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DETERMINATION OF TRACE METAL LEVELS AND FLUXES IN SEDIMENTS ALONG A SEGMENT OF QUA IBOE RIVER IN SOUTHERN NIGERIA.

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ABSTRACT: Levels and calculated fluxes of some trace metals (Pb, Fe, Cu, Cd and Zn) in sediments along a segment of Qua Iboe River in Ikot Ebak, Essien Udim Local Government Headquarters in Akwa Ibom State of Nigeria are presented. In areas with high anthropogenic activities, metal levels were observed to be high perhaps due to the discharge of municipal and industrial effluents particularly from the battery industry (when it was operational) into a tributary of the river. Hence the levels of the metals were much higher in downstream samples compared to upstream samples. The trends of Pb and Zn were however almost similar with that for Pb being $D_{S1}>D_2>US_2$ and that for Zn being $D_{S1}>DS_2>MS>US_2>US_1$. The DS_1 sample also contained the highest levels of Cu (9.770 μgg^{-1} and Cd (0. 190 μgg^{-1}) compared to other samples.

INTRODUCTION

The introduction of metals into the environment by anthropogenic activities is well documented[1,2]. Studies on sediments from different sources have provided adequate information on increased trace metal mobilization into the environment[3,4,5]. These studies have indicated the effects of metals from various anthropogenic sources including battery production[6], smelting processes[7], mining processes[2], burning of hazardous waste[8], shipping activities[9], the input of municipal sewage[10], the introduction of metal-rich industrial effluent[11,12] as well as the dumping of waste[13].

According to[14] sediments are repositories for physical and biological debris and sinks for a wide variety of chemicals. Yahya and Song (1994) who said that since sediments are both sinks and sources of trace metals in aquatic system, numerous reactions could take place within the sediment column between sediments and water share this view. These reactions play fundamental role in the mobilization and fluxes of heavy metals and with changes in pH and Eh, new equilibrium conditions could result.

Metals in sediments are obtained in water from geological formations such as rock weathering. Thus in addition to being primary sources of trace metals in water, sediments are known to be traps and reservoirs for these metals[16].

In the sediment, these trace metals could form complexes' with both organic and inorganic substances including clay and silt. But according to[17] because sediment is a reservoir and not merely a sink, there may exist a flux across the sediment- water interface in either direction depending on the ambient conditions at the time. Therefore sediments may either concentrate metals from the water or release metals to the water. Apart from trace metals, sediments could also be enriched with nutrients such as nitrogenous compounds, phosphorus and potassium either naturally or from untreated or partially treated wastes that contain nutrients. The release of these substances from sediments in soluble forms could result in water pollution by providing additional internal loading in the amount of polluting substances in water.

Currently, there is a great deal of concern regarding contaminated sediments and their impacts on ecosystem health[18]. The concern associated with the chemicals sorbed to sediments is that many commercial species and food chain organisms spend a major portion of their life cycle living in or on aquatic sediments. This provides a pathway for these chemicals to be consumed by higher aquatic life and humans[14]. Direct transfer of chemicals from sediments to organisms is now considered to be a major route of exposure for many species. These issues are focusing attention on sediment contamination and highlight the fact that sediments are important resource.

Since these sediments are both carriers and potential sources of contaminants in aquatic system, these substances could also affect ground water quality and agricultural products when disposed on land. Moreover, because contaminants are not necessarily fixed permanently in the sediments, they could be remobilized when physico-chemical conditions change. Bioavailability of toxic chemicals and food chain transfer could also be strongly affected by such processes and by the types of chemicals binding on the sediment particles. If concentrations in the water phase are low, sediment bound contaminants may have greater impact on aquatic organisms than dissolved concentrations. The basic premise has been to restrict contaminants from occurring in water at concentrations above the known chronic or toxic levels. This approach should also apply for sediments but it has to include the long-term behaviour of contaminants which is determined by the physico-chemical reactions in the system[14].

Analyses of metal distribution and available tidal hydraulic data indicate that metal concentrations are due to a combination of source and tidal hydraulics[17]. The fate of heavy metals such as lead, iron, copper, cadmium and zinc in the aquatic environment is of extreme significance due to their impact on the ecosystem. This is particularly true if the water course passes through an urban area where the inputs are non-point in nature and include municipal and industrial discharge, urban runoff and atmospheric contributions. The metals in such environment can be accommodated in three basic reservoirs: water, sediment and biota. The biota reservoir however is small compared to water, which in turn is much smaller than the sediment reservoir.

Studies on sediments such as the determination of levels and distribution as well as the fluxes of metals such as Fe, Pb, Cd, Cu and Zn in Qua Iboe River sediments could provide useful information on the processes going on within the river. Therefore the work was carried out to trace the various anthropogenic sources of trace metals into a segment of Qua Iboe River, quantify their levels and compute their fluxes in the sediments. Since there is no documentary evidence to show that any sedimentary work on metal fluxes in this part of the river had been carried out before, the data from this work could be used as baseline information.

THE STUDY AREA:

The study was concentrated on a segment of Qua Iboe River in Essien Udim Local Government Area of Akwa Ibom State. This area is within a typical tropical humid climate zone that is generally characterized by distinct dry and wet seasons.

The wet season sometimes begins in March or April and is often characterized by heavy storms of short duration. Sometimes strong winds that destroy crops and building occur. The annual average rainfall is about 2,168mm[19], although [20]had recorded mean annual rainfall of between 2,000 and 3,000mm.

The dry season which normally lasts between three and five months is often influenced by the hot north-easterly winds blowing from the Sahara desert. The mean annual temperature is 26°C with a high relative humidity (70-80%) particularly along the coast of Qua Iboe River.

The area is undulating with a gradient of less than 5%. The peculiar geological formation which ranges from coarse to fine sands accords the Qua Iboe River its sparkling quality particularly during the dry season when discharge through runoff is minimal[19,20]. However, during the rainy season, tremendous runoff from the thiny vegetated slopes interfere with the sparkling water and turns it into a diluted mixture of red clay and mud [20].

Occupationally, a high percentage of the citizens are peasant farmers who scarcely use chemical fertilizers and insecticides to raise their crops. Apart from a negligible few citizens who avail themselves of bore hole water, the rest depend on Qua Iboe River and its tributaries for their water supply.

MATERIALS AND METHODS

Sample cores were taken from five points viz. US_1, US_2, MS, DS_1 and DS in the sampling sites of Qua Iboe River and Atan stream (a tributary of the river) (Fig. 1). The sampling, which took place between January and October in 1997, was carried out at two points for each of the upstream and downstream sites. On the other hand, only one sampling point was chosen at the midstream site. Twenty core samples were obtained upstream made up of ten from US_1 and ten from US_2. Similarly, twenty samples were collected downstream made up of ten from DS_1 and ten from DS_2 while ten core samples were obtained from midstream (MS) site.

All the samples collected were put into brown calico bags and taken to the laboratory for preservation. Samples meant for metal analysis were air-dried while those for density and porosity determination were transferred into an oven set at a temperature of 105°C. The air-dried samples were then homogenized and passed through a 250µm sieve before sub-sampling for metal analysis. All the samples were then carried to China in November, 1997 where they were appropriately preserved and later analyzed in January, 1998 at The State Key Laboratory of Environmental Aquatic Chemistry (SKLEAC) in Beijing, China.

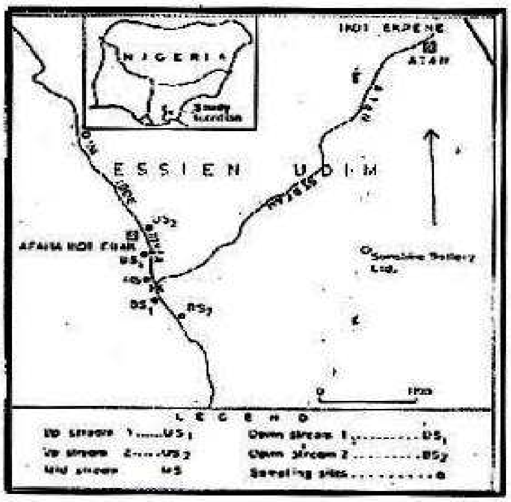

Fig. 1: Qua Iboe River at Afaha Ikot Ebak showing sampling sites.

Exactly 0.5000g of the samples were weighed using an automated Basic Sartorius Balance, model BA 61, into CEM Advanced Composite Teflon digestion vessels.

Into each of the samples prepared in a clean laboratory equipped with laminar flow bench and fume hood, 11cm^3 of the mixture of HNO_3/HCI/F|HF were carefully added in the ratio of 8:2:1[21]. The content of each vessel was carefully swirled to ensure complete mixture with the reagents. The vessels were then properly corked and made airtight prior to digestion. A microwave digestion equipment (CEM Corporation), model MDS-2000 was used to digest the sediment samples. The samples were put into Advanced Composite Teflon PFA digestion vessels, one of which was equipped with a pressure relief control that allowed a maximum operation pressure of 138 kpa. These were then placed in a rotatory table of the equipment, which is capable of accommodating a maximum of 12 digestion vessels at a time. The microwave power ranged between 0 (zero) and 100% (630 W) and the highest operating temperature was 200^{0}C. After digestion, each sample was diluted and made up to 25cm^3 with deionised water in flat bottomed flasks that had been thoroughly washed and rinsed. The solution was swirled to mix prior to analysis. Analyses of the samples were carried out using a Perking Elmer model 3100 Atomic Absorption Spectrometer, equipped with a deuterium arc background correction system, and a GFA model AS-60 auto-sampler. Argon was used as the inert flow gas. Elements analysed for were Fe, Pb, Cd, Cu and Zn. The results were recorded by the instrument in $\mu g l^{-1}$ but had to be converted to $\mu g g^{-1}$. Trace metal fluxes were calculated using the equation below:

$$F = R\,(1-\theta)\,\sigma\,C$$ [22]

Where F= flux, R= sedimentation rate, θ = porosity; σ = dry density, C= metal concentration.

RESULTS AND DISCUSSION

Table I contain the results of the analysis for concentrations of the metals in the sediments, while Table 2 contains the trace metal fluxes on site basis. Fe concentration was highest in MS and lowest in US_2. This may have been due to the proximity of MS to Atan stream, a tributary of Qua Iboe River, which received the battery factory effluent when it was operational. The trend indicates that the middle part of the river which received effluent from the factory recorded very high level of Fe (10,511.000 µgg^{-1}) which confirms the assertion by some authors that sediments are not only traps for metals but sinks for them[14]. On the contrary, low value (3,924.330-µgg^{-1}) was recorded at the upper part of the river which was not influenced by any industrial effluent. The trend for Fe concentration was $MS>DS_2>US_1>US_2>DS_1$. This gives a distribution pattern similar to that obtained for Ligurian coast sediments where the level of Fe at a particular point was relatively higher than the levels at other points[23]. The DS_1 sample was observed to record the highest Pb level (350.00 µgg^{-1}). The trend for Pb levels in the samples was $DS_2>MS>DS_1>US_1>US_2$. The trend shows that DS_1, MS and US_1 which were directly influenced by the runoff from the factory and the adjoining local streams contained higher Pb metal than US_2 which was further away from this influence (Fg. 1). Similarly high lead levels have been recorded for Newark Bay sediments[17], some Ligurian coast sediments[23], Long Isand sound sediments[24], Genesee river sediments[25] and Bermuda sediments[22]. The trend for Pb is almost similar to that for Fe particularly with respect to DS_2 and US_2 samples. Similarly Zn level was highest in DS_1 (30.020µgg^{-1}) indicating a concentration by other non point source of Zinc such as the adjoining farmlands and Essien Udim local Government Headquarters. (which was undergoing construction at this time). The trend for Zn distribution was $DS_1>DS_2>US_2>US_1$. The DS_2 sample also contained the highest levels of Cu (9.770 µgg^{-1}) compared to other samples. The trend for Cu distribution was $DS_2>US_2>DS_1>MS>US_1$. This trend resembles the distribution pattern for Cd in Bermuda sediments[22]. The DS_1 core yielded the maximum values of Pb, Zn, Cu and Cd in the river. It therefore appears the industrial effluent was the major source of the trace metals judging from the results obtained.

Metal fluxes, the product of total concentration and discharge varied directly with the discharge. It was also observed that the fluxes of the metal showed no definite trend (from DS_2 to US_2), except for Cd that showed flux increase from DS_2 to MS. In all, the metals maximum fluxes occurred in Fe (Table 2), which also exhibited the lowest flux corresponding to the lowest concentrations in the samples. Fe showed a maximum flux of 1641.8 10µg cm^{-2} S^{-1} at the MS site and a minimum flux of 44.540µg cm^{-2} S^{-1} at the US_1. The magnitude of Fe in the Qua Iboe River sediments was comparable to those obtained in the Ligurian coast and Genesee sediments[23,25]. The trend of fluxes for Fe in Qua Iboe River sediments was therefore $MS>DS_2>US_2>DS_1>US_1$.

TABLE 1. RESULTS OF ANALYSIS OF SEDIMENTS ALONG A SEGMENT OF QUA IBOE RIVER IN SOUTHERN NIGERIA

PARAMETERS	SAMPLES						SD	C.V
	DS_1	DS_2	MS	US_1	US_2	X		
Sed. Rate (cm^{-1})	7.500	3.500	21.600	21.600	27.100	18.340	6.992	38.124
Dry Density (cm^{-3})	0.010	0.0014	0.010	0.005	0.003	0.006	0.004	66.667
Bulk Density (cm^{-3})	1.934	1.408	1.867	2.012	1.674	1.779	0.217	12.198
Porosity	0.270	0.470	0.290	0.240	0.370	0.328	0.083	25.305
Fe (ug/g)	66.24.330	10217.670	10511.000	5554.000	3924.330	7366.266	2596.211	35.244
Pb (ug/g)	24.570	350.710	31.620	5.170	5.080	128.030	143.793	112.312
Cd (ug/g)	0.030	0.190	0.180	0.000	0.000	0.080	0.086	100.500
Cu (ug/g)	2.930	9.770	2.620	1.470	2.960	3.896	2.980	76.489
Zn (ug/g)	36.170	30.020	12.500	9.980	19.100	19.554	7.680	39.276

TABLE 2: TRACE METAL FLUXES (μg cm^2S^{-1}) ON SITE BASIS

SAMPLE	Fe	Pb	Cd	Cu	Zn
DS_2	362.680	13.850	0.0016	0.160	1.430
DS_1	102.680	3.510	0.0019	0.018	0.300
MS	1641.810	4.940	0.828	0.410	1.950
US_1	44.540	0.420	0.000	0.012	0.800
US_2	207.600	0.270	0.000	0.140	0.960
X	552.260	4.540	0.0063	0.164	1.088
S.D	557.700	5.040	0.010	0.13	0.560
C.V	100.990	111.010	158.730	19.270	91.470

Maximum Pb flux of 13.850μg cm^{-2} S^{-1} was obtained in the DS_2 sample while US_2 showed a minimum Pb flux of 0.270μg cm^{-2} S^{-1}. The flux pattern for Pb showed that more Pb had probably been introduced into the upper part of the river (with respect to the location of the battery industry), than the lower part.

Cd showed a definite trend of increased flux from the DS_2 to the MS with no metal flux into US_1 and US_2. The values show that DS_2 had a flux of 0.0016μg cm^{-2} S^{-1}, MS had a flux of 0.828μg cm^{-2} S^{-1} while DS_1 had a flux of 0.0019μg cm^{-2} S^{-1}. Cd flux into Qua Iboe River sediments resembled that observed in the Genesee river sediment[25] and Bermuda ocean sediment[22].

Cu showed the highest flux at MS (0.410 μg cm^{-2} S^{-1}) and a minimum flux at US_1 (0.012μg cm^{-2} S^{-1}). The trend was $MS>DS_2>US_2>DS_1>US_1$. The flux patterns were similar to those observed for Bermuda ocean and Genesee river sediments.

Zn showed no definite trend in its flux patterns. The highest flux value was however recorded at MS (1.950μg cm^{-2} S^{-1}) and the lowest at DS_1 (0.300μg cm^{-2} S^{-1}). The trend showed that $MS>DS_2>US_2>US_1>DS_1$, indicating that more Zn-laden runoff from the neighboring Local Government Headquarters (which was under construction at the time of this investigation) and the cultivated slopes was introduced into MS site than the US and DS sites.

On the whole the flux values show that influx of metals into the upper segment of Qua Iboe River through anthropogenic activities notably batteries production (when the factory was operational) and those contributed by the construction of the new Local Government Headquarters were greater than in the lower segment of the river.

It was generally observed that metal levels, as well as their fluxes were highest at sites close to a battery manufacturing industry and a Local Government Headquarters. Thus in addition to giving an information on the role usually played by anthropogenic activities in environmental pollution, the study also reveals the fact that sediments do not only act as metal traps but are also capable of retaining these metals for years.

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