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# SEASONAL VARIATIONS OF HEAVY METAL CONCENTRATIONS IN QUA IBOE RIVER ESTUARY, NIGERIA.

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**ABSTRACT**

Concentrations of six heavy metals namely Pb, Ni, V, Fe, C and Cd were determined in water samples from Qua Iboe river estuary and its associated creeks for six months (January to June, 1999). Results obtained indicate the following mean concentrations for the metals: Pb, 0.167mg/1 ± 0.148; Ni, 0.112mg/1 ± 0.089; V, 0.019mg/1 ± 0.042; Fe, 0.118mg/1 ± 0.077; Cu, 0.020mg/1 ± 0.026 and Cd, 0.036mg/1 ± 0.036. These concentrations were higher in the wet season than the dry season. On comparing these results with the WHO standard, it was observed that the mean concentrations of Pb and Ni were higher than the acceptable limit while the coefficient of variations of the metals were correspondingly high with the high degree of fluctuations in their concentrations from station to station and from season to season. The location of the river estuary correlated positively with its observed high metal concentrations. The environmental implications of these metals are discussed with reference to existing water quality of the river.

**KEYWORDS: Heavy metals, water sample, pollution, Qua Iboe River.**

## INTRODUCTION

Modern technologies have brought about a rapid increase in world population, industrialization and urbanization. These have in turn caused a corresponding increase in the volume of domestic and industrial wastes generated, but the improper management of these wastes results in environmental pollution problems. These problems affect both the developed and underdeveloped nations though to different extents, hence it becomes pertinent that adequate focus be placed on its control to avoid a disaster which may be similar to the incidence of methyl mercury poisoning which occurred in Japan (Christian *et al*, 1974; Young and Blevins, (1981).

Sastry and Tyagi (1982), pointed out that, water pollution by 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 of heavy metals contamination has caused great concern about its possible effects on plants, animals and human beings.

Koli and Whitemore (1983), have through their various works on the contamination of fishes, found out that pollutants, especially heavy metals, can cause serious damage to aquatic lives particularly fishes.

Some authors have indicated certain process that could be affected by heavy metal levels in fish to include: physiological balance and respiratory processes (Hemmandez and Diaz, 1986); cardiac respiratory rhythms (Skidmoll, 1970); oxygen consumption of the gill tissue and enzymatic activities (Hughes and Averey, 1977 and Tort *et al.*, 1982). And these effects on fish according to Jacki (1974) have a high tendency of manifesting in human.

In Pakistan, like other developing countries of the world, the level of metal pollution of freshwater bodies, especially the rivers, is no longer within safe limits for human consumption. Earlier baseline studies have identified high concentrations of certain heavy metals in local freshwater systems especially rivers and lakes (Ashraf & Jaffer, 1990; Ashraf *et al*, 1991, 1992), arising mainly from agricultural and industrial processes.

Although aquatic environment naturally contains little amounts of heavy metals in a highly industrialized area such as the one under study, the levels of these metals could be unexpectedly high. Ibeno, where a lot of downstream industries are located including Mobil Producing Nigeria Unlimited (MPNU), which involves in petroleum exploitation and production activities in the area can contaminate or pollute the environment.

This study was taken to assess the quality of the aquatic environment, the impact of local industries located nearby and other sources of anthropogenic input that may affect the heavy metal content of the study area, bearing in mind its effect on man and other living resources. This paper presents a work undertaken to evaluate the concentrations of six heavy metals in Qua Iboe river estuary and its associated creeks.

## STUDY AREA

Qua Iboe river (Fig. 1) lies within latitude 4° 30' to 4° 54'N and longitude 7° 30' to 8° 00E on the southeastern Nigerian coastline. It originated from Umuahia hills in Abia State and traverses mainly sedimentary terrains which develops into a big river before emptying into the Atlantic Ocean. Creeks are common throughout the length of the estuary but the most outstanding ones are Stubb and Douglas creeks. The river is turbid due to high quantities of suspended and dissolved solids in it. Although sandy beaches are found in some parts of the estuary, most of the shorelines are fringed with tidal mudflats and mangrove swamps in which *Rhizophora racemosa, R harrisonii, R manglel* and brackish water palm *Nypa tructicans* the commonest floral species.

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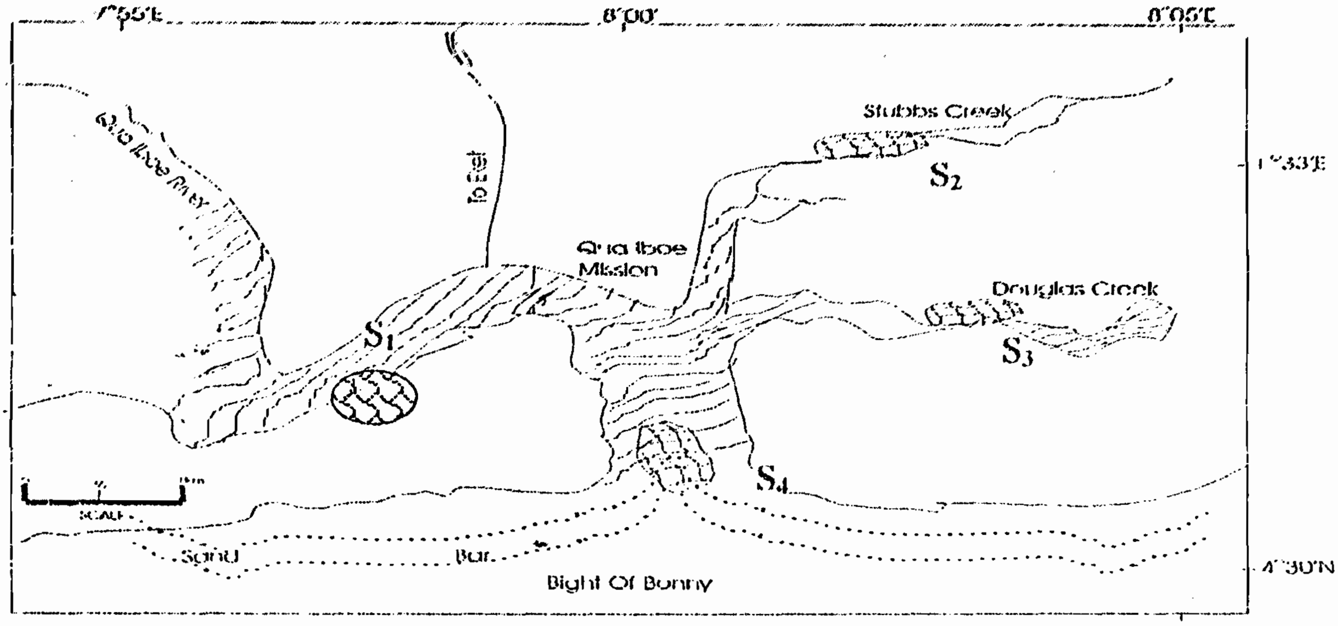


*Fig. 1: Distribution of trace metals in Qua Iboe River*

*Sample site*

## SAMPLING AND ANALYSIS

### Sampling

Sampling was carried out for six months between January and June 1999, spanning the wet and dry seasons of the year. Samples were collected with 2.5 litre black polythene bottles at the four designated stations (Fig 1) after rinsing the bottles several times with the samples and carefully filling them to avoid the trapping of air bubbles in the bottles (Polprasert, 1982; and Udosen et al, 1990). The samples were acidified with 1ml of concentrated $HNO_3$ and transported to the central laboratory of the University of Uyo, Uyo for analysis.

### Metal Analysis

A total of six heavy metals (Pb, Ni, V, Fe, Cu and Cd) were analyzed for, following the procedures of Milner and Whitefield (1981), using atomic absorption spectrophotometer (AAS) Unicam 919 model. This was done by aspirating the sample solution into the air acetylene flame of the AAS. Before the analysis of the sample was carried out, a calibration curve of the metal was prepared using standard stock solution of the metal analyzed for. From the curve, the concentration of the metal in sample was determined (Whiteside, 1979). All analysis was done in triplicates.

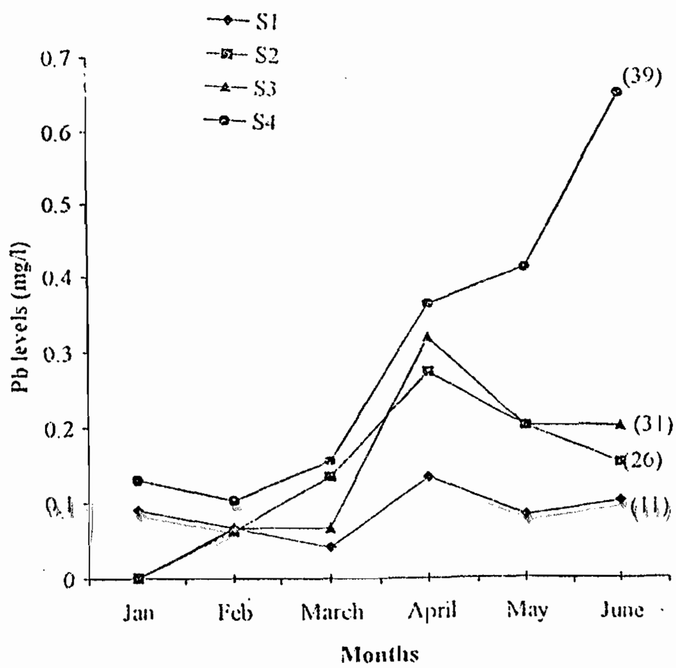


*Fig. 2: Lead levels in water from the different sampling stations (coefficient of variation in parenthesis).*

## RESULTS AND DISCUSSION

The mean concentration of the six metals Pb, Ni, V, Fe, Cu and Cd in all the stations are summarized in Tables 1–6 respectively. The spatial variations of the metals are also depicted in Figs. 2 to 7.

Seasonal variations in the concentration of these metals were observed and the levels were higher in the wet season than the dry season. The coefficients of variation are also given in Figs. 2 to 7 to indicate the distribution pattern of the metals for the different months and stations. The results obtained indicate that station 4

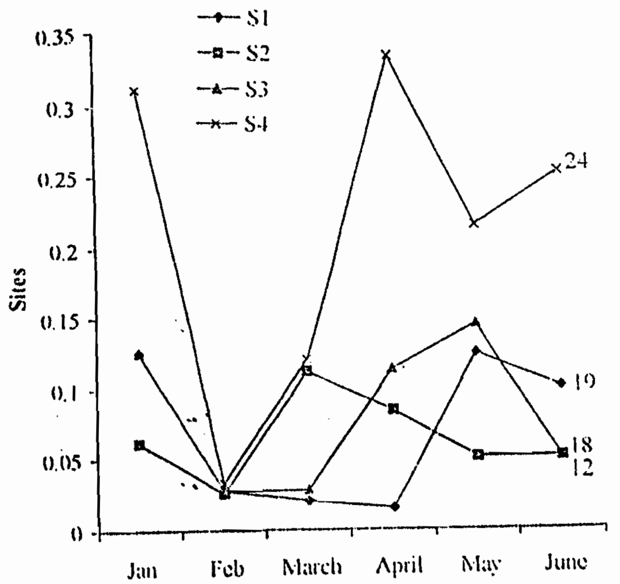


*Fig. 3: Nickel levels in water from the different sampling stations (coefficient of variation in parenthesis).*

(river estuary) recorded very high concentrations for all the metals analyzed especially during the wet season.

**Lead**

This metal is known to exist in many forms in the earth's crust, some of which are galena (PbS), Cerrusite ($PbCO_3$) and anglesite ($PbSO_4$) (Mills, 1971). Based on its great density and resistance to corrosion, it is used for many industrial applications. But being a toxic metal, it is capable of inducing abdominal pains, vomiting, drowsiness, convulsion, malfunction of the kidney, reproductive system, liver, brain and the A range of 0.043 to 0.650mg/l was obtained for Pb, with station IV recording the highest concentration (0.650mg/l) while station I had the lowest concentration (0.043 mg/l). This central nervous system (Goldsmith and Hildyard, 1988). range was found to be high when compared with WHO (1991) standards (0.05 mg/l) for drinking water and could be detrimental to human and other organisms found in and around the river. The high level of the metal in station 4 during the wet season was attributed to run-offs, activities of oil exploitation industries and the impact of the Atlantic Ocean on the river estuary. The distribution pattern of Pb is shown in Fig. 2 with station 4 recording highest coefficient of variation (39%) while station I had the lowest Pb value of 11%.

Nickel

Nickel is known to constitute most of the core of the earth, and exists mostly as, pentlandite (Ni, Cu, Fe)S and garnierite (hydrated Mg-Ni silicate of variable composition) (Takahashi and Bassett, 1965). And, due to its hardness, resistance to corrosion and high reflectivity when polished, the metal is widely used in the plating of other metals and in alloy formation. The range of nickel (0.020-0.333mg/l) obtained in this work was higher than the permissible limit in drinking water by WHO (1991)(Table 7). According to Sharma *et al* (1992), high Ni levels can cause cancer of the lungs, nose, bone and dermatitis (nickel itch).The trend of Ni distribution was not consistent as indicated in Fig. 3. The highest fluctuations were recorded at station 4 with a coefficient of variation 25%, while station 2 had the least (12%). Ni's highest concentration of 0.333mg/l was recorded at station 4 during wet season and this was attributed to the location of the station being the receiving end of all the contaminants/pollutants, the activities of oil companies and the additional source of contamination by run-off, while station I used as the control recorded the lowest concentration of Ni (0.02mg/l) also in the wet season. This may be attributed to the station being the upper part of the river and the absence of the impact of oil industry on the area.

The high fluctuation in the concentration of Nickel in

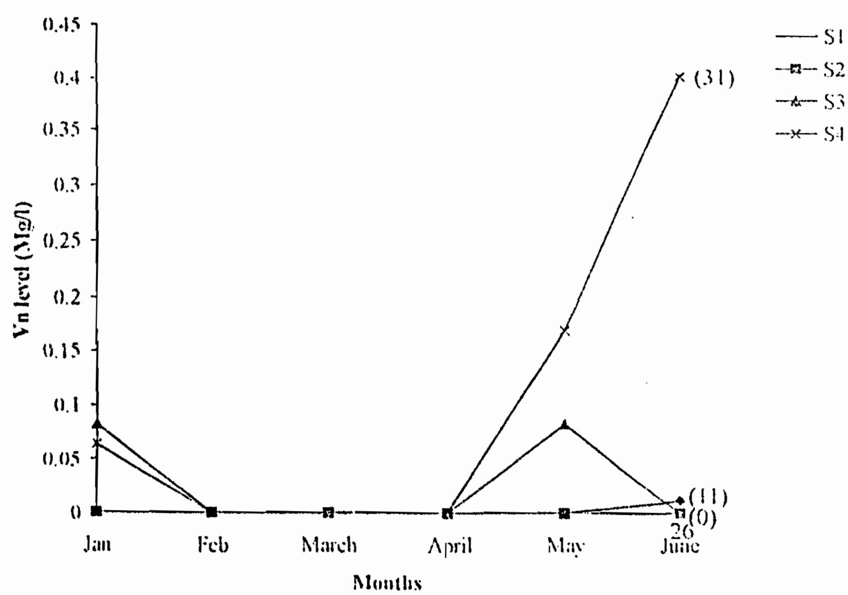


*Fig. 4: Vanadium levels in water from the different sampling stations (coefficient of variation in parenthesis).*

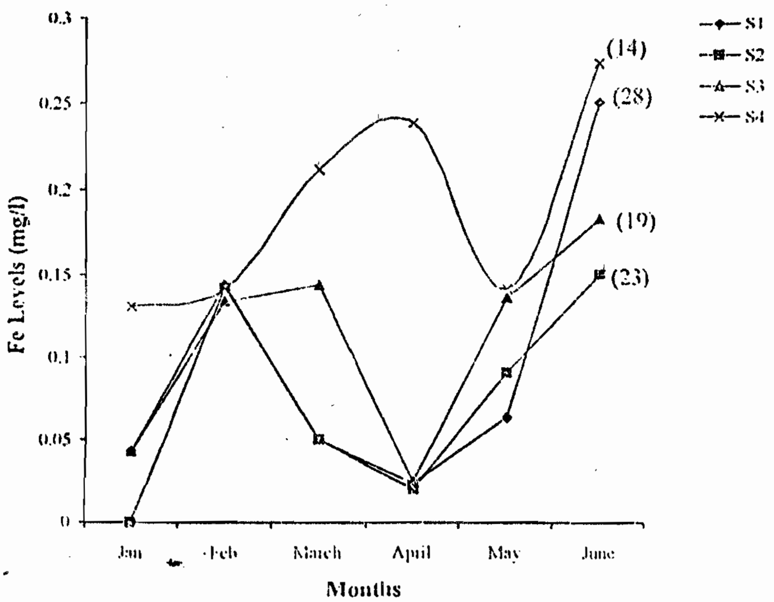


*Fig. 5: Iron levels in water from the different sampling stations (coefficient of variation in parenthesis).*

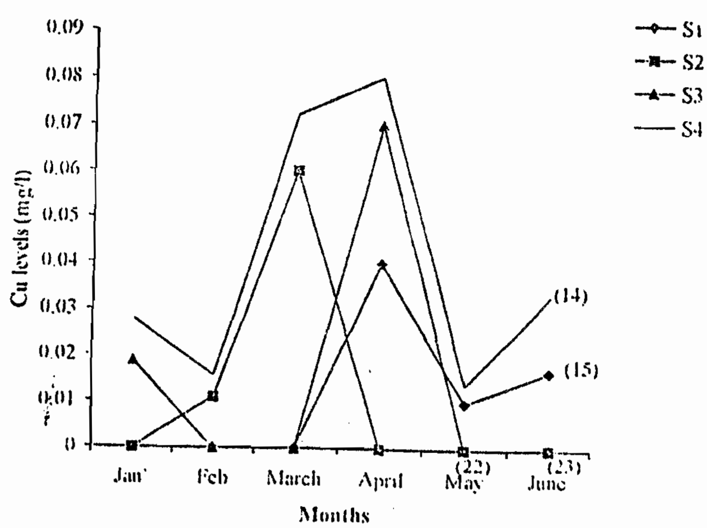


*Fig. 6: Copper levels in water from the different sampling stations (coefficient of variation in parenthesis).*

Table 1: Concentration of heavy metals in water samples from Qua Iboe river estuary in January 1999*

| METAL CONC (mg/l) | $S_1$ | $S_2$ | $S_3$ | $S_4$ |
|---|---|---|---|---|
| Pb | 0.090 ± 0.002 | BDL | BDL | 0.130 ± 0.001 |
| Ni | 0.125 ± 0.001 | 0.063 ± 0.002 | 0.125 ± 0.002 | 0.313 ± 0.002 |
| V | BDL | BDL | 0.081 ± 0.001 | 0.063 ± 0.003 |
| Fe | 0.043 ± 0.003 | BDL | 0.043 ± 0.002 | 0.130 ± 0.001 |
| Cu | BDL | BDL | 0.019 ± 0.001 | 0.028 ± 0.001 |
| Cd | 0.050 ± 0.002 | 0.008 ± 0.002 | 0.017 ± 0.03 | 0.033 ± 0.002 |

**Table 2: Concentration of heavy metals in water samples from Que Iboe river estuary in February 1999***

| METAL CONC (mg/l) | $S_1$ | $S_2$ | $S_3$ | $S_4$ |
|---|---|---|---|---|
| Pb | 0.067 + 0.002 | 0.064 + 0.002 | 0.067 + 0.002 | 0.102 + 0.003 |
| Ni | 0.028 + 0.002 | 0.026 + 0.002 | 0.027 + 0.003 | 0.033 + 0.002 |
| V | BDL | BDL | BDL | BDL |
| Fe | 0.143 + 0.001 | 0.141 + 0.002 | 0.133 + 0.002 | 0.140 + 0.002 |
| Cu | BDL | 0.011 + 0.003 | BDL | 0.016 + 0.001 |
| Cd | 0.028 + 0.002 | 0.031 + 0.002 | 0.012 + 0.001 | 0.051 + 0.002 |

**Table 3: Concentration of heavy metals in water Samples from Quo Iboe river estuary in March 1999***

| METAL CONC (Mg/l) | $S_1$ | $S_2$ | $S_3$ | $S_4$ |
|---|---|---|---|---|
| Pb . | 0.043 + 0.001 | 0.133 + 0.002 | 0.068 + 0.001 | 0.154 + 0.002 |
| Ni | 0.020 + 0.002 | 0.111 + 0.001 | 0.028 + 0.002 | 0.120 + 0.003 |
| V | BDL | BDL | BDL | BDL |
| Fe | 0.055 + 0.001 | 0.050 + 0.001 | 0.143 + 0.002 | 0.211 + 0.001 |
| Cu | BDL | 0.060 + 0.003 | BDL | 0.072 + 0.002 |
| Cd | 0.032 + 0.002 | 0.051 + 0.002 | BDL | 0.091 + 0.001 |

Table 4: **Concentration of heavy metals in water Samples from Quo Iboe river estuary in April 1999*.**

| METAL CONC (mg/l) | $S_1$ | $S_2$ | $S_3$ | $S_4$ |
|---|---|---|---|---|
| Pb | 0.133 + 0.002 | 0.273 + 0.001 | 0.318 + 0.001 | 0.364 + 0.001 |
| Ni | 0.167 + 0.001 | 0.083 + 0.001 | 0.112 + 0.002 | 0.333 + 0.001 |
| V | BDL | BDL | BDL | BDL |
| Fe | 0.024 + 0.001 | 0.020 + 0.002 | 0.025 + 0.002 | 0.238 + 0.001 |
| Cu | 0.040 + 0.003 | BDL | 0.070 + 0.002 | 0.080 + 0.002 |
| Cd | 0.050 + 0.002 | BDL | 0.050 + 0.002 | 0.150 + 0.001 |

the area of study may be attributed to the inconsistency in levels of this metal being added anthropogenically to the different sampling stations and the variations in the rate at which the metal is added to the area with that at which dilution is taking place from one station to the other and from one season to the other.

Vanadium

Vanadium according to Takahashi and Basset (1965) is a very rare metal in the earth's crust and is used with chromium in stainless steel while some of its compounds are used in glass, ceramics and colour industries. High concentrations of the metal can cause irritation of the respiratory tract, hemorrhage, coughing, nausea, vomiting and late nervousness and dizziness (Brooks and Jacobs, 1958). Vanadium results obtained in this study were consistent with the observation of Takahashi and Basset (1965), V levels were below detectable limits, at most of the stations due to low level of the metal in the earth's crust and non-availability of rainfall during the dry season that would have washed the metal from the adjoining land and air environment into river. The distribution pattern of the metal has shown that, station 1 recorded the lowest concentration (0.011mg/l) during the wet season while the highest concentration (0.170mg/l) was recorded at station 4 also in the wet season. The non- prevalence of the metal in the area of study could be observed in Fig. 4 as the coefficient of variation of all the stations were very low excepting station 2 with no value at all. Station 4 had the highest fluctuation pattern with a CV of 31%.

**Iron**

Iron ranks second in abundance among the metals and fourth among all elements in the earth's crust (Nebergall *et al*, 1975). It is mostly found in the forms: hematite ($Fe_2O_3$), magnetite ($Fe_3O_4$), limonite ($Fe_2O_3.H_2O$), lodestone ($Fe_3O_4$), taconite ($Fe_3O_4$), siderite ($FeCO_3$) and pyrite ($FeS_2$)(Sienko and Plane, 1976). Due to its abundance, ductility and high tensile strength, the metal is widely used for the manufacture of tools and weapons used domestically and industrially; thus it is expected to be found in large amount in the environment.

Copper

Copper exists in nature in many forms, some of which are chalcocite ($Cu_2S$), chalcopyrite ($CuFeS_2$), cuprites ($Cu_2O$), melaconite ($CuO$) and malachite ($Cu_2(OH)_2CO_3$) (Cahalan, 1973). It is found in the brightly coloured feathers of certain birds and in the blood of certain marine animals such as lobsters, oysters and cuttlefish where it serves the oxygen-carrying function (Frieden, 1968). Copper, due to its ductility and malleability is widely used in the electrical, printing, photographic and alloy industries. Thus it is expected to be found in a high concentration in the environment (Cahalan, 1973). A Cu level above 1.00mg/l in drinking water produces harmful effects such as nausea, vomiting, pallor, diarrhoea, symptoms of collapse and heart failure on humans (Brooks and Jacobs, 1958).

Copper ranged between 0.011 and 0.080mg/l in the

**Table 5:** **Concentration of heavy metals in water Samples from Quo Iboe river estuary in May 1999*.**

| METAL CONC (mg/l) | $S_1$ | $S_2$ | $S_3$ | $S_4$ |
|---|---|---|---|---|
| Pb | 0.083 ± 0.002 | 0.200 ± 0.001 | 0.200 ± 0.001 | 0.410 ± 0.001 |
| Ni | 0.123 ± 0.002 | 0.050 ± 0.002 | 0.143 ± 0.001 | 0.214 ± 0.001 |
| V | BDL | BDL | 0.082 ± 0.002 | 0.040 ± 0.001 |
| Fe | 0.064 ± 0.002 | 0.091 ± 0.002 | 0.136 ± 0.003 | 0.141 ± 0.001 |
| Cu | 0.010 ± 0.003 | BDL | BDL | 0.014 ± 0.002 |
| Cd | BDL | 0.017 ± 0.002 | BDL | 0.070 ± 0.002 |

**Table 6:** **Concentration of heavy metals in water Samples from Quo Iboe river estuary in June 1999*.**

| METAL CONC (mg/l) | $S_1$ | $S_2$ | $S_3$ | $S_4$ |
|---|---|---|---|---|
| Pb | 0.100 ± 0.002 | 0.150 ± 0.001 | 0.200 ± 0.001 | 0.650 ± 0.001 |
| Ni | 0.100 ± 0.002 | 0.050 ± 0.003 | 0.051 ± 0.002 | 0.250 ± 0.001 |
| V | 0.011 ± 0.003 | BDL | BDL | 0.170 ± 0.001 |
| Fe | 0.250 ± 0.001 | 0.150 ± 0.002 | 0.182 ± 0.001 | 0.273 ± 0.001 |
| Cu | 0.017 ± 0.002 | BDL | BDL | 0.033 ± 0.003 |
| Cd | 0.025 ± 0.003 | 0.017 ± 0.002 | 0.008 ± 0.002 | 0.083 ± 0.002 |

**Table 7:** **World Health Organization standard for water (1991)**

| SUBSTANCE | FOR DOMESTIC | FOR DRINKING |
|---|---|---|
| Cd | - | 0.05 |
| Fe | 1.00 | 0.30 |
| Ni | - | 0.05 |
| Pb | - | 0.05 |
| Cr | - | 0.50 |
| Co | - | 0.05 |
| Cu | 1.50 | 1.0 |
| Zn | - | - |
| Mn | 150 | 150 |

* Mean of three determinations.
BDL = Below Detection Limit
$S_1$ = River Upstream at Mkpanak
$S_2$ = Stubbs Creeks
$S_3$ = Douglas Creek
$S_4$ = River Estuary
Mg/l = Milligram per Litre

area, and based on WHO (1991) standard, the obtained levels does not pose any threat to human life and other higher animals using the water.

The degree of variability of the metal as shown in Fig. 6 was very high with station 3 recording the highest value (23%) while station 4 had the lowest value (14%). Also observed in the Figure is that the concentration of Cu in the months of March and April were higher and this was attributed to the period being the onset of rainfall in the area of study; thus this metal in the air, land and upper part of the river was washed down to the river but with prolonged rainfall; the metal concentration dropped as observed in the month of May due to dilution while the level in the month of June at the river estuary was the highest due to the ocean dynamics and the retention time of the pollutants and contaminants there from other parts of the river.

Cadmium

Cadmium is found in the earth mineral greenowickite (Cds) and in small amounts in general zinc ores. Cadmium-plated metals are known to be more resistant to corrosion, more easily soldered, and more attractive in appearance than galvanized metals, and is used in making a number of alloys (Nebergall *et al*, 1975).

The range obtained for cadmium was 0.008 to 0.150mg/l with station 4 recording the highest concentration (0.150mg/l) while stations 2 and 3 had the lowest value of 0.008mg/l. comparatively, the Cd range obtained (0.008 – 0.150mg/l) was higher than acceptable standards, and the metal level in the area was therefore seen as reaching a nuisance level that can result in harmful consequences. The pattern of

Although, it is a component of haemoglobin of the blood, a concentration above 0.3mg/l in water can cause toxicity in higher animals (WHO, 1991). The range of iron recorded in this study was 0.020-0.273mg/l; therefore, the metal was not regarded as pollutant in the area. Iron results also indicate a seasonal variation as higher concentrations were recorded in wet season than in dry season. This was attributed to the impact of rainwater and run-offs. Also, the degree of variability of the metal in the area was high as seen in Fig. 5 with station 1 recording the highest value (28%), while station 4, with very high levels of Fe ranked lowest with 14%.

distribution of the metal and its degree of variability is given in Fig 7. Station 4 recorded the highest level of Cd due to the area being the receiving end of all the pollutants/contaminants from other stations and additional inputs from Atlantic Ocean. The station also indicated the highest CV for Cd due to Ocean dynamics and high fluctuations in the rate of deposition of Cd with that of dilution in the area.

The study gives the distribution pattern of six heavy metals analyzed for in the study area. Some have been found to be above the widely acceptable standards thereby constituting a nuisance in the area. These high levels are believed to be caused by anthropogenic inputs into the study area. The general results have also indicate that most of the metals recorded their highest concentrations at station 4 especially during the wet season which indicates that during the rainy season, those pollutants in the atmosphere, adjourning lands and even in the upper part of the river were washed down to the estuary where they are retained until their residence time expires before they can be emptied into the Atlantic ocean.

## REFERENCES


Ashraf, M and Jaffar M., 1990. Contents of selected micro-nutrients in various local fresh water fish. Pak. J. Sc. & Ind. Res. 33: 278 – 280.

Ashraf, M., Jaleel, T. and Jaffar, M., 1991. Contents of trace metals in fish, sediment and water from three fresh water reservoirs on the Indus river. Pakistan Fish. Res. 12: 355 – 364.

Ashraf, M., Jaffar M. and Jaleel, T., 1992. Annual variations of selected trace metals in freshwater lake fish, Labeo rohita, as an index of environmental pollution. Toxicol. Environ. Chem. 35: 1-7

AWWA, American Water Works Association, 1980. Standard methods for the examination of water and waste water 15th ed. APHA-AWWA-WPCF. Pp148 – 157.

Brookes, V. J. and Jacobs, M. B., 1958. Poisons: Properties, chemical identification, symptoms and emergency treatment. 2nd ed. Van Nostrand Reinhold company, New York. P. 161, 166, 185.

Cahalan, M. J., 1973. Resources utilization – Copper from Low Grade ores, Chem. in Britain

Christian, R. F. mar, B. T. O; Welch E. B; Charison, R. F., 1974. The Natural environment: waste and control. Revised edition. Goodyear publication Co. Inc. California. Pp 93 – 94.

Frieden, E., 1968. The biochemistry of copper. Sci. American. Pp 102.

Goldsmith, E. and Hildyard N., 1988. The earth report. The essential guide to global ecological issues. Price Sterm Sloan Inc; Los Angeles, California. Pp 173.

Hemmandez, F. and Diaz, J., 1986. Bul. Environment Contam Toxicol 36: p851.

Hughes, G. M. and Averey, R. J., 1977. Water Res. 11: p1069

Jacki, 1974. Pollution and physiology of marine organisms. Vernberg F. J. and Keraberg W. D. Ed. New York Academy Press.

Koli, A. K. and Whitemore, R., 1983. Trace elements in fish from the Savannah River Nuclear Plant. Environmental International. 9: 361 – 365.

Mills, A. L., 1971. Lead in the Environment, Chem. in Britain, 7: p160

Milner, B. A. and Whiteside, P, J. 1981. Atomic spectrophotometry. 1st ed. Pye Unicam Ltd. pp14 – 75.

Nebergall, W. H., Schmodt, J. and Holtclaw, H. F., 1975. College Chemistry with Qualitative Analysis 5th edn. D. C. Health Publishing Co. California. Pp 843 – 926.

Polprasert, C., 1982. Heavy metal pollution in the Chofhray river estuary, Thaland. Water research, 16: 775 – 784.

Sastry, K. V. and Tyagi., 1982. Toxic effects of Chromium in fresh Teleost fish; *Channa punctatus*, Toxicology Letters 11: 17 – 21.

Sharma, Y. C. Prasand, G; and Rupainwar, D. C., 1992. Heavy metal pollution of river banga in Mirzapur, India. Inter. J. Environ. Studies. 40: 41 – 53.

Sienko, Michell J. and Plane, Robert, A., 1976. Chemistry 5th Edn McGraw-Hill Kogakusha Ltd. Pp 380.

Skidmoll, J. K. Q., 1970. Rev. Biol. 39: p 227.

Takahashi, T and Basset, W. A., 1965. The composition of the earth's interior. Sci. American. pp100.

Tort L., Cespo S. and Balash J., 1982. Comp. Biochem. Physol 72: p142

Udosen, E. D; Ibok, U. J. and Udoessien, E. I., 1987. Environmental implications of the sunshine batteries industry in Ikot Ekpene in Akwa Ibom State of Nigeria. A paper presented at the 12th Annual conference of the Chemistry Society of Nigeria (C.S.N) held at Calabar.

Udosen, E. D; Udoessien, E. I. and Ibok, U. J., 1990. Evaluation of some heavy metals in industrial wastes from a paint industry and their environmental pollution implications. Nig. Tech. Res. 271-77.

Warren, I. J., 1981. Contamination of sediment by lead, zinc and cadmium. A Review Environmental Pollution (Serial B) 2: 401 – 436.