

*Full Length Research Paper*

Relative estimation of lead and zinc in the Niger Delta

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ABSTRACT

This study was conducted to determine and compare the concentration of lead (Pb) and zinc (Zn) in sediment in two different places. Ten sediment samples each from Ilaje area of Ondo State and Qua Iboe river of Akwa Ibom State were analyzed quantitatively for lead and zinc content using aqua-regia (HNO_3 : HCl in the ratio of 1:3) for digestion and Buck Scientific Model 210VGP Atomic Absorption Spectrophotometer for analysis of the metal content. The results from this study shows that the maximum value of lead in Ondo state was recorded in Obenla with a value of $43.05\mu\text{g/g}$ while the minimum value was recorded in Ikorigo with a value of $4.65\mu\text{g/g}$. Value of zinc for this area ranged from $39.38\mu\text{g/g}$ to $138.72\mu\text{g/g}$. The value of zinc in the sediment samples of Qua Iboe river in Akwa Ibom State ranged from $24.26\mu\text{g/g}$ to $131.52\mu\text{g/g}$ while the maximum value of lead obtained in sediment of this area was recorded in Okorutip with a value of $232.95\mu\text{g/g}$ and the minimum value recorded in Esuk with a value of $2.40\mu\text{g/g}$.

Keywords: Pollution, assessment, sediment, heavy metals and remediation.

INTRODUCTION

Chronic pollution and/or contamination of the marine environment by heavy metals have become a severe problem especially in estuaries. In recent years, there has been an increasing concern about the growing exposure of humans to potential toxic chemicals. This potential exposure in many instances is due to initial contamination of water, air and soil, followed by various transport routes to man. As such, demands have increased for the design of monitoring systems that will identify and define the concentration, the chemical and physical behaviour of pollutants in soil (Brown, 1980). Pollution occurs when air, water or anywhere on earth gets contaminated. Contamination means that something is dirty, grimy and impure. All the different types of pollution on our earth that are caused by humans are contaminating the environment and making it not fit for use or at least they are decreasing the efficiency of it (Yagdi, 2000). Exposure to chemicals in the environment is an inescapable part of life as a result of industrialization which contributes to the development of the country. The introduction of harmful substances into the environment has been shown to have many adverse effects on human health, agricultural productivity and natural ecosystem. Many of the chemical substances have been held responsible for the major or minor sickness to which we are prone; they are pesticides and herbicides, preservatives, food additives, fertilizers, and several metals including Hg, Cd, Pb and other metals (Karen,

2005). The presence of heavy metals in aquatic systems originates from the natural interactions between the water sediments and atmosphere with which water is in contact. Man, through industrialization and technology, have developed the capacity to alter these natural interactions to the extent that the very water and aquatic life there in have been threatened to a devastating point (Karen, 2005). Estuaries and coastal areas are complex and dynamic aquatic environment (Moris et al., 1995), which are the main study areas: physical, chemical and biological interactions between fresh water and salt water systems can have profound influence on the transport and fate of the heavy metals.

The distribution of heavy metals through complex process of material exchange within this aquatic environment can also be affected by anthropogenic inputs. Often, such influence is more apparent in estuaries and surrounding coastal areas than in an open ocean due to the intense human activities (Moris et al., 1995). The transport of heavy metals from estuaries and then to the open ocean is dependent on the partitioning pattern of heavy metals between dissolved and particulate phases and other environment conditions (Carman et al., 2006). Nevertheless, physical, chemical transport and geochemical interactions within these areas may be the key factors controlling land-derived natural and pollutant chemicals into the coastal areas (Carman et al., 2006).

Sediment

Sediment is the loose sand, clay silt and other soil particles that settle at the bottom of water body (Davies and Abowei, 2009). The erosion of bedrock and soil lead to accumulation of sediment of past or on-going natural and anthropogenic processes and components. Sediment is a habitat and major nutrient source for aquatic organisms. Sediment analysis is important in evaluating 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 systems (Davies and Abowei, 2009). The traces of the heavy metals in plants and animals are not toxic (De Vries et al., 2007). Pb, Cd, and Hg are exceptions; they are toxic even in low concentrations (Galas – Gorcher, 1991).

Heavy metals

The term “heavy metals” refers to any metallic elements that has a relatively high density and is toxic or poisonous even at low concentration (Lenntech, 2004). “Heavy metals” is a general collective term, which applies to a group of metals and metalloids with atomic density greater than 4g/cm^3 , or 5 times or more, greater than water (Huton and Symon, 1986; Battarbee et al., 1988; Nriagu and Pacyna, 1990; Nriagu, 1989; Garbarino et al., 1995; Hawks, 1997). However, the metals include Lead (Pb), Zinc (Zn), Mercury (Hg), Arsenic (As), Cadmium (Cd), Silver (Ag), Chromium (Cr), Copper (Cu), Iron (Fe) and the platinum-group elements.

Heavy metal emission

Geological and anthropogenic activities are sources of heavy metal contamination (Dembitsky, 2003). Sources of anthropogenic metal contamination include industrial effluents, fuel production, mining, smelting processes, metal operations, utilization of agricultural chemicals, small-scale industries (including battery production, metal products, metal smelting and cable coating industries) brick kilns and coal combustion (Zhen-Guo et al., 2002). One of the prominent sources contributing to increased lead soil contamination is disposal of municipal solid waste (MSW). These wastes are either dumped on road-sides or used as land-fills while sewage is used for irrigation. Although useful as a source of nutrient, they are also sources of carcinogens and toxic metals. Apart from mining operations, mercury is introduced into the environment through cosmetic products as well as manufacturing processes like making sodium hydroxide (NaOH). Heavy metals are emitted both in elemental and compound (organic and inorganic) forms. Anthropogenic sources of emission are the various industrial point sources including former and present mining sites foundaries, and smelters, combustion

by-products and traffics (UNEP/GPA, 2004). Cadmium is released as by-product of Zinc (and occasionally Pb) refining; lead is emitted during its mining and smelting activities from automobile exhausts by combustion of petroleum fuels treated with tetra-ethyl (lead anti-knock agent) and from old lead paints, mercury is emitted by the degassing of the earth's crust (Lenntech, 2004). Generally, metals are emitted during their mining and processing activities (Lenntech, 2004). Environmental population by heavy metals is very prominent in areas of mining and old mine sites (Peplow, 1999). These metals are leached out and sloppy areas are carried by acid water downstream of run-off to the sea. Through mining activities, water bodies are most empirically polluted (Garbarino et al., 1995; INECAR, 2000). The potential for contamination is increased when mining exposes metal-bearing ores rather than natural exposures of ore bodies through erosion (Garbarino et al., 1995) and when mined ones are dumped on earth surface in manual dressing processes. Through rivers and streams, the metals are transported as either dissolved species in water or as in transported as either dissolved species in water as in integral part as suspended sediments (dissolved species in water have the greatest potential of causing the most deleterious effects). They may then be stored in river bed sediments or seep into underground water, thereby contaminating water from underground sources, particularly wells; and the extent of contamination will depend on the nearness of the well to the mining site. Wells located near mining sites have been reported to contain heavy at levels that exceed drinking water criteria (Garbarino et al., 1995; Peplow, 1999).

Heavy metal poisoning and bio-toxicity

The bio-toxic effects of heavy metals refer to the harmful effect of heavy metals to the body when consumed above the bio-recommended limits. Although individual metals exhibits specific signs of their toxicity, the following have been reported as general signs associated with Cadmium, Lead, Arsenic, Mercury, Zinc, Copper and Aluminium poisoning; gastro intestinal (GI) disorders, diarrhoea, stomatitis, tremor, haemoglobin causing a rust red colour to stool, a taxia paralysis, vomiting and convulsion, depression and pneumonia when volatile vapours and fumes are inhaled (McCluggage, 1991). The nature of the effects could be toxic (acute, chronic or sub-chronic), neurotoxic, carcinogenic, mutagenic or tetratogenic.

Cadmium

Cadmium is toxic at extremely low levels. In humans, long term exposure results in renal dysfunction, characterized by tabular proteinuria. High exposure can lead to obstructive disease, cadmium pneumonitis, resulting from inhaled dusts and fumes. It is characterized by chest pains, cough with foamy and

bloody sputum, and death of the lining of the lung tissues because of excessive accumulation of watery fluids (McCluggage, 1991). Cadmium is also associated with bone defects, viz: ostomalacia, osteoporosis and spontaneous fractures increased blood pressure and myocardial dysfunction. Depending on the severity of exposure, the symptoms of effects include nausea, vomiting, abdominal cramps, dyspnoea and muscular weakness. Severe exposure may result in pulmonary oedema and death. Pulmonary effects (emphysema, bronchitis and alveolitis) and renal effects may occur following sub-chronic inhalation exposure to cadmium and its compounds (McCluggage, 1991; INECAR, 2001, European Union, 2002, Young, 2005).

Lead (Pb)

Lead (Pb) is the significant toxin of the heavy metals and the inorganic forms are absorbed through ingestion by food and water, and inhalation (Ferner, 2001). A notable serious effect of lead toxicity is its tetragenic effect. Lead poisoning also causes inhibition of the synthesis of haemoglobin dysfunctions in the kidneys, joints and reproductive systems, cardiovascular system and acute and chronic damage to the central nervous system (CNS) and peripheral nervous system (PNS) (Ogwuegbu and Muhanga, 2005). Other effects include damage to gastro intestinal tract (GIT) and urinary tract resulting in bloody urine, neurological disorder and cause severe and permanent brain damage. While inorganic forms of Pb typically affect the CNS, PNS, GIT and other biosystems, organic forms predominantly affect the CNS (McCluggage, 1991; INECAR, 2000; Ferner, 2001; Lenntech, 2004). Pb affects children by leading to the poor development of the brain, thereby resulting in poor intelligence quotient (IQ) (Udedi, 2003). Its adsorption in the body is enhanced by Ca and Zn deficiencies. Acute and chronic effects of Pb result in psychosis (Udedi, 2003).

Zinc (Zn)

Zinc has been reported to cause the same signs of illness and does lead, and can easily be mistakenly diagnosed as Lead poisoning (McCluggage, 1991). Zinc is considered to be relatively non-toxic especially if taken orally. However, excess amount can cause system dysfunctions that result in impairment of growth and reproduction (INECAR, 2000; Nolan, 2003). The clinical signs of zinc toxicities have been reported as vomiting, diarrhoea, blood urine, uterus (yellow mucus membrane) liver failure, kidney failure and anaemia (Fosmire, 1990).

Mercury (Hg)

Mercury is toxic and has no known function in human biochemistry and physiology. Inorganic forms of mercury cause spontaneous abortion, congenital

malformation and GI disorder like corrosive esophagitis and hematochezia (Fosmire, 1990). Poisoning by its organic forms, which include monoethyl and dimethyl mercury presents with erethism (an abnormal irritation or sensitivity of an organ or body part to stimulation), acrodynia (pink disease, which is characterized by rash and desquamation off the hands and feet) gingivitis, stomatitis, neurological disorders, total damage to the brain and CNS and are also associated with congenital malfunction (Ferner, 2001; Lenntech, 2004).

Arsenic (As)

As with Lead (Pb) and Hg, arsenic toxicity symptoms depend on the chemical form ingested (Holum, 1983; Ferner, 2001). Arsenic acts to coagulate protein form complexes with co-enzymes and inhibits the production of adenosine triphosphate (ATP) during respiration (INECAR, 2000). It is possibly carcinogenic in compounds of all its oxidation state and high-level exposure can cause death (Ogwuegbu and Ijioma, 2003; USDOL, 2004). Arsenic toxicity also presents a disorder, which is similar to, and often confused with Guillain-Barre syndrome, an anti-immune disorder that occurs when the body's immune system mistakenly attacks part of the body resulting in nerve inflammation that causes muscle weakness (Kanfor, 2006; NINDS, 2007).

MATERIALS AND METHODS

Collection of Samples

Van Veen grab sampler was employed for sampling in each of the sampling points. The samples were kept in polythene bag and taken to the laboratory. In the laboratory, the samples were air-dried, ground with pestle and mortar, sieved with 2mm mesh and analyzed for Zn and Pb content.

METHOD

The already air-dried, ground and sieved samples were digested using aqua regia. 1g of each of the samples was weighed into small beakers and 20ml each of the aqua-regia was quantitatively transferred into the beakers containing the samples and were heated for 30 minutes at 105°C. The samples were then allowed to cool and filtered, using Whatman filter paper, into the sample bottles, made up to 30ml mark with 1M HNO₃ and were analyzed for Zn and Pb, using Atomic Absorption Spectrophotometer (Buck Scientific Model 210 VGP).

Quality Assurance

All the glass wares used during the course of the analysis were soaked overnight in acidified potassium

Table 1. Lead and Zinc concentration in Ondo State Samples

Sample	Sample Code	Pb(x±SD)µg/g	Zn(x±SD)µg/g
Awoye	N ₁	15.15±0.21	83.97±0.21
Ilepete	N ₂	9.15±0.21	39.38±0.02
Idi-Ogba	N ₃	26.55±0.21	87.42±0.00
Ilowo	N ₄	10.20±0.21	138.72±0.00
Odonla	N ₅	7.45±0.21	82.17±0.21
Uku-Aba	N ₆	11.85±0.21	84.42±0.00
Obenla	N ₇	43.05±0.21	116.67±0.21
Ojumole	N ₈	15.15±0.21	90.27±0.21
Ikongo	N ₉	4.65±0.99	109.32±0.00
Ibijimi	N ₁₀	13.05±0.99	90.57±0.21

Table 2. Lead and Zinc concentration in Akwa Ibom state samples

Sample	Sample Code	Pb(x±S.D)µg/g	Zn(x±S.D)µg/g
Oma bridge head	S ₁	4.95±0.21	85.32±0.00
Esuk	S ₂	2.40±0.42	25.34±0.02
Ikot Edibang	S ₃	7.20±0.42	25.34±0.02
Ikot Akpa Etek	S ₄	5.1±0.00	37.62±0.00
Ique	S ₅	10.80 ±0.00	131.52±0.42
Odio	S ₆	8.85±0.21	36.44±0.02
Nditia	S ₇	3.30±0.00	29.4±0.00
Okorutip	S ₈	7.80±0.00	42.92±0.02
Upenekang	S ₉	232.95±0.02	40.52±0.02
Ina Abasi	S ₁₀	9.30±0.00	29.84±0.02

heptaaxodichromate (VI) solution to remove any traces of metal. The glass wares were then washed with detergent and rinsed copiously with distilled water. The samples were also prepared in duplicate and analyzed for the metal content, to avoid error.

RESULTS AND DISCUSSION

Comparison of Lead Concentration in Ondo and Akwa Ibom States' samples

Zinc is an ubiquitous essential trace mineral (Asonye et al., 2007). All the sediments sampled contained zinc at concentrations relatively high. Although, zinc does not accumulate like other heavy metal does with continued exposure (Asonye et al., 2007) rather body content is modulated by homeostatic mechanisms that act mainly on absorption and liver levels (Walshe et al., 1994). The highest concentration of zinc was recorded

in Ilowo area of Ondo State ($138.72 \pm 0.00 \mu\text{g/g}$) and this may be attributed to the geochemical nature of the coastal region coupled with the dumping of zinc containing municipal and domestic wastes into the rivers, by the people living in the area. In all the areas that were sampled in Ondo State, the range of zinc concentration is $39.3 \pm 0.02 \mu\text{g/g}$ to $138.72 \mu\text{g/g}$ of Ilepete and Ilowo areas respectively while in Akwa Ibom State, the concentration ranges from $25.22 \mu\text{g/g}$ to $131.94 \mu\text{g/g}$ of Esuk and Ique respectively (Figures 1 and 2). The reason for the differences in zinc concentration may be as a result of differences in sources of zinc pollution from different anthropogenic

into the respective river; as well as the ability of sediment to act as sink (Kalu and Osibanjo, 1988; Benedict and Oladapo, 1991). In Akwa Ibom State, the lowest zinc concentration was recorded in Esuk with $25.20 \pm 0.04 \mu\text{g/g}$.

The order for zinc distribution in Akwa Ibom State follow: Ique>Oma bridgehead>Upenekang>Okorutip>IkotaKpa Etek>Odio>Ina Abasi> Nditia> Ikot Edibang> Esuk. In Ondo State, however, the only site that is less contaminated with zinc is Ilepete ($39.38 \pm 0.02 \mu\text{g/g}$), since its value is below the USEPA maximum permissible level (MPL) while other sites (Awoye, Idi-Ogba, Ilowo, Odonla, Uku-Aba, Obena, Ojumole, Ikongo and Ibijimi sites) are polluted with zinc with their zinc level greater than the maximum permissible level by USEPA.

In Akwa Ibom State, Oma bridge head ($85.32 \pm 0.00 \mu\text{g/g}$) and Ique ($131.52 \pm 0.40 \mu\text{g/g}$) are polluted with zinc while the other remaining eight sites are contaminated with their zinc concentration less than the maximum permissible level.

Comparison of Mean Concentration of Zinc in Ondo and Akwa Ibom States' samples

The mean concentration of zinc in the two states were compared using the unpaired t-test at 95% confidence level and it was found that there is a significant difference between the two means. The t-calculated (3.241) is greater than the t-tabulated (2.101) and this could be as a result of differences in geochemical nature of the region and likely activities with Ondo State samples having the highest mean (92.29).

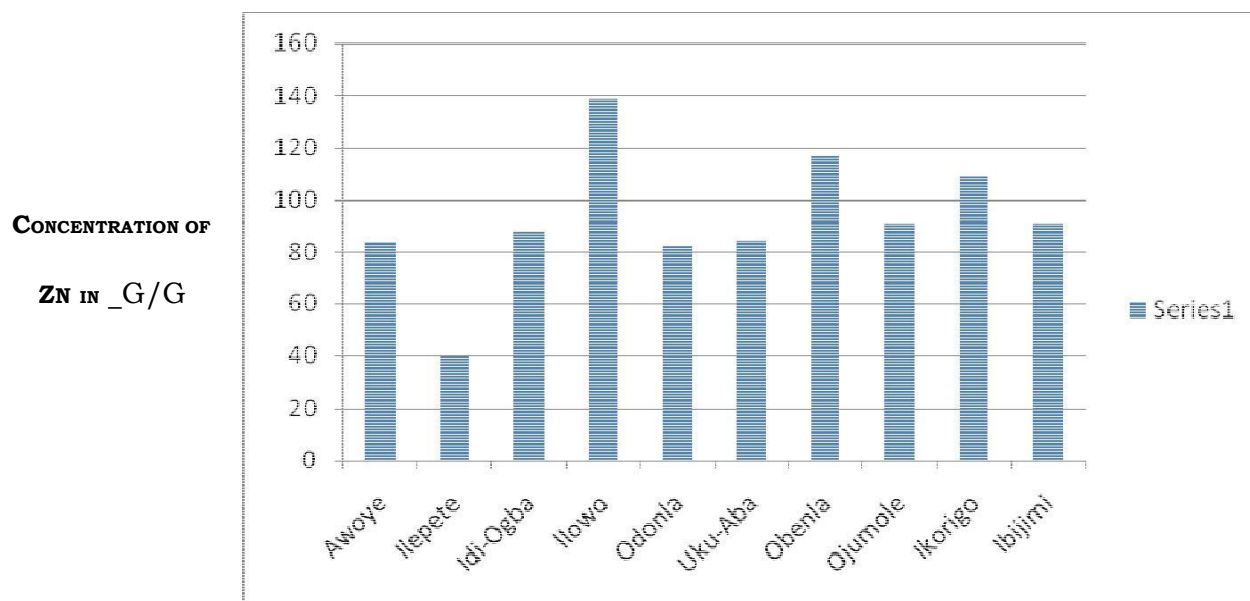


Figure 1. Concentration of zinc in ppm in Ilaje area of Ondo State

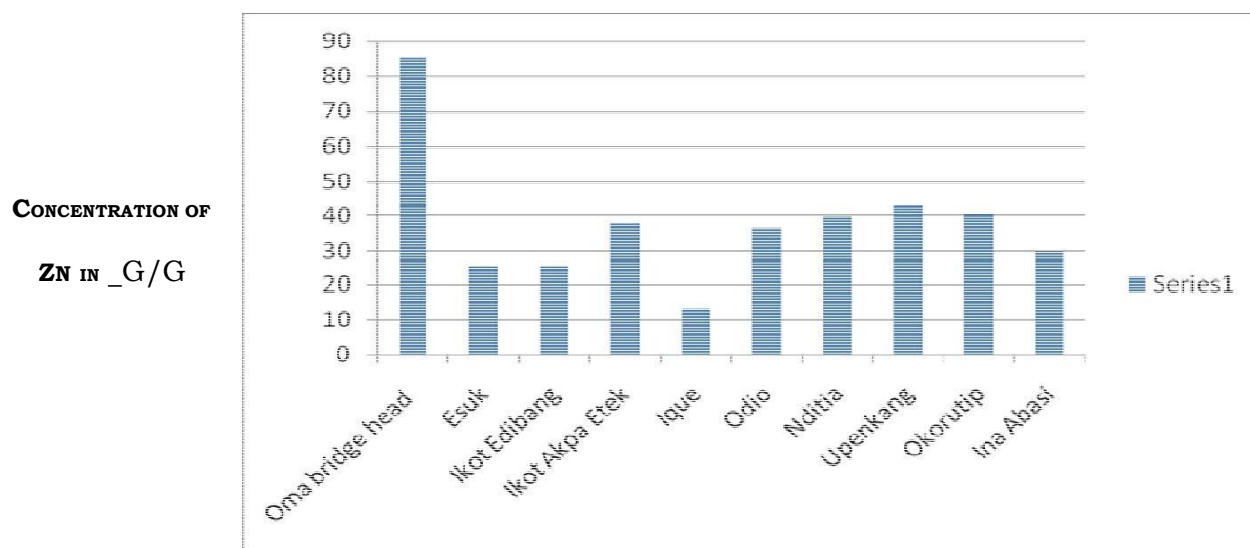


Figure 2. Concentration of zinc in ppm in Qua Iboe River of Akwa Ibom state

Comparison of Lead Concentration in Ondo And Akwa Ibom States' samples

Lead is the most ubiquitous toxicant in the environment (Goyer, 1993). Lead may impair renal function, red blood cell production, the nervous system and causes blindness (Asonye et al., 2007). Water, especially lead polluted water, is a major source of lead toxicity (Asonye et al., 2007). In Ondo State sites, the lowest and highest lead concentrations were recorded in Ikongo and Obenla sites respectively; hence, the range for the concentration of lead in Ondo State sites is from $4.65 \pm 0.99 \mu\text{g/g}$ to $43.05 \pm 0.21 \mu\text{g/g}$ for Ikorigo and

Obenla sites respectively. The order for the distribution of Pb in this area is Obenla > Idi-ogba > Awoye > Ojumole > Ibijimi > Uku > Abia > Ilowo > Ilepete > Odonla > Ikorigo, according to figure 2.

The values obtained for lead in Ondo State sample are all below the United State Environmental Protection Agency maximum permissible level (MPL) of $40 \mu\text{g/g}$. It can therefore be concluded that all the areas are contaminated with lead and the sources of contamination could be attributed to lead occurring naturally in crude oil taking place in the area; could be a likely source (the major industrial activity taking place in the area). Since the samples collected from Ondo

CONCENTRATION OF
PB IN _G/G

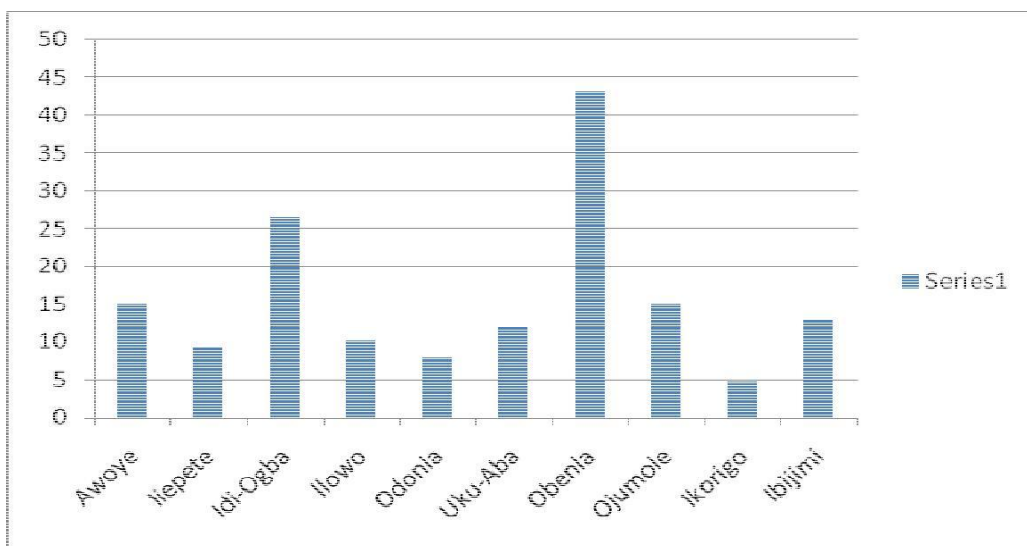


Figure 3. Concentration of Pb in ppm in Ilaje area of Ondo State

CONCENTRATION OF
PB IN _G/G

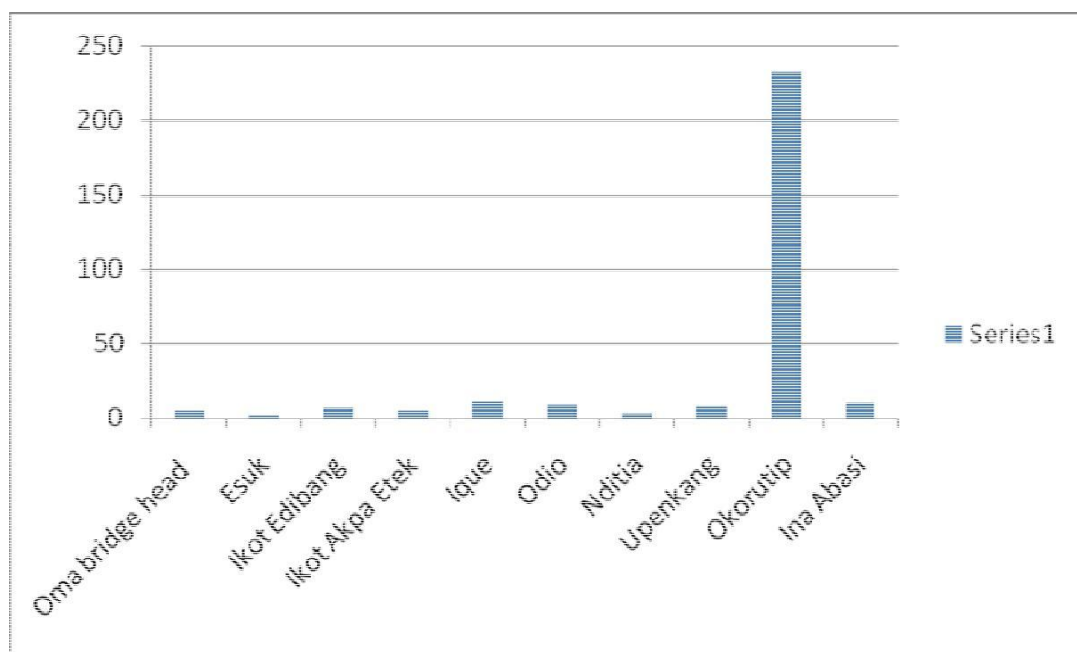


Figure 4. Concentration of Pb in µg/g Akwa Ibom State samples

State contained Pb at concentration below the USEPA standard one may conclude that the level of the metal in the sample would not constitute any health hazard.

In Akwa Ibom State, the highest concentration was recorded in Okorutip site ($232.95 \pm 0.21 \mu\text{g/g}$). According to the USEPA maximum permissible levels for Pb ($40 \mu\text{g/g}$), only Okorutip is polluted while others are contaminated with lead. Exxon Mobil crude oil exploration and exportation taking place in these areas may be one the sources of Pb since its only the exploration activities (industrial activities) that is the

major anthropogenic source.

Figure 4.3 shows the order for the distribution of lead in these areas is: Okorutip > Ique > Ina-Abasi > Odio > Upenkang > Ikot-Edibang > Ikota Akpa Etek > Oma bridge head > Nditia > Esuk.

Bioaccumulation and magnification is capable of leading to toxic level of these metals in fish in these areas, even when the exposure is low. Hence the study of the heavy metal content of aquatic animals in these areas is highly essential to know their suitability for intake; since fishes are notorious for their ability to

concentrate heavy metals in their muscles and to ensure that toxic heavy metals are not being transferred to man through fish consumption (Olowu et al., 2010); since sediments have been reported to form the major repository of heavy metal in aquatic system while both allochthonous and autochthonous influences could make a concentration of heavy significance (Olowu et al., 2010).

Comparison of Mean Concentration of Zinc in Ondo and Akwa Ibom States' samples

The unpaired t-test at 95% confidence level was also used which shows that there is no significant difference between the mean concentration of lead in the two states. The t-calculated (0.5928) was lower than the t-tabulated (2.101) and may be due to the similarity in the major anthropogenic source of pollution which is the crude oil exploration in the two states.

CONCLUSION

It was found that the estuary of the coastal area of Ondo State has been heavily polluted with zinc which can be linked to the municipal and domestic discharge into the estuary. Hence, there should be monitoring for proper discharge of any waste into the estuary and Atlantic Ocean to prevent the ecosystem from heavy metal hazard. Due to the toxicity of the metals and ability of fishes to bioaccumulate these metals, their distributions in fishes is also needed to be carried out to determine whether they are safe for intake. In Akwa Ibom State, the level of zinc distribution is not alarming and only one of the sites contained lead at a level greater than the maximum permissible level by USEPA; nevertheless, there is need for continuous heavy metal assessment in this area. Although, all the sites contained lead at levels that are not enough to cause pollution, but all the sites are contaminated with lead. Lead is contained naturally in crude oil and this could be the major source of contamination. Hence, companies involved in exploring, exporting and/or refining crude oil in these areas must be properly monitored by government agency to ensure that their wastes are properly treated and discharged to reduce environmental pollution, due to heavy metal and hydrocarbons which will invariably prevent health hazard.

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