Journal of Applied Sciences. 7 (2) : 4229 – 4240 June 2004

VARIATIONS IN TRACE METAL LEVELS IN SEDIMENTS FROM IKPA RIVER IN ITU AREA OF AKWA IBOM STATE, NIGERIA.

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(Accepted 16 October 2003)

ABSTRACT

The levels of six trace metals (Ni, Cu, Mn, Pb, Zn and Fe) in sediments collected from Ikpa River which receives rubber effluent and those of one of its tributaries were determined during wet and dry seasons using atomic absorption spectrophotometer. The levels of all metals in water from an effluent discharge point in Ikpa River (S_2) and ravine water, down stream (S_5) were higher than those from upstream ravine water samples (S_3 and S_4). The coefficients of variation of these metals were 15.05% and 29.84% for Ni; 54.99% and 48.19% for Cu; 59.38% and 68.43% for Mn; 28.35% and 39.87% for Pb; 47.79% and 118.49% for Zn and 6.97% and 6.29% for Fe during wet and dry seasons respectively. Similarly the degree of accumulation of all the metals at S_1 was 1.00 while variations in the degree of accumulation of these metals occurred at other sites depending on the types of the metals and the corresponding sites. The health implications of the presence and accumulation of these metals in the river and its tributary on man have been discussed based on national and international standards.

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 creating. The majority of these industries are sited near natural water bodies and their wastes containing metals are often discharged directly or indirectly into them (1).

The toxic metals (Ni, Pb, Zn and Cr) can enter the terrestrial environment via natural processes such as rock and soil weathering as well as geothermal reactions. They could also be introduced into the aquatic environment anthropogenically through industrial processes and other activities. All the above activities contribute directly or indirectly to increase levels of these metals in tissues of living organisms (2).

When industries discharge their wastes into any aquatic and / or terrestrial environments, the wastes are transformed depending on the nature of the receiving environment and the prevailing conditions. For instance, speciation of metals may occur in a reducing environment resulting in their easy absorption by plants. However, the concentration of these metals especially in vegetables and fruits depends largely on factors such as inherent qualities of plants, trace element content of sediment and soil, geographical location as well as the use of fertilizers and fungicides (3).

Trace metals trapped by sediments and their mobilities and reactions in the sediments and subsequent uptake and distribution in plants are therefore of critical importance in relation to man's health. Stream sediments appear to serve as the storage reservoir and primary sources of heavy metal bio-concentration. However, metals are not necessarily retained permanently by the sediment but can be recycled via biological and chemical agents into the water column.

The study area

Ikpa River is a small perennial rainforest tributary stream that is located in the lower ridges of the Cross River in South Eastern Nigerian. The stream has a main channel with a total length of

53.57 km from its source in Ikono Local Government Area of Akwa Ibom State and discharges into the Cross River close to Nwaniba (Fig. 1).

Ikpa River has a watershed area of 516km^2 of which 76m^2 (14.8%) of the lower ridges is liable to annual flooding of the fringing low land. The non-flooding zone of the upper ridges has a basin area of 440km^2 (85.2%) and mean depth and width of 12.5m respectively. The entire length of the main channel of the stream lies at the interface of two different geological deposits viz. tertiary sediment or rocks and cretaceous deposits (4).

MATERIALS AND METHOD

Portions of the sediments were collected with a core sampler. Samples from each site were then made into composite samples 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 downstream of Ikpa River (S_1), effluent discharge point (S_2), upstream (S_3), ravine upstream (S_4), and ravine downstream (S_5). 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 hr to eliminate undesirable materials. The dried samples were ground and homogenized using mortar and pestle before sieving through a 2mm screen.

Each sample (1.0g) was weighed into a beaker (100cm^3) and 10cm^3 nitric acid was added. This was then heated to dryness. Thereafter HNO_3 (10cm^3) and $HClO_4$ (3cm^3) were added and the solution heated to fume.

The sample solution was obtained by processing the residue with hot 6mol/HCl (4cm^3) and then filtered and diluted with water to 50cm^3. This solution was then used for metal determinations in Atomic Absorption Spectrophotometer (5).

RESULTS AND DISCUSSION

The seasonal concentrations of the metals Ni, Cu, Mn, Pb, Zn and Fe and their coefficients of variation are given (Table I, Figs. 2 and 3). The first two metals exhibited very low concentrations in sediments when compared to Mn and Zn, which were high. Iron exhibited the highest concentration in sediments during both dry and wet seasons with correspondingly low coefficient of variation (Tables I and II). Lead levels at the five site varied slightly during both seasons as shown by the coefficients of variation for wet season (28.35%) and dry season (39.87%) (Tables I and II).

However, although zinc levels were low, variations between sites were high, being 47.79% and 118.49% respectively for wet and dry seasons (Tables I and II). Apart from Ni with the highest mean concentration of 0.17μgg^{-1} occurring at two sites (S_1 and S_5), the other metals except Fe were less accumulated in S_2 sediments. Similarly, the mean levels of these metals except Ni were generally high in S_5 site (Table III).

The concentration of metals at one point in water could be influenced by their concentrations at other points and their corresponding sediments. The concentration of Fe in a discharged rubber 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. Fishes could easily take up this metal since most of their food is derived from sediment and on consumption could be lethal to man. This is likely to apply to other metals also present in the discharged effluent.

The results of analysis of the river sediments from five sites during wet and dry seasons show that mean levels of Fe were 37.28μgg^{-1} in S_1; 41.56μgg^{-1} in S_2; 37.57 in S_3; 40.96μgg^{-1} in S_4 and 42.53μgg^{-1} in S_5 giving a trend of
$S_5 > S_2 > S_3 > S_2 > S_1$ (Table3). Fe levels in sediments from all the other sites were higher than the levels of Fe in S_1 sample. The levels of Fe in aquatic lives including fishes are likely to be affected by the levels of Fe in these sediments. The metal levels

varied more during the wet season than in the dry season (Tables I and II). The very high levels of Fe in S_5 compared to S_3 sample must have been due to contribution of Fe to this site by the discharged effluent. The mean level of Fe in sediment was higher in site S_5 than S_4 due possibly to the slow movement of the water and the possible high absorption ability of the metals by this sediment. Thus, the high Fe levels in S_2, S_3, S_4 and S_5 sediment suggest possible contamination of these sediments by Fe metal.

The mean seasonal concentrations of Mn in the sediments from the five sites were S_1 (0.72 μgg^{-1}), S_2 (0.64μgg^{-1}), S_3 (0.67μgg^{-1}), S4 (0.69μgg^{-1}) and S_5 (1.96μgg^{-1}). The trend was therefore $S_5 > S_1 > S_4 > S_3 > S_2$ (Table III). The concentration of manganese was higher in S_5 sediment than in S_1 sediment. This must have been due to the contribution of Mn to the S_5 sediment by urban runoff. This suggests that the rubber effluent did not contribute to Mn contamination in the river. The mean seasonal concentrations of Pb in sediments at S_2 and S_4 sites were (0.37μgg^{-1}), while the levels in S_3, S_1 and S_5 sediments were 0.52μgg^{-1}, 0.52μgg^{-1} and 0.69μgg^{-1} respectively (Table III). These gave a trend of $S_5 > S_1 > S_3 > S_2 = S_4$.

The level of Pb in S_5 was significantly greater than in S_3 sediment. This may mean that S_5 site received more Pb- laden wastes from Uyo metropolis and the ravine, which receive mixed wastes from several sources including mechanic workshops and the University of Uyo medical centre. It was established that any polluted sediment should have much Pb deposit in it (6). The presence of lead is still risky to life since fishes and other fauna are particularly very sensitive to lead and often retain about 1% of ingested lead which could be taken up by man, the ultimate consumer (7).

The seasonal levels of copper in the sediments from the five sites were S_1 (0.42μgg^{-1}); S_2 (0,16μgg^{-1}), S_3 (0.20μgg^{-1}), S_4 (0.19μgg^{-1}) and S_5 (0.51μgg^{-1}) (Table III). These gave a trend of $S_5 > S_1 > S_3 > S_4 > S_2$. The source of high copper level in S_5 may have been natural or anthropogenic or a combination of both. The high level in S_1 suggests a contribution of copper by the factory effluent to the sediment. Runoff from town could have also introduced copper to the river and the sediment could have trapped this.

The mean seasonal levels of Ni in the river sediment from the five sites were S_1 ($0.17\mu gg^{-1}$); S_2 ($0.16\mu gg^{-1}$); S_3 ($0.14\mu gg^{-1}$); S_4 ($0.14\mu gg^{-1}$) and S_5 ($0.17\mu gg^{-1}$) (Table III). These gave the trend $S_1 = S_5 > S_2 > S_3 = S_4$. The degree of variation in the nickel levels in the sediments from the five sites during wet and dry seasons were 15.0% and 29.27% respectively. This may have been due to Ni present in the effluent in addition to natural occurrence.

Generally, the presence of these metals, especially their salts in the environment is risky since these salts are poisonous (8). When discharged into a river, the metals can enter the food chain, become bio-accumulated in fish and later bio-transferred to man, the ultimate consumer of fish (1). This metal could become a threat to aquatic lives particularly fishes, which happen to take the bulk of their food from sediment.

The consumption of Pb in high concentration could result in the deadening of nerve receptors, decline intelligence in children, impairment of hair, red blood nucleotide metabolism, perturbation of calcium homeostasis in the hepatocytes, and bone cells. Generally, acute Pb poisoning causes stomach pains, headaches, tiredness, lassitude, dizziness, anaemia, tremor, fatigue, constipation, neuritis, seizures, general weakness, insomnia, hypertension, renal dysfunction, sperm count suppression and in severe cases coma and death (2 and 9).

The high levels of Cu recorded in the samples could be absorbed by plants and subsequently transferred to animals and man. When taken in excess the metal could lead to mucosal irritation, nausea, vomiting, diarrhea, intestinal cramps, severe capillary damage, hepatic or renal damage and of course nervous system irritation followed by depression. Possible necrotic changes in the liver and kidney could also occur (10 and 11)

Iron is an essential element in human nutrition (12). However, iron could also present serious pollution problems when available in high concentration. Above 0.3mg/1 it could result in a condition known as haemochromatosis wherein tissue damage results from its accumulation. Small children have been poisoned following the ingestion of large quantities of iron tablets (13). Consumption of excess amount of Mn could lead to cardiovascular mortality (14). Absorbed Mn leaves the blood stream quickly and concentrates in the liver. When Mn concentrates in the liver, it conjugates in the liver. There might be an association between Mn deficiency and disorders such as anaemia and abnormalities in children (15).

Ni in some forms is likely to be carcinogenic in human even though clinical or epidemiological studies were not available on the effects of oral ingestion of Ni (16). According to them in addition to evidence of statistically significant elevations of respiratory cancers among refinery workers, very high concentrations of this metal have also been recorded in the liver, kidney and brain of humans. This presupposes that Ni could accumulate in tissues of organisms with high metabolic activity whenever it occurs in excess.

Excessive intake of Zn may lead to vomiting, dehydration, electrolyte imbalance, abdominal pain, nausea, lethargy, dizziness and lack of muscular coordination (17). Acute renal failure caused by zinc chloride has been reported.

CONCLUSION

All metal levels except Ni were higher in S_5 sediments than S_1 sediments indicating probable contribution of some amount of these metals by anthropogenic sources to the Ikpa River tributary (ravine stream). Fe was found to be exceptionally high in S_5 during wet season indicating the presence of large amount of Fe in the

Table I. Levels of metals in sediment (μgg^{-1}) during wet season and their coefficients of variation.

Metal	S_1	S_2	S_3	S_4	S_5	X	S.D	CV
Ni	0.297	0.234	0.211	0.2008	0.239	0.238	0.036	15.05
Cu	0.723	0.224	0.298	0.302	0.736	0.457	0.251	54.99
Mn	1.095	0.820	0.744	0.715	2.317	1.138	0.676	59.38
Pb	0.816	0.459	0.816	0.502	0.875	0.694	0.197	28.35
Zn	1.856	0.591	0.937	1.164	2.116	1.333	0.637	47.79
Fe	40.80	45.174	39.28	42.562	46.496	42.86	2.99	6.97

Table II. Levels of metals in sediment (μgg^{-1}) during dry season and their coefficients of variation.

Metal	S_1	S_2	S_3	S_4	S_5	X	S.D	CV
Ni	0.045	0.072	0.076	0.081	0.109	0.077	0.023	29.84
Cu	0.122	0.111	0.095	0.148	0.275	0.150	0.072	48.19
Mn	0.349	0.461	0.587	0.655	1.599	0.730	0.499	68.43
Pb	0.292	0.275	0.221	0.232	0.522	0.308	0.123	39.87
Zn	0.407	0.413	0.261	0.565	2.704	0.870	1.031	118.49
Fe	33.759	38.544	35.89	39.36	38.55	37.22	2.34	6.29

Table III. Mean seasonal levels of metals in sediment (μgg^{-1}) and their degree of accumulation (in parenthesis).

Metal	S_1	S_2	S_3	S_4	S_5
Ni	0.17 (1.00)	0.16 (0.94)	0.14 (0.82)	0.14 (0.82)	0.17 (1.00)
Cu	0.42 (1.00)	0.16 (0.38)	0.20 (0.48)	0.19 (0.45)	0.51 (1.21)
Mn	0.72 (1.00)	0.64 (0.89)	0.67 (0.93)	0.69 (0.96)	1.96 (2.72)
Pb	0.55 (1.00)	0.37 (0.67)	0.52 (6.95)	0.37 (0.67)	0.69 (1.25)
Zn	1.13 (1.00)	1.00 (0.88)	0.59 (0.52)	0.86 (0.76)	2.41 (2.13)
Fe	37.28 (1.00)	41.56 (1.11)	37.59 (1.01)	40.96 (1.09)	42.53 (1.14)

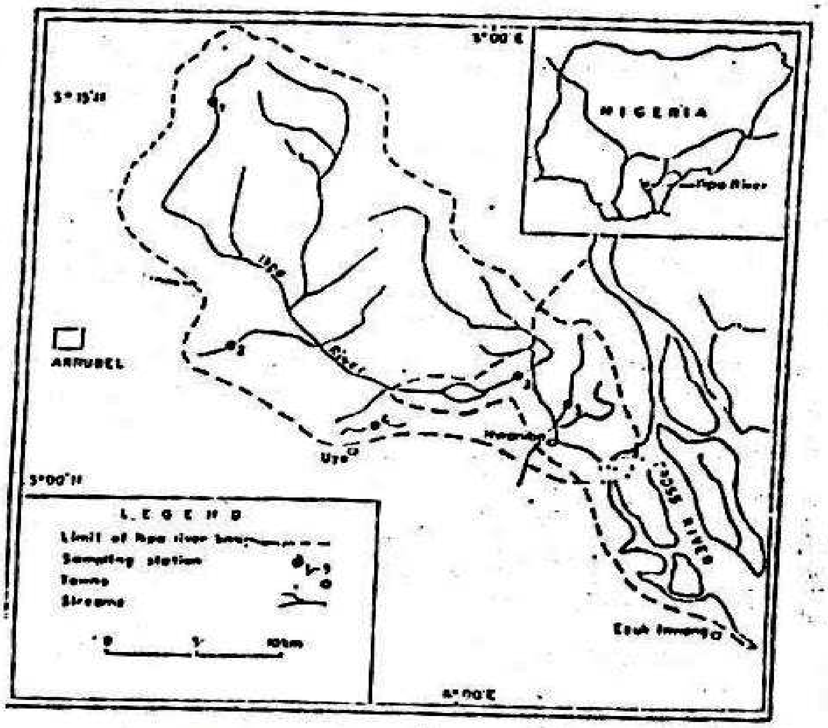

Fig. 1. Ikpa River showing the sampling stations

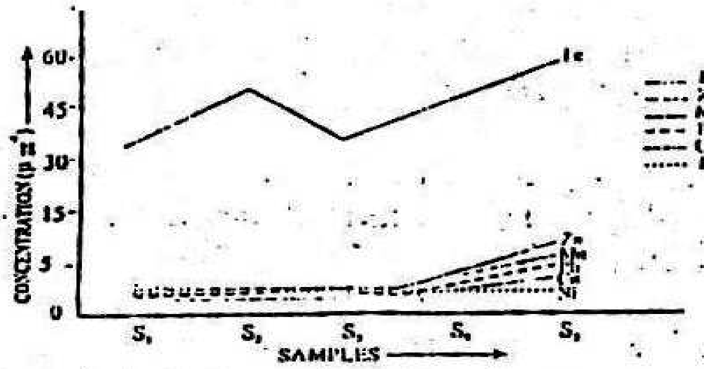

Fig. 2. Mean concentration ($\mu g g^{-1}$) of Ni, Cu, Mn, Pb, Zn and Fe in sediments

runoff from town and University of Uyo ravine. The accumulation of all these metals in all the samples supports the general view that sediments are not just traps or sinks for trace metals, but their reservoir.

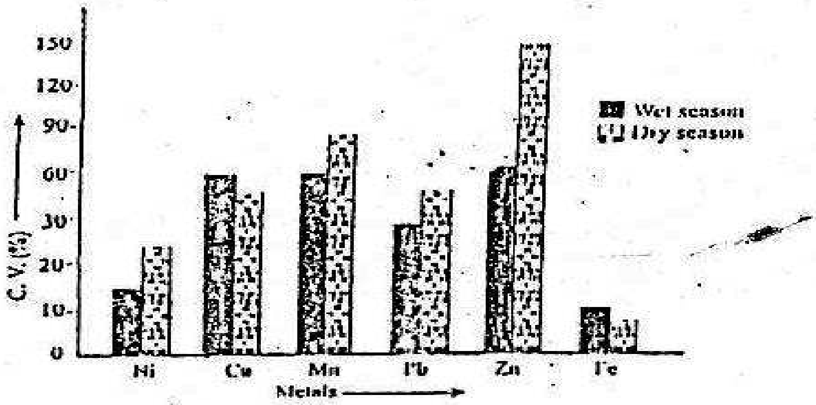

Fig. 3. Mean seasonal coefficient of variation of metals in the sediment during (a) wet season and (b) dry season.

REFERENCES

n, E. D. Levels of Trace Metals in Sediments from ›oc River and its Tributaries. J. Sc. Engr. Tech. 5 (1) : 982 - 991. 1998.

2. Udosen, E. D. Levels of Toxic Metals in *Achatina achatina* from parts of Akwa Ibom State, Nigeria. Journal of Environmental Science Beijing, China. 12 (1) : 68 - 74. 2000.
3. Rao, M. N. The Need for More Information on the Trace Element of Food for Improving Human Nutrition. International Atomic Energy Agency. Vienna. Technical Reports Series. 197 : 29 - 37. 1980.

4. Clausen, H. S. Correlation of Ichthyofaunal Distribution with Distribution of Geological deposits and Chemical Composition of Fresh Water in Nigeria. Videnak. Medd. Fra Danski Nulurh foren Bd. 126 : 317 - 333. 1964.
5. Alegria, A., Barbera, R., Errecalde, F., Farre, R., and Lagarda, M. J. Environmental Cadmium, Lead and Nickel Contamination: Possible Relationship Between Soil and Vegetable Content. Fresenius. Journal of Anal. Chem. 339 : 654 - 657. 1991.
6. Mantei, E. J. and Coonrod, D. D. Heavy Metal content in the stream sediments adjacent to a sanitary Landfill. Environ. Geol. Water Sci. 13 (1) : 51 - 58. 1989.
7. Young, G. J. and Blevins, R. D. Heavy Metal Concentrations in the Holston River Basin (Tennessee) Archives of Environmental Contamination and Toxicology. 10(5): 541-560.
8. Buser, A. I and Efimov, I. P. Chemistry Definitions, Notions, Terminology. Mir Publishers Moscow. 1984.
9. Moore, C. V. In: Goodyear, R. S. and Shils, M. E. ed. Modern Nutrition in health and Disease, Philadelphia Lea and Febiger. P. 297. 1973.
10. Nriagu, J. O. Silent Epidemic of Environmental Metal Poisoning. Environmental Pollution. 50 : 139 - 161. 1988.
11. World Health Organization (WHO). Guidelines for Drinking Water Quality. Health Criteria and Other Supporting Information. W. H. O. Geneva. PP. 85 - 315. 1984.
12. Watt, B. K. and Merill, A. L. Composition of food-raw, processed, prepared. Washington D. C. Revised USDA Agriculture Handbook. B : 112. 1963.
13. Stein, M. Acute Iron Poisoning in Children. Western Journal of Medicine. 125 : 289. 1976.

14. Masironi, R. International Studies on Trace Elements in Etiology of Cardiovascular Disease. Nutrition Reports International. 7 : 51. 1973.
15. Pier, S. M. The role of heavy metals in human health. Texas reports on biology and medicine. 33 : 85. 1975.
16. Coogan, T. P., Latta, D. M. Snow, E. T. and Costa, M. Toxicity and Coacinogenicity of Nickel Compounds. CRC Critical Reviews in Toxicology. 19 : 341 - 384. 1989.
17. Prased, A. S. and Oberleas, D. eds. Trace Element in Human Health Disease. 1 : 377. 1974.