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HEAVY METAL LEVELS IN WATER AND FISH FROM STREAMS IN IKOT EKPENE (NIGERIA) IN RELATION TO INDUSTRIAL AND MUNICIPAL DISCHARGES.

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ABSTRACT

Results of an investigation of the baseline and post impact levels of metals in water and fish from Atan stream receiving a batteries factory effluent further downstream, and from a point below its confluence with Qua Iboe River (QIR) at Ikot Ekpene are presented.

The 5 metals (Cu, Sb, Cd, Pb, and Zn) examined showed increasing concentrations from the head water of Atan stream to the site after the effluent discharge point. While mean Cu and Zn levels continue to increase below the confluence of this stream, Sb, Cd, and Pb levels decrease. In water, all metal levels and physicochemical variables below the effluent discharge point are significantly higher than those from the site upstream of Atan regarded as baseline levels, while metal levels before the point discharge and upstream of Atan are not significantly different, except for Sb.

In fish, trends of increasing concentrations downstream are apparent for Cu in *Tilapia mariae* and *Auchenoglanis fasciatus*; Pb in *T. mariae* and *T. zillii*, and Zn in *T. mariae*, *T. zillii* and *A. fasciatus*. Except for a decreasing trend downstream for Cd in *T. zillii*, others show fluctuating levels. Pb levels in fish appear to be higher than internationally recommended limits.

INTRODUCTION

Many reports on various aspects of heavy metal contamination of water from other parts of the world are available but there is a dearth of information on the baseline levels of these metals as well as pollution data generally in Nigeria. This lack of pollution data has been attributable to low levels of industrialization and urbanization which lead to low pollutional stress that can be accommodated by the natural self-purification capacity of the rivers

(Ajayi & Osibanjo, 1981).

It appears that governmental concern is focussed mainly on the coastal waters (particularly during oil spills) (see Imevbore and Odu, 1985 on the Funiwa blow-out of January, 1980), perhaps due to the overt manifestations of the incident, while the rather "insidious" effects of heavy metal contamination are overlooked, possibly until disaster strikes. Increasing number of factories are being established in Nigeria but there appears to be no concern over the possible ecological disturbances the factory effluents (treated or untreated) might create in streams which are usually the sinks. Thus the management of pollutional crises could be cumbersome in the absence of pre-impact assessment data.

This baseline study was undertaken to obtain data on five heavy metals in water and fish from Atan stream which receives a batteries factory effluent further down its course, and from Qua Iboe river below its confluence with Atan stream. Also examined were the levels of physicochemical variables in the water and their relationships with the metals.

STUDY AREA

The Qua Iboe River (Fig. 1) rises 13km south-west of Umuahia in Imo State, Nigeria. Here the surface consists of consolidated sand formations with islands of sandstone outcrops. From here the river flows through coastal sand plains in west and central Akwa Ibom State and empties into the Bight of Bonny. These geological formations accord the river its peculiar quality notably during the dry season (November – March) when discharge through run off is at its minimum, but during the rains (April – October) runoff from the thinly vegetated slopes interfere with the water quality turning it into a diluted mixture of red clay and mud. The water quality is also disrupted due to the commercial exploitation of gravel and fine sand reserves from the river bed.

Atan stream (Fig. 1), a tributary of Qua Iboe River at Ikot Ekpene, rises from the outskirts of the town and runs through a sparsely populated area, with insignificant domestic pollution

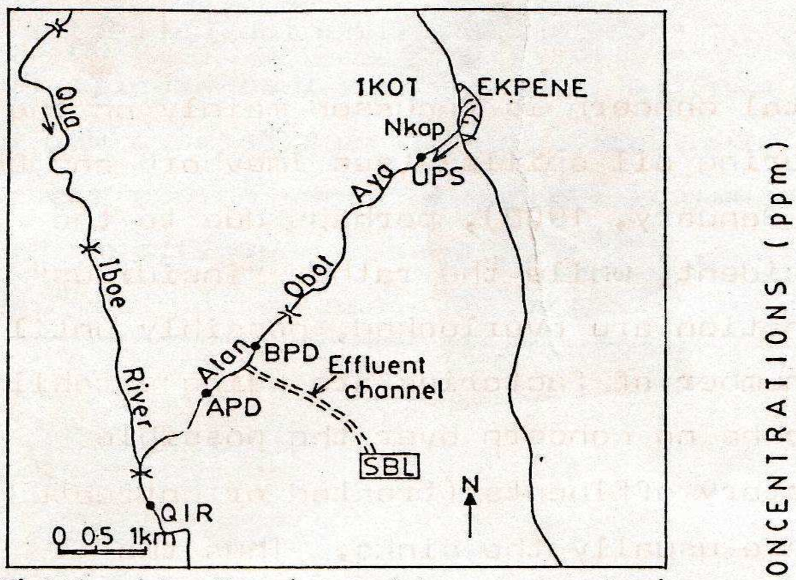

Fig.1. Map of Qua Iboe river and Atan stream showing sampling sites and the Sunshine Batteries factory location.
UPS = upstream; BPD = before point discharge of factory effluent; APD = after point discharge of factory effluent; QIR = Qua Iboe river; SBL = Sunshine Batteries Ltd.

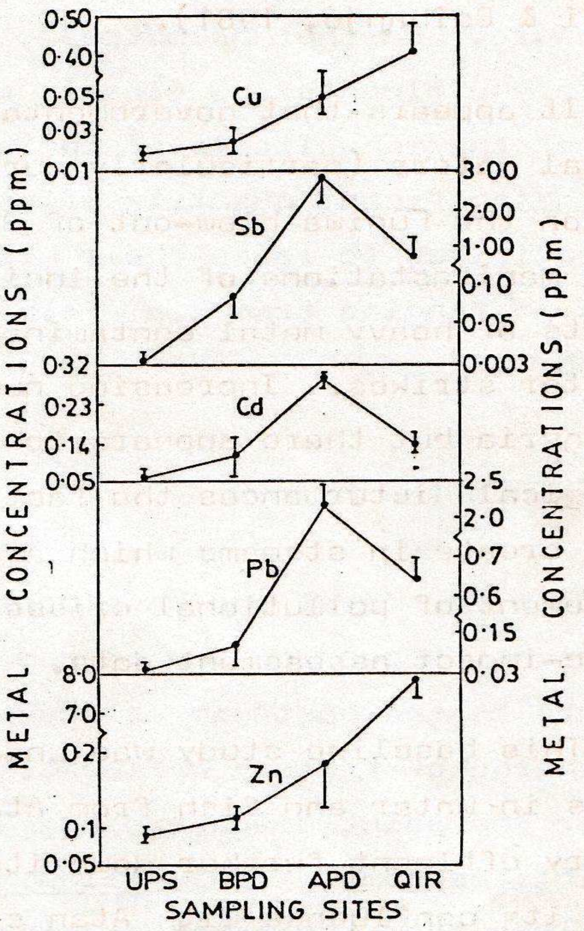

Fig.2. Mean metal concentration (ppm) ± S.E. (vertical bars) in water from the four sites investigated. Site abbreviations as in fig. 1.

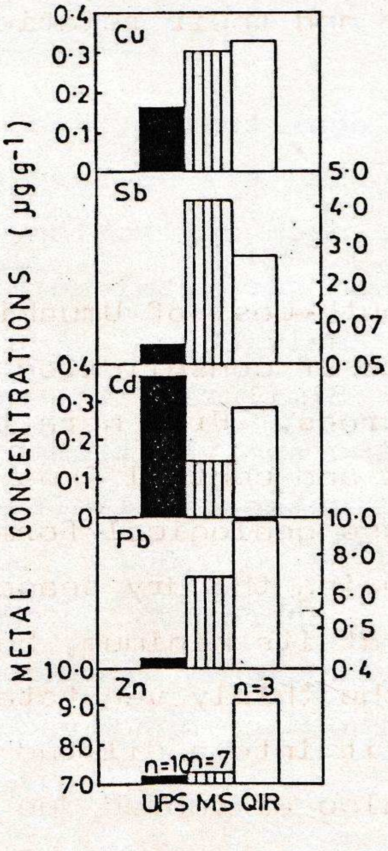

Fig. 3 Mean metal concentration (µg g^{-1}) in T. mariae from the three sites investigated.
MS = Midstream of Atan.

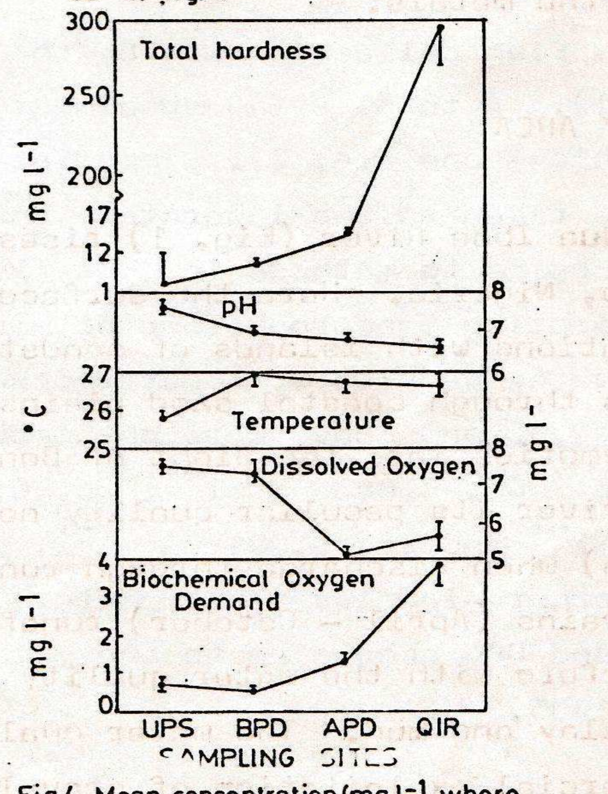

Fig.4. Mean concentration (mg l^{-1} where applicable) ± SE (vertical bar) of physicochemical variables from the four sites investigated.

pressure. Further downstream, it receives the Sunshine Batteries factory effluents and finally empties into the Qua Iboe River. Over 70% of the inhabitants of the study area are peasant farmers who use an insignificant quantity of chemical fertilizers and hardly any insecticides to raise their crops. The soils are generally acidic with pH ranging from 3.5 - 4.5 with scattered areas having marginally higher values.

MATERIALS AND METHOD

Samples for metal and physicochemical analyses were collected at four stations, three in Atan stream and one in Qua Iboe River (Fig. 1). UPS refers to the upstream or headwater site while BPD means before point discharge of factory effluent. APD denotes samples collected about 200m after the point discharge and QIR, the site on the Qua Iboe River. Of the fishes sampled only Tilapia mariae was represented by more than 1 specimen from the 3 sites, viz, upstream (UPS), midstream (MS) and Qua Iboe River (QIR).

Fish collection was by the use of local traps (Ikpa) (see Essien, 1981). A total of 49 specimens representing six species were collected (Table 1 and Fig. 2). Immediately after each collection, the fishes were taken to the laboratory and processed for metal determination according to methods in AWWA (1980) and analysed on a Pye Unicam Atomic Absorption Spectrophotometer model SP9. Similarly, the metal levels in water samples were determined using the same instrument. Recoveries of 99.5% and above were obtained and the detection limits for the metals were: Cu, C.003 g ml^{-1}; Sb, 0.02 g ml^{-1}; Cd 0.002 g ml^{-1}; Pb, 0.01 g ml^{-1} and Zn, 0.001 g ml^{-1}. Surface temperature was determined with a mercury-in-glass thermometer; total hardness by EDTA titration; pH, DO and BOD according to the methods in the Hach handbook series DR-EL/5 of 1985.

RESULTS AND DISCUSSION

Fig. 2 illustrates the average concentrations of the 5 heavy metals in water from the 4 sites examined. All metals exhibit increasing concentrations from UPS to APD but two trends emerge when considering

Table 1. Mean Metal concentrations (ug g^{-1}) in fish species (excluding *Tilapia mariae*). UPS = upstream; MS = midstream; QIR = Qua Iboe river.

Site/species	n	Metals Cu	Sb	Cd	Pb	Zn
UPS						
Auchenoglanis fasciatus	4	0.12[a]	0.063	0.88	0.13	7.99[a]
Tilapia zillii	1	0.15	0.30	1.50[b]	0.02[a]	8.00[a]
MS						
A. fasciatus	3	0.43	1.50	0.15	0.12	10.13
T. zillii	3	0.88	0.75	0.23	6.85	8.59
Papyrocranus afer	3	0.78	3.25	0.21	5.91	5.92
Chromidotilapia guntheri	2	0.53	0.85	0.57	2.75	6.66
Channa obscurus	2	1.23	2.00	0.23	3.93	8.59
QIR						
A. fasciatus	1	1.67	0.00	0.18	3.90	12.10
T. zillii	1	0.24	0.00	0.15	16.50	15.10
P. afer	4	1.14	1.76	0.49	7.36	11.15
C. guntheri	3	0.72	0.80	0.12	1.93	8.60
C. obscurus	2	0.52	1.82	0.25	1.40	12.60

a = Increase downstream

b = Decrease downstream

the QIR site concentrations. Firstly, there is an increase in the concentrations of Cu and Zn. Secondly, the concentrations of Sb, Cd, and Pb dropped in QIR. In each case, the drop in concentration was higher than the UPS and BPD values from Atan stream. Of the 5 metals, Sb had the lowest mean concentration (0.004 ppm) at the UPS while Zn had the highest mean value (7.75 ppm) at QIR site.

Results of the statistical comparison of mean metal levels between UPS and other sites (Table 2) indicate that apart from Sb the mean metal concentrations between UPS and BPD were not significantly different. With the exception of Sb, the mean metal levels between UPS and QIR were significantly different, being higher in QIR site than UPS of Atan stream. All mean metal values were significantly higher for APD site than UPS.

Mean metal values at UPS site were taken as baseline values and in water they were lower than values from other sites. The lack of differences in mean Cu, Cd, Pb, and Zn between UPS and BPD sites is indicative of the absence of source(s) of inputs that could lead to increases in their levels before the point discharge of factory effluents. This, however, is not the case with Sb whose level for BPD site is significantly higher than the UPS level (Table 2), indicating some degree of input before the point discharge of the factory effluent.

Sb and Pb are the two metals very likely to appear in the batteries effluent due to the use of antimonial lead in the batteries manufacturing process (Ibok et al., 1989). It is difficult to understand why Sb concentration is higher for BPD site than UPS. However, considering the low baseline level (UPS site) and the lack of significant difference between UPS and QIR values (Table 2) it is plausible to argue that the possibility of introducing materials likely to add antimony to the water before the point discharge of the effluent may not be ruled out. All metal levels were higher for APD site than UPS, indicating contribution of some quantity of these metals from the factory effluent to Atan stream. The significantly higher concentrations of metals (except Sb) from QIR site than the baseline levels indicates major contribution from urban drainage and seepage, especially Cu and Zn. The drop in levels of Sb, Cd, and Pb at QIR site could be attributed to either low levels of input from the environment or dilution by a larger body

Table 2. Comparison of mean metal values in water using Student's t-test. Site abbreviations as in Fig. 1.
n.s. = not significant; *, **; *** = 95%, 99% and 99.9% level of significance respectively.

Metals	Site pairs	Statistical result/inference
Copper		
	UPS and BPD	$0.05^{n.s.}$
	" " APD	0.05^{*}
	" " QIR	0.001^{***}
Antimony		
	UPS and BPD	0.05^{*}
	" " APD	0.001^{***}
	" " QIR	$0.05^{n.s.}$
Cadmium		
	UPS and BPD	$0.05^{n.s.}$
	" " APD	0.001^{***}
	" " QIR	0.01^{**}
Lead		
	UPS and BPD	$0.05^{n.s.}$
	" " APD	0.001^{***}
	" " AIR	0.001^{***}
Zinc		
	UPS and BPD	$0.05^{n.s.}$
	" " APD	0.001^{***}
	" " QIR	0.001^{***}

of water.

Metal concentrations in fish (Fig. 3; Table 1) do not show the kind of trend apparent in water, although 3, and not 4, locations were considered in fish survey. However, Cu, Pb, and Zn in T. mariae increased from upstream of Atan to QIR, while concentrations of Sb and Cd fluctuated at the 3 sites. In this species, Cd was the only metal with the highest concentration (0.37 ug g^{-1}) upstream, relative to the other two sites. While Sb had the lowest level (0.06 ug g^{-1}) in T. mariae from upstream site, Pb had the highest level (9.88 ug g^{-1}) at QIR.

Overlooking the constraint of single specimens of some species from some locations, trends of increasing levels downstream are apparent for Cu in A. fasciatus; Pb in T. zillii, as well as Zn in both A. fasciatus and T. zillii, while a trend of decreasing levels downstream occurs for Cd in T. zillii. Pb had the lowest (0.02 ug g^{-1}) and the highest (16.50 ug g^{-1}) concentrations in T. zillii from UPS and QIR sites respectively (Table 1).

Apart from T. mariae and A. fasciatus in this study Kakulu et al. (1987) have reported trace metal concentrations (except Sb) in the other four fish species from the Niger Delta but it is apparent that with the exception of Cu in T. zillii and Zn in C. guntheri, higher metal concentrations have been recorded in the present study (Table 4). Generally, open water metal concentrations were lower in fish tissue in line with established patterns (Cross et al; 1970; Namings et al; 1974; Mathis and Cummings, 1971; Naminga, 1975; Udoidiong, 1990).

Of the 5 physicochemical variables, totel hardness and BOD increased downstream (Fig. 4). Correlation between these two variables and Cu and Zn respectively, were low except for BOD and Zn, with $r = 0.6763$ ($df = 7$; $P < 0.05$). Dissolved oxygen decreased downstream of Atan but increased at QIR. There was a drop in temperature from BPD to QIR after an initial rise, while pH decreased downstream to QIR. Mean values of total hardness, BOD and DO between UPS and BPD (Table 3) were not significantly different while others were significantly higher than UPS levels.

Table 3. Comparison of mean concentrations of physicochemical variables using Student's t-test. Abbreviations and notations as in Table 2.

Variable	Site pairs	Statistical results/inference
pH		
	UPS and BPD	0.05*
	" " APD	0.01**
	" " QIR	0.001***
Temperature		
	UPS and BPD	0.001***
	" " APD	0.01**
	" " QIR	0.001***
Total hardness		
	UPS and BPD	0.05 n.s.
	" " APD	0.01**
	" " QIR	0.001***
BOD		
	UPS and BPD	0.05 n.s.
	" " APD	0.01**
	" " QIR	0.001***
DO		
	UPS and BPD	0.05 n.s.
	" " APD	0.001***
	" " QIR	0.001***

Table 4. Mean metal levels (ug g^{-1}) in fish and ranges (in parentheses) from this study, compared with those from Kakulu *et al.* (1987) below each parenthesis where applicable.

Species	n	Metals Cu	Sb	Cd	Pb	Zn
P. afer	7	0.98 (0.20-2.50) 0.53	2.40 (1.80-4.[illegible]0) -	0.37 (0.06-1.90) 0.02	6.74 (0.15-18.52) 0.37	8.91 (0.11-14.60) 4.75
C. obscurus	4	0.87 (0.09-1.80) 0.69	1.91 (1.23-2.50) -	0.24 (0.04-0.45) 0.02	2.67 (1.30-3.93) 0.29	10.60 (6.24-13.00) 4.89
C. guntheri	5	0.65 (0.30-1.20) 0.21	0.82 (0.90-1.70) -	0.30 (0.08-0.75) 0.01	2.26 (0.55-4.20) 0.41	7.82 (5.65-11.30) 10.18
T. zillii	5	0.61 (0.1-1.30) 0.82	0.51 (0.30-1.24) -	0.47 (0.1-1.50) -	7.41 (0.02-16.50) 0.41	9.77 (4.92-15.84) 6.12
T. mariae	20	0.23 (0.05-0.65) -	1.86 (0.05-7.[illegible]0) -	0.27 (0.01-0.85) -	4.10 (0.08-19.50) -	7.51 (0.07-23.11) -
A. fasciatus	8	0.43 (0.05-1.67) -	0.59 (0.10-1.50) -	0.52 (0.15-2.25) -	3.60 (0.07-18.08) -	9.31 (6.77-12.24) -

The higher levels of total hardness and BOD at the QIR site vis-a-vis the other three sites in Atan stream is a reflection of the level of its disturbance. Of interest is the BOD value which shows that the level of organic pollution of QIR is higher than that of Atan stream (c.f Ibok et al; 1989).

The comparison of data from a study like this with international standards is fraught with problems because "disparate standards" are given by different agencies and countries. For example, Dangerfield (1983) reported the following WHO standards in water, which are the maximum permissible levels (in mg 1^{-1}) : Cu, 1.5; Pb, 0.05; Zn, 15.00; Hardness ($Ca\ CO_3$), 300; pH, 6.5 - 9.2 units. The National Health and Medical Research Council (NHMRC) of Australia gives the following concentrations as standards in seafoods (Cebbington et al; 1977): Cd, 2.0; Cu, 30; Lead, 2.0; and Zinc, 1000 (in ppm). Oni (1987) reported United States Environmental Agency (USEPA) and World Health Organisation (WHO) standards in water for the following metals: Cu, 1.0; Zn, 5.0; Cd, 0.01; Sb, 0.01; and Pb, 0.05 (in mg 1^{-1}).

Using the Australian NHMRC standards, only Pb levels in fish from the present study are above the recommended limit. In water, the Cu levels are well below United States Environmental Protection Agency (EPA) standards. Sb, Cd, and Pb levels are higher from the present study while Zn concentration is higher than recommended USEPA limit and below NHMRC limit at the QIR site. Results of the effluent quality measurements (Table 5) indicate that Atan stream below the point discharge, does not remain a relatively uncontaminated surface water.

For example, the ammonia level of 2.83 mg 1^{-1} and suspended solids level of 410.25mg 1^{-1} in the treated effluent are high, and using the classification scheme of surface water by Prati et al. (1971), water with such levels of substances is polluted. Accordingly Atan stream would invariably be a polluted stream. Again, Pb level of 0.20 mg 1^{-1} in the treated effluent is four times higher than the international limit of 0.05 mg 1^{-1} for that metal in water. Although Sb and Cd levels in the treated effluent were below detection, it is reported that occasional overflows of untreated effluent occur and this may be responsible for the higher metal concentrations below the point discharge.

Table 5. Effluent quality measurements within and outside the batteries factory (mean values). PS = production site; BT = before treatment; AT = after treatment.

Variable		Locations		
		PS	BT	AT
Temperature (^{o}C)		28.82	27.07	27.45
pH		2.42	6.75	6.62
Conductivity (mhos cm^{-1})		1335.29	2390.08	27.28
Suspended solids (mg l^{-1})		789.00	2410.10	410.25
Total solids	"	5620.00	7895.00	450.25
Hardness	"	-	13.33	352.00
Ammonia	"	0.50	0.65	2.83
Sulphite	"	27.30	14.50	15.33
Sulphace	"	120.06	79.66	35.37
Copper	"	2.22	5.48	0.22
Antimony	"	0.02	0.03	BD
Cadmium	"	BD	BD	BD
Lead	"	34.00	37.00	0.20
Iron	"	38.77	0.54	13.21

BD = below detection

If more technical expertise and prudence are shown by staff of the treatment unit, lower levels of the metals could be achieved. The absence of any metal - related catastrophy should not imply lack of impact on the stream biota and man and consequently should not lead to complacency on the part of management of the factory on further reducing the levels of toxicants in the effluents.

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