sediments act as sinks or traps for metals carried into them by feeder tributaries (4). Meyerson et al (3) however regard sediments not merely as sinks but reservoirs which may either concentrate metals from the water or release metals to the water. Thus, stream and river sediments appear to serve as the storage reservoirs and primary sources of metal biocentration. Stream sediments adjacent to a sanitary landfill contain high levels of Ag, Zn, Cu and Pb metals compared with samples not affected by the landfill (5). Whitton and Harding (6) also revealed the enrichment of sediments with Zn and Pb as a result of urban and industrial pollution in Southern Lake Michigan. In the Pb - Zn belt of Benue Trough in Nigeria, Olade et al (7) recorded levels of Pb up to 10^{-9} ppm while Voogt et al (8) discovered that the sediment in Jintsu river in Japan near a Zinc mine contained up to 400mg Cd/litre whereas the river water contained only 9 µg/litre.

Apart from health hazards and sanitary nuisance, water pollution could lead to severe economic and social consequences. For instance, there have been general discontentment and occasional clashes between some oil companies and citizens of Iko and Uquo Ibene in Akwa Ibom State of Nigeria over the pollution of their fishing settlements and creeks.

Qua Iboe River is one of the most important waterways in the south eastern part of Nigeria. It traverses many Local Government Areas in Abia and Akwa Ibom States before emptying into the Atlantic Ocean via Bight of Bonny. It therefore means that Qua Iboe River and its tributaries are the major sources of water for the inhabitants of the Local Government Areas through which they

traverse. The dumping of industrial wastes into this river or any of its tributaries could be dangerous not only to the immediate neighbours of the affected waterways but also to inhabitants downstream since most of the pollutions are bound to flow downwards.

MATERIALS AND METHOD

Portions of the sediments were superficially collected by hand (9). These were made into composite samples at each site and the wet samples put into metal-free brown calico bags, labelled and taken to the laboratory for further treatment and analysis.

Sampling was carried out upstream (QIR²) and downstream (QIR¹) in Qua Iboe River. In Atan stream (a tributary of Qua Iboe River) which received the battery effluent, sampling was carried out at three sites: upstream (ATS²), downstream (ATS¹) and before effluent discharge point (BPD). (ATS²) served as the baseline site, being the headwater of Atan stream (Fig. 1). Sampling was carried out monthly for ten months covering dry and wet seasons.

Sample Treatment and Analysis

The samples were air-dried and later oven-dried at a temperature of 105°C for 6 hours to eliminate undesirable materials. The dried samples were disaggregated and homogenised using mortar and pestle before sieving through a 2mm screen. The homogenised samples were then subsectioned for metal analysis (10).

Each sample (1.0g) was digested twice under reflux with 2.0cm³ of analar grade nitric acid (HNO₃) and 4.0cm³ of hydrogen peroxide (H₂O₂). After the second digestion, the solution was left to evaporate to dryness using a hot sand bath. The sample was later dissolved in 1:1 HCl (2.0cm³) and diluted to 100cm³ with ultrapure water before analysing for the metals via a flame Atomic Absorption Spectrophotometer.

The concentrations of these metals obtained in μgg^{-1} on a dry weight basis were multiplied by the dilution factors. Procedural blanks were also prepared and analysed for the same metals. The detection limits in parts per million (ppm) for the metals using the instrument were Pb (0.01), Sb (0.035), Cd (0.001), Cu (0.004) and Co (0.005). Recoveries carried out on the test metals were above 98%, confirming the reliability of the method used.

RESULTS AND DISCUSSION

The seasonal concentrations of the metals Pb, Cu, Co, Cd and Sb and their coefficients of variation are given (Table 1, Figs. 2 and 3). The last two metals exhibited very low concentrations in the sediments when compared to Cu and Co which were high. Lead exhibited the highest concentration in the sediments during both dry and wet seasons with correspondingly high coefficients of variation (Table 1, Fig. 3). Cadmium levels at the five sites varied slightly during both seasons as shown by the coefficients of variation for dry season (3.91%) and wet season (5.16%).

However, although antimony levels were low, variations between sites were high, being 61.62% and 73.81% respectively for dry and wet seasons, although relatively lower than those for cobalt (109.25% and 107.91%) respectively (Table 1). Apart from Cd with the highest mean concentration of $0.48 \mu\text{gg}^{-1}$ occurring at three sites (ATS², ATS¹ and QIR¹), the other four metals had their highest mean levels at ATS¹ site (Table II).

The metal levels in the sediments between site pairs have been compared using student's t-test (Table III). Mean concentrations of Co was not significantly different between ATS² and BPD. However, mean concentrations of Pb, Sb, and Cd were significantly higher at ATS² site than BPD site (Table III). Cadmium was the only metal in which its sediment levels at ATS² site were not significantly different from those at ATS¹ site. For the other metals ATS¹ levels were the only metals without significant differences between their ATS² mean levels and those at QIR¹ site.

Only the mean concentrations of lead and copper were higher at BPD site than at ATS² site. The degrees of accumulation of these metals in the sediment samples over the baseline values indicated that all metals were highly accumulated at ATS¹ sediments (Table II). Expectedly all other metals except Cu were less accumulated in BPD sediments. Similarly the levels of these metals except Cu were higher in QIR¹ and in QIR² sites (Table II).

The concentrations of metals at one point in water could influence their concentrations at other points and their corresponding sediments. The concentration of Pb, in a discharged battery effluent influenced the concentration of this metal in the receiving water which in turn could have influenced the level of the metal in the corresponding sediment (II). Since fishes derive most of their food from sediments, this metal could easily be taken up by them which on consumption by man could be lethal. This is likely to apply to other metals also present in the discharged effluent.

The results of analysis of stream and the river sediments from five sites during dry and wet seasons show that the mean levels of Pb were 40.37 $\mu\text{g g}^{-1}$ in ATS²; 60.14 $\mu\text{g g}^{-1}$ in BPD; 740.80 $\mu\text{g g}^{-1}$ in ATS¹; 400.15 $\mu\text{g g}^{-1}$ in QIR¹ and 178.55 $\mu\text{g g}^{-1}$ in QIR² giving a trend of ATS¹ > QIR¹ > QIR² > BPD > ATS² (Table II, Fig. 1). Pb levels in the sediments in all the other sites were higher than the levels of Pb in ATS² samples ($P < 0.001$ in case) (Table III). The levels of Pb in aquatic lives including fishes are likely to be affected by the levels in these sediments. The lead level in QIR¹ must have been influenced to some extent by the levels in QIR² and ATS¹ sites. The metal levels varied more during the wet season than dry season (Table 1). The very high level of Pb in ATS¹ sediment compared to the level in BPD sample must have been due to contribution of Pb to this site by discharged effluent. The level must have been higher in ATS¹ than QIR¹ owing to the slow movement of the stream water and the possible high absorption ability of the metals by these sediments. The high Pb levels in ATS¹, QIR¹, QIR² and BPD sediments suggest possible contamination of these sediments by lead metal.

The mean seasonal concentrations of Sb in the sediments from the five sites were ATS² (0.91 $\mu\text{g g}^{-1}$), BPD (0.31 $\mu\text{g g}^{-1}$), ATS¹ (1.40 $\mu\text{g g}^{-1}$), QIR¹ (0.54 $\mu\text{g g}^{-1}$) and QIR² (0.38 $\mu\text{g g}^{-1}$). The trend was therefore ATS¹ > ATS² > QIR¹ > QIR² > BPD (Table II, Fig. 1). The concentration of antimony was higher in ATS¹ sediments than in ATS² sediments but surprisingly the concentration in ATS² sediments was higher than in QIR¹. The former must have been due to the contribution of Sb to the ATS¹ sediment by the battery effluent in addition to contribution by runoff, and whereas ATS² sediments were influenced by town runoff, QIR¹ sediments were not. This explains why Sb level in ATS² sediment was higher than in QIR¹ sediment. The mean seasonal concentrations of Cd in the sediments at ATS², ATS¹ sites were all the same (0.48 $\mu\text{g g}^{-1}$), while the levels in QIR² and BPD sediments were respectively 0.45 $\mu\text{g g}^{-1}$ and 0.44 $\mu\text{g g}^{-1}$ (Table II). These gave the trend ATS² = ATS¹ = QIR¹ > QIR² > BPD. The level of Cd in ATS² sediment was significantly greater than in BPD sediment. This may mean that ATS² site received more Cd-laden wastes from the town and the government reserved areas (GRA) through which the stream traverses. Voogt et al (8) had established that any polluted sediment should have much Cd deposit on it. The presence of cadmium is still risky to life since fishes are particularly very sensitive to cadmium and often retain about 1% of ingested cadmium which could be taken up by man, the consumer (12).

The seasonal levels of cobalt in the sediments from the five sites were ATS² (6.10 $\mu\text{g g}^{-1}$), BPD (6.00 $\mu\text{g g}^{-1}$), ATS¹ (64.00 $\mu\text{g g}^{-1}$), QIR¹ (40.00 $\mu\text{g g}^{-1}$) and QIR² (6.14 $\mu\text{g g}^{-1}$) (Table 1). These gave the trend ATS¹ > QIR¹ > QIR² > ATS² > BPD. The source of the high level of Cd in QIR¹ may have been natural or anthropogenic or a combination of both. The high level in ATS¹ suggests a contribution of cobalt by the factory effluent to the sediment. Cobalt could be easily introduced anthropogenically into an environment through its application in agriculture as microfertilizer. Runoff from the town could also introduce cobalt into the stream and this could be taken up by the sediments.

The seasonal levels of Cu in the river and stream sediments from the five sites were ATS² (15.00 $\mu\text{g g}^{-1}$), BPD (17.97 $\mu\text{g g}^{-1}$), ATS¹ (25.00 $\mu\text{g g}^{-1}$), QIR¹ (14.55 $\mu\text{g g}^{-1}$) and QIR² (17.23 $\mu\text{g g}^{-1}$) (Table 1). These gave the trend ATS¹ > BPD > QIR² > ATS² > QIR¹ (Fig. 3). The degrees of variation in copper levels in the sediments from the five sites during dry and wet seasons were almost the same, being 23.34% and 23.55% respectively. This may have been from Cu present in paint pigments employed in decorating buildings and machines in the factory in addition to natural occurrence.

Generally the presence of these metals especially their salts in the environment is risky since these salts are poisonous (13). When discharged into water, the metals can enter the food chain, become bioaccumulated in fish and later biotransferred to man, the ultimate consumer of fish. By being differentially accumulated in the sediments particularly in ATS¹, QIR¹ and QIR² sites, these metals could become a threat to aquatic lives particularly fishes which happen to derive the bulk of their food from sediments. When fishes and plants obtained from these sites are consumed by man, ailments associated with these trace metals could be contracted. 0.29 mg/l of Cd, 0.1 - 3 mg/l of Co, 0.5 - 5 mg/l Cu and 3 - 20 mg/l of Pb are toxic to plant (14). Similarly 3 - 330 mg/day of Cd, 500 mg/day of Co; 250 mg/day of Cu; 1mg/day of Pb and 100mg/day of Sb are toxic to man while 1.5 - 9g/day of Cd and 10g/day of Pb are lethal to man. There have been documentations of the effects of these metals in man (15, 16 and 17).

The consumption of Pb in high concentration could result in the deadening of nerve receptors, impairment of haeme, vitamin D and red blood nucleotide metabolism, perturbations of calcium homeostasis in the hepatocytes, bone cells and brain in asymptomatic children. Generally, acute Pb poisoning causes stomach pains, headaches, tiredness, lassitude, dizziness, anaemia, tremor, irritability and in severe cases coma and death. Since the effects of this metal are often cumulative, the high levels recorded in the sediments could lead to any of the above ailments after

continuously consuming lead-contaminated fish and/or plants (Table 1).

Antimony could present serious pollution problem when available in high concentration of up to 0.5 mg/l and apart from being toxic to the heart and capable of causing sudden death in large doses it also damages the kidneys (18).

The accumulation of Cd in these sediments is expected to affect the fishes and plants in that water and when consumed by man, several ailments such as severe kidney and liver damage, hyperglycaemia, proteinuria, glucosuria, amino-acid uria, bronchitis, pneumonitis, hypertension, anaemia and emphysema result (19, 20).

Consumption of excess amount of Co could lead to heart disease and increased red blood cells. Cobalt could also initiate or promote carcinogenic activity in animals (2). Since Co levels are relatively high, plants growing on the sediments are likely to absorb the metals and subsequently get it transferred to animals and finally to man who is at the end of the food chain (Table 1).

The high levels of Cu recorded in the samples could be absorbed by plants and subsequently transferred to animals and man; and when taken in excess the metal could lead to mucosal irritation, nausea, vomiting, diarrhoea, intestinal cramps, severe gastrointestinal irritation, widespread capillary damage, hepatic, or renal damage and of course nervous system irritation followed by depression. Possible necrotic changes in the liver and kidneys could also occur (19 and 21).

CONCLUSION

All metal levels except Cd were higher in ATS¹ sediments than in ATS² sediments indicating probable contribution of some amount of these metals by anthropogenic sources to the Qua Iboe River tributary. Lead was found to be exceptionally high in ATS¹ samples throughout the seasons indicating the presence of large amount of lead in the discharge effluent. Since ATS¹ was a site few metres away from the discharge point, it also means that a good

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proportion of lead discharged into the stream was immediately absorbed by the sediments. Since the levels of these metals except Cu were equally comparatively higher in QIR¹ (downstream) than in QIR² (upstream) samples, it could be concluded that their levels in Qua Iboe River were influenced by contributions by the factory effluent. On the whole the accumulation of these metals in all the sediment samples supports the general assertion that sediments are not just traps or sinks for heavy metals, but their reservoirs.

Table 1: Seasonal concentrations ($\mu\text{g g}^{-1}$) of metals in sediments and their coefficients of variation (%).

Metals	SITES/SEASONS											
	ATS ²		BPD		ATS ¹		QIR ¹		QIR ²		C.V	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
Lead (Pb)	40.24	40.50	161.10	159.18	748.08	733.52	402.24	398.06	191.06	166.04	90.15	91.85
Antimony (Sb)	1.17	0.65	0.40	0.22	1.40	1.40	0.46	0.54	0.43	0.33	61.62	73.81
Cadmium (Cd)	0.47	0.49	0.44	0.44	0.48	0.48	0.48	0.48	0.45	0.44	3.91	5.16
Cobalt (Co)	6.00	6.19	5.98	6.02	64.44	63.56	40.06	39.94	6.00	6.28	109.25	107.91
Copper (Cu)	14.56	15.44	18.18	17.76	24.78	25.08	14.80	14.30	17.39	17.06	23.34	23.55

Table II: Mean seasonal levels of metals in the sediments ($\mu\text{g g}^{-1}$) and their degrees of accumulation (in parenthesis).

	ATS ²	BPD	ATS ¹	QIR ¹	QIR ²
Lead (Pb)	40.37 (1.00)	160.00 (3.97)	740.80 (18.35)	400.15 (9.91)	178.55 (4.42)
Anthmony (Sb)	0.91 (1.00)	0.31 (0.34)	1.40 (1.54)	0.54 (0.55)	0.38 (0.42)
Cadmium (Cd)	0.48 (1.00)	0.44 (0.92)	0.48 (1.00)	0.48 (1.00)	0.45 (0.94)
Cobalt (Co)	6.10 (1.00)	6.00 (0.98)	64.00 (10.49)	40.00 (6.56)	6.14 (1.01)
Copper (Cu)	15.00 (1.00)	17.97 (1.20)	25.00 (1.67)	14.55 (0.97)	17.23 (1.15)

Table III. Comparison of mean metal values in sediment between site pairs using student's t-test.

Metal	Site Pair	Level of Significance	Difference between sites
Lead (Pb)	ATS ² and BPD	$P < 0.001$	$\text{BPD} > \text{ATS}^2$
	" " ATS ¹	$P < 0.001$	$\text{ATS}^1 > \text{ATS}^2$
	ATS ¹² and QIR	$P < 0.001$	$\text{QIR} > \text{ATS}^2$
Antimony (Sb)	ATS ² and BPD	$P < 0.001$	$\text{ATS}^2 > \text{BPD}$
	" " ATS ²	$P < 0.05$	$\text{ATS}^1 > \text{ATS}^2$
	" " QIR	$P < 0.05$	$\text{QIR} > \text{ATS}^2$
Cadmium (Cd)	" " BPD	$P < 0.001$	$\text{ATS} > \text{BPD}$
	" " ATS ¹	$P > 0.05^{\text{n.s}}$	$\text{ATS}^2 = \text{ATS}^1$
	" " QIR	$P > 0.05^{\text{n.s}}$	$\text{ATS}^2 = \text{QIR}$
Copper (Cu)	" " BPD	$P < 0.001$	$\text{BPD} > \text{ATS}^2$
	" " ATS ¹	$P < 0.001$	$\text{ATS}^1 > \text{ATS}^2$
	" " QIR	$P > 0.05^{\text{n.s}}$	$\text{ATS}^2 = \text{QIR}$
Cobalt (Co)	" " BPD	$P > 0.05^{\text{n.s}}$	$\text{ATS}^2 = \text{BPD}$
	" " APD	$P < 0.001$	$\text{ATS}^1 > \text{ATS}^2$
	" " QIR	$P < 0.001$	$\text{QIR} > \text{ATS}$

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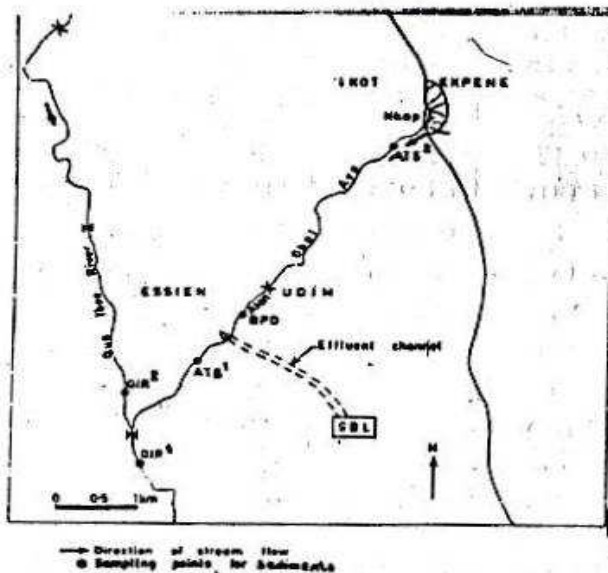


Fig. 1. Map of Qua Iboe river and Atan Stream showing sampling sites and the sunshine batteries factory location. ATS^1 = after point discharge of factory effluent; ATS^2 = upstream; BPD = before point discharge of factory effluent; QIR^1 = Qua Iboe river downstream; QIR^2 = Qua Iboe river upstream; SBL = Sunshine Batteries Ltd.

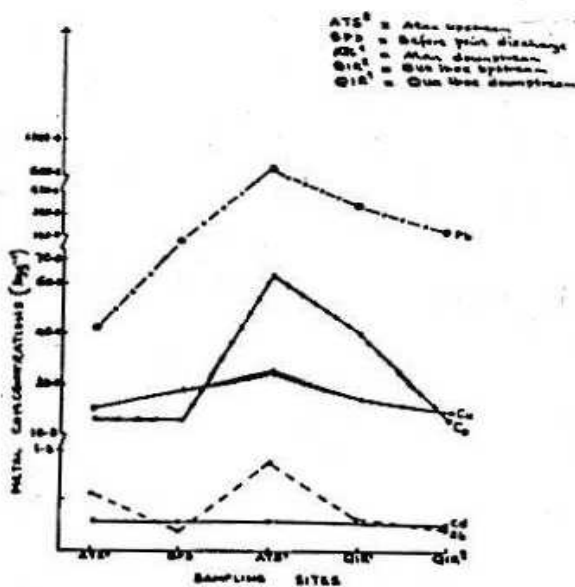


Fig. 2. Mean concentrations ($\mu\text{g g}^{-1}$) of Pb, Cu, Cd, Co and Sb in sediments

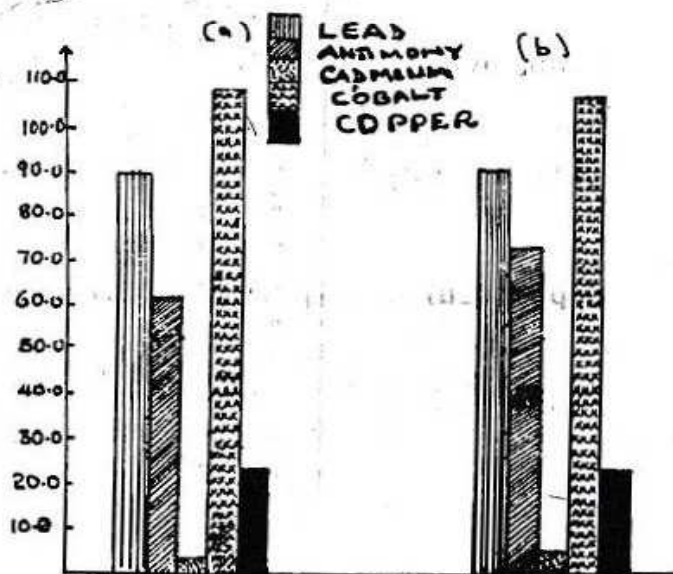


Fig. 3. Mean seasonal coefficients of variation of metals in the sediments during (a) Dry season and (b) Wet season

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(Accepted 20 December 1996)