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SEDIMENT QUALITY: ASSESSMENT OF SELECTED HEAVY METALS IN THE SEDIMENTS OF THREE RIVERS IN THE NIGER DELTA REGION OF NIGERIA

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ABSTRACT

The aim of this study was to determine heavy metals levels (Pb, Cd, Cr, Ni, As, Hg, Cu, Znand Fe), in the sediments of three rivers (Orashi River, Aluu River and Woji River). Nine sediment samples were collected from the three rivers (.3 samples from each river). The samples were digested .by placing 10 g of each sample into beakers, then 20 cm^3 of concentrated trioxonitrate (v) acid was added, and were carefully heated on a hot plate. The samples were cooled and 2-4 cm^3 of perchloric acid ($HClO_4$) was added and heated until a cleared sample solution was obtained. The samples were diluted and filtered into 100cm^3 volumetric flasks and the concentrations of the metals were determined by atomic absorption spectrometry (AAS). The results showed that Fe, Pb, Cd, Cu and Ni were the main contaminants. It was noted that the concentrations of Pb and Cd, which are poisonous metals, were high in the sediment samples, compared to the World Health Organisation (WHO) maximum allowable limit of 0.01 mg/L for both lead and cadmium.

Key words: Heavy metal, AAS, Sediment, Rivers, Niger Delta.

INTRODUCTION

Heavy metals are metallic elements with high atomic weight and density. These include the transition metals, some metalloids, lanthanides and actinides. Being metals ions, heavy metals cannot be degraded or destroyed, therefore, their stability makes them persistent toxic substances in environment [1-3]. Heavy metals as the environmental contaminants can be found in the air, soil and water, which pose health hazard to the public [4, 5]. Various reports on impact on the environment have been reported. Cruz-Guzman *et al* [6] reported that water pollution at the Gulf of Thailand, which was caused by combination of heavy metals and nutrients, together with eutrophication, had resulted in their habitat to be degraded, particularly mangrove forest and coral reef.

Sediment is the sink of toxicants in the aquatic environment [7]. This is because pollutants from the surrounding environment wash into surface water systems and bind to particulate matter in the river [8]. Through the process of sedimentation, particulate matter settles into the sediment therefore, increasing the concentrations of the pollutants in the sediment.

Several studies have been carried out on sediment quality in terms of metal accumulation and contamination [9-11]. Research has shown that there is an affinity for organic and inorganic contaminants (such as metals) to particulate matter [12-14]. This has resulted in the storage of several potentially toxic substances in sediments. The stability of these contaminants is controlled by a combination of physical and chemical processes, which can see toxic metals held down for long periods, reducing the risk of toxicity. The major physical process is the very low agitation usually brought about by wave disturbance that takes place in ocean sedimentary levels, bioturbation and the property of the sedimentary material, i.e. surface area, sediment porosity (packing of the material), the particle size of the sedimentary materials [15].

Research conducted by Zhang *et al* [16] studied the elemental concentrations of sediments. Addy *et al* [17], studied the distribution of trace elements in the surface of water and sediments from Crayford Creek in Warri, Delta State, Nigeria. They discovered that the sediment and water were contaminated with Cu, Cr, Mn, Pb, Ni, Cd, Fe and Zn. Similarly, research has shown that some rivers and creeks in the Niger Delta region of Nigeria were contaminated with heavy metals [18-22]. Sediments influence environmental fate of many toxic and bio-accumulative substances in aquatic ecosystems [23]. Many substances in aquatic systems and elements associate themselves with particulate matter and are eventually dragged down into the sediment bed [24]. They also act as sources of pollution to the biological environments where they are found because they accumulate contaminants, nutrients, metals, pathogens, inorganic and organic chemicals. When this occurs in large quantities, the sediments assimilate large volumes of contaminants, which disrupt the ecosystem through the loss of biotic species. Many researches have been carried out to state the importance of sediment contamination for ecosystem quality and the widespread incidence of sediment contamination [25, 26]. Impacts on the ecosystem from sediment-associated contaminants have been studied and results have shown to range from direct effects on benthic communities [27-29] to substantial contributions to contaminant loads and effects on upper tropic levels through food chain contamination. Sediment contamination occurs because many chemicals bind themselves to organic or inorganic particles that eventually settle to the bottom of streams, rivers, reservoirs, estuaries and marine waters. In addition, sediment contaminants adhere to small, fine-grained particles and settle in depositional areas. Such contaminants include metals that could be toxic to the ecosystem, but are held in a stable state by the sediment particles.

The aim of this study is to determine some toxic heavy metals in Mbiama, Aluu and Woji rivers of Niger Delta region.

MATERIALS AND METHODS

Description of the study area

This research work covers both fresh water and brackish water. The rivers include Orashi River, Aluu River and Woji Creek. Orashi and Aluu rivers are both fresh water while Woji creek is brackish water in Port Harcourt, River State, Nigeria. Orashi river (also known as Urashi or Ulasi), is a river of the lower Niger River basin, and a tributary of Oguta Lake, Southeastern Nigeria. It is located on the East – West road, Mbiama. For Aluu River, its alternative names are Allua, Alia and Aluu. Woji creek passes through many communities including Oginigba, Woji Azubiae, Okujagu, Okuru-Ama, Abuloma, Ojimba, Oba, Kalio-Ama and Okrika. The occupation of the people around Woji creek includes fishing, farming, boating and dredging. Water from the creek is used for washing, cooking and even drinking. The vegetation is dominated by Nypa palms (*Nypa fructicans*) and mangrove (*Avicennia nitida* and *Rhizophora racemosa*) an important fluvial system in the city of Port Harcourt, which serves as a source of food (fishes and other edible aquatic organisms) and transportation. The region lies within the longitudes 6^o 55'E - 7^o 05'E and Latitude 4^o 48'N - 4^o 57’N of southern oil rich Niger Delta region.

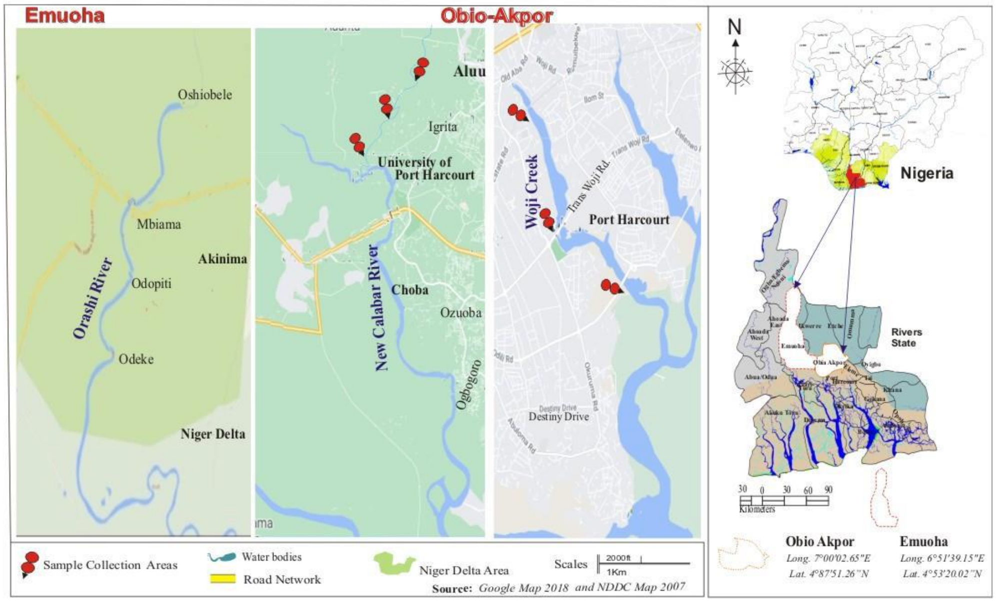

Figure 1: Map showing the study areas

Sampling preparation and samples collections

Sampling preparation

Sample containers were properly labeled to reflect date, time of sampling, and locations of various samples. Sampling containers were rinsed several times with the water of the sediment to be sampled before collecting the representative sample for analysis. Samples were properly preserved before onward transportation to laboratory for analysis.

Samples Collection

A random sampling technique was adopted as described byNayak *et al* [30]; in collecting the sediments samples from the three rivers (Orashi River, Aluu River and Woji Creek). Nine samples (3 samples from each river) were collected from the three rivers. Sample were taken to a depth of 60 cm to account for the toxic zone where aerobic respiration takes place and therefore, ease of chemical flow from the sediment to the water column. Samples were randomly collected with a good distance depending on the size and shape of the river. The samples were collected to represent the whole river.

Preparation of Standards

Standards solution of chromium, iron, nickel, zinc, arsenic, mercury, copper, cadmium and lead were prepared using Iron (III) chloride, Manganese (II) chloride, Zinc nitrate, Cadmium chloride, Chromium nitrate, Nickel (II) nitrate, Cobalt (II) nitrate and Lead nitrate salts, for the calibration of the instrument. Stock standards solutions of the metals of interest were prepared by weighing out the appropriate salt of the metal out as calculated in relation to the formula weight, dissolved in 1 dm^3 volumetric flask and made up to mark with deionized water [31, 32]. The working standards of appropriate concentrations were prepared from the stock solutions by diluting appropriate volume with deionized water and made up to mark in 100 cm^3 volumetric flask and used for calibrating the AAS equipment.

Sample digestion

Exactly 1.0 g of each sample was placed into beakers, added 20 cm^3 of concentrated trioxonitrate (v) acid, and kept for 24 hours after which they were carefully heated on a hot plate connected sand-bath in fume hood chamber with periodic addition of 10-20 cm^3 concentrated trioxonitrate (v) acid until the production of red nitrous oxide (NO_2) ceased. The samples were cooled and 2-4 cm^3 of perchloric acid ($HClO_4$) was added and heated until a clear sample solution was obtained. The samples were diluted with deionized water, filtered into 100 cm^3 volumetric flasks, made up to mark and transferred into a capped labeled plastic bottle and was analyzed immediately. The ratio of the acids, HNO_3:$HClO_4$, used for the digestion was 5:1 [33, 34]. Blank sample was also prepared by digesting the same proportion of the reagents used in the sample digestion under the same experimental condition without the sample.

Analysis of the samples

The filtrates obtained from the digestion process were subsequently analyzed for heavy metals (Pb, Cd, Fe, Ni, Cu, Hg, Zn, Cr and As) using atomic absorption spectrophotometer (UNICAM, 969), while mercury was determined by cold vapour atomic absorption spectrometry usingF732-S spectrophotometer. The laboratory analysis was carried out at Tudaka Environmental Consultants' facility, in Port Harcourt, River State, Nigeria.

RESULTS AND DISCUSSION

The results of the concentrations of heavy metals from the study locations are shown in Tables 1-3.

Table 1: Heavy metal concentration (mg/kg) of Mbiama River sediment

Parameter	Station 1	Station 2	Station 3
Cd	1.010	1.602	3.602
Cu	10.40	2.404	8.301
Fe	20670	4380	5194
Pb	10.80	10.30	17.90
Ni	31.60	32.40	26.30
Zn	ND	ND	ND
As	ND	ND	ND
Hg	ND	ND	ND
Cr	ND	ND	ND

ND = not detected

Table 2: Heavy metal concentration (mg/kg) of Aluu River sediment

Parameter	Station 1	Station 2	Station 3
Cd	14.40	ND	ND
Cu	ND	ND	7.280
Fe	302.3	38.62	133.4
Pb	ND	ND	ND
Ni	11.89	ND	ND
Zn	1.490	1.290	10.68
As	ND	ND	ND
Hg	ND	ND	ND
Cr	184.5	79.20	201.5

Table 3: Heavy metal concentration (mg/kg) of Woji River sediment

Parameter	Station 1	Station 2	Station 3
Cd	4.470	5.286	0.061
Cu	34.81	0.179	58.87
Fe	2024	3112	876.7
Pb	0.034	13.97	73.77
Ni	0.733	0.955	0.443
Zn	10.32	14.66	32.85
As	ND	ND	ND
Hg	ND	ND	ND
Cr	0.004	136.6	0.045

Heavy metal concentration in the analyzed samples signifies some degree of contamination in the area under investigation. The highest values of the selected heavy metals were recorded for Fe in Mbiama River, with a ranged value of 4380 – 20670 mg/kg in Table 1. The values of Fe maybe attributed to iron ores like hematite (Fe_2O_3), which is red, magnetite (Fe_3O_4) (black in colour), limonite ($2Fe_2O_3.3H_2O$), which is brown or siderite ($FeCO_3$), (pale brown) which may be present in the region. They may leach or wash into the river, then later settle under the river bed [36]. There is a noticeable moderate value for Ni, Pb and Cu in Table 1 as well, that ranged from 26.30 – 32.40 mg/kg, 10.30 – 17.90 mg/kg, and 2.404 – 10.40 mg/kg respectively. The case Pb can be attributed to the plumbo-solvent action of the acidic water, poorly cased borehole, leaching from waste in the battery chargers and mechanic workshops as well as vehicular emissions from the exhaust pipes [37]. Arsenic, zinc, chromium and mercury were not detected in the sediments (in Table1).

In Table2, the heavy metals result in Aluu River showed that Fe and Cr had highest concentrations, having a ranged value of 38.62–302.3 mg/kg and 79.20 – 201.5 mg/kg respectively, compared to Zn that ranged from 1.290 – 10.68 mg/kg and Ni (11.89 mg/kg). Ni and Cd were detected in just one of the stations. Pb, As and Hg were not detected in the sediments in River Aluu. The high concentrations of Fe and Cr values in the sediment may be due to the minerals in the soil or it is caused by industrial and human activities in the area that release much of these minerals into the rivers that later settle under the river bed. Metals are strongly associated with particles in runoffs [35].

There is a noticeable high value of Fe in Woji river in Table3, a ranged value of 876.7-3112 mg/kg, compared to Cr and Ni that ranged from 0.004 – 136.6 mg/kg and 0.443- 0.955 mg/kg respectively. Also, As and Hg were not detected. The other metals were detected. The Fe value in the sediment may be due to minerals in the soil, which might move into the sediment from soil that entered the water. The presence of all these metals in the River Woji may be due to leaching of heavy metal toxicant wastes containing them. It is evident that there has been some degree of contamination due to heavy metals in the study area.

CONCLUSION

The results of the heavy metal analysis of the sediments samples indicated the presence of Fe, Pb, Cd, Cu and Ni. Heavy metal concentration in sediment samples signifies some degree of contamination in the area under investigation. Sediment samples in the area were enriched in some heavy metals, though some were low and some were not detected in the three rivers (e.g. arsenic and mercury). Fe was relatively higher in concentration than other metals (Tables 1-3). The study revealed high concentrations of Pb and Cd, in the sediment samples, of which Pb and Cd are poisonous metals. They were above the maximum allowable limit of the World Health Organization of 0.01 mg/L [38], which is dangerous to human health. This can cause lead poison and eventually lead to death of human. Human can consume those poisonous metals through direct drinking of the water or indirectly through feeding on those fishes (which feed on the sediments) from the rivers.

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