PRELIMINARY OBSERVATIONS ON DISSOLVED TRACE-METAL CONCENTRATIONS AND DISTRIBUTIONS IN THE SURFACE WATERS OF QUA IBOE RIVER ESTUARY, SOUTH-EASTERN NIGERIA.

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ABSTRACT

The concentration and distribution patterns of some selected trace-metals (Fe, Pb, Cu, Zn, Cr, Mn, Ni & Co) in the surface waters of Qua Iboe River estuary have been determined over a complete tidal cycle in March, 2004. The measured trace-metal concentrations in the surface waters of Qua Iboe River estuary measured were low and fall within the acceptable limits based on WHO and Ministry of Environment (Nigeria) standards. Metal levels displayed both spatial and tidal variations, which are due to both anthropogenic discharge and natural processes in the ecosystem. Some metals like Ni and Cr were completely below detection level over the salinity gradient sampled (5ppt – 20ppt) and hence were not detected. This may be due to adsorption by suspended particles. Cu (0.012 – 0.019 mg/l), Zn (0.002 – 0.081mg/l) and Mn (0.027 – 0.039mg/l) concentrations were very low and at some periods of sampling were not detected. This may be due to the role played by diatoms and phytoplanktons in assimilation of these metals for regulation of biochemical processes. The analysis of the result shows that Fe was negatively correlated with pH (r_1 = -0.52, r_2 = -0.40 and r_3 = -0.59, n=13). Pb on the other hand was positively correlated with pH (r_1=0.08, r_3=0.77, n=13) on the 1st and 3rd day, except on the 2nd day, where a weak negative correlation (r_2 = -0.09, n=13) was obtained.

KEYWORDS: Dissolved trace-metal, diurnal cycles, estuary, surface waters, Nigeria.

INTRODUCTION

The presence of trace-metals in aquatic environment has been the major concern of environmental chemists, geologists and other environmental experts for the past decades. This is because some of them when present, even in trace amounts, lead to pollution of the aquatic environment. Moreover, people's livelihoods in these areas are intimately linked to the resources from these coastal zones. An estuary as defined by Montgomery (2000) is a body of water along a coastline, open to the sea, in which the tide rises and falls and in which fresh and salt water meet and mix to create brackish water. The mixing is severe at the transition zone due to increase tidal turbulence and fluvial discharge. Transition zone is also an area in which physical mixing of marine and fluvial matter occurs (Kerner and Krogmann, 1994). Metal concentrations in surface waters of aquatic ecosystem such as estuary can fluctuate by several orders of magnitude over a diurnal cycle due to inter-play of tide and physicochemical factors. Other factors include biological processes, chemical reactions, degree of resuspension and factor of dilution. Metals, such as Mn, Zn and Cu are taken up by organisms for the physiological functioning of their living tissues (Chapman and Kimstach, 1996). These metals also regulate many biological and chemical processes.

According to Gangaiya et al (2001), heavy metals in an unperturbed environment are preferentially transferred from the dissolved to the particulate phase and as a result metal concentrations in sediments are generally much higher than in the overlying waters. As a result, most researchers in the field tend to analyzed only the sediments in the assessment of trace – metal distribution/concentration patterns. The importance of these elements in the surface waters cannot be over emphasized as some organisms in estuarine ecosystem which plays a vital role in food relationship are surface dwellers. Also, water circulation in estuaries is often very limited (Montgomery, 2000). This makes them especially vulnerable to pollution; because they are not freely flushed out by vigorous water flow, pollutants can therefore accumulate. It is therefore of great scientific

interest to determine the concentration and distribution patterns of the latter in the surface waters as some fishes, shellfishes and other estuarine organisms absorbed these minerals directly from the water through their gills and other tissues. However, the source of most of the pollutants found in aquatic organisms is via the food chain. First, phytoplankton, bacteria, fungi and other small organisms absorb these materials. In turn, these are eaten by larger animals, eventually ending up in the organisms eaten by man. Unlike many organic contaminants that lose toxicity with biodegradation, metals cannot be degraded further and their toxic effects can be long lasting (Clark, 1992), as it shift from one compartment to the other within the ecosystem because trace-metal lack natural elimination methods.

Metals in natural waters can exist in truly dissolved, colloidal and suspended forms. The proportion of these forms varies for different metals and for different water bodies. Consequently, the toxicity and sedimentation potential of metals change, depending on their form (Kerner and Krogmann, 1994). This paper examines the concentration and distribution patterns of selected dissolved trace-metals at a turbulent estuary such as Qua Iboe River estuary in South-Eastern Nigeria. The results of such a study would be useful in understanding the pattern of variations of the trace-metal in the ecosystem; determining the extent to which the ecosystem can support life based on the available metals and assessing the water quality status of Qua Iboe River estuary. The results would also be useful in interpretation of long-term trends and detection of abnormal trends.

MATERIALS AND METHODS

The study area is located at Qua Iboe River estuary (Figure 1). The estuary lies close to longitude $7^0 57^1$ East and latitude $4^0 35^1$ North. The area is characterized with fine to very fine sands as dominant constituents. The anchor station was located near Mobil Jetty in the outer Qua Iboe River estuary ($4^0 32^1 36.8^{11}$N; $7^0 59^1 22.36^{11}$E) (Figure 1). The station was occupied over a complete tidal cycle (600am to

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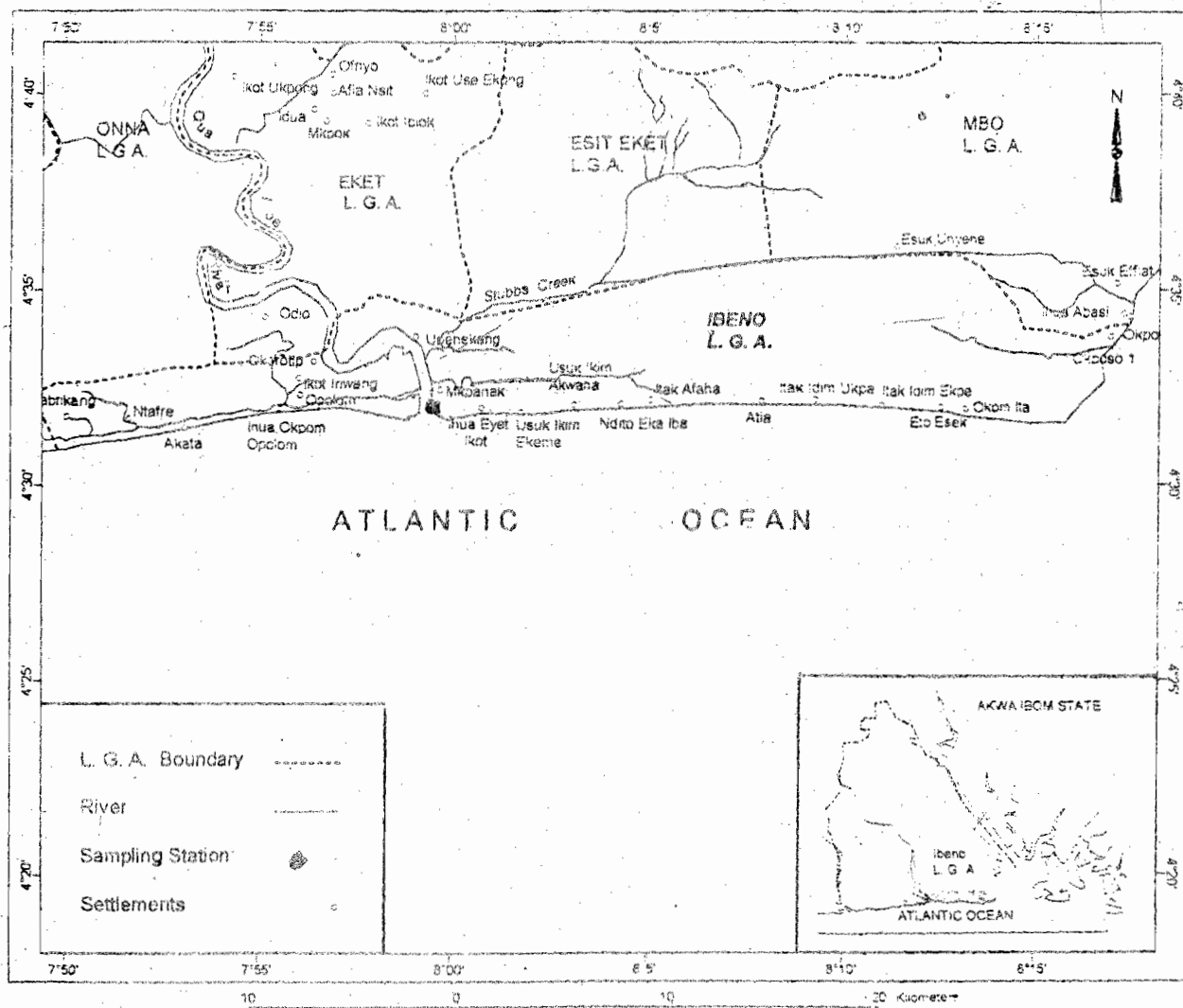
Fig. 1: Ibeno Local Government Area showing Sampling Stations

1800pm) on 27th – 29th March, 2004 with high water (HW) at 14.00pm and low water(LW) at 8.00am. Sample collection was carried out at hourly intervals. Salinity and pH measurements were determined in-situ using portable electronic equipment. Samples for dissolved trace – metal determination were collected in acid – cleaned 1 litre linear polyethylene plastic containers. The samples were preserved in ice-block stored in coolers in the field.

Samples for trace-metals analysis were filtered on the same day through preweighed acid-washed $0.45\mu m$ pore-size polycarbonate filters and filtrates were acidified with 1 cm^3 of high-purity trioxonitrate (v) acid (HNO_3). Trace-metals in the water samples were determined using a unicam atomic absorption spectrophotometer (APHA, 1985).

RESULTS AND DISCUSSION

Tables 1-3 give the analytical results for the concentrations of dissolved trace-metals salinity and pH in the surface waters of Qua Iboe River estuary during the diurnal cycles. Dissolved trace-metal (Cu, Fe, Zn, Cr, Mn, Pb, Co and Ni) concentrations during the present study are generally low. This could be linked to the fact that sediments of Qua Iboe River estuary and its transition zone as observed in the field composed of a lot of terrigeneous material which has a higher binding capacity for metal. Although no measurements on sediment composition were made, visual observations indicated significant amounts of

terrigeneous material. Also studies in the sediments of adjacent Qua Iboe River (Ekwere et al., 1992) shows that the concentration of Ni (10-72ppm), Cr (8-35.6ppm) Cu (14-60ppm), Zn (226-1,416ppm) and Pb (15-40ppm) in the sediments are higher compared to the result obtained in this studies. Sediments containing a lot of terrigeneous material could have greater capacity to bind metals than marine – derived sediments because of the presence in the former of materials such as iron and aluminnium oxides and hydroxides which bind metals strongly (Gangaiya et al., 2001). Dissolved Cr and Ni were not detected through out the three days of sampling (Tables 1, 2 and 3). One of the reasons for complete absence of these metals could be association of trace-metals with particles. Kerner and Krogmann (1994) attributed low concentration of dissolved trace-metals to its association with particles. Dissolved concentration of trace-metals – Cu, Zn and Mn were very low such that at some periods of sampling were not detected (Tables 1, 2 and 3). This may be due to the fact that these metals are being taken up by diatoms and phytoplankton. Mn, Zn and Cu, when present even in trace concentrations are important for the physiological functions of living tissue and regulate many biochemical processes (Chapman and Kimstach, 1996). Yoshiaki et al (2004) explains that diatoms can take heavy metals through complex formation with some kinds of polysaccharides and amino acids, of which the valve walls of algae composed.

TABLE 1: SUMMARY OF DISSOLVED TRACE-METAL CONCENTRATIONS AND PHYSICOCHEMICAL PARAMETERS FOR SURFACE WATERS DURING THE TIDAL CYCLE FOR DAY ONE (27TH MARCH, 2004)

Time (hr)	Fe (mg/l)	Pb (mg/l)	Cu (mg/l)	Zn (mg/l)	Cr (mg/l)	Mn (mg/l)	Ni (mg/l)	Co (mg/l)	pH	Sal. ppt
6.00	0.172+0.001	0.023+0.001	Nd	0.002+0.000	Nd	0.037+0.001	Nd	0.084+0.001	7.60+0.01	06±1.414
7.00	0.166+0.001	0.026+0.001	Nd	0.003+0.001	Nd	Nd	Nd	0.037+0.001	7.21±0.00	06±1.414
8.00	0.267+0.001	0.063+0.001	Nd	Nd	Nd	Nd	Nd	0.017+0.001	7.11±0.01	07±0.000
9.00	0.368+0.009	0.068+0.001	Nd	Nd	Nd	Nd	Nd	0.018+0.001	7.02±0.01	07±0.000
10.00	0.146+0.001	0.011+0.000	Nd	0.004+0.000	Nd	Nd	Nd	0.027+0.001	7.22±0.16	12±2.828
11.00	0.168+0.001	Nd	Nd	0.003+0.001	Nd	Nd	Nd	0.168+0.001	7.50±0.00	11±2.828
12.00	0.149+0.001	0.087+0.001	Nd	Nd	Nd	Nd	Nd	0.123+0.001	7.55±0.01	10±1.414
13.00	0.093+0.001	0.028+0.001	Nd	0.020+0.000	Nd	Nd	Nd	Nd	7.49±0.01	10±1.414
14.00	0.086+0.001	0.067+0.001	Nd	0.004+0.000	Nd	Nd	Nd	0.084+0.001	7.48±0.01	11±1.414
15.00	0.107+0.001	0.029+0.001	Nd	0.014+0.001	Nd	Nd	Nd	Nd	7.03±0.01	10±0.000
16.00	0.113+0.001	0.068+0.001	Nd	0.013+0.001	Nd	Nd	Nd	Nd	7.54±0.00	07±1.414
17.00	0.163+0.001	0.028+0.001	0.017+0.001	0.081+0.000	Nd	Nd	Nd	0.039+0.001	7.39±0.10	07±1.414
18.00	0.181+0.001	0.080+0.000	Nd	0.062+0.001	Nd	0.037+0.001	Nd	0.063+0.001	7.50±0.01	10±1.414

Note that Nd = Not detected

TABLE 2: SUMMARY OF DISSOLVED TRACE-METAL CONCENTRATIONS AND PHYSICOCHEMICAL PARAMETERS FOR SURFACE WATERS DURING THE TIDAL CYCLE FOR DAY TWO (28TH MARCH, 2004)

Time (hr)	Fe (mg/l)	Pb (mg/l)	Cu (mg/l)	Zn (mg/l)	Cr (mg/l)	Mn (mg/l)	Ni (mg/l)	Co (mg/l)	pH	Sal. Ppt
600	0.104+0.001	0.069+0.001	Nd	0.002+0.000	Nd	Nd	Nd	Nd	6.93±0.01	05±1.41
700	0.081+0.001	0.068+0.000	Nd	Nd	Nd	Nd	Nd	Nd	7.51±0.01	06±1.41
800	0.113+0.001	Nd	Nd	0.004+0.001	Nd	Nd	Nd	Nd	7.84±0.00	11±0.00
900	0.177+0.001	0.126+0.001	Nd	Nd	Nd	Nd	Nd	Nd	7.69±0.01	10±1.41
1000	0.191+0.001	0.020+0.001	Nd	0.006+0.001	Nd	Nd	Nd	0.083+0.001	7.21±0.01	13±1.41
1100	0.163+0.001	0.026+0.001	Nd	Nd	Nd	Nd	Nd	0.093+0.001	7.64±0.01	10±1.41
1200	0.166+0.001	0.089+0.001	Nd	Nd	Nd	Nd	Nd	0.027+0.001	7.09±0.01	11±1.41
1300	0.162+0.001	0.137+0.000	0.019+0.001	0.002+0.000	Nd	0.038+0.001	Nd	0.168+0.001	7.59±0.01	11±0.00
1400	0.083+0.001	0.122+0.000	Nd	Nd	Nd	0.034+0.001	Nd	0.083+0.001	7.74±0.01	10±1.41
1500	0.094+0.001	0.023+0.000	0.019+0.000	0.013+0.001	Nd	0.027+0.001	Nd	0.117+0.001	7.85±0.01	11±1.41
1600	0.074+0.001	0.024+0.000	Nd	0.017+0.001	Nd	Nd	Nd	0.129+0.001	7.47±0.01	09±1.41
1700	0.086+0.001	Nd	0.018+0.001	0.013+0.000	Nd	Nd	Nd	0.382+0.001	7.56±0.01	10±1.41
1800	0.103+0.001	0.023+0.001	Nd	0.002+0.000	Nd	Nd	Nd	0.017+0.001	7.51±0.01	10±1.41

Note that Nd = Not detected

TABLE 3: SUMMARY OF DISSOLVED TRACE-METAL CONCENTRATIONS AND PHYSIOCHEMICAL PARAMETERS FOR SURFACE WATERS DURING THE TIDAL CYCLE FOR DAY THREE (29TH MARCH 2004)

Time (hr)	Fe (mg/l)	Pb (mg/l)	Cu (mg/l)	Zn (mg/l)	Cr (mg/l)	Mn (mg/l)	Ni (mg/l)	Co (mg/l)	pH	Sal ppt
6.00	0.129+0.001	0.016+0.00	0.017+0.001	0.002+0.000	Nd	Nd	Nd	0.242+0.001	7.32±0.014	08±0.00
7.00	0.232+0.002	0.030+0.001	Nd	Nd	Nd	0.037+0.001	Nd	0.223+0.001	7.47±0.014	07±1.41
8.00	0.126+0.000	Nd	Nd	0.002+0.001	Nd	Nd	Nd	0.184+0.001	7.52±0.014	07±1.41
9.00	0.313+0.001	0.019+0.001	Nd	0.005+0.001	Nd	Nd	Nd	0.163+0.001	7.53±0.014	08±1.41
10.00	0.105+0.001	0.090+0.001	Nd	0.002+0.000	Nd	Nd	Nd	0.383+0.001	7.63±0.04	12±0.00
11.00	0.114+0.001	0.161+0.002	Nd	0.004+0.001	Nd	0.037+0.001	Nd	0.418+0.001	8.11±0.014	20±1.41
12.00	0.104+0.001	0.092+0.001	Nd	0.002+0.000	Nd	Nd	Nd	0.094+0.001	8.55±0.007	16±1.41
13.00	0.082+0.00	0.106+0.000	Nd	Nd	Nd	Nd	Nd	0.083+0.001	8.67±0.014	19±1.41
14.00	0.084+0.001	0.129+0.001	0.012+0.001	Nd	Nd	Nd	Nd	0.412+0.001	8.54±0.04	15±1.41
15.00	0.094+0.001	0.113+0.001	Nd	Nd	Nd	0.039+0.001	Nd	0.419+0.001	8.86±0.014	13±1.41
16.00	0.125+0.001	0.084+0.002	Nd	0.002+0.000	Nd	Nd	Nd	0.334+0.001	7.80±0.014	09±0.00
17.00	0.137+0.001	0.024+0.000	Nd	Nd	Nd	Nd	Nd	0.168+0.001	7.64±0.014	09±0.00
18.00	0.183+0.001	0.021+0.001	Nd	Nd	Nd	Nd	Nd	0.138+0.001	7.56±0.007	10±1.41

Note that Nd = Not detected

On day two, maximum dissolved Cu concentration of 0.019mg/l was observed by 1300pm and 1500pm (Table 2) during flooding and onset of ebbing respectively. This was the highest concentration of Cu throughout the sampling periods, while a concentration value of 0.018mg/l was evident by 1700pm towards the end of sampling during ebbing. The present low concentrations of dissolved Mn could also be attributed to co-precipitation with Ca and Mg being the major ions in hard water. The evidence for the hardness of these waters could be seen by the species of marine shale organisms found in the ecosystem. Basically shale organisms require a lot of Ca and Mg for the shale formation; their presence suggests hardness of water.

Maximum Zn concentration of 0.081mg/l, 0.017mg/l and 0.05mg/l (Tables 1, 2 and 3) were obtained for the three days during ebbing respectively while minimum concentration of 0.002mg/l was evident for the three days. The Zn concentration of 0.081mg/l observed on day one (Table 1) three hours after HW could be attributed to desorption of this element from suspended matter and sediment to the underlying water during estuarine mixing. A decrease in salinity was also observed during this period (from 11ppt to 7ppt), suggesting that desorption is favoured at low salinity (see Table 1).

Tables 1-3 show the concentration and distribution patterns of Pb in mg/l for surface waters as a function of time (hr.) during the tidal cycles for the three days sampled. Maximum concentrations of 0.087mg/l and 0.137mg/l were obtained on first day and second day by 1200noon and 1300pm during flooding respectively. while maximum Pb concentration of 0.161mg/l was evident on day three 1100am- three hours after LW (see Table 3). The present distribution of Pb may be due to resuspension of sediment rich in Pb which had been brought in by anthropogenic input during wet season through surface run – off loaded with municipal wastes and atmospheric wash – out. About 15% of the world's lead is consumed in gasoline additives with almost the entire lead content being emitted into the ambient air during combustion (Akpan et al., 2002). Pb was not detected on 2nd and 3rd day at 800am and on day one at 1100am and day two at 1700pm (Tables 1, 2 and 3). Removal of Pb was also observed by Balls et al (1984) at Fourth estuary of Scotland. Elbaz – Poulichet et al (1984) also reported removal of Pb at Gironde estuary. This removal which is also evident in this study may be linked to the role of particles in removal of Pb from solution. Pb shows a significantly weak positive correlation with pH on day one (r_1=0.08, n=13) and a significantly strong positive

correlation on day three (r_3=0.77, n=13). While negative weak correlation was obtained on day two (r = -0.09, n=13). This suggests that there is no specific relationship between lead and pH in the surface waters of Qua Iboe River Estuary.

Fe concentration and distribution patterns for surface waters as a function of time (hr.) during the tidal cycles are shown in Tables 1 - 3. Maximum concentration of Fe of 0.368mg/l was observed on day one, one hour after LW (Table 1), during the onset of flooding. Minimum concentration of 0.086mg/l was observed at exactly high water (HW). On day two, highest concentration of 0.19mg/l was observed two hours after LW during flooding, while lowest concentrations of 0.07mg/l was observed two hours after HW during ebbing. Similar trend was obtained on day three, maximum Fe concentration of 0.313mg/l was obtained one hour after LW, while minimum concentration of 0.082mg/l was observed one hour before HW during flooding. The present distribution patterns of Fe reflect the influence of the local geology, as this area is uninfluenced by short-range anthropogenic discharge of Fe. Fe – pH relationship shows negative correlation for the three days sampled (r_1 = -0.52, r_2 = -0.40 and r_3 = -0.59, n=13). Fe-salinity on the other hand show negative correlation for days one and three (r_1 = -0.44, r_3 = -0.57, n = 13) and positive correlation on day two (r_2 = 0.55, n = 13). The present observation may be due to the formation of iron – solids complex with some anions at high pH which sinks to the bottom sediment as flocs or particulate matter. This observation also suggests that Fe is soluble at low pH and salinities.

Maximum Co concentration of 0.168mg/l (Table 1) was observed on the first day three hours after LW. Minimum concentration of 0.017mg/l was observed at 800am (LW) (Table 1). On day two, Co was not detected at the first four hours of sampling. Maximum concentration of 0.382mg/l (Table 2) was observed three hours after HW during ebbing and minimum concentration of 0.017mg/l was observed immediately after maximum concentration, that is, by 1800pm during ebbing. For day three, maximum concentration of 0.419mg/l (Table 3) was obtained one hour after HW during ebbing, while minimum concentration of 0.083mg/l was observed one hour towards HW during flooding. Co exhibits essentially conservative mixing with lower concentrations at high salinities. This may be attributable to increasing solubilization of Co by complexation with chlorides ions. This is supported by correlation coefficients of Co with salinity for the three days which shows weak positive correlations (r_1 = 0.31, r_2 =0.24 and r_3 = 0.20, n = 13). Also Co-pH relationship revealed a significantly fairly strong to weak positive correlations for the three days (r_1 = 0.54, r_2 =0.16 and r_3 = 0.20, n = 13), suggesting increase complexation of Co with chlorides. Metal concentrations in the surface waters of Qua Iboe River estuary were generally low and in most cases lower than global average shale values (Turekian and Wedepohl, 1961).

CONCLUSION

The dissolved trace metals (Fe, Pb, Zn and Co) of Qua Iboe River estuary displayed spatial and tidal variations over a short – term interval (diurnal cycle) due to the influence of anthropogenic discharge, meteorological and natural hydrographic factors. It is evident from the study that some trace metals are of measurable concentrations in the surface waters. This implies that water pollution by heavy metals as a result of human activities could be deleterious. This situation is aggravated by the lack of natural elimination processes for metals. As a result, metals shift from one compartment within the aquatic environment to another, including the biota, with maximum concentration occurring in the sediment.

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