EVALUATION OF SOME HEAVY METALS ON THE SURFACE WATER OF WARRI RIVER, WARRI, DELTA STATE, NIGERIA

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Abstract

The objective of the study was to investigate the presence of some heavy metals in this often polluted water body. For this examination to be accomplished, standard analytical procedures were used to determine surface water samples collected from Warri River, between April and September 2012. Atomic Absorption Spectrophotometer (ASS) was used to evaluate the presence of heavy metal in this all popular water body. The sampling stations examined were chosen as a result of ease of accessibility. Concentration of heavy metals in this river was compared with (WHO, 1982 and FEPA, 1991) recommended standards for aquatic organisms and portable water for human usage. The study showed that the mean concentrations of the following metals (Iron =6.75 mg/l, Copper =1.69 mg/l, Lead =0.45 mg/l, Manganese = 2.22 mg/l, Cadmium =0.18 mg/l and Chromium =0.24 mg/l) except Zinc (4.21 mg/l), exceeded the maximum limit recommended for human lives, indicating that the water body was harmful to humans, but posed no danger to aquatic organisms. It is therefore recommended that the river be closely monitored from time to time in order to alert the general public of the incidence of any future increase in pollution in the same water body. Since the level of aquatic pollution are bound to change overtime, through natural and/or artificial means, there is need to enforce existing industrial and environmental wastes discharge/recycling laws to ensure reduced, more efficient and planned waste discharges, especially into the aquatic ecosystem. This measure will avert future metal bio-accumulation in water and in aquatic organisms as well as reduce the concentration of metals that may be ingested by man through fish food and or portable water.

Keywords: Heavy metals, polluted water, Warri River, Nigeria

Introduction

Availability of good quality water in the aquatic environment is an indispensable feature for improving life's qualities (Oluduro and Aderiye, 2007). Natural water contains heavy metals whose nature and concentration, vary with water source. These water sources could be contaminated with oil spillage, domestic and/or industrial effluence. Also the increased use of metal-based fertilizers in aquaculture, results in continuous rise in heavy metal pollution of fresh water bodies through flood. Metals have been introduced into aquatic systems through weathering of rocks, leaching of soils, dissolution of aerosol particles from the atmosphere and human activities including mining, processing and use of metal based materials in the manufacture of certain products (Ipinmoroti and Oshodi, 1993; Adeyeye, 1994; Asaolu *et al*., 1997). The bye-products emanating from these activities together with the metals contained in them, affects water bodies adversely, altering their chemical composition and causing harm to both humans and aquatic organisms depending on such water bodies for fish food and portable water supply (Adewoye, 1998).

Heavy metals attract public health interests, because affected persons exhibit behaviors similar to those affected with persistent toxic chemicals (Obayori *et al*., 2009). Unlike many organic contaminants that lose toxicity with biodegradation, heavy metals cannot be degraded further. In addition, their toxic effects could become long lasting, whilst their concentration in the organisms increase through bioaccumulation. Toxic metals are of low concentrations in their natural environment (lbeto and Okoye, 2010), but resulting from industrialization and other technological processes, they often occur at higher concentrations, other than those naturally occurring. When they occur at elevated levels in natural aquatic systems, they become toxic to organisms (Adeyinwo *et al*., 2005).

Polluted water samples for analytical studies are used for the detection of low, toxic and significant amounts of heavy metals. A continuous monitoring of such metals in the aquatic system is essential as their concentrations reflect contamination load over a period of time (Adeyinwo *et al*., 2005). In Nigeria, there are reports of various types of pollutants from chemical and industrialized areas especially those emanating from crude oil spills into various water bodies. Aquatic pollution through these contaminants, often result in adverse consequences to the organisms. To date, some studies have been carried out on heavy metal pollution in Warri River, but none of the finding is in relation to their recent concentration; hence the present study. It compared the heavy metal isolated from this river with those allowable for aquatic organisms and human lives as recommended (WHO, 1982; FEPA 1991 and Dietz *et al*., 2000).

Materials and Methods

Description of the study area

Warri River is located at latitude 5^0. 27^1 to 5^0. 33^1 N and longitude 5^0. 33^1 to 5^0. 41^1 E (Figure 1). The river is located in South Western Nigeria, as a tributary of River Niger. It flows for 57 kilometres, ending at the Bight of Benin, around the Gulf of Guinea and empties into the Atlantic Ocean. The river, which has a depth of about 30 cm (98ft) on the average, was the most important channel for crude oil shipment. Chevron, a major United States oil company has its main Nigerian oil production facility located at the mouth of the river.

Collection of samples

Surface water samples were collected the same day from each of the three stations. Each station sample was kept in one litre plastic bottle. Such bottles were previously washed in 10% HNO_3 and 1:1 HCl and HNO_3 for 48 hours and labelled. To the water in the one litre plastic bottle, was added a few drops of HNO_3, in order to prevent loss of metals and probable attack by bacterial or fungal growths. Water samples were transported to the Ministry of Petroleum and Environment, in Owerri, Imo State, for heavy metal isolation and analysis. Sampling was carried out for six months with three replicates per station.

Sample analysis

Fifty mills of surface water sample was measured out from the one litre plastic bottle collected from each station into 250 ml conical flask and digested with 10 ml $HN0_3$ acid. The mixture was heated on a hot plate to a reduced volume of 5 to 7 ml. Digested samples were filtered using Whatman No.4 filter paper. Deionised water was added to it to the 100 ml mark. Samples were then mixed properly and transferred into polythene bottles. A blank was also prepared as illustrated using distilled water. Each sample was read off the Atomic Absorption Spectrophotometer (ASS) UNICAM, 919 Model. Calibration was done by using standards for each metal under investigation at wave lengths of 324.7nm for copper, 248.3 nm for iron, 283.3 nm for lead, 228.8 nm for cadmium, 357.9 nm for chromium, 279.5 nm for manganese and 213.9 nm for zinc. These results were tabulated for interpretation.

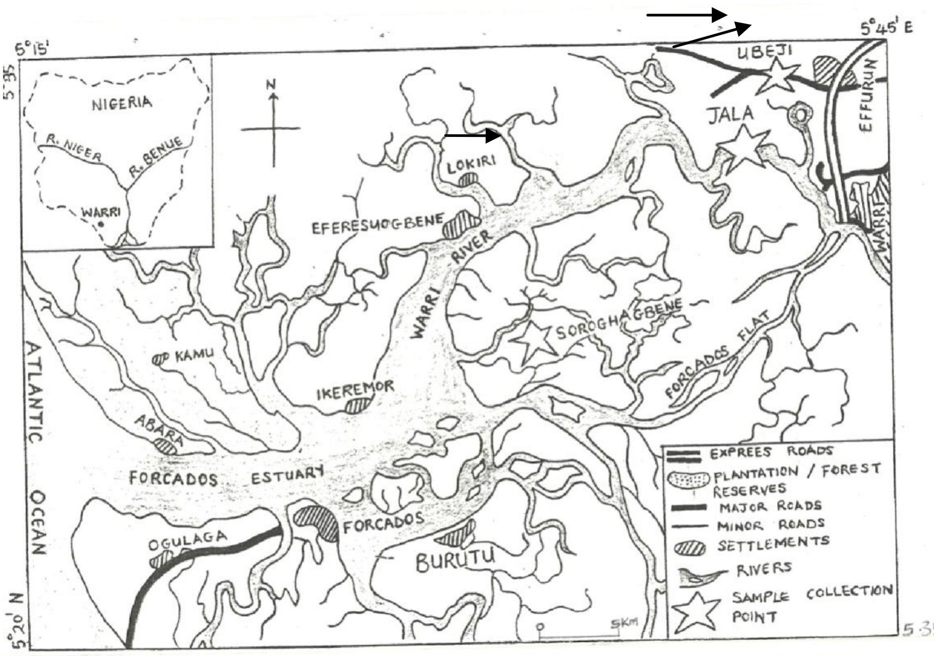

Fig. 1: Map of Warri River and environs, showing the study stations (Soroghagbene, Jala and Ubeji)

Statistical Analysis

Data generated from the study were analyzed statistically by calculating means and standard deviation according to Steel and Torrie (1960).

Results

Table 1 revealed that Iron (1.42 ± 1.51 mg/l) had the highest mean concentration, while Chromium (0.08 ± 0.08 mg/l) had the least concentration. Data in this table revealed a decreasing order of metal distribution from April through to September at each station.

The data in Table 2, revealed that Iron (3.03 ± 1.01 mg/l) had the highest mean concentration, Zinc (0.48 ± 0.59 mg/l) took the intermediate position while Chromium (0.19 ± 0.11 mg/l) was the least occurring heavy metal in station 'B'. This observation also showed a decreasing order in the distribution of metals at the stations from April to September.

As observed in tables 1 and 2, data in Table 3, also showed the same pattern of heavy metal concentration/distribution during the months. Iron, accounted for the highest concentration amongst those isolated. Chromium was the least occurring metal isolated during the study, Table 4. The table also revealed that the mean concentration of Iron was the highest in April compared with metal concentrations during the other months.

Discussion

The results of the present study revealed that the mean concentration of each metal was highest in the month of April, but decreased progressively to the month of September. The reason for this observation could be that the influence of reduced rainfall or low precipitation was experienced more in April when there was more sunshine during that month than in other months. Increased metal concentration was highest in April as the water body which was subject to evaporation, left the surface water highly concentrated. As the intensity of rainfall increased, the concentrations of heavy metals decreased also through dilution.

The recent amount of heavy metals in the study area may be associated with human activities such as pollutants from localized industries, oil spills and the use of chemical based fertilizers by farmers. The same observation was reported by (Egila and Nimyel, 2002) who reported that the discharges settled more in the sediments of some dams in Plateau State, than at their surface water. It was also observed that iron had the highest mean concentration throughout the study. The highest concentrations of all metals were sampled in the month of April while the least were sampled in the months of June/July. It was also reported that iron occurred at higher concentration in the sediments of Ondo State Coastal areas than at surface water (Asaolu *et al*., 1997; Asaolu and Olaofe, 2004) as well as in the sediments of the Lagos lagoon, than at surface water Nwajei and Gagophien, 2000). These observations were in contrast to that of the present study where metal concentration was very high at water surface.

On the average, the distribution of mean concentrations of Chromium (0.24 mg/l), lead (0.45 mg/l) Copper (1.69 mg/l), and all other heavy metals detected in the study area varied from one station to another station, but maintained the same pattern of distribution in each station throughout the study period. This pattern of metal distribution could be attributed to geological occurrence of minerals that vary from one location to the other. Similar variations were reported in sediment of major dams in Ekiti State (Adefemi *et al*., 2007).

The concentration of zinc in the present study ranged between 2.19-6.70 mg/l with an average value of 4.21±0.42 mg/l. The highest concentration (6.70 mg/l) was obtained in April. This concentration may have been associated with domestic activities, including the use of these chemicals in the local industries and zinc based fertilizers by farmers (Egila and Nimyel, 2002). According to Obodo (2002), Zinc was prevalent at the lower reaches of River Niger. Zinc concentration in that locality was comparable with those of the present study. Zinc is a neurotoxin, causing neuronal cell death in a dose dependent manner. Fortunately, the concentration of zinc at surface region during the present study (4.21) was below (76.6) the recommended standards (WHO, 1982; FEPA, 1991 and Dietz *et al*., 2000), reported as harmful to aquatic organisms. This indicates that the present concentration of Zinc in Warri River may not be harmful to the organisms in that environment.

Table 1: Temporal distribution of heavy metals isolated from surface water in Soroghagbene.

Parameters	April	May	June	July	Aug	Sept	± SD
Iron (mg/l)	3.81	2.82	0.12	0.59	0.49	0.71	1.42±1.51
Copper (mg/l)	0.24	0.14	0.13	0.04	0.31	0.03	0.79±1.22
Lead (mg/l)	0.15	0.13	0.11	0.01	0.06	0.08	0.09±0.05
Cadmium (mg/l)	0.28	0.22	0.04	0.03	0.05	0.01	0.09±0.08
Chromium (mg/l)	0.18	0.10	0.03	0.03	0.04	0.05	0.08±0.08
Zinc (mg/l)	1.06	1.04	0.70	0.23	0.53	0.32	0.22±0.30
Manganese (mg/l)	0.76	0.64	0.33	0.21	0.42	0.89	0.29±0.31

Table 2: Temporal distribution of heavy metals isolated from surface water in Jala,

Parameters	April	May	June	July	Aug	Sept	± SD
Iron (mg/l)	4.31	4.03	3.34	2.43	2.23	1.84	3.03±1.01
Copper (mg/l)	1.72	1.63	0.89	0.88	0.74	0.54	2.05±1.23
Lead (mg/l)	0.35	0.23	0.10	0.11	0.13	0.34	0.21± 0.11
Cadmium (mg/l)	0.41	0.24	0.19	0.21	0.13	0.33	0.23± 0.11
Chromium (mg/l)	0.22	0.13	0.10	0.09	0.11	0.04	0.19± 0.11
Zinc (mg/l)	2.03	2.01	1.19	1.12	0.63	1.31	0.48± 0.59
Manganese (mg/l)	0.81	1.10	0.43	0.42	0.90	0.93	0.54± 0.55

Table 3: Temporal distribution of heavy metals, from surface water in Ubeji

Parameters	April	May	June	July	Aug.	Sept.	±SD
Iron (mg/l)	3.61	3.34	2.96	1.21	1.47	1.19	2.29±1.13
Copper (mg/l)	0.61	0.48	0.32	0.33	0.62	0.53	1.39±1.22
Lead (mg/l)	0.34	0.24	0.11	0.02	0.10	0.09	0.15±0.11
Cadmium (mg/l)	0.23	0.11	0.02	0.08	0.08	0.23	0.14±0.09
Chromium (mg/l)	0.10	0.02	0.11	0.03	0.04	0.04	0.11±0.09
Zinc (mg/l)	3.61	3.44	1.63	1.41	1.03	2.07	0.63±1.05
Manganese (mg/l)	1.74	1.13	0.87	0.42	0.44	0.90	0.68±0.96

Table 4: Comparative mean concentration of metals isolated with those recommended for humans and aquatics life, FEPA (1991) .

Parameter	Potable water (mg/l)	Aquatic life (µ/l)	Present study	April	May	June	July	Aug.	Sept.
Iron (mg/l)	1.0	7.00	**6.75	11.73	10.19	6.42	4.23	4.19	3.74
Copper (mg/l)	0.2-1.0	2.90	**1.69	2.57	2.25	1.34	1.25	1.67	1.10
Lead (mg/l)	0.05	5.80	**0.45	0.84	0.60	0.32	0.14	0.29	0.51
Cadmium (mg/l)	0.01	8.00	** 0.18	0.92	0.57	0.25	0.32	0.26	0.57
Chromium (mg/l)	0.1	10.0	** 0.24	0.50	0.25	0.24	0.15	0.19	0.13
Zinc (mg/l)	5.0	76.6	*4.21	6.70	6.49	3.52	2.76	2.19	3.70
Manganese (mg/l)	0.2	5.00	** 2.22	3.31	2.87	1.63	1.05	1.76	2.72

*Limits below that recommended for portable water

Cadmium occurs naturally in association with Lead/ Zinc. Their concentrations during the present study exceeded the tolerable level; hence consumers of food from this region should take the present discovery seriously. According to Bichi, (2000) the acute neurological effects of lead toxicity manifests in the form of nausea and abdominal cramps, bloody diarrhoea and vomiting, dizziness and chest-pain. These diseases which were reported in Japan, after the Second World War, were traced to Cadmium contaminated rice field. Human consuming fish polluted by both metals could be down with rheumatic arthritis and muscular pain. Wassen (1995) reported that coal and fossil fuels are known sources of Cadmium pollution. The residual deposits of the metal from oil spillage may be another source of Cadmium, Obodo (2002) in River Niger, Nwajei and Gagophien (2000) in Lagos Lagoon.

Copper is an essential substance required for normal functioning in human life, but because its concentration exceeded the WHO (1982) limit for portable water, it may result in anaemia, damage to the liver and kidney, as well as result to stomach and intestinal irritation. These observations were also reported by (Asaolu and Olaofe, 2004). Persons suffering from these ailments were at greater risk of secondary infections. Copper normally occur in portable water because of their release from copper pipes as well as their release form additives designed to control algal growth as reported by (Adeyinwo *et al.*, 2005) who also sampled Warri River.

Conclusion

The present study revealed that surface water from Warri River were contaminated with heavy metals, at levels not harmful to aquatic lives, but harmful to human lives when taken in portable water. The concentration of all metal isolation from the study area, except Zinc was higher than those recommended by FEPA (1991) for portable water. Iron concentration was relatively the highest in comparison to other metals (Copper, Lead, Zinc, Manganese, Chromium and Cadmium) isolated. The concentration of these metal pollutants in this frequently used water body, portends danger for its inhabitants (man and livestock), who drink the water or consume other products, without realizing the danger they are exposed to.

Recommendation

The following steps which were already in existence could be re-enforced as ways of avoiding and controlling future occurrences and effects of metal discharge into waters bodies.

Industries should enforce, adopt and maintain environmental wastes recycling laws and standards to enable them reduce the amount of wastes channelled into the aquatic environment.

Industrial effluents especially those containing heavy metals should be properly treated before being discharged on land or released into the aquatic environment.

Government should organize seminars and workshops to enlighten the public on safe and proper disposal of waste that contains heavy metals and the problem it could result in, when warnings are neglected.

Government policies on prevention and control of oil pollution should be strictly adhered to for improved fish production.

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