J. Sci. Engr. Tech. 8 (2) : 3312 - 3321 June 2001

LEVELS OF LEAD, COPPER AND IRON IN FISH FROM SOME STREAMS WITHIN A RAVINE IN UYO MUNICIPALITY, NIGERIA.

E.D. Udosen+ and J.P. Essien*
Department of Chemistry and Biochemistry
University of Uyo, Uyo , Nigeria.

ABSTRACT

The levels of three toxic metals (Pb, Cu and Fe) were determined in seven species of fish: Malapterurus electricus (F_1), Auchenoglanis fasciatus (F_2), Brienomyrus brachyistius (F_3), Chromidotilapia guntheri (F_4), Hopsetus (F_5), Papyrocranus afer (F_6), and Bryarius longipinnis (F_7) from some streams within a ravine in Uyo municipality in Akwa Ibom State of Nigeria. The results obtained showed very high mean concentrations of Pb (13.12 ugg^{-1}) in F_1, (12.04ugg^{-1}) in F_6 and (8.76ugg^{-1}) in F_7 samples while levels of Fe were high only in F_1 (11.03 ugg^{-1}), F_5 (11.23 ugg^{-1}) and F_7 (9.71 ugg^{-1}). Mean levels of Cu were equally high in all fish samples except F_4, F_5 and F_6. The coefficient of variation (C.V) also remained highest for Pb in F_3 (43.52%) while that for Cu in F_6 was the least (0.00%). When compared with other research findings and international standards, the results revealed that the streams investigated were relatively polluted by lead, copper and iron.

INTRODUCTION

Heavy metals are common components of natural waters and although some are essential for living organisms, others may become highly toxic when present in high concentration (1). When present in natural waters, these metals could enter the food chain, become bioaccumulated in aquatic organisms including fish and later become biotransferred to man, the ultimate consumer of these organisms. Moreover, metals cannot be degraded biochemically in nature. The stability of these metals therefore allows them to be transported for considerable distances by water. As a result of this process, the levels of metals in the upper members of a food

+ To whom all correspondence should be addressed.
* Present address: Department of Botany and Microbiology, University of Uyo, Uyo, Nigeria.

chain can reach values sufficiently high to become health hazards when such organisms are used as food.

The pollution of our natural waters by metals commonly results from the discharge of industrial effluents into these waters (2). Such effluents often accelerate the degradation of the water quality and increases the mortality rate of aquatic organisms living in the waters.

The uptake of metals in fish and fish organs and the potential use of fish in environmental assessment programmes depend on factors such as species of fish, fish organs, modes of metal uptake and release and environmental factors (3). Metal concentrations in fish have also been related to morphology of fish, differences among species and fish weight within populations (4-7). Thus acting singly or in contact with other factors, pollutants such as toxic metals could cause large numbers of organisms to die more or less simultaneously. Hester (8) identified some toxic metals including Pb and Cu to be potentially hazardous to aquatic organisms or to man through consumption of such organisms. Many recent works on water pollution have shown that heavy metals are the commonest contaminants and that these metals often cause damage to aquatic plants and animals particularly fish (1 and 2). For a country like Nigeria where fish is the commonest source of protein, contamination of aquatic environments deserve serious attention. All the streams found within Uyo ravine (which receive most of the municipal run off and effluents discharge from the University of Uyo and a Public Hospital at Anua) finally empty into Ntak Inyang river which is a tributary of Cross River that flows into the Atlantic Ocean. Since fish is a reliable bioindicator of pollution, the determination of heavy metal levels in fish from the ravine could serve as a reliable method of assessing the extent of contribution to the pollution load of the Ntak Inyang river and hence of Cross River by the already polluted streams within the ravine.

Primarily, the aim of this study was to determine for nutritional purposes the content of Pb, Cu and Fe in seven fresh water fish commonly found in some streams within a ravine in Uyo municipality. Attempt was not made at correlating toxic metals and degree of contamination of the streams. Moreover the control of contamination of these streams is very difficult since the streams do not belong to a particular interest group or community.

MATERIALS AND METHOD

Several species of fish were randomly sampled over a period of six months from four different streams within the Uyo ravine (Fig. 1). Three sampling gears including the use of hook and line, nets and local traps (Ikpa) were employed. The nets and local traps (Ikpa) were usually set at dusk and inspected at dawn (9).

After collection, the fishes were usually put into a portable aquarium and taken to the laboratory for identification and classification and later stored in a refrigerator prior to metal determination (10). A total of seventy specimens representing seven species were selected and used for the investigation.

Each fish was filleted both sides using a stainless knife. The muscle was homogenized by grinding it in a mortar. The homogenized sample (5.0g) was digested with a mixture of trioxonitrate (V) acid (HNO_3) and tetraoxochlorate (VII) acid ($HCLO_4$) in the ratio of 2: 1 (i.e. $10cm^3$ of HNO_3 to $5cm^3$ of $HCLO_4$). The mixture was then evaporated in a sand bath inside a fume cupboard. The white cake residue formed was dissolved in $10cm^3$ of nitric acid (20%). The solution was then finally diluted to $30cm^3$ with ultrapure water and later analysed using an atomic absorption spectrometer (A.A.S), Unicam 9.9. Solar system. No correction for background absorption was made since the background absorption was found to be very low. Detection limits were: Pb (0.01), Cu (0.004) and Fe (0.006). Recoveries of over 98% were obtained for each element.

RESULTS AND DISCUSSION

Table 1 contains the mean concentrations and range as well as the standard deviations and coefficients of variation of the three metals (Pb, Cu and Fe) in each of the seven species ($F_1 - F_7$) of fish collected within the sampling site (Fig. 1). Fig. 2 gives the comparison of mean metal concentrations in the fish samples. Fig. 3 illustrates the coefficients of variation of metals in the fish samples.

There seems to be no particular concentration pattern in the different fish species sampled. In *Malapterurus electricus* (F_1), mean Pb level was the highest ($13.12\mu gg^{-1}$) while mean Cu content was the least ($1.07\mu gg^{-1}$). Lead (Pb) also had the highest coefficient of variation of 18.83% (Table 11). In *Auchenoganis fasciatus* (F_1), Pb content was still the highest ($6.56\mu gg^{-1}$) while Cu was the least ($0.45\mu gg^{-1}$). The coefficient of variation was equally the highest for Pb (16.31%) followed by that for Fe (13.29%). In the case of *Brienomyrus brachyistus* (F_3), Fe had the highest mean value of 3.31μgg^{-1} followed by Pb with a mean level of 2.16μgg^{-1}. However, the coefficient of variation remained the highest for Pb (43.52%) followed by Fe (11.78%). *Chromidotilapia guntheri* (F_4) recorded the highest mean Fe content of 3.31μgg^{-1} followed by a mean concentration of 4.53μgg^{-1} for Pb and 0.10μgg^{-1} for Cu. Surprisingly, Cu had the highest coefficient of variation of 20.00%. In *Hepsetus odoe* (F_5), Fe content was the highest (11.25μgg^{-1}), followed by Pb (6.90μgg^{-1}). However, the coefficient of variation for Pb was the highest (10.00%), followed by that for Fe (3.38%). In the cases of *Papyrocranus ager* (F_6) and *Bryanus longipinnus* (F_7), Pb levels were the highest (12.04μgg^{-1}) and (8.76μgg^{-1}) respectively while Cu contents were the least (0.00μgg^{-1}) and (0.07μgg^{-1}) respectively (Table 1). The coefficients of variation was found to be comparatively much higher (42.86%) for Cu in *Brycinus longipinnus* (F_7) species than in *Papyrocranus ager* (F_6) species (0.00%).

Considering the metal levels in the species, Pb was found to exhibit the following trend: $F_1 > F_6 > F_7 > F_5 > F_2 > F_3$ (Table 1). For Cu, the trend was $F_5 > F_1 > F_2 = F_3 > F_4 > F_7 > F_6$ while for Fe, the trend was $F_5 > F_1 > F_7 > F_6 > F_2 = F_3 = F_4$ (Table 1). There was therefore no definite or regular trend in the metal levels in all the fish species analysed.

Since the Pb concentration in all the fish species fell outside the range of 0.003 – 0.07μgg^{-1} obtained for fish from unpolluted waters in other parts of the world, the streams within Uyo ravine could be said to be polluted by Pb (11 – 13). Moreover, based on standards set up by the Australian National Health and Medical Research Council (NMRC) for Pb (2.0μgg^{-1}) in sea food, the mean levels of 13. 12μgg^{-1} in F_1, 6.56μgg^{-1} in F_2, 2.16μgg^{-1} in F_3, 4.53μgg^{-1}in F_4, 6.90μgg^{-1}, in F_5, 12.04μgg^{-1}, in F_6 and 8.76μgg^{-1} in F_7, samples are high enough to cause serious health problems to individuals who may happen to consume them (2 and 14).

This deduction is arrived at following the experimental evidence for the existence of carcinogenicity (renal tumours) of inorganic lead in rat after oral ingestion of high doses of Pb (15). Moreover, at concentratiobn lower than 0.05 ppm which is the maximum total lead permitted in drinking water in the United States and Nigeria, fish may suffer toxic effects or become adversely affected (16 and 17).

The levels of Cu in all the fish samples particularly F_1, F_2, and F_5, were quite high and worrisome. Cu is almost always elevated in the gills, Liver, pancreas and other internal organs (15). Copper is one of the most toxic heavy metals to fish and its toxicity depends on the degree of hardness of the water in which they live. The LC $_{50}$ of copper typically ranges between 0.02 and 1.0mg Cu/L in fresh water (18). An increase in water hardness to approximately 500mg/L as $CaCO_3$is said to increase the enhanced synergistically by combinations of C/Al/Zn, Cu/Cd/Zn, Cu/Zn, Cu/Zn/Ni, Cu/Zn/phenol, and Cu/H^+ (18). However organic sequestration always significantly reduces acute toxicity. Therefore although several species of fish have the ability to adapt to potentially toxic copper levels, at least temporarily, yet this ability reduces if the water is reasonably hard owing to the presence of $CaCO_3$, ionic (Cu^{2+}) and its hydroxides ($Cu_2OH_2^{2+}$, $CuOH^+$) which are very toxic (18) There are however only a few cases of acute poisoning by Cu and its salt. The chief symptoms following ingestion of Cu are epigastric burning, nausea, vomiting, and diarrhea (19). There may also be lesions in the gastrointestinal tract and induction to hemolytic anemia. On the whole, chronic Cu poisonings is rarely reported, except for individuals suffering from a congenital disorder known as Wilson's disease.

The levels of Fe were generally quite high to warrant concern particularly in F_1, F_2, F_5, and F_7 species. However, Fe is rarely a toxicologically significant contaminant of fish tissue and often occur in high concentration (20-22). Since the lethal concentration (LC_{50}) of total Fe to fish generally range from 0.3 to >10mg/L depending on species and test conditions, the levels of Fe in the fish samples could lead to some of the health effects such as vomiting, gastrointestinal bleeding, pneumonities, convulsion, coma and jaundice often associated with acute exposure to Fe (15). In some cases, a generalized increase in Fe content (known as Remosiderosis) occurs, in other instances, a specific deposition may lead to localized fibrosis. Although this condition is relatively benign, some studies have indicated that it is accompanied by abnormal glucose metabolism and increase heart disease.

CONCLUSION

The results of the research have revealed that the streams within the ravine are to some extent polluted by the heavy metals Pb, Cu and Fe. It is suspected that the metals may have been introduced into these streams by the discharges into the ravine by small scale industries, production.

industries, other industries associated with these metals and run off through refuse dumps, mechanic workshops, petrol filling stations and agricultural farms. Infact Udosen et al (23) had earlier warned of the dumping of paint wastes into this ravine. The metals so accumulated by the fish in these streams could become biomagnified in the muscles and later biotransferred to consumers. The result could be undue interference with the normal physiological functioning of the body which in turn could cause untold damages ranging from nervous malfunctioning to death.

TABLE 1. METAL CONCENTRATIONS (μgg^{-1}) IN FISH SAMPLES

S/N	SAMPLE		METALS/CONCENTRATIONS		
			Pb	Cu	Fe
1	F_1	Mean	13.12	1.07	11.03
		Range	9.05-16.11	0.98-1.20	10.01-11.90
		Std. Dev.	2.47	0.07	0.47
		Coeff. Of Variation	18.83%	5.54%	4.26%
2	F_2	Mean	6.56	2.45	8.31
		Range	5.00-8.30	0.60-3.50	2.77-4.00
		Std. Dev.	1.07	0.03	0.44
		Coeff. Of Variation	16.31%	6,67%	13.29%
3	F_3	Mean	2.16	0.45	3.31
		Range	1.03-3.60	0.40-0.50	2.78-3.79
		Std. Dev.	0.94	0.03	0.39
		Coeff. Of Variation	43.52%	6.67%	11.78%
4	F_4	Mean	4.53	0.01	3.31
		Range	3.60-5.60	0.07-0.15	2.79-86
		Std. Dev.	0.73	0.02	0.36
		Coeff. Of Variation	16.11%	20.00%	10.88%
5	F_5	Mean	6.90	1.16	11.25
		Range	5.88-8.00	1.13-1.19	10.67-11.90
		Std. Dev.	0.69	0.02	0.38
		Coeff. Of Variation	10.00%	1.72%	3.38%
6	F_6	Mean	12.04	0.00	5.07
		Range	10.33-13.05	0.00	4.50-5.90
		Std. Dev.	0.91	0.00	0.36
		Coeff. Of Variation	7.56%	0.00%	6.90%
		Mean	8.76	0.07	9.71

7	F_7	Range Std. Dev. Coeff. Of Variation	7.50-9.98 0.65 7.48%	0.04-0.12 0.3 42.86%	9.05-11.30 0.63 6.49%

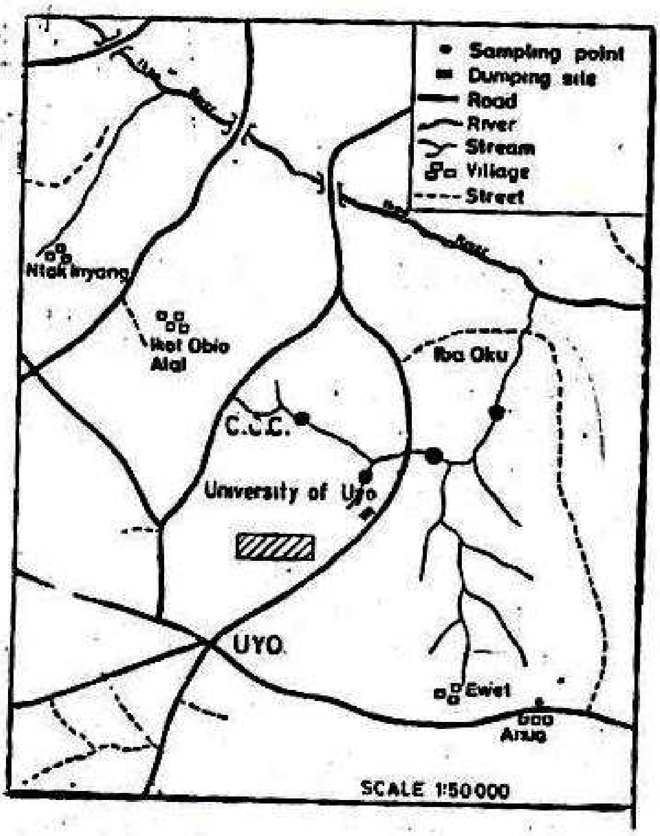

Fig. 1. Part of Uyo showing the sampling site.

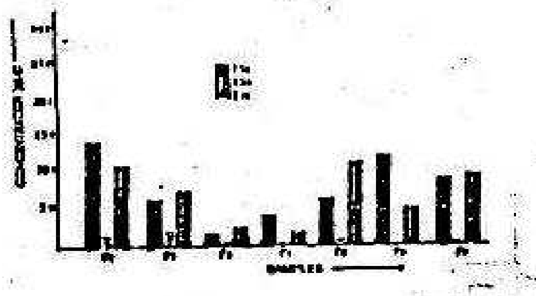

Fig. 2. Comparative levels of metals in the fish samples.

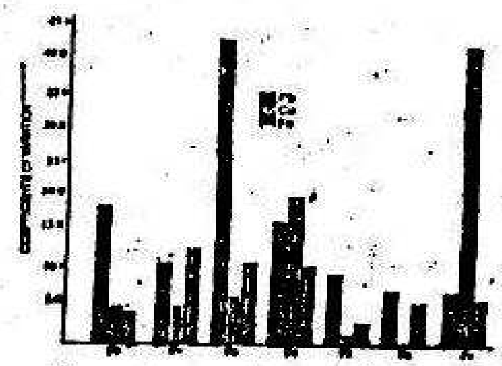

Fig.3. Comparative coefficients of variation of metals in the samples.

REFERENCES

1. Ibok,U.J.,Udosen,E.D.and Udoidiong, O.M.Heavy metals in fishes from some streams in Ikot Ekpene Area of Nigeria. Nig.J.Tech.Res. 1: 61-68.1989.
2. Udosen, E.D.Trace metal levels in *Arthropteris orientalis* from battery industrial environment. Global J. of Pure and Applied Sciences.4(1): 35 42.1998.
3. Hakanson, L. Metal in fish sediments from the river Kolbacksan water system. Arch. Hydrobiol.101:373-400.1984.
4. Johnson, G.M.Trace elements loadings to sediments of fourteen Ontario Lakes and correlations with concentration in fish . Canad. J. Fish Aquat. Sci. 44:3-13.1987.
5. Saiki.K.M. and May, W.T. Trace residues in bluegills and common carp from the lower San Joaquin river, California and its tributaries. Sci. Total Environ. 74:199-217.1988.

6. Wren, D.C. and MacCrimmon. R.H. Comparative bioaccumulation of mercury in two adjacent freshwater ecosystems. Water Res.20: 763-769.1986.

7. Wren, D.C., MacCrimmon.R.H. and Loescher, R.B. Examination of bioaccumulation and biomagnification of metals in a Precambrian shield lake. Water, Air and Soil Pollution. 19:277-291.1983.
8. Hester, F.J. Economic aspects of the effects of pollution on the marine and Anadromous Fisheries of the Western United States of America. FAO Fish Tech. Pap. 162:34.1976.
9. Udoidiong, O.M. A comparative survey of the fish communities of two Nigerian Headwater streams in relation to man made perturbations. 45: 93-108.1988.
10. A.W.W.A. Standard Methods for the examination of water and waste water includind bottom sediment and sludges. 15th ed.APHA-AWWA-WPCF. PP.148-157.1980.
11. Byran.G.W.Some aspects of heavy metals tolerance in aquatic organisms. In: Lockwood A.P.M.(ed.). Effects of pollutants on aquatic organisms. Cambridge University Press. Cambridge. P.7. 1976.
12. FAO. Co-ordinated project on pollution in the Mediterranan- A Report, No. 3. Cir. Gen.Fish. Coun. Mediterr. 7.1978.
13. Udosen, E.D. Aquo-Terrestrial Environmental Pollution Studies of inorganic substances from two industrial firms un Akwa Ibom State, Nigeria.Ph.D. Thesis. P.575.1991.
14. W.H.O. Guidelines for Drinking Water Quality. Vol.2. Health and other supporting information. World Health Organisation, Geneva. PP.85-315.1984.
15. Moore, James W. Inorganic contaminants of surface water. Springer- Verlag. New York. P.334.1991.
16. F.E.P.A. Guidelines and Standards for Environmental Pollution Control in Nigeria. Federal Environmental Pollution Agency (FEPA) . P.238. !991.
17. W.H.O. In W.H.O. Technical Report Series No.505. Evaluation of certain food additives and the contaminants: Mercury, Leadand Cadmium. PP.85-119. 1972.