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# ASSESSMENT OF CD, FE, CR, CU, MN AND PB CONCENTRATION IN WATER AND SEDIMENT FROM ALADJA AND OLERI RIVER, DELTA STATE, NIGERIA

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## ABSTRACT

This study assessed the concentrations of heavy metals such as Cd, Fe, Cr, Cu, Mn and Pb in water and sediment samples collected from the Aladja and Oleri River. Sediment samples were collected from four sample sites namely, Jeti Area, Aladja River, Oleri River and Aladja community. Heavy metals in water samples were extracted with concentrated HCl and preserved in a refrigerator prior to metal analysis. Sediment samples were digested by the mixture of $2cm^3$ of 60% concentrated Perchloric acid and $15cm^3$ of concentrated nitric acid in a ratio 2:1 acid. Results from this study reveal that Ni, Pb, Mn and Cd were below detectable limit in the water samples. Fe, Cu, Cr and Zn observed an appreciable amount of the metal concentration but all concentration exist below the FEPA maximum acceptable limit. The concentrations of the metals in the sediment samples for Ni ranges from 11.84 ± 0.06 and 14.23 ± 0.06 mg/kg; Pb: 7.45 ± 0.04 and 11.22 ± 0.67 mg/kg; Fe: 3084 ± 4.51and 6045 ± 5.03 mg/kg; Cu: 54.17 ± 0.04 and 92.29 ± 0.05 mg/kg; Cr: 3.81 ± 0.05 and 4.84 ± 0,05 mg/kg; Zn: 38.58 ± 0.05 and 57.74 ± 0.05; Mn: 78.40 ± 0.05 and 186.47 ± 0.06 mg/kg and Cd: 3.14 ± 0.04 and 4.53 ± 0.03 mg/kg respectively. Analysis reveals that all the metals under investigation were within the FEPA maximum detectable limit. By comparing the accumulation of heavy metals in both water and sediments, it can be concluded that the heavy metals are highly accumulated in sediments than water, since the sediments act as reservoir for all contaminants and dead organic matter descending from the ecosystem above. However, the concentration of heavy metals in the sediments shows a degree of pollution. The short and long – term impact of the effluents discharged into the surrounding environment by the Delta Steel Company, Aladja may results to be fatal to both aquatic and human life. Hence, with this study aimed at assessing the effect of the activities of the Delta Steel Company in the Aladja and Oleri River, Delta State, Nigeria for the level of heavy metal enrichment in the sediments as well as the contamination status at the various discharge points, the continued discharge of improperly treated effluent may further compound the environmental problems of these immediate communities. Therefore the treatment of water is essential before been discharged into the outside rivers, streams, lakes or water bodies.



KEYWORDS: FEPA, Aladja river, oleri river, effluents and heavy metals, assessment, sediment, water.

## INTRODUCTION

Sediment is the loose sand, clay, silt and other soil particles that is deposited at the bottom of body of water or accumulated at other depositional sites. Sediments can emanate from the erosion of bedrocks and soil or from the decomposition of plants and animals (Akpan and Thompson, 2013). Sediments are normally mixtures of several components including different mineral species as well as organic debris (Gibbs, 1977). Sediments represent one of the ultimate sinks for heavy metals discharge into the environment (Luoma, and Bryan, 1981). In the aquatic environment, sediment has a high storage capacity for contaminants (.Karbassi *et. al.,* 2007). In the hydrological cycle, less than 0.1% of the metals are actually dissolved in the water and more than 99.9% are stored in sediments and soils (Pradit *et. al.,* 2009). Sediments are frequently containing higher concentrations of pollutants. They act as carriers and possible sources of pollution due to the fact that heavy metals are not permanently fixed by them and can be released back to the water by changes in environmental conditions, therefore they may become sufficiently polluted to disrupt the natural biological communities – the ecosystem (Toluna *et. al.,* 2001). Contaminated sediments are known to be responsible for degradation of water quality in the natural waters table especially in the shallow and enclosed water systems (Venugopal *et. al.,* 2009). Heavy metals, such as arsenic, mercury, Cadmium, Lead and Chromium, are commonly detected in lakes (Anshumali *et. al.,* 2009). The Delta Steel Company is a metal steel company whose operation base is in Aladja, Udu Local Government Area, in Delta State Nigeria and has several operations that produce huge amount of gaseous, liquid and solid waste. The important operations include preparation of raw materials, such as processing of limestone, pelletizing of Iron Ore, reduction of iron ore to metallic iron using direct reduction process, hot metal and billet production using electric arc furnace, steel making and rolled products like rods. Each of these processes produces pollutants that is either gaseous, liquid or solids. Therefore, steel industry is a major source of environmental pollution, though; the pollution is not confined to a single processing stage. Effluents from the plant are discharged into Aladja and Oleri Rivers, both rivers serve the community's need for water. The available quantity and quality of this water as well as its management contribute to the sustainability of the community as well as the growth and development of any nation's economy. Sediment analysis is vital to assessing qualities of total ecosystem of a water body in addition to water sample analysis practiced for many years, because it reflects the long term quality situation independent of the current inputs. Since sediments are normally the final pathway for both natural and anthropogenic components produced or derived to the environment, thus, this study is aimed at assessing the effect of the activities of the Delta Steel Company in the Aladja and Oleri River, Delta State, Nigeria for the level of heavy metal enrichment in the sediments as well as the contamination status at the various discharge points.

## MATERIALS AND METHODS

Water samples were collected from Oleri River and two discharge outlets in Aladja River from the plant, often called (Jeti Area) and the community area often called (Aladja Area). The Aladja River is a discharge point of effluents from the Delta Steel Plant, Ovwian – Aladja with river serving as tributary to the Oleri River. Sediment samples were collected from four sites (Jeti Area, Aladja River, Oleri River and Aladja community). These sites are around the steel plant. Water and sediment samples were collected in plastic containers previously cleaned by washing in non - ionic detergent, rinsed with tap water and later soaked in 10%$HNO_3$ for 24 hours and finally rinsed with deionised water prior to usage.

## SAMPLE PREPARATION

2g portions of the soil samples were weighed into 125cm$^3$ Erlenmeyer Flasks that were previously washed with nitric acid and rinsed with distilled water. A mixture of 2cm$^3$ of 60% concentrated Perchloric acid, 15cm$^3$ of concentrated nitric acid in a ratio 2 : 1 acid and 1cm$^3$ concentrated tetraoxosulphate (VI) acid was added to the flasks. The mixture was heated for 30minutes until dense white fume appeared. The flasks were cooled and 50cm$^3$distilled water was added, the flasks were heated again for 3minutes and the mixture were filtered with a Whatman No. 42 Filter Paper into 100cm$^3$ volumetric flasks. The filtrate was made to 100cm$^3$ mark with distilled water and obtained analyte for various heavy metals (Dawson, 1978). Using the Atomic Absorption Spectrophotometer (Pye Unicam SP 2900 Model). Heavy metals in water samples were extracted with conc. HCl and preserved in a refrigerator prior to metal analysis

## RESULTS AND DISCUSSIONS

### Results

| Parameter Mg/l | Jeti Area | Aladja Area | Oleri River | FEPA Std |
|---|---|---|---|---|
| Nickel | ND | ND | ND | < 1 |
| Lead | ND | ND | ND | < 1 |
| Iron | 0.91±0.01 | 0.94±0.01 | 0.62±0.02 | 20 |
| Copper | 0.02±0.01 | 0.01±0.01 | 0.02±0.1 | < 1 |
| Chromium | 0.02±0.01 | 0.01±0.01 | ND | < 1 |
| Zinc | 0.11±0.15 | 0.45±0.58 | 0.40±0.1 | < 1 |
| Manganese | ND | ND | ND | 5 |
| Cadmium | ND | ND | ND | < 1 |

*Results are mean of triplicate determination ± standard deviation ND = Not detectable*

**Table 2:** Shows the mean standard deviation concentration of (Nickel, Lead, Iron, Copper, Chromium, Zinc, Manganese, Cadmium) in the different sediment

| Parameters mg/kg | Jeti Area | Aladja River | Olori River | Aladja Comm. |
|---|---|---|---|---|
| Nickel | 14.23±0.06 | 13.81±0.10 | 14.56±0.05 | 11.84±0.06 |
| Lead | 11.22±0.67 | 7.45±0.04 | 8.61±0.03 | 8.52±0.04 |
| Iron | 6045.00±5.03 | 3084±4.51 | 4815.00±4.00 | 5015±4.04 |
| Copper | 54.17±0.04 | 62.15±0.04 | 92.29±0.05 | 68.23±0.07 |
| Chromium | 3.81±0.10 | 3.94±0.04 | 3.77±0.31 | 4.84±0.05 |
| Zinc | 44.07±0.03 | 38.58±0.05 | 57.74±0.05 | 50.20±0.10 |
| Manganese | 104.30±0.05 | 78.40±0.05 | 186.47±0.06 | 141.41±0.10 |
| Cadmium | 3.84±0.05 | 3.14±0.04 | 4.08±0.03 | 4.53±0.03 |

*Results are mean of triplicate determinations ± standard deviation*

## DISCUSSIONS

The results obtained for the sediment analysis are shown in table (2). The metals concentrations in sediment varied widely and exhibit fluctuations between the different sample point, especially in values of Fe, Cu, Mn, and Pb but no noteworthy differences were observed in the Cd concentrations among the various rivers studied. Fe attained its highest value in the Jeti area of the river follow by the Aladja community river. This could be that effluent from the industrial process was discharged at the Jeti area which then flow through the Aladja community point. The maximum value for Mn, Zn, Cu and Ni were recorded in the Oleri River. Cr reaches the highest concentration at the Aladja community point while Fe reaches its maximum at the Jeti Area. Results from analysis from table 2 reveals that nickel in the sediment samples were observed to range from 11.84 ± 0.06mg/kg and 14.56 ± 0.05mg/kg. Sediment samples were observed to be below the intervention values of Ni to be 210mg/kg as recommended by the Netherlands Sediment Quality Guidelines (Department of Soil Protection, Netherlands, (1994). The Lead concentration in the various sediments reveals that the lowest concentration level was observed in Jeti Area sediment. The increase in the Lead concentration in the sediment and the variation of the lead concentration in the various samples may be due to the presence of both natural and anthropogenic activities such as spill of leaded petrol from fishing boats and dust which holds a huge amount of lead from the combustion of petrol in automobile cars within the boundaries of the different locations. The practice of gas flaring could also be a cause of the deposit of lead. Natural gas is used in the steel and the excess is flared and smelting process in production metal with the ecosystem serving as an ultimate recipient for the Pb particle discharged into the environment. While humans inhale this Pb particle, the rest are deposited on soil and vegetations (Ademoroti, 1996).

The data obtained from this study reveals that the concentration of lead ranged from 7.45 ± 0.04 and 11.22 ± 0.67 mg/kg. The values were below the intervention value (530 mg Pb/kg). This study witnesses a drastic increase in the concentration of Fe as compare to the various metals analyzed with the Jeti area witnessing the highest concentration 6045 ± 5.03 mg/kg and the Aladja River sediment with 3084 ± 4.51mg/kg. This significantly higher concentration of Fe strongly indicate the presence of the metal pollution from this highly industrialize areas where Fe has been the main raw material in the production of Iron and Steel. However, Fe has been found to occur at high concentrations in Nigeria soil (Adefemi *et. al.,* 2007). The high concentrations of these metals in the soil samples may also be due to the natural lithogenic and pedogenic processes (Woolhouse, 1983), as well as anthropogenic factors resulting in environmental pollution (Knezevic *et. al.,* 2009). It was further reported that the Fe content in soil layers varies within a wide range of 100 to 100,000 mg/kg. Prolong exposure of Fe from the sludge into soils may contaminate it and change the soil structure and thus make it harmful for cultivation. Samntaray and Das, (2001) reported the concentration of Fe content to range from 1422.5 - 1593.0 mg/kg in agricultural soils near a metalliferous Chromite mine soil in India. The Fe contents observed in the sludge samples in this study were higher than those reported in (Samntaray and Das, (2001). The concentration of Cu in the sediment samples ranged from 54.17 ± 0.10 mg/kg to 92.29 ± 0.05 mg/kg with the Oleri River having the highest concentration of the metal and the Jeti area have the lowest concentration. The concentration of copper is significantly higher than that of in China (≤ 35 mg/kg) and India (20 – 30 mg/kg).The high concentration of the metal may be due to the facts that the metal is used in the purification and isolation of other metals for quantitative analysis and also to form a mold in Iron and Steel industries. The concentration of Cu on the sediment at the various discharge point ranges from 54.17 ± 0.04 mg/kg to 92.29 ± 0.5 mg/kg. The concentration of the metal is below the Netherland intervention value of 190 mg/kg. The concentration of Cr in the sediment ranged from 3.81 ± 0.10 to 4.84 ± 0.05 mg/kg. It is observed that sediment around the Aladja River has lower concentration of Cr. The metal is an ingredient in several important catalysts. The chief use of chromium is to form alloys with iron, nickel or cobalt. The addition of Cr imparts hardness, strength, and corrosion resistance to the alloy. Imperatively, the Cr deposit on the sediment could be attributed to the activities carried out in the steel plant. The concentration of Cr is below the limit of 100 mg/kg recommended by EU.

The maximum content of Cr reported by (Kabata and Pendias, 2000) in soil used in cultivation was 100 mg/kg. Natural background of Cr in agricultural soil in China is < 90 mg/kg. The concentration of Mn in the sediment ranges between 78.40 ± 0.05 to 186.47 ± 0.06 mg/kg with the sediment from the Aladja river indicating the lowest concentration while the sediment from the Olori river indicate the highest concentration of the metal. Mn is used principally in the form of alloys with iron, obtained by treating pyrolusite in a blast furnace with iron ore and carbon. The presence of Mn in the various sediments could be attributed to the industrial activities by the steel plant. Mn is one of the trace materials in soil that build cells and tissues needed for growth in plants. The levels of Mn in soils were relatively low. The highest level of Mn obtained was 186.47 ± 0.06 mg/kg. Soil generally contains 200 – 3000 mg/kg of manganese with an average value of 600 mg/kg (Lindsay and Norvell, 1979). The concentration of Mn obtained in this study is lower than the EU regulatory standard of 1500 mg/kg. Data from this study reveals that the concentration of Cd ranges from 3.14 ± 0.04 to 4.53 ± 0.03 mg/kg with the metal concentration from the sediment of the Aladja river been the lowest and that of Aladja community highest. Cd may be electrolytically deposited as a coat on metals, chiefly iron or steel. The significant concentration of cadmium in the sediment could be attributed to the activity of the Delta Steel Plant. Natural background concentration level for Cd in agricultural soil in China is ≤ 0.2 mg/2kg (Wong *et.*

*al.*, 2002), Cd concentration in the present study fell the within permissible limits as compared with those reported by the Dutch agricultural authority. The concentration of heavy metal present in the water samples at the various discharge points (table 1) reveals that Ni, Pb, Cd and Mn were below the detectable limit in the water samples. Fe, Cu, Cr and Zn were detected in the water samples collected in the various locations except for the Oleri River where Cr concentration were below detectable limit. All the metal detected in the various water samples were below the FEPA maximum permissible limits. Cd is a toxic metal with no metabolic benefits to human and aquatic biota. Its presence in any compartment of the aquatic ecosystem indicates contamination (Opaluwa *et. al.*, 2012).

Very high Cd levels in drinking water may lead to vomiting and diarrhea, and sometimes death while taking lower levels over a long period will cause kidney damage and fragile bones (Cleveland 2008). Pb like Cd has no known purpose in our bodies and could cause permanent damage to the health of both children and adults as reported by King County, Public Health, Seattle (2013). Adults and children who drink water containing Pb in excess could experience kidney problems or high blood pressure and delays in their physical or mental development respectively (USEPA, 2012). The metal concentration of Zn in water samples at the various discharge point may be due to considerable amounts of zinc leached from protection plates of boats containing the active zinc as mentioned by Hamed, (1998). Residents in these areas face the risk of getting various diseases by drinking the waters contaminated with these trace elements. Extreme care is needed to be taken. The water concentrations for Zn, Cu, Cr and Fe in the study areas were less than the accepted maximum levels in water and may pose no problem to man. By comparing the accumulation of heavy metals in water and sediments, it can be concluded that the heavy metals are highly accumulated in sediments than water, since the sediments act as reservoir for all contaminants and dead organic matter descending from the ecosystem above. Similar findings were reported by other authors (Hamed, 1998; Samir, and Ibrahim 2008; Nguyen, *et. al., 2005).*

## CONCLUSION

This study reveals that the concentration of heavy metals in the sediment of the various discharged point is greater than those for water when compared. The study further reveals that the metal concentration in the sediment was generally low except for the Fe whose concentration ranges from 3084 ± 4.51 to 6045 ± 5.03mg/kg. However, the concentration of heavy metals in the sediments shows a degree of pollution. The short and long – term impact of the effluents discharged into the surrounding environment by the Delta Steel Company, Aladja may results to be fatal to both aquatic and human life. Continued discharge of improperly treated effluent may further compound the environmental problems of the communities living around this company. Therefore the treatment of water is essential before releasing to the outside streams, lakes, water bodies

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