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HEAVY METALS IN FISHES FROM SOME STREAMS IN IKOT EKPENE AREA OF NIGERIA

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Abstract: Concentrations of eight metals (Hg, Zn, Cu, Co, Sb, Cd, Pb, and Cr) were determined in four species of fish from three streams *(Tilapia mariae* and *Chromidotilapia guntheri* from Atan stream; *Tilapia mariae* and *Auchenoglanis fasciatus* from Nkap stream; and *Channa Obscurus* from Qua Iboe River) in Ikot Ekpene. The levels of ten physicochemical variables were also determined in the three streams. Differences in all mean concentrations of metals and physicochemical variables were analysed by the use of t-tests and comparisons were made between Atan and Nkap; Atan and Qua Iboe, and Nkap and Qua Iboe streams. Significant differences ($p < 0.05$) were revealed between the levels of some metals, and physicochemical variables in the three pairs of streams examined. The results obtained indicate that Nkap stream is relatively unpolluted whereas Atan and Qua Iboe are significantly polluted. The results further reveal that the levels of metals in fish in the three streams follow the order: Atan stream > Qua Iboe River >> Nkap stream. Details of this and other analytical findings are discussed and possible reasons given.

Introduction

It is now recognised that advancement in technology as well as growth in population have led to high levels of industrialization and urbanization which in turn have led to environmental pollution resulting from the discharge of industrial effluents replete with most common heavy metals such as Hg, Zn, Cu, Co, Sb, Cd, Pb and Cr into our environments, particularly natural waters. Writing on Water Quality Surveillance and treatment, Oni (1987) pointed out that industrial manufacturers may endanger public health by discharging toxic substances (including heavy metals) into water which may cause taste and odour problems, contaminating irrigated food crops and killing fishes and other natural life in rivers. As noted by Udosen *et al* (1987), the pollution of these environments result from man's determination to match desire with production through the establishment of various industries with potentials to pollute our environments.

According to Sastry and Tyagi (1982), water pollution by such heavy metals has become a health hazard in recent years. Similarly, Warren (1981) noted that man's activities have increased the quantity and distribution of heavy metals in the atmosphere, on land and in rivers, lakes and seas. The extent of this widespread but generally diffuse contamination has caused concern about its possible effects on plants, animals and human beings. Writing on the environmental implications of Sunshine batteries industry at Ikot Ekpene, Udosen *et al* (1987) warned against gross pollution of streams flowing through towns and cities and especially industrial areas by wastes and effluents from domestic, commercial and industrial sources. According to them, although concentrations of metals in the batteries effluents were not high enough to present serious pollution problems, their concentrations could increase in future if steps were not taken to stop the rising trend in the amounts that enter the streams.

Brooks (1974), Bebbington *et al* (1977), Young and Blevins (1981); Koli and Whitmore (1983); and Sastry and Tyagi (1982) amongst others have through their various works on the contamination of fishes found out that pollutants, especially the heavy metals could cause serious damage to aquatic life particularly fishes. In countries where fish is regarded as one of the commonest sources of proteins, contamination of bodies of water deserves greater attention. An example of a disaster resulting from contamination of the environment by heavy metals was the outbreak of minamata disease in Japan which was caused by methyl-mercury poisoning (Christman *et al,* 1974; Young and Blevins, 1981). According to Christman, this mercury poisoning through food chain build up occurred in Japan's Minamata Bay which received industrial wastes containing mercury compounds. Fish in the bay accumulated mercury compounds through the food chain and were in turn caught and eaten by people as well as cats that frequented the dock area. Consequently, between 1953 and 1961, forty four people died from mercury poisoning as a result of eating fish caught in the bay (Christman *et al,* 1974). Moriber (1974), also found out that consumption of waste water from a mine which produced cadmium, zinc and lead resulted in a rickets-like disease known as itai-itai. Middle Brooks (1979), reported that toxic compounds are common constituents of some industrial processes and frequently find their way into streams. Accordingly, such streams are often degraded when these toxic compounds are discharged into them to the extent that beneficial uses are no longer

Table 1: Mean metal concentrations ($\mu g\ g^{-1}$) and ranges (in parentheses) in *tilapia marie* and *channa obscurus*

Stream/Fish	*Metal ($\mu g\ g^{-1}$)*							
	Hg	*Zn*	*Cu*	*Co*	*Sb*	*Cd*	*Pb*	*Cr*
Atan	0.032	11.64	0.77	1.67	2.09	0.33	6.69	5.28
	(.015—.048)	(6.60—15.84)	(.31—1.20)	(1.25—2.75)	(1.50—3.00)	(.15—.75	(.078—18.08)	(4.00—9.50)
T. mariae								
No of specimens	6	6	4	6	5	5	6	5
Nkap	0.024	7.85	0.16	2.69	0.17	0.98	0.48	5.13
	(.01—.04)	(5.20—10.50)	(.052—.35)	(.50—7.50)	(0.1—0.25)	(0.30—2.25)	(0.13—1.20)	(4.40—6.50)
T. mariae								
No. of specimens	6	6	6	4	3	4	6	4
Qua Iboe	0.035	11.05	0.84	1.58	1.80	0.39	4.88	4.28
	(.012—.058)	(5.65—15.10)	(0.09—2.50)	(0.58—3.25)	(0.90—3.25)	(0.04—1.90)	(0.13—18.52)	(2.50—6.00)
C. obscurus								
No of specimens	12	12	12	8	7	9	12	9

* Numbers below ranges refer to the number of specimens from which metals were detected, out of 6 specimens of *T. mariae* and 12 of *C. obscurus.*

Table 2: Mean concentrations of metals ($ug\ g^{-1}$) in chromidatilapia guntheria and auchenoglanis fasciatus.
Figures in parentheses and below, as in Table 1

Stream/Fish	*Metal*							
	Hg	*Zn*	*Cu*	*Co*	*Sb*	*Cd*	*Pb*	*Cr*
Atan	0.028	7.25	1.07	1.44	1.95	0.24	2.82	4.8
C. guntheri	(.01—.45)	(4.92—10.94)	(.32—1.80)	(1.25—1.50)	(1.24—3.0)	(.15—.38)	(.79—3.93)	(=)
No of specimens	6	6	6	4	5	6	6	3
Nkap	0.023	7.72	0.14	1.14	0.067	0.45	0.25	4.24
	(.012—.051	(5.64—10.00)	(0.78—.285)	(.75—1.50)	(.05—.10)	(.01—1.10)	(.07—.66)	(3.10—4.80)
A. fasciatus								
No of specimen	6	6	6	4	3	4	6	5

possible. For instance, the author found out that settleable matter could impede fish hatching. Tebutt (1977), also found out that the effect of potentially toxic materials on streams and rivers are normally measured by their action on fish.

Heavy metals are common components of natural waters and although some are essential for living organisms, yet they may become highly toxic when present in high concentrations. Thus heavy metals could remain for a long time in sea foods and by a series of reaction mechanisms accumulate in them and are transported in large concentrations to animals or human beings when consumed (Fadrus *et al,* 1979). Since the physiology of fish the world over seems to be the same, the authors believe that effects elsewhere as a result of high concentration or accumulation of any heavy metal is bound to occur anywhere such metals are found in concentrations exceeding those set by National Health Medical Research Council (NHMRC).

Since the people of Ikot Ekpene and indeed many other Nigerians depend on fish caught locally to supplement their protein requirement, the research on levels of heavy metals in fish including their sources could be seen as one bold step towards preserving our natural environments. So, the three streams; Nkap, Atan and Qua Iboe, selected for this work are significant in different ways. Nkap stream for instance, runs through a sparsely populated reserve area in Ikot Ekpene town and empties into Atan stream which passes through an industrial area on the outskirts of the town. These two streams — Nkap and Atan, then empty into Qua Iboe River, which also receives some other smaller streams.

Materials and Methods

The fish specimens and the physicochemical data were collected at two sites which were about 300m apart in each stream. Local traps (Ikpa) were the only gear used in the collection of fish, and were usually set at dusk and inspected at dawn. A total of 36 specimens of 4 fish species (6 specimens from each site) were collected for metal analysis. Immediately after each inspection, the fishes were taken to the laboratory and the muscle tissue prepared by filleting the fish on both sides. 5.00g of the muscle (representing the two fillets from each fish) was weighed from each fish, homogenized and digested with a mixture

Table 3: Mean levels and ranges (in parentheses) of physicochemical variables to the three streams

	~~Physio~~ Physicochemical Variable				
Stream	pH	Temperature (°C)	Conductivity (umho cm^{-1})	Total Solids (mg l^{-1})	Total Hardness (mg $l^{-1}CaCo_3$)
Atan	6.93 (6.7—7.4)	26.53 (26.3—27.2)	139.92 (22.50—260.51)	864.34 (764.30—956.10)	12.54 (4.00—20.00)
Nkap	7.56 (6.8—8.0	25.76 (25.3—26.4)	52.57 (21.70—125.30)	629.48 (440.00—810.00)	8.06 (4.00—12.00)
Qua Iboe	6.72 (6.3—7.4)	26.94 (25.9—27.5)	360.38 (15.80—1500.00)	3802.08 (108.00—11,602.00)	293.71 (155.00—362.00)

	Physiochemical Variables				
	Suspended Solids (mg l^{-1})	Total Dissolved Solids (mg l^{-1})	B. O.D. (mg l^{-1})	C. O. D. (mg l^{-1})	Dissolved Oxygen (mg l^{-1})
Atan	656.96 (198.40—1420.00)	377.03 (95.00—640.10)	0.88 (0.35—1.52)	3.19 (.20—7.05)	6.16 (4.55—8.00)
Nkap	273.79 (126.80—415.10)	163.21 (68.50—250.40)	0.67 (0.32—1.20)	1.42 (0.50—3.35)	7.52 (6.80—8.90)
Qua Iboe	855.41 (400.30—1360.12)	142.04 (85.00—250.7)	3.86 (1.30—7.05)	15.05 (8.50—21.55)	5.56 (3.90—7.46)

Table 4: Comparison of mean metal concentrations in fish (µg g^{-1}) among stream pairs. Figures in parentheses refer to number of fish specimens examined (pooled data from sites 1 and 2 in each stream)

	Metal							
Stream Pair/ Probability	Mg	Zn	Cu	Co	Sb	Cd	Pb	Cr
Atan			0.95(10)		2.02(10)	0.28(12)	4.76(12)	
Nkap			0.15(12)		0.12	0.72(8)	0.36(12)	
P			< 0.001		< 0.001	< 0.001	< 0.05	
Atan								5.10(8)
Qua Iboe								4.28(9)
P								< 0.05
Nkap		7.79(12)	0.15(12)		0.12			
Qua Iboe		11.05(12)	0.84(12)		1.80(7)			
P		< 0.01	< 0.01		< 0.001			

P = Level of significance

of nitric and perchloric acids in the ratio of 2 : 1. The resultant solution was evaporated to dryness on a hot plate and the white residue formed dissolved in 10 ml of 20% nitric acid. The sample solution was diluted to 30 cm^3 with de-ionized water and analyzed on a Perkin Elmer Absorption Spectrophotometer model SP — 9, (1978), for Zn, Cu, Co, Sb, Cd, Pb and Cr. Mercury (Hg) was determined colorimetrically after extraction with dithizone in carbon tetrachloride. All analyses were carried out in duplicates and recoveries of over 99.5% were obtained. The detection limits for the metals were: Hg. 0.10 ppm; Zn, 0.01 ppm; Cu, 0.035 ppm; Co, 0.048 ppm; Sb, 0.20 ppm; Cd, 0.02 ppm; Pb, 0.10 ppm; Cr, 0.04 ppm.

For the physicochemical parameters of the stream waters, the following methods were employed: The temperature measurements were taken on site at the time of sampling. Both sample and ambient temperature readings were read to 0.5°C. The total suspended matter was determined gravimetrically by filtration method (Hanson, 1973), while total dissolved solids was determined by evaporation method (Hanson, 1973). On the other hand pH, D.O., B.O.D., and C.O.D. were determined following the methods in the HACH Handbook, Model Dr-El/5 (1985) while total Hardness determination was by EDTA titration using solochrome Black T as the indicator.

Results

Apart from lead and chromium, mean metal concentrations in fish were relatively low in the three streams investigated, with mercury having the least concentrations (Tables 1 and 2). There were no significant differences in mean metal concentrations between sites 1 and 2 in all four species in the three streams. A one-way analysis of variance of metal concentrations in individual species on site basis revealed significant differences in mean metal concentrations of *Tilapia mariae* from Atan stream ($p < 0.001$); *Channa obscurus* from site 1 in Qua Iboe River ($p < 0.05$) and the pooled data (sites 1 and 2) of *Channa obscurus* from Qua Iboe River ($p < 0.001$). A summary of the mean values and ranges of physicochemical variables of the three streams is given in Table 3.

Differences in mean values of the following physicochemical variables between sites 1 and 2 have been obtained: Total solids in Atan; Total hardness in Nkap; suspended solids in Atan and Qua Iboe; Total dissolved solids in Atan; BOD in the three streams; COD in Qua Iboe, and DO in Atan. Only the relationships between BOD/COD and BOD/DO in Qua Iboe and Atan respectively, showed good fits to linear regressions. Accordingly, values of each of the variables could be predicted from the respective regression lines in Fig. 1.

Table 5: Comparison of mean values of physicochemical variables among stream pairs

	Physicochemical Variable									
Stream Pair/ Probability	*PH P*	*Temp. (°C)*	*Cond. (umho cm^{-1})*	*Total Solids (mg l^{-1})*	*Total Hardness (mg l^{-1})*	*Tot. Diss. Solids (mg l^{-1})*	*B. O. D. (mg l^{-1})*	*C. O. D. (mg l^{-1})*	*D. O. (mg l^{-1})*	*Susp-ended Solids (mg l^{-1})*
Atan	6.93	26.63		864.34	12.54	377.03		3.19	6.16	
Nkap	7.56	25.76		629.48	8.08	163.21		1.42	7.52	
P	0.01	0.001		0.001	0.001	0.05		0.05	0.05	
Atan					12.54	377.03	0.883	3.19		
Qua Iboe					293.71	142.04	3.86	15.25		
P					0.001	0.05	0.01	0.001		
Nkap	7.56	25.76			8.06		0.67	1.42	7.52	273.97
Qua Iboe	6.72	26.94			293.71		13.86	15.25	5.56	855.41
P	0.01	0.01			0.001		0.01	0.001	0.01	0.001

P = Level of significance

Figures 2 and 3 show mean metal concentrations in the four fish species from the three streams. Mean concentrations of zinc (11.64 ug g^{-1} copper (0.77 ug g^{-1}) and antimony (2.09 ug g^{-1}). in *T. mariae* from Atan stream were significantly higher than the mean values of 7.85, 0.16 and 0.17 ug g^{-1} for the corresponding metals in *T. mariae* from Nkap stream (striped bars). Conversely, mean cadmium concentration (0.98 ug g^{-1}) in *T. mariae* from Nkap stream is significantly higher than 0.33 ug g^{-1} mean value for the same species from Atan stream.

In Fig. 3, copper, antimony and lead concentrations averaged 1.07, 1.95 and 2.82 ug g^{-1} respectively in *Chromidotilphia* Guntheri from Atan stream, and are significantly higher than the average values of 0.14, 0.067 and 0.25 ug g^{-1} for the respective metal (striped bars) in *Auchenoglanis fasciatus* from Nkap stream. Similarly the 2.09 ug g^{-1} average concentration of antimony in *T. mariae* from Atan stream and 1.80 ug g^{-1} average in *C. obscurus* from Qua Iboe river are higher than the 0.17 ug g^{-1} average of the same metal in *T. mariae* from Nkap stream (Fig. 2, striped bars). Again in Fig. 3, *C. guntheri* from Atan stream has a higher mean concentration of antimony than *A. fascistus* from Nkap stream. However, the mean concentration of this metal in *C. guntheri* from Atan stream is not significantly different from its mean concentration in *C. obscurus* from Qua Iboe river.

Data on metals in fish, and physicochemical variables in water from the two sampling sites in each stream were pooled (in fish, irrespective of species) and the average values used in making comparisons between stream pairs (Tables 4 and 5). Only metals and physicochemical variables that differed significantly between stream pairs are shown. In Table 4, it is evident that mean concentrations of copper, antimony and lead are higher in Atan stream fishes than in fishes from Nkap stream, whereas cadmium level are higher in Nkap stream fishes than in Atan. For the comparison between Atan stream and Qua Iboe river, only the mean chromium concentration is higher in Atan stream fishes than in *C. obscurus* from Qua Iboe river. The mean concentra-

Table 6: Physicochemical Characteristics of the Sunshine Battery effluent before and after neutralization

Characteristics		*Location*		
		Within Factory	*Before Treatment*	*After Treatment*
Temperature (°C)		30.50	30.50	26.50
PH		3.00	3.50	6.90
Conductivity (umhos cm^{-1})		1348.00	2440.00	25.50
Suspended Solids (mg l^{-1})		4720.00	5560.00	80.00
Dissolved Solids	”	880.00	2320.00	440.00
Total Solids	”	5600.00	7880.00	520.00
Total hardness	”	ND	ND	28.00
BOD	”	”	”	1.46
COD	”	”	”	2.40
Mercury	”	”	”	ND
Zinc	”	”	”	3.78
Cobalt	”	”	”	0.35
Copper	”	2.22	5.48	0.22
Antimony	”	0.02	0.03	BDL
Cadmium	”	BDL	BDL	”
Chromium	”	”	”	”
Lead	”	34.00	37.00	0.20

ND = Not determined BOD = Biochemical Oxygen Demand BDL = Below detection limit
COD = Chemical Oxygen Demand.

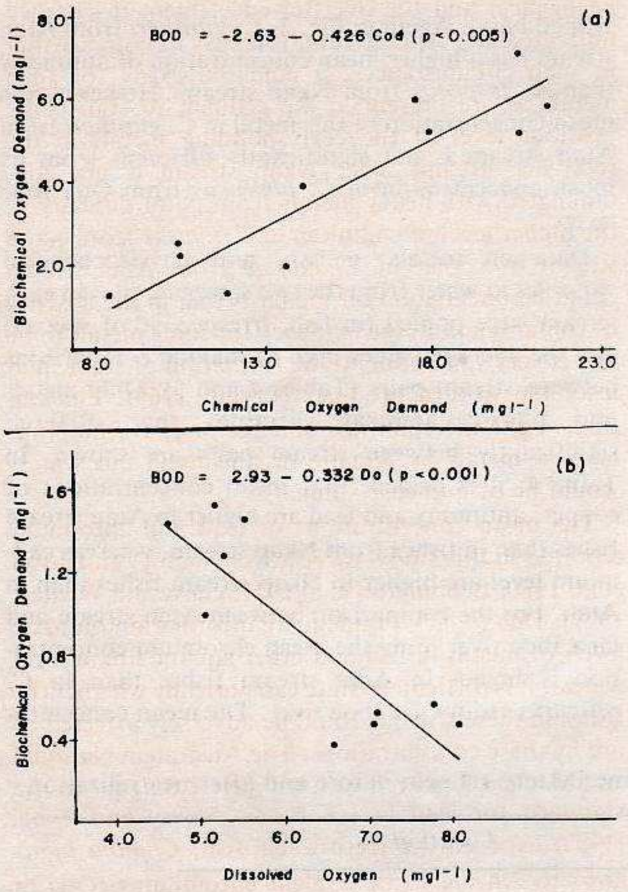

Fig. 1: Relationships between (a) BOD and COD in Qua Iboe River; (b) BOD and DO in Atan Stream

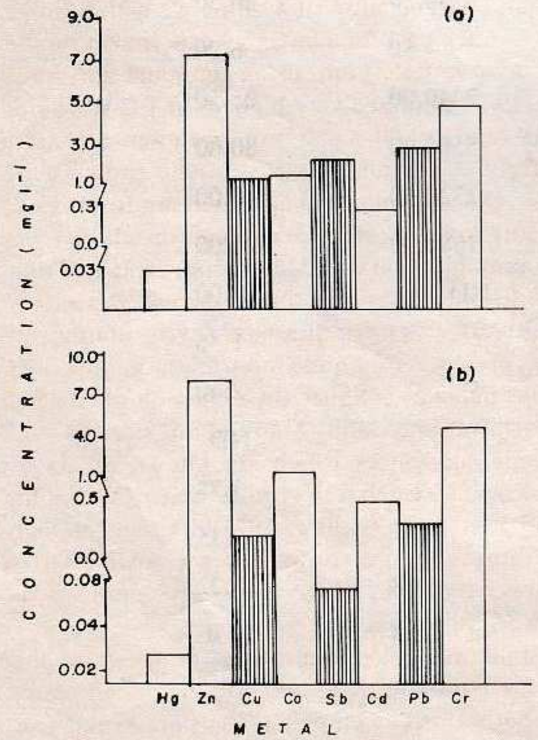

Fig. 3: Histogram of mean metal concentrations in (a) *C. gunther;* from Atan stream;

(b) *A. fasciatus* from Nkap steam.

Stripped bars show metals with significant differences between means.

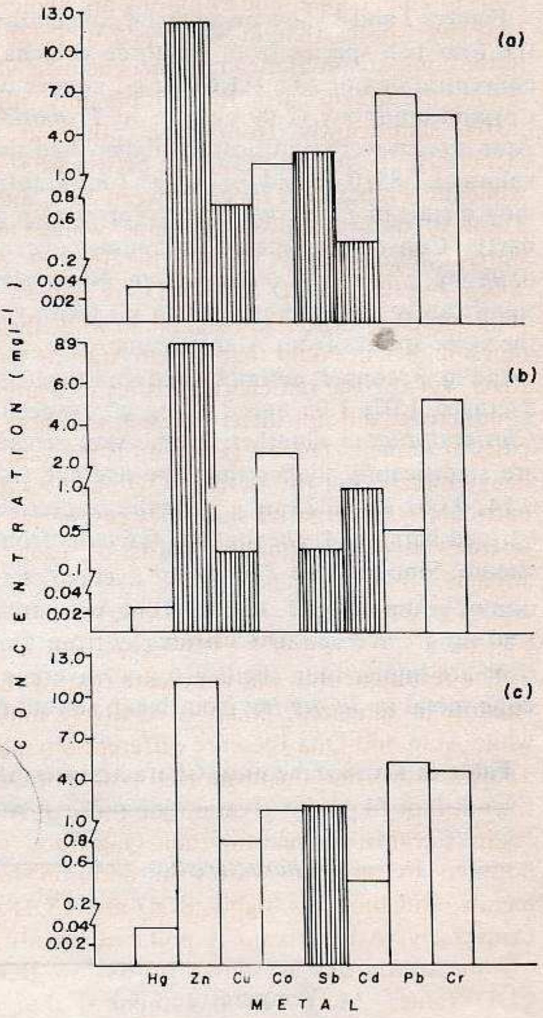

Fig. 2: Histogram of mean metal concentrations in
(a) *T. mariae* from Atan stream
(b) *T. mariae* from Nkap stream
(c) *C. obscurus* from Qua Iboe River

tions of zinc, copper and antimony are higher in Qua Iboe river species than in Nkap species. Table 5 refers to the comparison of mean physicochemical variables among the stream pairs. In the table only values that differ significantly from each other are given. Generally, the pH values range between 6.0 and 8.0 while the temperature range between 25 °C and 27 °C. Total solids are almost the same while Qua Iboe water is much harder than either that of Atan or Nkap. Similarly BOD and COD are highest in Qua Iboe compared with Atan and Nkap while the D.O. is much higher in Nkap than either Atan or Qua Iboe River. Of the the ten characteristics measured, only conductivity did not differ between the three stream pairs examined. The overall trend is the same as for heavy metals, but the BOD, COD and DO data are particularly informative since they emphasize the differences in water quality status of each of the streams.

Discussion

The results of this study indicate that of the three streams investigated, Nkap is relatively unpolluted while Atan and Qua Iboe are differentially polluted. Table 5 shows that the mean BOD value of Qua Iboe river at Ikot Ekpene is greater than those of Atan and Nkap streams, indicating that Qua Iboe river is polluted by organic wastes in addition to trace metals, and thus has higher BOD and COD values. Conversely, Atan stream is polluted mainly by inorganic substances as shown by its low BOD and COD values. Mara (1976) contended that in hot climates the natural BOD of river can be higher. Citing Meadows (1974), he mentioned River Turkwell in a remote area of Northern Kenya, with a BOD of 2045 µg g^{-1}, as an example. However, since Qua Iboe river at Ikot Ekpene receives drainage and seepage from an unsewered urban area, the BOD level reported in this study does not represent the natural BOD, especially when viewed against the BOD levels in the other two streams. It is therefore plausible to regard it as indicating pollution.

A closer look at Table 6 shows that the level of the measured physicochemical characteristics of the neutralized batteries factory effluents are satisfactory, but since Atan stream receives the treated effluents, it was initially difficult to link the higher concentrations of some metals in Atan stream fishes (*T mariae* and *C. guntheri*) against the lower concentrations of the same metals in Nkap stream fishes (*T mariae* and *A. fasciatus*) to the batteries factory effluents, especially since cadmium concentration in *T. mariae* from Nkap stream is higher than that in *T. mariae* from Atan *stream*. Interestingly however, factory sources revealed that occasionally the raw effluents in the neutralization tank may overflow before actual treatment is effected (due probably to negligence) and the overflowed effluent discharged untreated into Atan stream. It is easy to visualize that in such circumstances, a potential exists for such metals as are present in the effluent to add to the previous level of the corresponding metals in the receiving stream. Since Nkap stream is not contaminated with heavy metals from point discharges, the higher level of cadmium in *T. mariae* from Nkap stream over that in *T. mariae* from Atan stream could be understood on the basis that in the absence of contamination, the tendency for some metals to be lost is very small, due to the formation of stable and insoluble storage products (Bryan, 1969). Elucidation of the merchanisms and factors governing uptake of metals by aquatic organisms in our waters would be of immense value.

The mean concentrations of lead and chromium reported in this study are relatively high (Van Hassel et al. 1980, Bebbington et al 1977; Giesy and Wiener, 1977). Due to lack of adequate information on toxic levels of metals in fish and other aquatic life in local waters, it is difficult to state categorically whether the fishes in these streams could be adversely affected or not by these concentrations. The Australian National and Medical Research Council gave 2.0 µg g^{-1} as the standard for lead in sea foods. Sastry and Tyagi (1982) exposed the fresh-water fish, *Channa punctatus* to 2.6 mg l^{-1} hexavalent chromium Cr(VI) (a concentration described as sublethal) for 30 days and reported physiological indices of stress in the exposed fish. *Chana obscurus* in the present study has a mean chromium concentration of 4.28 ug g^{-1} with a range of 2.50 — 6.0 µg g^{-1}. In a bioassay experiment on the clam, *Eqeria radiata* Lam, using cadmium and lead, Akpan (1987) obtained very high 96-hr LC 50 values of 21.38 and 219.00 mg l^{-1} for cadmium and lead respectively. Cadmium toxicity in the presence of lead was reduced while lead appeared not to have exhibited any toxicity than when alone. Imevbore (personal communication with Udoidiong) explained that the high LC 50 values were due to the use of the river (Cross River) water for the bioassay, pointing out that the presence of humic substances in the river water was likely to enhance the reduction of toxicity of the metals to the clams. Many of our streams contain humic substances which are known to act as chelating agents. Chelation keeps the element in solution and non toxic (Odum, 1971), though at high concentrations humic substances are toxic (Barter and Carey, 1982), in which case they could act as light-absorbing sensitizers.

The similarity in concentrations of mercury and chromium in the four fish species in the three streams suggest natural occurrence, but the same is not true for other metals particularly zinc and Lead. Higher zinc and lead levels in Qua Iboe river possibly derive from both domestic sewage and drainage from automobile workshops as well as possible negligence on the part of the staff attached to the neutralization unit of the Sunshine batteries industry are suspected to be responsible for elevated levels of the metals in Atan stream. The standards set by the Australian National Health and Medical Research Council for some metal concentrations in sea foods are Hg (0.5 µg g^{-1}); Cd (2.0 µg g^{-1}); Cu (30.0 µg g^{-1}); Pb (2.0 µg g^{-1}); Zn (1000.0 µg g^{-1}), (Bebbington et al; 1977).

Based on these standards, zinc concentrations reported here are well below the 1000.0 µg g^{-1} (wet weight) recommended. Similarly Cu, Cd and Hg have respective mean concentrations of 30.0 µg g^{-1}, 2.0 µg g^{-1} and 0.5 µg g^{-1}. These are well above those reported for these metals in this study. The above four metals (Zn, Cu, Cd and Hg) do not therefore pose health hazards.

On the other hand, lead, cobalt, antimony and Chromium have relatively high concentrations. Lead antimony concentrations are high because antimonial lead is one of the raw materials used in the production of batteries. Chromium, Cobalt and lead are constituents of paints and it is reasonable to presume their presence in run-off waters which may contain among other materials, paint wastes containing pigments from spraying workshops, new or renovated buildings. All the above metals also occur naturally especially in water.

It is pertinent at this stage to point out that our failure to formulate trace metal standards suitable for our environment, and complacency on the use of standards from temperate countries to explain tropical data, is fraught with danger and should be reappraised if our research reports on trace metals and pollution generally are to be meaningful, especially now that we are witnessing increased urbanization and industrialization in the country.

Conclusion

From results of analyses, levels of metals in fish in the three streams under study are found to be in general in the order: Atan stream > Qua Iboe River >> Nkap stream. These results which show Atan as the most polluted of the three streams reveal that fishes are better specimens for use in the study of contamination levels of natural waters than the water samples.

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