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Comparative Study of Heavy Metal Pollution of Sediments in Odo-Owa and Yemoji Streams, Ijebu-Ode Local Government Area, Sw Nigeria

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Abstract: *This study aims at determining the elemental concentrations of Cu, Zn, Cr, Pb, Ni, Co and Cd in the sediment samples from Odo-Owa and Yemoji streams in Ijebu-Ode Local Government Area (L.G.A), South Western (SW) Nigeria, using Atomic Absorption Spectrophotometer* and *comparing the concentration of these metals in the two streams with other studies and with acceptable concentration values for metals in water. There was no detectable Cd in any of the samples; however all the samples contained a detectable amount of one or more of the other metals of interest. The trend of heavy metals in sediments of Odo-Owa stream is Zn>Pb>Cu>Cr (151.3 mg/kg, 17.74 mg/kg, 6.16 mg/kg, 2.30 mg/kg) while Yemoji is Zn>Cr>Pb>Cu (3.63 mg/kg, 2.37 mg/kg, 1.67 mg/kg, 1.43 mg/kg). Statistical analysis of t-test showed a great significant difference ($p<0.05$) among metals in Odo-Owa and Yemoji downstream except for Cr. Except for Zn metal (151.3 mg/kg) in Odo-Owa (downstream), the mean concentrations of the metals were below the values obtained from other studies and were within the set by National Oceanic and Atmospheric Administration (NOAA) limits (SQGs for Zn-150 mg/kg, Cu-34 mg/kg, Cr-81 mg/kg, Pb-46.7 mg/kg), so not considered to be a cause for toxicology concern.*

Keywords: *Heavy Metals, Pollution, Sediments.*

I. Introduction

The environment is an important component necessary for the existence of both man and other biotic organisms. Thus, Bankole (2008) reported that “Environment” refers to the physical surroundings of man, of which he is a part and on which he depends for his activities, like physiological functioning, production, and consumption. His physical environment stretches from air, water, and land to natural resources like metals, energy carriers, soil, and plants, animals, and ecosystems. For urbanized man, a large part of his environment is man-made. But even then, the artificial environments (buildings, roads) and implements (clothes, automobiles) are the result of an input of both labour and natural resources.

Pollution is an undesirable change in the physical, chemical or biological characteristics of air, water and soil that may harmfully affect life or create a potential health hazard to any living organism. Any substance which causes pollution is called a pollutant. A pollutant can also be defined as any solid, liquid or gaseous substances present in such concentration as may be or tend to be injurious to the environment (Bhatia, 2009). Pollution of the natural environment by heavy metals is a global problem because of their indestructible nature and most of them have toxic effects on living organisms (Dalman et al., 2006).

In recent years, there has been significant concern regarding urban soil contamination due to rapid industrialization and urbanization, especially contamination due to various heavy metals (Chen et al., 2007). Heavy metals are natural components of the environment, being present in rocks, soil, plants and animals. They occur in different forms: as minerals in rock, sand and soil; bound in organic or inorganic molecules or attached to particles in the air (Tam and Wong, 2000). But most of the heavy metals occurrences in urban soils tend to originate from anthropogenic sources such as industrial, urban development and transport activities (Charles worth et al., 2003, Strivastava et al., 2007). Heavy metals are one of the serious pollutants in natural environment due to their toxicity, persistence and bioaccumulation problems (Pekey, 2006; Nouri et al., 2006).They are not chemically or biologically degraded; thus the pollutants stay for longer period in the environment.

Many different definitions have been proposed-some based on density, some on atomic number or atomic weight and some on chemical properties or toxicity. Most recently, the term "heavy metal" has been used as a general term for those metals and semimetals with potential human or environmental toxicity (Samara and Richard, 2009). Any metal having an atomic weight greater than that of sodium, a density greater than 5 g/cm^3 and possesses some notion of toxicity are classified as “heavy metals”(Suciu et al., 2008). Many of the elements that can be considered heavy metals have no known benefit for human physiology. Lead, mercury, and cadmium are prime examples of such "toxic metals." Yet, other metals (zinc, copper, cobalt) are essential to human biochemical processes. Any of these elements may have pernicious effects if taken in quantity or if the usual mechanisms of elimination are impaired (Samara and Richard, 2009).

Sediment is the loose sand, clay, silt and other soil particles that settle at the bottom of the body of water. The erosion of bedrock and soils leads to accumulation of sediments of past or on-going natural and anthropogenic processes and components. Data from sediments can provide information on the impact of distant human activity on the wider ecosystem. The composition of sediment sequences provides the best natural archives of recent environmental changes (Davies and Abowei, 2009). Sediment is a habitat and major nutrient source for aquatic organisms. Sediment analysis is important in evaluating qualities of total ecosystem of a body of water in addition to water sample analysis practiced for many years because it reflects the long term quality situation independent of the current inputs (Adeyemo et al., 2008) and it is the ultimate sink of contaminants in the aquatic system (Davies and Abowei, 2009).

Monitoring of the contamination of soil and sediment with heavy metals is of interest due to their influence on ground water and surface water and also on plants, animals and humans (Suciu et al., 2008). Heavy metals from incoming tidal water and fresh water sources are rapidly removed from the water body and deposited onto the sediments (Tam and Wong, 2000; Samarghandi et al., 2007).

Odo-Owa is a typical municipal stream subjects to pollution threat arising from human activities. The stream is a popular source for domestic uses, car wash, waste and other human activities. Close to it is a fuel station suspected to be discharging fuel waste into it. Yemoji stream on the other hand is a primary source of water for Water Corporation in providing potable water for the community with considerable population size. Therefore, domestic activities in the stream are very minimal. Nigerian Brewery is located few meters away from this stream and it is suspected to be discharging toxic wastes into the stream, the allegation that was refuted by the authorities of the brewery. The findings of this study support their rebuttal.

1.1 Heavy Metal Pollution

Pollution of the aquatic environment by inorganic chemicals has been considered a major threat to aquatic organisms including fishes. The agricultural drainage water containing pesticides and fertilizers and effluents of industrial activities and runoffs in addition to sewage effluents supply the water bodies and sediment with huge quantities of inorganic anions and heavy metals (ECDG, 2002). The most anthropogenic sources of metals are industrial, petroleum contamination and sewage disposal (Santos et al., 2005).

Accumulation of trace metals occur in upper sediment in aquatic environment by biological and geochemical mechanisms and become toxic to sediment-dwelling organisms and fish, resulting in death, reduced growth, or in impaired reproduction and lower species diversity (Praveena et al., 2008). Heavy metal contamination in sediments can affect water quality and thus the bioassimilation and bioaccumulation of metals in aquatic organisms, with potential long-term implications for human health and the ecosystem. Human may be contaminated by organic and inorganic pollutants associated with aquatic systems by consumption of contaminated fish and other aquatic foods in the environment (Mackay and Clarck, 1991). This fact is due to the capacity of some aquatic organisms to concentrate heavy metals up to 105 times the concentration present in the water (Guimarães et al., 1982).

In Nigeria today, residents have to look for alternative ground water sources such as shallow wells and boreholes because the government is unable to meet the ever-increasing water demand. The quality of these ground water sources are affected by the characteristics of the media through which the water passes on its way to the ground water zone of saturation (Adeyemi et al., 2007). The heavy metals discharged by industries, traffic, municipal waste, hazardous waste sites as well as from fertilizers for agricultural purposes and accidental oil spillages from tankers can result in a steady rise in contamination of ground water (Igwilo et al., 2006).

Many studies indicated that levels of metals were higher in sediment than in water. Studies conducted on metal accumulation in sediment showed increase in metal levels in sediment with addition of sewage, industrial effluents and agricultural wastes (Fernandez et al., 2007; Wang et al., 2001). The aim of this study is to evaluate heavy metal pollution status in sediments of Odo-Owa and Yemoji streams in Ijebu-Ode L.G.A. An attempt is also made in comparing the mean concentration between the two streams, and also compare with the standard sediment quality criteria and with studies from other countries.

II. Materials And Methods

2.1 Sample Collection and Preparation

Forty sediment samples were randomly collected during the short dry spell in the month of August. The identifiable landmarks in adjoining land areas to the sampling points were also recorded. The sediments were drained of water and subsequently air-dried for few days under room temperature. The dried samples were disaggregated, sieved to remove materials such as wastes, animal shells and plant roots and later grinded into a homogenous mixture using a porcelain mortar and pestle, sieved through 2 mm sieve to achieve fine powder before they were analyzed for their elemental constituents.

2.2 Digestion of Samples

The digestion of the sediment sample was carried out according to the method described by Maff (1981). 2 g of each sample was weighed into a digestion flask, 20 mL of the digesting acid, agua-regia [HNO_3: HCl (3:1)] was measured in a fume cupboard and added to the sample in the digestion flask. Digestion was carried out on a hot plate in a fume chamber avoiding splattering. Digestion was continued until the entire volume was reduced to about 15 mL. The beaker was removed and allowed to cool. The samples were cooled, filtered then diluted to 25 mL with distilled water and stored in a sample bottle before they were analyzed for their elemental constituents. The essence of the digestion before analysis was to reduce organic matter interference and convert metal to a form that can be analyzed by AAS.

2.3 Sample Analysis

The filtrates were analyzed for heavy metals (Cu, Zn, Cr, Pb, Ni, Co, Cd) using Atomic Absorption Spectrophotometer (Buck Scientific 210/211VGP) for concentration by using specific cathode lamp. AAS was calibrated for each element using standard solution of known concentration before sample injection. The digest and blind duplicates were reported on a wet basis.

III. Results

The metals detected in the sediments include chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), cobalt (Co) and zinc (Zn). Ni and Co were not detected in Yemoji stream while their concentration in Odo-owa varies. Cd was not detected in all the sampled streams (Tables 1 and 2).

3.1 Sampling Locations

Fig 1: Ijebu-Ode L.G.A Road Map Showing Odo-Owa and Yemoji Streams

Table 1: Concentrations (mg/kg) of heavy metals in upstream (US) and downstream (DS) sediments of Odo-Owa.

Sampling sites	Cu	Zn	Cr	Pb	Ni	Co	Cd
ODS1	7.14	18.8	2.38	9.3	1	1.13	BDL
ODS2	2.44	14.7	1.315	4.69	BDL	1	BDL
ODS3	10.89	216.7	2.125	26.3	BDL	BDL	BDL
ODS4	3.63	14.15	1.565	4.625	BDL	BDL	BDL
ODS5	6.88	453.5	2.19	12.95	BDL	BDL	BDL
ODS6	7.13	167.9	2.75	12.82	BDL	BDL	BDL
ODS7	6.815	139.9	2.815	9.005	20.9	BDL	BDL
ODS8	4.38	184.8	3.25	14.22	1.63	BDL	BDL
Mean±SD	6.16±2.47	151.3±137.9	2.30±0.61	11.74±6.47	BDL	BDL	BDL
OUS1	3.94	10.78	2.19	7.19	BDL	BDL	BDL
OUS2	2.44	6.25	3.38	3.565	BDL	BDL	BDL
Mean±SD	3.19±0.75	8.513±2.26	2.785±0.60	5.378±1.81	BDL	BDL	BDL

* ODS – Odo-Owa downstream; OUS – Odo-Owa upstream; SD – Standard deviation; BDL – Below detection limit

3.2Analysis

Turkey T-test and Pairwise Correlation Analysis was used to evaluate the significant difference in the concentration of the studied metals with respect to different streams. A probability at level of 0.05 or less was considered significant; however, no statistical analysis was carried out for Ni, Co and Cd since they were below detection limits. Bar plot was also employed to show the significant difference in Odo-Owa and Yemoji downstream. Analyses carried out are represented thus:

IV. Discussion

The average metal concentrations in sediment varied between Odo-Owa and Yemoji streams especially in Cu, Zn and Pb but no significant differences were observed in Cr concentrations between the two streams. Cr concentration may be as a result of same bedrock and soils which had accumulated from past or on-going natural processes (parent material). Ni, Co and Cd were below detection limits.

The high level of Zn in sediment of Odo-Owa could be attributed to high traffic density as well as highly populated area, lack of appropriate land fill, industrial and agricultural discharges which are distributed along Okeowa vicinity compared with Yemoji stream in Imagbon locality which is rural. Also, the fuel station and car wash (which uses detergents),livestock and poultry cultivation sited in proximity to Odo-Owa stream could be the likely causes of increased Zn content. Zn, being one of the constituents in biocides, alloys, batteries, paints and

Table 2: Concentrations (mg/kg) of heavy metals in upstream (US) and downstream (DS) sediments of Yemoji.

Sampling sites	Cu	Zn	Cr	Pb	Ni	Co	Cd
YDS1	1.065	2.44	1.88	1.065	BDL	BDL	BDL
YDS2	1.75	2.315	1.88	0.94	BDL	BDL	BDL
YDS3	1.19	3.065	2.125	0.94	BDL	BDL	BDL
YDS4	1.815	3.565	2.315	2.69	BDL	BDL	BDL
YDS5	1.815	4.94	3.505	2.75	BDL	BDL	BDL
YDS6	1.38	3.75	1.94	1.125	BDL	BDL	BDL
YDS7	1.13	2.88	2.19	0.94	BDL	BDL	BDL
YDS8	1.315	6.065	3.125	2.88	BDL	BDL	BDL
Mean±SD	1.433±0.30	3.628±1.21	2.37±0.57	1.666±0.86	BDL	BDL	BDL
YUS1	3.125	1.565	3.25	3.19	BDL	BDL	BDL
YUS2	1.565	1.25	2.44	2.94	BDL	BDL	BDL
Mean	2.345±0.78	1.408±0.16	2.845±0.41	3.065±0.13	BDL	BDL	BDL

* YDS – Yemoji downstream; YUS – Yemoji upstream

refineries, may be primarily attributed to fertilizers used nearby the stream. Automobile tyres contain large quantities of ZnO that is used as an accelerator in vulcanization (Tijani and Onodera, 2009). Corrosion of galvanized metal and tyre wear in urban runoff, runoff from street, road and high way surfaces can contribute significant quantities of Zn to the aquatic environment.

Table 3: T-Test Results for Odo-Owa and Yemoji Down Streams

METALS	ODO-OWA DOWNSTREAM	YEMOJI DOWNSTREAM	P – VALUE
Cu and Cu	6.163±2.47	1.433±0.30	0.002
Zn and Zn	151.3±137.9	3.628±1.21	0.025
Cr and Cr	2.299±0.61	2.37±0.57	0.795
Pb and Pb	11.74±6.47	1.666±0.86	0.005

In conclusion the results showed that the metal, Zn, have been introduced into the media by anthropogenic sources which includes paints, corrosion of metal, tyre wears, all from car-wash activities. Poultry, fuel station and high traffic congestion along Odo-Owa, equally contribute to the high concentration of Zn.

The mean levels of heavy metals in the sediments of Odo-Owa and Yemoji streams showed that concentration of the metals were generally low compared to that from other countries and fall within the acceptable limits described by Long et al. (1998), except for Zn (151.30 mg/kg) in Odo-Owa which is higher than the acceptable values in sediment samples.

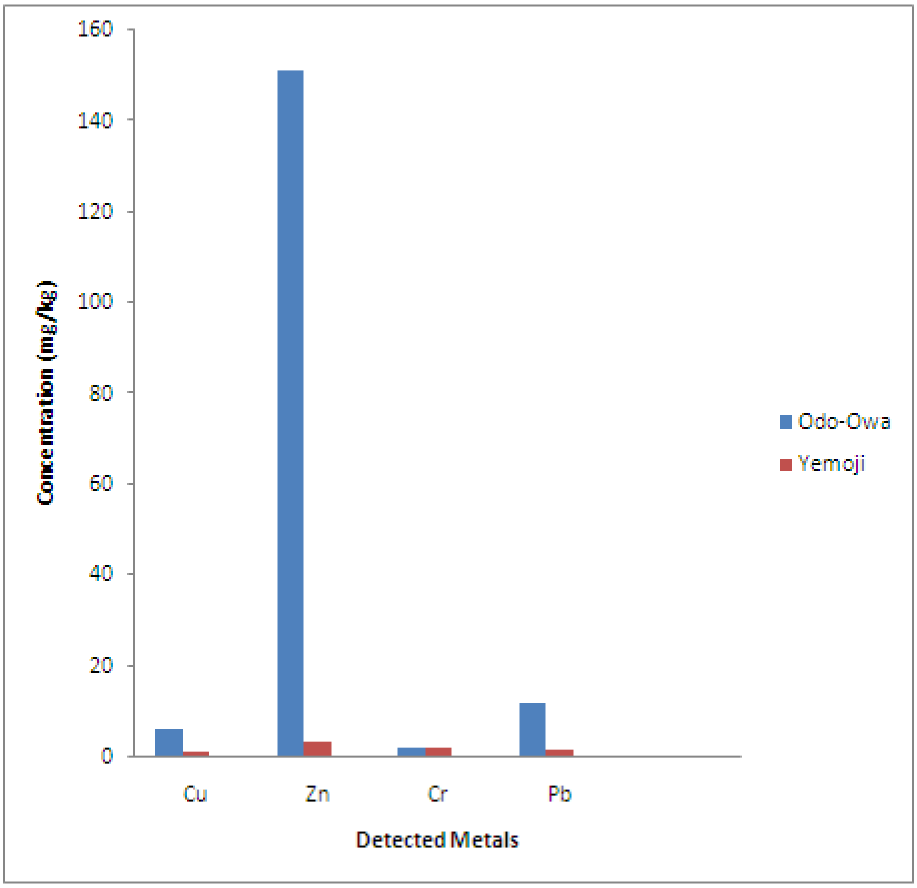

Fig 2: Barplot of metal deposits in Odo-Owa and Yemoji downstream.

Table 4: Comparison of metal concentrations (mg/kg) in this study with sediment guidelines, and metal concentration in contaminated sediments from other countries

	THIS STUDY		SQG, NOAA		Dou et al. (2013)	Yu et al. (2008)
METALS	ODS	YDS	ERL	ERM	Eastern Beibu Bay	Quanzhou Bay China
Cu	6.163±2.47	1.433±0.30	34	270	58.26	71.4
Zn	151.3±137.9	3.628±1.21	150	410	67.28	179.6
Cr	2.299±0.61	2.37±0.57	81	370	53.65	82
Pb	11.74±6.47	1.666±0.86	46.7	218	27.99	67.7
Ni	-	-	20.9	51.6	-	-
Co	-	-	-	-	-	-
Cd	-	-	1.2	9.6	0.16	0.59

*SQG – Sediment Quality Guidelines; NOAA – National Oceanic and Atmospheric Administration; ERL – Effect Range Low; ERM – Effect Range Medium

V. Conclusion

The result of this study provides valuable information about heavy metal contents in sediment from the two sampling stations, Odo-Owa and Yemoji, Ijebu-Ode metropolis.

All the metals studied did not appear to pose any threat. The levels of the elemental concentrations are very low compared with the values obtained from other studies from other parts of the country and also within acceptable limits and not considered to be a cause for toxicology concern. The bearable level of these metals could be related to a constant flow of the streams. However, the concern is higher values recorded for Zn that is more than that of the limits. If this continues unabated, it could have adverse implications on health since Zn has been linked to gastrointestinal distress, sebaceous gland closure, skin eczema and blister.

In conclusion, Zinc is an essential element in the environment. The possibility exists for both a deficiency and excess of this metal. For this reason it is important that regulatory criteria for Zinc, while protecting against toxicity, are not set so low as to drive zinc levels into the deficiency area. (IPCS, 1996).Based on the results of this study, consumption of large amount of compounds which contain zinc should be controlled and limited. Further studies to evaluate and determine changes due to usage of zinc containing compounds should be encouraged. The bottom line here is the fact that regulatory bodies for metals currently apply only to the potentially hazardous elements such as cadmium, lead and mercury.

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