# EVALUATION OF TRACE METAL LEVELS AND SPECIATION PATTERN IN THE SURFACE WATER OF AIBA RESERVOIUR, AFTER SORPTION ON AMBERLITE XAD-16 RESIN

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**Abstract:** A study was carried out to assess the concentration of five trace metals and speciation pattern in surface water Aiba reservoir in Iwo , South-Western Nigeria, after sorption with Amberlite XAD-16. Atomic absorption spectrophotometer was used for estimation of trace metals. The total mean concentrations of trace metals in the surface water of the reservoir was in the decreasing order of Fe $(0.47 \pm 0.15)$ > Mn $(0.26 \pm 0.09)$ > Zn $(0.16 \pm 0.07)$ > Cu $(0.07 \pm 0.02)$ > Pb $(0.005 \pm 0.001)$ mg/L. Fe and Mn were above the (WHO, 2006) specified limit, Zn and Cu were below limit and Pb was exactly equal to the specified limit. The speciation pattern revealed that suspended metal had the highest percentage distribution in Mn and Fe, while organic bound had the highest percentage distribution in Pb and free metal ions had the highest percentage distribution in Zn and Cu. The suspended particulate metals and those that are bound by humic and fulvic acid present in natural organic matter in waters, have very low toxicity. In this study where Zn and Cu had the highest percentage in free metal ion showed that their potential to be toxic was very high and this may have adverse effects on the aquatic habitats living in the reservoir.
[Godwin Oladele Olutona\*; John Chijoke Ajaelu; Modupe O. Dawodu. **EVALUATION OF TRACE METAL LEVELS AND SPECIATION PATTERN IN THE SURFACE WATER OF AIBA RESERVOIUR, AFTER SORPTION ON AMBERLITE XAD-16 RESIN.** *Rep Opinion* 2012;4(10):4-13]. (ISSN: 1553-9873). http://www.sciencepub.net/report. 2

## 1. Introduction

The speciation of trace metals in natural waters has received considerable attention for some time now (Nkono et al.1999).The trace elements existing in fresh waters are present in various physico-chemical  forms , which include simple hydrated ions, hydroxo complexes, inorganic complexes, and colloidal particles (Mizuike,1987;Tokalioglu *et al*., 2000). Trace metals are also frequently adsorbed on, occluded in, or included in, inorganic, organic or biological suspended particulate matter (Mizuike 1987).  The transport, behaviour and fate in the environment as well as biological effects – mobility, bioavailability and potential toxicity of the elements to human and aquatic organisms of a trace metal will differ greatly depending on its physicochemical forms (Muzuike 1987; Nkono et al. 1999).Thus, information on the physicochemical forms of trace metals in fresh waters is very useful in studies of geochemistry, biological sciences, environmental problems and water treatment (Mizuike 1987). Moreover, Hg, Ag and Cu are strongly bound  by(or adsorbed to) organic matter in natural waters, and Pb is largely hydrolysed, Cd, which is only weakly complexed by organic ligands and less hydrolysed is often found to be the most toxic metal on the basis of the total dissolved metals. This is one of the reasons why the speciation analysis of metal in water sample is so important; strongly-bound metals usually exhibit low toxicity of dissolved metals cannot be assessed if only total metal concentrations are available (Morrison and Florence 1989). Moreover, total metal do not allow for the degree of liability to be measured and offer no indication in which the metal bound, i.e organic or inorganic (Stockdale 2005).

Speciation is the determination of the species or the physico-chemical forms of an element which together comprise its total concentration in a given sample (Horsfall et al. 1999). Korfali and Jurdi (2010) further defined speciation as the identification and quantification of the different species, forms, or phases present in a material. Stockdale (2005) refers chemical speciation to the form of ions in solution and their interaction with other constituents, both aqueous and solid. Scoullos and Pavlidou (2000) contributed that the term speciation encompasses two slightly different connotations of speciation –the functional and the operational ones. Functionally, we may identify and distinguish between species that are, for example available to plant or ecotoxic`; species of an element that are more easily exchangeable in mineral surface than others. However, operationally speciation is determined by the physico-chemical properties of the real natural entities which are the so called 'species'. Scoullos and Pavlidou (2000) therefore defined speciation as the determination of the concentration of various 'fractions' which clusters

of species with different physico-chemical properties are such as are 'extractable' or detectable under specific condition with specific means.

The biological or chemical forms of species may affect all aspects of the metal behaviour and biological effects for different natural water systems which contain different proportion of the various species (Charles 1989).However, the principal purpose of studying metal speciation in natural water relates to determining their relative nutrients or toxic effects with respects to biota and to understand the behaviour of metal pollutant in the aquatic environment (Stockdale 2005).

Heavy metal speciation can be classified using the division of operationally defined 'liable' and 'non-liable' forms. Liable metals are those which are electrochemically active for anodic stripping voltametry (AVS) determination. This includes the free metal ion and those metal complex which can dissociate immediately in the diffusion layer giving the free metal ions and producing AVS, while the remaining fraction are the non-liable (or bound) heavy metals i.e metal complexes or fine colloidal which dissociate very slowly compared to the approximate diffusion time (Forstner and Wittman 1983; Scoullos and Pavlidou 2000). Fractionation procedures can help to distinguish those metals having a lithogenic origin from those with an anthropogenic origin (Korfali and Jurdi 2010). Metals of anthropogenic origin occur mainly in the early fractions whereas metals having a lithogenic source are found in the residual fraction (Rubio et al. 1991).

Humic substances, deriving from soil where they originate from biological tissues, are the major organic constituents of fresh waters(Mizuike 1987).Humic substances are usually described as acidic, hydrophilic, aromatic polymers containing carboxylic, phenolic hydroxyl and alcoholic groups despite their chemical structure is still incompletely known (Mizuike 1987). They play an important role in fresh waters, interacting with metal ions, hydrated metal oxides, clay minerals and organic compounds (Mizuike 1987; Tokalioglu et al. 2000). Humic substances, major organic constituent of natural waters, interact strongly with various heavy metals to form humic complexes and affect adsorption-desorption behaviour of metals (Tokalioglu et al. 2000). Heavy metals complexes with humic substances can be selectively separated from other metal species by sorption on macro reticular anion exchangers or non-ionic synthetic polymers (Mizuike 1987).

Solid phase extraction is one of the most effective multi-element separation pre-concentration techniques because of its simplicity, rapidity and ability to attain a high concentration (Mizuike 1981; Soylak et al. 2001). Column and or batch technique could be applied to solid phase extraction of trace heavy metal ions (Soylak et al. 2003.

In solid phase extraction, several sorbent especially ion-exchange resin such as Amberlite CG50, Chelex 100 have been used for the preconcentration separation of the trace metal ions from various media such as natural water research as well as sea water, urine, geological samples etc to concentrate metals from solution onto the resin active sites (Soylak et al. 2003; Stockdale 2005). Amberlite CG50 and Chelex 100 have been used routinely in aquatic research. Amberlite CG50 is a weak cation exchanger and is less efficient than Chelex, which has a functional group with a high affinity for trace metals (Stockdale 2005). Moreover, the synthetic adsorbent resins, especially Amberlite XAD series (XAD-2, -4, -7, -8, -11, -16, -1180 and -2000 etc) have been widely used to enrich trace metal from aqueous solutions; due to the fact that the resins have good physical properties such as porosity, uniform pore size distribution, high surface area and good adsorbent properties (Tokalioglu et al. 2002; Soylak et al. 2003). Among the Amberlite XAD series adsorbent, Amberlite XAD-16, which is an adsorbent based on polystyrene divinylbenzene-copolymer was chosen for this study. The reason is due to the fact that the resin has excellent physical resistance, hydraulic characteristics and thermally stable. In addition, the resin has high porosity, low polarity and the largest surface area of $825 \text{ m}^2\text{g}^{-1}$(Tokalioglu et al. 2000& 2002).

Many factors could influence the chemical speciation of heavy metals, such as sediment particle-size distribution, organic matter content, salinity, pH and redox potential (Soon et al. 1999; Dollar et al. 2001). Lim and Kiu (1995) opined that changes in the environmental conditions such as pH and redox potential may result in the remobilization of some trapped metals; hence heavy metals in sediments can become potential source of pollution.

Aiba reservoir is the second oldest impoundment of Osun River Basin and was created primarily for the provision of potable water with fisheries development as an ancillary benefit to Iwo and surrounding communities (Atobatele and Ugwumba 2008). Construction of residential houses is encroaching into the north-eastern part of the reservoir. Other anthropogenic influences in and around the reservoir include intense fishing activity, washing of domestic wares and automobiles, bathing and fetching of water for construction and domestic purposes.

A small reservoir such as Aiba reservoir is more susceptible to pollution than large lakes (Wetzel 1992; Dinar et al. 1995). Despite increasing anthropogenic influences due to the rapid development of Iwo, there is little information regarding the chemical speciation of heavy metal content. More so, in recent times, there has been rising concerns about the state of our environment (Atobatele and Ugwumba 2008). Speciation study of heavy metals in surface water reservoir are usually conducted in the areas subjected to enhanced anthropogenic factors since an increased level of heavy metal presence is a consequence of man's activity (Sobczynski and Siepak 2001).

The objective of this study is to investigate the abundance of some heavy metals in surface water within each chemical fraction and potential risk of these bound metals to the aquatic system.

## 2. Materials and Methods
## 2.1 Description of the Study Area

Aiba reservoir is a manmade lake located in Iwo city in the south-western part of Nigeria (Fig. 1). The reservoir lies between longitude00 $4^0$ 11′ to $004^0$ 13′ East of the Greenwich and Latitude $07^0$ 38′ to $07^0$ 39′ North of the Equator. The reservoir has a catchments area of 54.39 $km^2$ (32 hectares). The reservoir drains the Aiba, Osun and Onikan streams and later flows into the Oba River, which is a tributary of River Oshun (Atobatele and Ugwumba 2008).
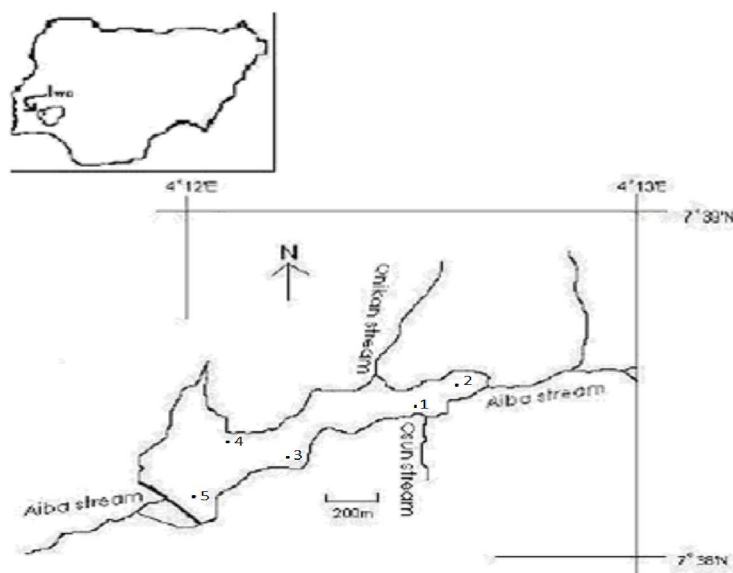


**Figure. 1. Map of Aiba reservoir showing sampling locations**

Five sampling locations in the reservoir were selected for sample collection (Figure 1). Location 1 is one of the entry point and receives water from Osun stream. This area is also an agricultural area. Location 2 is the source of Aiba reservoir. Location 3 is the agricultural area and receive agro-allied chemicals from the surrounding farmland. Location 4 is the residential area and adjacent to the main road. This area receives sewage and domestic effluents from the surrounding residential houses. Location 5 is the spillway area of the reservoir.

## 2.2 Collection of Water Samples

The plastic bottles meant for sampling were thoroughly washed with non ionic detergent, rinsed with tap water and then soaked in 10 % $HNO_3$ for 48 h prior to sampling for chemical analyses. Containers were thereafter rinsed with distilled water and finally rinsed thrice on site with harbour waters being sampled. All glassware were also washed with non-ionic detergents, rinsed with tap water soaked in 10 % $HNO_3$ for 48 h and then rinsed with distilled water to preclude trace metal contaminations.

About 2 L reservoir surface water samples for heavy metal determination were collected form

five sampling locations Aiba reservoir. The samples were collected in pre labelled 2 L polythene bottles. The samples for metal analysis were immediately acidified with 5 mL conc. $HNO_3$ and transported to the laboratory for digestion, which usually took place within 24 h after collection. All the samples for metals analysis were stored in the refrigerator at about 4 $^o$C to in-activate the bacteria and to prevent change in volume due to evaporation.

### 2.3 Speciation of Heavy Metals
### 2.3.1 Resin and Column Preparation
The Amberlite XAD-16 of 20-40 mesh with pore size of about 10 nm and surface area of 825 $m^2$/g obtained from Aldrich South Africa was ground to enlarge the sorption surface and sieved to 60 – 80 mesh. The resin was respectively washed with methanol, water, 1 mol/L $HNO_3$ in acetone, water, 1 mol/L NaOH and water.
A 800 mg of Amberlite XAD-16 resin suspended in water was finally slurry packed into a glass burette column fitted with a glass mesh.

### 2.3.2 Speciation of Metal ions in Reservoir Surface Water
The water samples were filtered through a 0.45 μm membrane filter and then the filtrates were passed through the adsorbent column packed with Amberlite XAD-16 resin at a flow rate of 2 -2.5 mL/min, and the eluate was reserved for further analysis. The metal bound to organic substance retained on the resin were eluted with 1M HCl in acetone for determination by AAS. To determine the free metal ions present in water, the eluate was passed through another packed resin column using sodium tetraborate reagent (pH 9.18). The scheme of the speciation procedure in details is illustrated in Fig. 2

### 2.3.3 Suspended Particles
The water samples were filtered through a 0.45 μm Nuclepore membrane filter to investigate the metals bound to suspended particles, the filtrate was dissolved in 10 mL concentrated $HNO_3$, centrifuged, evaporated to near dryness and then collected in a volume of 2 mL with 2 mol /L $HNO_3$. Metals in suspended particles were then determined using AAS.

### 2.3.4 Separation of Metal-Humic Complexes from Free Metal Ions.
A 250 mL aliquot of the filtrate was passed through the column at a flow rate of 2 – 2.5 mL/min to absorb the metals bound to humic and fulvic substances. The effluent was reserved in order to determine the free metal ions. The metal sorbed on

the resin was eluted at a flow rate of 1 mL/min with 1 mol/L HCl in acetone. The eluate was evaporated to near dryness and the residue was dissolved in 0.7 mL of 2 mol/L nitric acid. The metals bound to humic and fulvic substances were then determined using AAS.

### 2.3.5 Free Metal Ions
A 0.95 g of sodium tetraborate reagent was added to the effluent in unit 3.20.3 above. The solution was passed through the column packed with Amberlite XAD-16 resin. The trace metals adsorbed on the resin were eluted again with 1 mol/L HCl in acetone. After the evaporation of the eluate to near dryness, the residue was dissolved in 0.7 mL of 2 mol/L nitric acid and then the free metal ions were analyzed by AAS.

### 2.4 Recovery Analysis
This was conducted to ascertain the precision of the analytical procedures used in this study, since reference water material was not available to us when this study was carried out. A 25 mL water sample was put into a Teflon beaker and was spiked with 25 mL of 50 μg/mL of the metals and digested as earlier described. The digested spiked sample was made up to the mark in a 25 mL volumetric flask with doubly distilled water. Also, a 25 mL each of 50 μg/mL of the standard heavy metal solution mixture was taken for AAS analysis. The results obtained were compared with those of the spiked water samples to obtain the recovery of the analysis. Generally, the quality control performed included daily analyses of standards and triplicate analyses of samples and blanks to further check the reproducibility of the methods used in this study. The instrument was calibrated using the method of standard addition in order to reduce matrix effect.

### 2.5 Atomic Absorption Analysis of Samples
Trace elements in the surface water samples were analyzed for their metal contents using a Buck Model 205 Flame Atomic Absorption Spectrophotometer (FAAS), available at the International Institute of Tropical Agriculture (IITA), Ibadan.

### 2.6 Statistical Analysis of Data
The statistical package for social sciences (SPSS) software, 15.0 for window evaluation version was used for all the analyses. Both descriptive and inferential statistical analyses were used to interpret the data in this study. Descriptive analysis, Pearson correlation, Principal component analysis (PCA), Cluster analysis and Aquoaccumulation Index were carried out.

## 3.0 Results and Discussions
### 3.1 Results of the Recovery Analysis

In order to for errors (contamination and adsorption losses) in the speciation procedure, recovery test were carried out. The result of the recovery analysis and analyses of the surface water samples drawn from five locations of Aiba reservoir are presented in the table below and discussed accordingly

Under the experimental conditions used, the standard calibration curves obtained showed high linearity level with $r^2$ values (Table 1) between 0.9856 for $Zn^{2+}$ and 0.9987 for $Cu^{2+}$. Recoveries of heavy metals in water ranged from 86.99 % for $Pb^{2+}$ to 98.02 % for $Mn^{2+}$ (Table 1). These values are adjudged acceptable, and hence, the results obtained are reliable.

**Table 1: Calibration Curve and % Recovery for Heavy Metals.**

| Metal | Cu | Fe | Mn | Pb | Zn |
|---|---|---|---|---|---|
| Calibration curve,r2 | 0.9794 | 0.9961 | 0.9898 | 0.9585 | 0.9896 |
| % Recovery of metal in $H_2O$* | 96.23±3.06 | 87.50±6.60 | 89.73±6.31 | 86.99±3.53 | 98.38±6.97 |

*Values are mean of triplicate analysis ± % RSD

### 3.2 Total Metal Concentrations

A high number of heavy metals that are previously occurring at very low concentrations in water are now found in high concentrations, thereby creating adverse effect on aquatic life (Patil and Shrivasta 2003). International regulations on water quality are lowering the maximum permissible levels of potentially toxic metals in humans (Tuzen and Soylak 2006). The total mean value of trace metals in the surface water of the reservoir was in the decreasing order of Fe > Mn > Zn > Cu > Pb (Figure 2)

Iron in drinking water is presented as $Fe^{2+}$, $Fe^{3+}$ in suspended form (Sonawane 2003). Fe enters into the water from natural geological sources, industrial waste, domestic discharge and also from by products (Patil and Ahmad 2011).The source of iron in the reservoir may be from alloys, soldiers roofing sheet and car wash. Fe causes staining in clothes and imparts a bitter taste. Excess amount of Fe (> 10 mg/kg) causes rapid increase in pulse rate and coagulation of blood vessels, hypertension and drowsiness (Patil and Ahmad 2011). The ranged of iron in the surface water of the reservoir was from 0.19 to 0.81 mg/L. The mean value of Fe in the reservoir was $0.47 \pm 0.15$ mg/L. The mean value of iron in the reservoir was above the maximum allowable concentrations of 0.3 mg/L proposed guideline by WHO (2006).

The ranged value of manganese in the reservoir was between 0.09 to 0.51 mg/L. the mean value was $0.26 \pm 0.09$ mg/L. WHO has recommended a guideline value of 0.1 mg/L of Mn in drinking water. The surface water of Aiba reservoir analyzed for Mn exceeded the limit permitted by WHO.

Zinc (Zn) is an essential micronutrient in human being and only at very high concentration; it may cause some toxic effect. Zinc compound are astringent corrosive to skin, eye and mucus membrane (Patil and Ahma 2011). They are known to cause special type of dermatitis known as "Zinc pox". Zn was also known to be irritating to digestive tract thereby causing nausea and vomiting. The main industrial uses of Zn are galvanization and preparation of alloys. The main source of Zn in natural waters including drinking water may be galvanized pipes and roofing sheets. The guidelines value for Zn in drinking water is given as 5.0 mg/L by WHO. Zn concentration in the reservoir ranged from 0.02 to 0.34 mg/L with mean values of $0.16 \pm 0.07$ mg/L.

Copper (Cu) a trace metal and an essential metal for cellular metabolism, may become extremely toxic for aquatic animals as its concentration increases in water (Carvalho and Fernandes 2006). Cu in the reservoir water ranged from 0.03 to 0.09 mg/L. Cu was considerably below the limit of 1.0 mg/L by WHO in drinking water. Mean values of Cu concentration was $0.07 \pm 0.02$ mg/L. consequently no contamination due to Cu in the investigated surface water.

Lead (Pb) enters in drinking water from industrial effluents, different waste and household sewage (Patil and Ahmad 2011). Toxic level of Pb in human body is 500 ppm beyond which it causes anaemia, brain damage and vomiting (Kanwar and Sharma 1987). Pb in the reservoir ranged from 0.002 to 0.01 mg/L with mean value of $0.005 \pm 0.001$ mg/L. The Pb content of the surface water was exactly equal with the recommended value of 0.005 mg/L recommended by WHO.
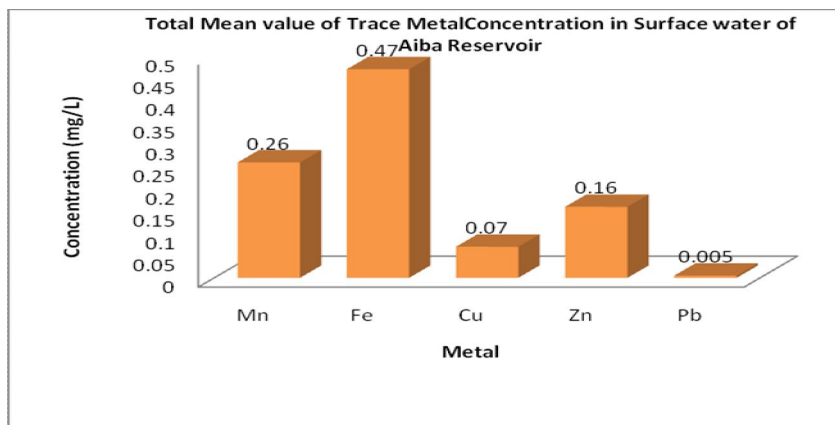
Fig.2 Mean Value of Trace Metals Concentration in Surface Water of Aiba Reservoir

## 3.3 Fractionating Studies

The speciation of metals in surface water of the reservoir is presented in the Figure 3 a-e below. The speciation of metal in water is very important to understand the metal behaviour in aquatic system as that of metal speciation in sediment (Korfali and Jurdi 2010).The forms of the chemical species of toxic metals in water column could be used as a predictor of bioavailability to particular aquatic organism (Korfali and Jurdi 2010). The free ion activity model states that there is a correlation between the toxicity of a metal to an organism and the thermodynamic activity of the free aqua metal ion in solution (Morel 1983).

The distribution of Mn in the water sample showed that suspended metals has 38 % while organic bound metal was 33% and free metal ions was 30 %. The distribution of Iron in the surface water of the reservoir revealed that suspended metal had the highest percentage of 36 while organic bound and free metal ions had 34 % and 30 % respectively. The distribution of Zinc showed that free metal ions had the highest percentage of 38, organic bound metal had the lowest percentage of 26 and suspended metal had 36 %. Pb showed that organic bound metals had the highest distribution of 38 % while both suspended metals and free metal ions had 31 % distributions respectively. The highest percentage distribution in Copper is essential to life both humans and aquatic animals. After Hg and Ag, ionic copper is the most toxic metal species to a wide range of aquatic organism (Stauber et al. 1996) Copper was found to be free metal ions with 38 % followed by suspended metals with 33 % distribution and organic bound metals with 29 % distribution.

As expected, the elements Mn and Fe were predominate in the particulate or suspended fractions (Figs. 3a and 3b). This result is in agreement with the findings of Nkono et al. 1999. It is well known fact that dominant forms of Pb, Fe and Mn are usually adsorbed or co-precipitated as hydroxides of basic salts (Benes and Steinnes 1975).

Cu and Zn were mainly predominant in the free metal ions - non-labile fraction (Figs.3c and 3e) i.e metal that pass through the column in form of complexes that do not dissociate on the column and, more likely, metal associated with colloidal material (Pik et al.1982).This results are in agreement with findings of (Benes and Steinnes 1975; Pik et al.1982; and Nkono et al. 1999) who reported that Cu and Zn were mainly distributed in the non-labile fraction. This finding proves that Cu ions associate strongly organic matter and colloidal iron oxide. (Nkono et al. 1999).

Pb was found predominant in the organic bound fraction (Fig. 3d). This finding indicates the presence of strong complexation of Pb metal in the reservoir water. This result is in disagreement with finding of Nkono et al. (1999) who reported Pb being predominate in the particulate fraction. The percentage distribution of both suspended metals and free metal ions are equal in this study.
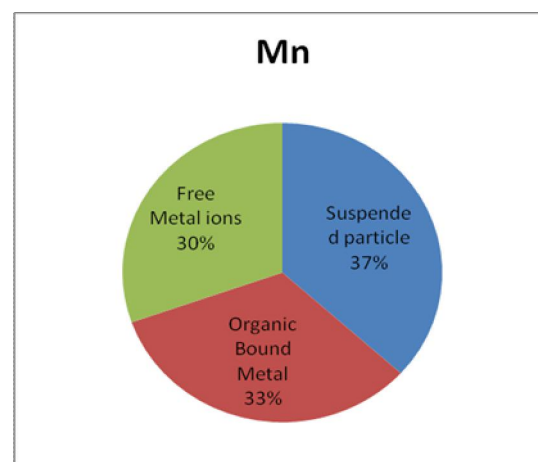


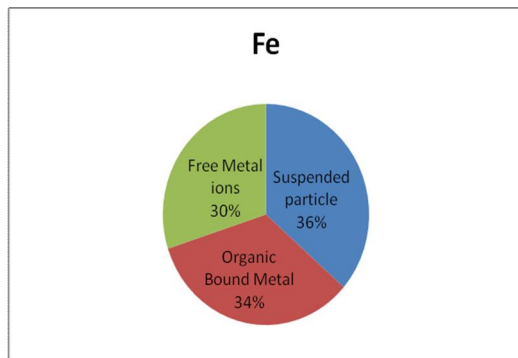Figure 3a: Distribution of Mn in surface water of Aiba reservoir

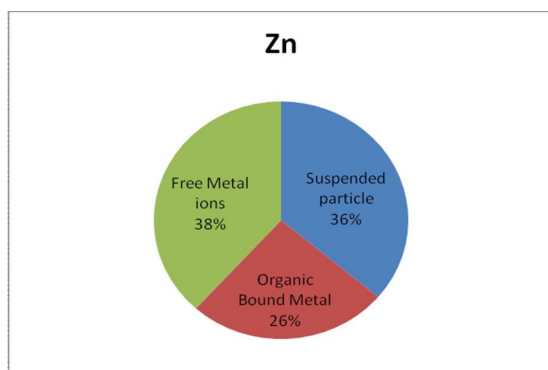Figure 3b: Distribution of Fe in surface of water of Aiba reservoir



Figure 3c: Distribution of Zn in surface of water of Aiba reservoir
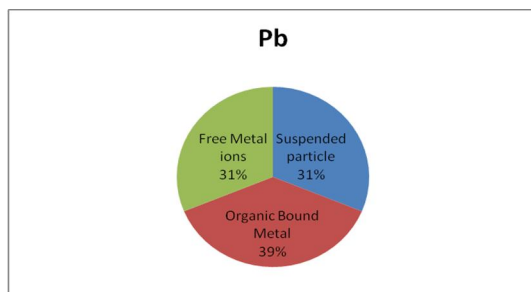


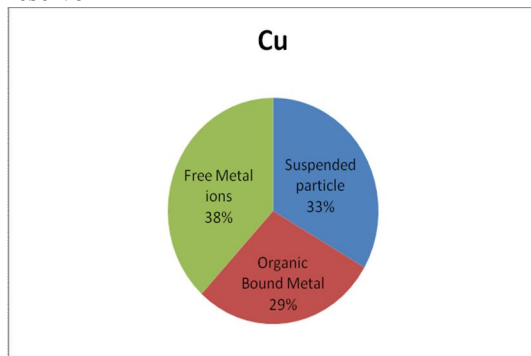Figure 3d: Distribution of Pb in surface water of Aiba reservoir



Figure 3e: Distribution of Cu in surface water of Aiba reservoir

In all, suspended metal had the highest percentage distribution in Mn and Fe, while organic bound had the highest percentage distribution in Pb and free metal ions had the highest percentage distribution in Zn and Cu. The toxicity of these trace metals are critically dependent on their physico-chemical forms the most toxic of these metals are the free metal ions. The suspended particulate metals and those that are bound by humic and fulvic acid present in natural organic matter in waters, have very low toxicity. In this study where Zn and Cu had the highest percentage in free metal ion showed that their potential to be toxic was very high and this may have adverse effects on the aquatic habitats living in the reservoir.

**3.4 Correlation Analysis**

Correlation analysis between analyzed trace metals in the reservoir surface water are shown in Table 2. The highest correlation in the reservoir surface water ($> 0.6$) was found between Fe and Mn. Two-tailed correlation coefficient showed that Mn and Fe as well as Zn and Cu was highly correlated at $P > 0.01$ level.

**Table 2: Two-tailed Pearson Correlation Analysis**

|       | Mn       | Fe      | Cu       | Zn      | Pb  |
|-------|----------|---------|----------|---------|-----|
| **Mn** | 1        |         |          |         |     |
| **Fe** | 0.650**  | 1       |          |         |     |
| **Cu** | 0.094    | -0.028  | 1        |         |     |
| **Zn** | 0.080    | 0.102   | 0.400**  | 1       |     |
| **Pb** | -0.0213  | -0.064  | 0.056    | -0.079  | 1   |

** Correlation is significant at the 0.01 level (2-tailed).

**3.5 Principal Component Analysis**

Principal component analysis pattern recognition techniques that attempts to explain the variance of a large dataset of inter-correlated variables with a smaller set of independent variables (Hopke 1985). PCA was employed in this study to compare the compositional pattern between the metals analysed in the reservoir surface water and to identify factors that influences each one. The first two components accounted for 62.289 % of the total variance of the metals analysed in the reservoir surface water (Table 3). The first PC accounted for 35.105 % of the total variance was correlated with Mn and Fe which is likely due to soil leaching, roofing sheet while the second PC accounted for 27.185 % of the total variance was correlated with Cu and Zn and is consider as represent anthropogenic activities due to wash off from roofing sheet.

**Table 3: Principal Component analysis for Aiba reservoir water**
**Eigens value**

| Component | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| % Variance | 35.105 | 27.185 | 19.455 | 12.159 | 6.097 |
| % Cumulative | 35.105 | 62.289 | 81.744 | 93.903 | 100.00 |

**PCA variable loadings**

| Metal | 1 | 2 |
|---|---|---|
| Mn | **0.874** | -0.224 |
| Fe | **0.822** | -0.284 |
| Cu | 0.251 | **0.811** |
| Zn | 0.372 | **0.741** |
| Pb | -0.336 | 0.147 |

### 3.6 Aqouaccumulation Index

The pollution intensity in the reservoiur water was assessed by adapting the Taylor and McLennan (1995) equation using FOREGS-EuroGeoSurveys mean values of dissolved metals in water as the background, Bn, values (Table 4) to arrive at what is here described as the "Aquoacumulation" Index (I-aquo).

$I\text{-geo} = \log_2 [C_n/1.5B_n]$,

where Cn is the measured total metal concentration in soil; $B_n$ is the background value; and 1.5 is the background matrix correction factor due to lithogenic effects.

The I-geo values are classified into seven classes (0 - 6) as follows:

| Value | Class | Grade/Pollution Intensity |
|---|---|---|
| I-geo $\leq$ 0 | 0 | Practically unpolluted (PU) |
| 0 < I-geo < 1 | 1 | Unpolluted (U) - Moderately polluted (MP) |
| 1 < I-geo < 2 | 2 | Moderately polluted (MP) |
| 2 < I-geo < 3 | 3 | Moderately polluted (MP) –Heavily Polluted |
| 3 < I-geo < 4 | 4 | Heavily polluted (HP) |
| 4 < I-geo < 5 | 5 | Heavily polluted – very heavily polluted |
| 5 < I-geo | 6 | Very heavily polluted (VHP). |

It was revealed that the reservoir was practically unpolluted with respect to all the metals considered in this study (Table 4).

Table 4 The Aquoaccumulation Index (I –aquo) Values in Aiba Reservoiur water

| Metal | $C_n$ | $B_n$ | I-aqou | Pollution Intensity |
|---|---|---|---|---|
| Mn | 0.26 | 56.7 | - 8.35 | PU |
| Fe | 0.47 | 268 | - 9.74 | PU |
| Cu | 0.007 | 1.23 | - 1.42 | PU |
| Zn | 0.16 | 6.01 | - 1.75 | PU |
| Pb | 0.005 | 0.224 | - 0.07 | PU |

### 3.7 Cluster Analysis

The dendrogram in Figure 4, derived from total centroid cluster analysis in respect of the trace metals relationship, differentiated the metals into four minor classes and three major groups: Cu and Pb and Zn; Mn and Fe. Generally, strong associations of chemical species in an environmental matrix speak of their close relationship in terms of their sources and factors responsible for their presence.

```
 C A S E     0     5    10    15    20    25
 Label   Num  +---------+---------+---------+---------+---------+

 Cu       3
 Pb       5
```

Zn                                                                          4

Mn        1
Fe                                                                                          2

**Figure 4: Dendrogram for trace metals in surface water of Aiba reservoir**

**4.0 Conclusion**

The trace metal concentrations and the speciation pattern of surface water of Aiba reservoir have been assessed. Results of our measurement reveals that Mn and Fe were above while Pb was equal to the WHO permissible level for drinking water and CU and Zn were below the permissible limit. The speciation pattern also reveals the presence of and Fe in high percentage in suspended metals, Pb in organic bound awhile Zn and Cu in the free metal ions fractions.

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8/20/2012