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Heavy Metals in Bioindicators of the River Niger about the Vicinity of the Ajaokuta Iron and Steel Industry in Kogi State of Nigeria

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ABSTRACT

The status of heavy metal pollutants of the River Niger within the vicinity of the Ajaokuta Iron and Steel Industrial complex was determined. The concentration levels of the metals- Cr, Pb, Fe, Co, Mn, V, Zn, Cu, Ni and Cd were determined in water, fish, soil and plant using Atomic Absorption Spectrophotometer. The results show that the concentrations of these heavy metals were higher in the plant samples (*Eichhornia crassipes*) than in other samples analysed. The heavy metal concentrations in the plant sample was in the order Fe > Mn > Zn > Cu > Ni > Cr > Co, while the other metals were not detected. Heavy metal concentration in the other samples were found to be low and mostly at undetectable levels.

Key words: Heavy metals, water, fish, soil, plant, pollution, anthropogenic sources

INTRODUCTION

Pollution is the introduction of contaminants into an environment that causes instability, disorder, harm or discomfort to the ecosystem i.e., physical systems or living organisms (Wikipedia, 2009). Pollution can take the form of chemical substances, or energy, such as noise, heat, or light. Environmental pollutants from many different sources contaminate water, air and land, putting humans and ecosystems at risk and often pitting people against industry. The term pollution of the environment herein refers to an increase of trace elements beyond the tolerable limits of the environment (Fifield and Haines, 1995). This increase may be related to human activities, which could be industrial and/or agricultural practices.

The iron and steel industry involves a myriad of operations which generate vast volumes of air emissions, liquid effluents and solid wastes (Bhargava, 1997). Improper management of solid waste is one of the main causes of environmental pollution and degradation in many cities, especially in developing countries. Many of these cities lack solid waste regulations and proper disposal facilities, including for harmful waste. Such waste may be infectious, toxic or radioactive.

Heavy metals are metallic elements that are present in both natural and contaminated environments. In natural environments, they occur at low concentrations. However, at high concentrations as is the case in contaminated environments, they result in public health impacts. The elements that are of concern include lead, mercury, cadmium, arsenic, chromium, zinc, nickel and copper. Heavy metals may be released into the environment from metal smelting and refining industries, scrap metal, plastic and rubber industries, various consumer products and from burning of waste containing these elements. On release to the air, the elements travel for large distances and are deposited onto the soil, vegetation and water depending on their density. Once deposited, these metals are not degraded and persist in the environment for many years poisoning humans through inhalation, ingestion and skin absorption. Acute exposure leads to nausea, anorexia, vomiting, gastrointestinal abnormalities and dermatitis (Njoroge and UNEP, 2007). For example, in the 1950, many fatalities occurred among a fishing community in Minamata Bay, Japan due to consumption of fish polluted by methyl mercury (Irukayama in Obasi, 1999; Okoye, 1989). Similar fish poisoning from methyl mercury was reported in Ghana in 1967 (Obodo, 1993). In 1968, the Japanese Ministry of Health and Welfare traced the cause of an unusual and painful disease Itai-Itai disease to chronic cadmium poisoning resulting from consumed fish (Forstner and Wittman, 1979).

The most polluted in the environment is the aquatic system. According to Okoye *et al.* (2002), water resources remain the main reservoirs of industrial, domestic and agricultural wastes in most developing countries. Hence streams, coastal environments including banks of rivers suffer from metallic pollutants due to increased industrialization. This is true because, air and soil contaminations ultimately end up in the aquatic system via local precipitation, water runoff and leaching of rocks and solid waste. A more serious pathway is the discharge of urban and industrial wastes, which contribute about one million different potential pollutants into aquatic system (Laws, 1981; Okoye, 2000; Egile and Nimyel, 2002; Obodo, 2002; Oguzie *et al.*, 2002).

Regulatory bodies have as a result been set up all over the world to study, monitor and protect its environment due to serious threats posed to life by pollutants. This includes the Environmental Protection Agency (EPA) in the United States of America, United Nation Environmental Programme (UNEP) and most recently the Federal Ministry of Environment (FME) in Abuja.

Following this concern, this work examines an aspect of environment quality assessment using water, fish, soil and aquatic plant found and used by the people around the Ajaokuta Iron and Steel Industrial Complex which is situated at the western bank of the River Niger, about 546 km North of the Atlantic Ocean in Nigeria.

This study is informed by the observation in the 1980s, when minor operations at the complex commenced. The villagers noticed a period of contamination of the water body leading to the death of the living organisms most especially fish which when picked up decayed fast.

Although, the company is not fully operational now, the Ajaokuta iron and steel industrial complex may be one of such pollution site of the environment and in particular the ecological system of the River Niger flowing behind the complex. The study may also provide a base-line data for future studies in the area when the plant is fully operational.

MATERIALS AND METHODS

Study area: The iron and steel complex is situated in Ajaokuta Local Government Area of Kogi state, South-central Nigeria, on the bank of the River Niger. Ajaokuta is located in approximately 7°33'22"N 6°39'18"E at an elevation of 54 m (FallingRain.com Gazetteer, 2007) and it is the home of the multi-million dollar Ajaokuta Rolling Mill. The Local Government has a population of about 122,321 people according to the 2006 census (NBS, 2006). There are few settlements (mainly fishing communities) along the bank of the river that has small farming activities.

Figure 1 shows the map of the Ajaokuta Local Government Area of Kogi State where the Ajaokuta Iron and Steel Industry is located. The Government Area has the eastern boundary with

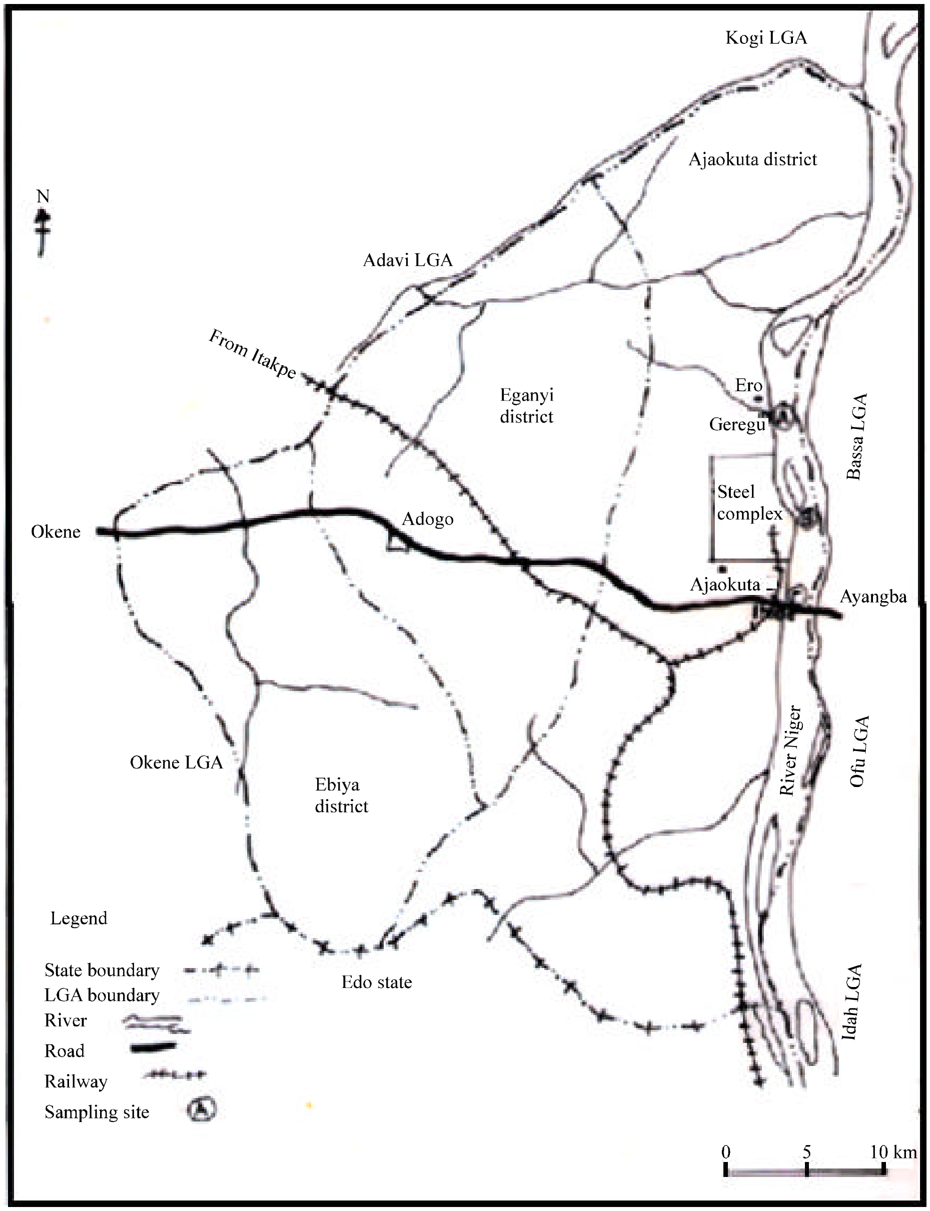

Fig. 1: Ajaokuta local government area map

the River Niger which flow down south just behind the vicinity of the Ajaokuta iron and steel industry. Ajaokuta iron and steel industry is the only industrial site located along the bank of the river and the choice of the site for the industry was motivated by the presence of the river for bulk transportation up-stream and down-stream of raw materials, consumable materials, finished products and the abundance of fresh water for the operation of the plant and domestic requirements. The effluent from the industry is also discharged into the river in addition to the other wastes that are discharged into the river due to the topography of the area.

Sampling point: Three sampling points were chosen (Fig. 1) for analysis of the heavy metals: the experimental sites which is directly behind the complex at the point the industry discharges the effluent into the river; the control site which is at the up-stream of the complex and then the down-stream about 2 km away from the complex to measure the recovery effect. The up-stream site is site A which is Geregu village serving as the control site. The experimental site, B is at Ajaokuta village directly behind the complex for studying the effects of the company's activities on the environment and the down-stream site C, is located at Itobe village bridge for studying the recovery effect.

Sampling and sample preparation: Four different materials were sampled for analysis from the three sampling sites. They are water, fish, soil and plant samples.

Grab surface water for analysis were collected from the three sites in treated polyethylene bottles and stored at 4°C in a refrigerator prior to analysis. This was done with the help of row canoe. The water samples from each site were labeled A_1, A_2 and A_3 i.e., water sample from A, B and C, respectively.

Six different fish species were sampled from each of the three sites mentioned above for analysis. These species are as shown in Table 1. They are known as good metal monitoring species (Obodo, 2002).

They were bought directly from fishermen and washed in the river and collected in polyethylene bags, which were leached with dilute HCL, rinsed with deionized water and stored in a refrigerator at 4°C before drying. The fish samples from site A were labeled F_1A to F_1F, those from site B were labeled F_2A to F_2F and those from site C were labeled F_3A to F_3F. F_1, F_2 and F_3 representing fish samples from site A, B and C, respectively. The A, B, C, D, E and F following each fish sample on each site represent the fish species as in Table 1. The fish sample was then dried in an oven at the temperature of 105°C for four days until a constant weight was observed. The samples were then pulverized in a mortar, labeled and stored in polyethylene containers which were leached, washed and dried.

Soil samples from the bank of the river from the three sites were also collected. A composite soil sample from each site was collected and stored in treated polyethylene containers. The samples were dried in an oven at 25°C until a constant weight was attained and then pulverized into finely ground soil and kept for digestion. The three soil samples were labeled S_1, S_2 and S_3 i.e., soil sample from site A, B and C, respectively.

A plant sample (water hyacinth: *Eichhornia crassipes*) from each site was also sampled for analysis. The plant is of the genus Eichhornia of tropical fresh water plant, which is highly prolific and producing mainly vegetatively. It was collected and washed with the river water and kept in treated polyethylene bags. The plant samples were dried in an oven at about 105°C for four days until a constant weight was observed. The samples were then pulverized into powder and stored for digestion. They were stored in treated polyethylene bags and labeled P_1, P_2 and P_3 i.e., plant samples from site A, B and C, respectively.

Table 1: Sampled fish species

Code	Scientific name	Common/English name
A	*Bagrus bayad*	Silver catfish
B	*Mormyrus rume*	Trunk fish
C	*Oreochromis niloticus*	Tilapia fish
D	*Pellonula afzeliusi*	Fresh water sardine
E	*Synodontis membranaceus*	Catfish
F	*Distichodus rostratus*	Grass eater

Digestion of sample: 200.00 cm^3 of the water sample was mixed with HCl/HNO_3 acid i.e., 3.00 cm^3 of 1:1 mixture of 8M HCL/8M HNO_3. The mixture was slight concentrated to 19.00 cm^3 by heating and this was made up to 25.00 cm^3, stored in a treated polyethylene bottle and made ready for AAS measurement (using UNICAM, 969).

One gram of the dried pulverized fish sample was weighed into a 200 cm^3 kjeldahl flask and 20 cm^3 of the digestion mixture (1:1 mixture of 8M HCl/8M HNO_3) was added. The mixture was allowed to stand for 24 h before digestion under reflux. The reflux lasted for 45 min and it was observed that the sample was soluble. This sample was later heated a little to remove the brown fumes (NO_2). The solution was then cooled and made up to 50 cm^3 with distilled water and stored in treated polythene bottle for AAS analysis.

0.5 g of soil sample was digested with 10 mL of aqua regia with temperature increasing to 110°C and 3 h digestion at this temperature. In the last 10 min, 2 mL of H_2O_2 was added; after which it was filtered and diluted with deionised water.

1.00 g of dried plant sample was digested with the mixture of concentrated nitric acid and perchloric acid in the ratio of 4:1 for 10 h on an electric plate. The resulting solution was evaporated and redissolved in 0.1 M HNO_3. It was then made up to 50 cm^3 mark and stored in a treated polyethylene bottle for AAS measurement.

RESULTS AND DISCUSSION

The results of the AAS analysis of metals in the samples are shown in Table 2-5.

Table 2: AAS analysis result of fish samples

	Metal concentration (ppm)									
Sample CODE	Zn	Mn	Fe	Pb	Ni	Cu	Cr	V	Co	Cd
F_1A	5.5	ND	8.1	ND	ND	ND	ND	ND	ND	ND
F_1B	13.2	ND	12.2	ND	ND	ND	ND	ND	ND	ND
F_1C	9.3	ND	12.2	ND	ND	ND	ND	ND	ND	ND
F_1D	10.2	ND	9.2	ND	ND	ND	ND	ND	ND	ND
F_1E	12.2	ND	13.2	ND	ND	ND	ND	ND	ND	ND
F_1F	1.3	ND	7.8	ND	ND	ND	ND	ND	ND	ND
F_2A	4.4	ND	10.0	ND	ND	ND	ND	ND	ND	ND
F_2B	10.3	ND	10.2	ND	ND	ND	ND	ND	ND	ND
F_2C	10.2	ND	11.5	ND	ND	ND	ND	ND	ND	ND
F_2D	3.8	ND	13.2	ND	ND	ND	ND	ND	ND	ND
F_2E	10.3	ND	13.1	ND	ND	ND	ND	ND	ND	ND
F_2F	4.3	ND	8.3	ND	ND	ND	ND	ND	ND	ND
F_3A	7.4	ND	11.3	ND	ND	0.4	ND	ND	ND	ND
F_3B	9.3	ND	9.2	ND	ND	ND	ND	ND	ND	ND
F_3C	10.3	ND	11.1	ND	ND	ND	ND	ND	ND	ND
F_3D	9.3	ND	10.2	ND	ND	ND	ND	ND	ND	ND
F_3E	11.8	ND	11.1	ND	ND	ND	ND	ND	ND	ND
F_3F	9.8	ND	11.3	ND	ND	1.5	ND	ND	ND	ND

F_1A-F_1F: Fish samples from Geregu (Site A); F_2A-F_2F: Fish samples from complex site (Site B); F_3A-F_3F: Fish sample from Itobe bridge (Site C); ND: Not detected

Table 3: AAS analysis result of plant, water and soil samples

	Metal concentration (ppm)									
Sample code	Zn	Mn	Fe	Pb	Cu	Ni	Cd	Cr	Co	V
A1	ND	ND	5.9	ND	ND	ND	ND	ND	ND	ND
A2	ND	ND	11.0	ND	ND	ND	ND	ND	ND	ND
A3	ND	ND	10.0	ND	ND	ND	ND	ND	ND	ND
S1	ND	5.2	115.2	ND	ND	0.5	ND	0.1	ND	ND
S2	ND	ND	118.0	ND	ND	ND	ND	ND	ND	ND
S3	ND	1.7	110.0	ND	ND	ND	ND	ND	ND	ND
P1	9.6	42.0	95.0	ND	2.0	1.6	ND	0.5	0.3	ND
P2	7.4	30.0	115.0	ND	2.3	1.4	ND	0.7	0.1	ND
P3	7.4	52.0	118.0	ND	1.3	1.1	ND	0.3	0.1	ND

A1: Water samples from Geregu (site A); A2: Water samples from complex (site B); A3: Water samples from Itobe (site C); S1: Soil samples from site A; S2: Soil samples from site B; S3: Soil samples from site C; P1: Plant sample from site A; P2: Plant sample from site B; P3: Plant sample from site C; ND: Not detected

Table 4: Zn concentration value (ppm)

Sample site	No. of sample	Mean concentration value	Concentration range	Minimum concentration	Maximum concentration
A	6	8.62	1.3-13.2	1.3	13.2
B	6	7.22	3.8-10.3	3.8	10.3
C	6	9.65	7.4-11.8	7.4	11.8

Table 5: Fe concentration value (ppm)

Sample site	No. of sample	Mean concentration value	Concentration range	Minimum concentration	Maximum concentration
A	6	10.45	7.8-13.2	7.8	13.2
B	6	11.05	8.3-13.2	8.3	13.3
C	6	10.70	9.2-11.3	9.2	11.3

Two metals namely iron (Fe) and zinc (Zn) were detectable in all the 18 fish samples analyzed from the three sampling site with traces of copper in two samples from site C. Other metals were at undetectable levels. All were below WHO standards of 1.5, 2.5, 0.15, 0.2, 0.4,150 and no value for Pb, Mn, Cr, Cd, Ni, Zn and Fe, respectively.

Zinc metal concentrations in the 18 samples show a mean value of 8.62 ppm in site A; 7.22 ppm in site B and 9.65 ppm in site C. This mean concentration values observed for Zn ranged from 7.4-11.8 ppm which is higher than in other sites and could be as a result of washed rusted zinc roofing of the settlement into the river through the drainage system because of the topography of the area. Table 4 shows a summary for zinc concentration value.

Iron metal concentrations in the 18 fish samples show a mean value of 10.45 ppm in site A, 11.05 ppm in site B and 10.70 ppm in site C. The highest mean concentration value was found at site B as can be seen in Table 5.

The iron concentration range observed in each of the sites is expected since the environment is filled with iron ore. This is why the difference between the mean values is insignificant.

Metal concentrations in most of the fish samples show higher metal concentrations in both the control site and the recovery site than in the experimental site. For instance Mormyrus rume (Trunk Fish) shows Zn and Fe concentration of 13.2 and 12.2 ppm at site A compared to that shown at site B (10.3 and 10.2, respectively). *Synodontis mebranaeus* (catfish) also shows a concentration 12.2 and 13.2 ppm for Zn and Fe respectively at site A compared to that shown for Zn and Fe at site B which is 10.3 and 13.1 ppm, respectively. The concentration at site C is also higher (11.8 ppm for Zn and 11.1 ppm for Fe). This could be as a result of the contribution into the pollution level by metal scraps, rusted zinc roofings which get washed into the river at both sites as a result of their topography different from that of site B. This trend was also observed in the plant and soil samples except for Fe metal.

The undetectable metal concentration level observed for most of the metals in fish samples was further confirmed by the same or similar result obtained for water and soil samples. This was however, not the case with plant samples where more metals were detected. Fe concentrations prevalent in all the samples analysed show its abundance in the environment not necessarily as a result of the industrial activity. This can also be confirmed from the high concentrations obtained from the soil and plant samples.

Synodontis membranaceus showed a high Fe concentration in all the three sites while *Mormyrus rume* (Trunk fish) show higher concentrations for Zn metal. These fish species tend to be high metal biaccumulators than *Oreochromis niloticus* (Tilapia fish). So catfish can be used to monitor Fe and Zn metal concentration than other species.

The traces of Cu found in fish samples in site C could be as a result of the clay nature of the soil in the environment, agricultural activities and sewage from the village.

Higher concentrations of metals similar to those in the sediments are always noticed in some fresh water and marine water organisms compared to terrestrial plants where the levels remain well below the level in the soil (Alloway, 1995). So some of the metals found in the plant samples i.e., Ni, Cr and Co could have been accumulated into the plant system a long time ago during the operational days of the industry.

The undetectable level of the remaining metal could be as a result of the long time effect caused by the non-operational nature of the iron and steel industry. The levels of these metals in the analysed samples are still less than the World Health Organization standards.

Though metal accumulation in fish is determined by the species, fish is still a very useful bioindicator for metal analysis. Fish species like Synodontis membranaceus (catfish) and *Tilapia zilli* (Tilapia or lady fish) have been discovered to be good bioindicators (Obodo, 2002). Plants have also been discovered to be useful in recovering heavy metals from the environment (especially soil) and so is a good bioindicator too for metal analysis (Shauibu and Ayodele, 2002; Fayed and Abdel-Shafy, 1985; Abdel-Shafy *et al.*, 1987).

CONCLUSION

Heavy metal pollutants in the environment are of immense concern globally because of their toxic nature to both plants and animals habitats. The Ajaokuta Iron and Steel Industry- an industry that can launch Nigeria into the era of industrialization, should be handled in such a way that direct awareness with particular respect to industrial friendly environment.

The results obtained in this study show that the metal concentrations obtained were within acceptable limits for portable water. Though the industry is not operational now, plans are underway to make it functional soon. And as such, the government should see that necessary control and treatment processes are put in place in readiness for a smooth takeoff of operations to ensure safety of lives.

There should be a creation of database bank to study the metal pollution to assist in the understanding of metal cycling in the environment; routine analysis carried out to monitor the extent of degradation of the environment. Other physico-chemical parameters can be further studied.

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