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A study of chemical speciation of metals in aquatic bottom sediment of Aiba reservoir, Iwo, Nigeria

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The species and total mean metal concentrations of some potentially environmental toxic metals (manganese (Mn), iron (Fe), copper (Cu), zinc (Zn), and lead (Pb)) in the sediments of Aiba reservoir were examined. The total mean value were in the order of Fe > Mn > Zn > Cu > Pb. The metal concentrations (mean ± standard deviation (SD) in µg/g dry weight) were Mn, 28 ± 0.88; Fe, 42.03 ± 1.11; Cu, 5.82 ± 0.21; Zn, 11.91 ± 0.37; and Pb, 0.44 ± 0.02. Some physico-chemical parameters of the bottom sediments were also measured and their average levels and range are pH, 6.2 to 6.6; conductivity, 104 ± 5 µScm^{-1} (50 to 170 µScm^{-1}); water absorbency, 54.66 ± 2.17 (50 to 63.3). The speciation result revealed that high levels of these metals studied (Mn, Fe, Cu, Zn, and Pb) were associated with exchangeable and carbonate bound fractions, pointing out that they are in potentially available forms and may pose serious problems to the reservoir ecosystem.

Key words: Bottom sediments, speciation, Aiba reservoir, metals.

INTRODUCTION

Natural waters, that is, seawaters and freshwaters, are extremely complex dynamic chemical systems consisting of different components, namely various solutes, organic matter and colloidal or particulate material. Hence, a number of chemical processes between metal pollutants dissolved in trace levels and each of these components is expected to take place in the aquatic reservoirs such as rivers, lakes and oceans, and it is the distribution of the trace metal pollutants between the different chemical species and forms which determines their geochemical and biological reactivity (Skvarta, 1998). Trace metals are of high ecological importance since they are not removed from water as a result of self purification, but accumulate in reservoir and enter the food chain (Loska and Wiechula 2002). The elevation of metal levels in a reservoir is shown mainly by an increase in their concen-trations in bottom sediment. Their occurrence in the environment results primarily from anthropogenic acti-vities (Ghrefat and Yusuf, 2006). Moreover, the natural process, such as weathering of rocks and volcanic

activities plays a noticeable role in enriching the water reservoirs with heavy metals (Forstner and Wittmann, 1981; Veena et al., 1997). In order to protect the aquatic life community, comprehensive methods for identifying and assessing the severity of sediments contamination have been introduced, since the determination of total concentration of heavy metals are not the best indicator of their mobility, bioavailability and toxicity (Lim and Kiu, 1994; Bunzl et al., 1999; Korfali and Jurdi, 2010).

Sediments are normally mixtures of several com-ponents, including different mineral species as well as organic debris (Ghrefat and Yusuf, 2006). Sediment can act as both a sink and a source for contaminants. It reflects the quality of surface water as well as provides information on the transportation and fate of pollutant (Santchi, 1984; Finney and Huh, 1989).

Sediments are vital components of aquatic ecosystems in which toxic metals accumulate through complex physical and chemical adsorption mechanism which depend on the nature of the sediment matrix and the properties of adsorbed compounds (Abul Kashem et al., 2007). Several processes lead to the association of heavy metals with solid phases, such as direct absorption by fine-grained inorganic particles of clays, adsorption of

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hydrous ferric and manganese oxides which may in turn be associated with clays, adsorption or complexation with natural organic substances, which may also be associated with inorganic particles, and direct precipitation as new solid phases (Gibbs, 1973). Several factors could influence the chemical speciation of heavy metals. Some of these factors include sediment particles, particle size distribution, organic and inorganic matter content, dissolved oxygen, pH, salinity, and redox potential and their presence in water phase of some anions and cations that can bind or co-precipitate the water-dissolved or suspended pollutants (Di Toro et al., 1991; Soon et al., 1999; Dollar et al., 2001).

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). Speciation can further be defined as the identification and quantification of the different species, forms, or phases present in a material (Korfali and Jurdi, 2000; Fytianos and Lourantou, 2004). However, the determination of specific chemical species is difficult and often hardly possible (Loska and Wiechula, 2002). Consequently, determinations of wider forms, for instance, the mobile or carbonate bound forms, depending on operational defined procedure can be a good compromise to give information on environmental contamination risks (Fytianos and Lourantou, 2003).

Several sequential extraction have been developed by many researchers which are variant on the Tessier procedure in which the exchangeable metals and those nominally associated with carbonate, Fe-Mn oxides, organic material and silicate residues were extracted with different reagents in order to address this issue to estimate the amounts and proportion of metals present in different forms in sediment samples (Tessier et al., 1979; Sobcynski and Siepak, 2001).

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 agricultural practices, intense fishing activity, washing of domestic wares and automobiles, bathing and fetching of water for construction and domestic purposes. These different anthropogenic sources around the reservoir may contribute in enhancing the metal pollution in sediment of the reservoir.

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 bottom sediments of 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). Therefore, it is of importance to establish the degree of trace metal contamination and to discuss the origin of these contaminants in the sediments of the reservoir.

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

MATERIALS AND METHODS

Study area

Aiba reservoir is a man-made lake located in Iwo city in the South-western part of Nigeria (Figure 1). The reservoir lies between longitudes 4° 11' to 4° 13' east of the Greenwich and latitude 07° 38' to 07° 39' north of the Equator. The reservoir has a catchment 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).

Experimental

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.

Sampling took place in the month of October, 2010. Triplicate samples of the bottom sediment for each of the five locations were collected with grab sampler. Sediment samples from each locations were made into composite representative samples and were stored in clean, sealable polythene bags already rinsed with acid and thoroughly washed with double distilled water. The samples were air-dried over an inert surface in a ventilated cupboard to minimise cross contamination of samples. The dried samples were seived through a polythene mesh of 2 mm pore size to get rid of pebbles and large particles.

A dried sediment sample (10.0 g) was weighed into a boiling tube. Distilled water (10 ml) was added and allowed to stand for 30 min and was stirred occasionally with a glass rod (IITA, 1979). A Eutech tester (pHTestr^{TM} 2) was inserted into partly settled suspension and the pH was measured. Sediment conductivity measurement was taken at the site, the suspension was not stirred during measurement, the electrode was rinsed with deionized water and wiped with clean tissue after each reading.

To determine water absorbency of the sediment, samples were oven-dried and crushed in a mortar using pestle. Thereafter, 3.0 g of sub-sample was weighed, soaked in water for 24 h, excess water was drained and the sample reweighed (Smith, 1996).

The analytical speciation scheme used in this study is a slightly modified version of selective sequential extraction procedure by Tessier et al. (1979). Except for the introduction of two important factors; water soluble and plant available. In this scheme, heavy metals were separated into nine operationally defined fractions (F):
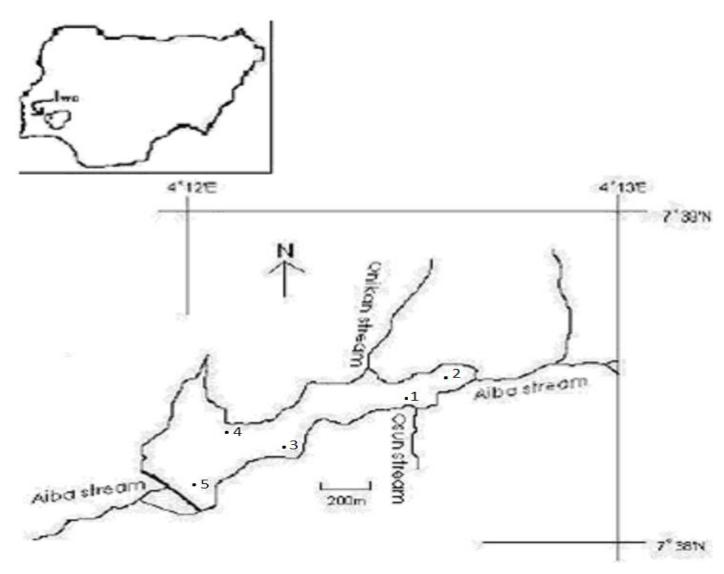
Figure 1. Map of Aiba reservoir showing sampling locations.

water soluble (F1), exchangeable (F2), bound to carbonate (F3), plant available (F4), bound to Mn (F5), bound to amorphous Fe oxide (F6), bound to crystalline oxide (F7), bound to organic matter (F8), and residual fraction (F9).

One gram of each soil sample was weighed and extractions were made through steps (F) by centrifugation and filtration at 10,000 rpm placing the sample in 100 ml conical flask. Deionised water was used to wash the residues following subsequent extractions in order to ensure selective dissolution and avoid possible inter-phase mixing between the extractants. All samples were run in duplicates.

Fraction 1: Water soluble metals

Water soluble metals were extracted with a solution of 50 ml distilled deionized water at pH 7.0 and at 28°C for 2 h.

Fraction 2: Exchangeable metals

The residue from (a; water soluble metals) was extracted with 25 ml of 1.0 M NH_4COOCH_3 (pH = 7.0). The suspension was shaken for 30 min at 28°C.

Fraction 3: Metals bound to carbonate

The residue from (b; exchangeable metals) was extracted with 3 M sodium acetate (CH_3COONa^+) adjusted to pH 5.0 with acetic acid (CH_3COOH). The suspension was shaken for 5 h.

Fraction 4: Plant available metals

The residue from (c; metals bound to carbonate) was extracted by shaking with a solution mixture of 50 ml of 0.025 M HCl + 0.05 M H_2SO_4 for 30 min at 28°C.

Fraction 5: Bound to Mn-oxide

The residue from (d; plant available metals) was shaken for 30 min

at 28°C with a solution of 25 ml 0.1 M $NH_2OH.HCl$ in 25% CH_3COOH (pH 2 to 3).

Fraction 6: Bound to amorphous Fe-oxide

The residue from (e; Mn-oxide) was extracted with 25 ml of 0.2 M $(NH_4)_2C_2O_4$ (pH 3.0) for 30 min at 50°C using a water bath with occasional stirring.

Fraction 7: Bound to crystalline Fe-oxide

The residue from (f; amorphous Fe-oxide) was extracted using 25 ml of 0.04 M $NH_2OH.HCl$ in 25% acetic acid (pH 2) and it was heated in a water bath with occasional stirring at 100°C for 6 h.

Fraction 8: Bound to organic matter

The residue from (g; crystalline Fe-oxide) was extracted with 10 ml of 0.02 M HNO_3 and 15 ml of 30% H_2O_2 (adjusted to pH 2 with HNO_3). The mixture was then heated to 85°C for 5 h with occasional agitation. A second 15 ml liqueur of 30% (pH 2 with HNO_3) was added and the mixture was heated again to 85°C for 3 h with intermittent agitation. After cooling, 5 ml of 3.2 M NH_4COOCH_3 in 20% (v/v) HNO_3 was added and the samples diluted to 20 ml and were agitated continuously for 30 min.

Fraction 9: Residual metals

The residue from (h; organic matter) was digested with a mixture of concentrated HNO_3 and $HClO_4$ for 8 h.

Instrumentation and statistical analysis of data

The metal content of all the extracts in the centrifuged solutions were determined by atomic absorption spectrophotometer using Buck Model 205 flame atomic absorption spectrophotometer, available at the International Institute of Tropical Agricultural (IITA), Ibadan.

The coefficient of variation measure the strength of a linear relationship between any two variables on a scale of -1 (perfect inverse relation) through 0 (no relation) to +1 (perfect sympatheic relation). In this study, raw data was used in calculating the correlation coefficient using the SPSS computer software package 15.0 for window evaluation version. Both descriptive and inferential statistical analyses were used to interpret the data in this study. Pearson correlation analysis was also carried out.

RESULTS AND DISCUSSION

Physico-chemical parameters of bottom sediment of Aiba reservoir

The physico-chemical parameters of the sediment show that pH range from 6.2 to 6.6 with highest value recorded in locations 1 and 3 and lowest value recorded in the location 5 (Table 1). The sediment pH is slightly acidic. This might be due to organic detritus deposited at the bottom of the reservoir. Conductivity of the sediment shows the range value of 50 to170 µS/cm with the mean

value of 104 ± 5.0 µS/cm. The highest value was recorded in location 3, the agricultural area, while the lowest value was recorded in location 5 (Table 1). Conductivity and pH are positively correlated. A linear relationship between conductivity and pH was observed in the sediment of the Aiba reservoir. The sediment in location 5 was most acidic (low pH) and had the lowest conductivity value, while sediment in location 3 had the highest pH value recorded and the highest conductivity. Water absorbency ranged from 50 to 63.3% with mean percentage of 54.66 ± 2.17%; the highest percentage was recorded in location 1, while the lowest value was recorded in locations 4 and 5. The bottom sediments from Aiba reservoir, the main source of drinking water from Iwo and environs were found to contain highly elevated levels of Iron (42.03 ± 1.11 µg/g), followed by Manganese (28.86 ± 0.88 µg/g), and Zinc (11.91 ± 0.37 µg/g). The levels of Copper (5.82 ± 0.21 µg/g) and lead (0.44 ± 0.02 µg/g) were the lowest (Figure 2).

This might be due to less pollution from automobile and removal of tetra ethyl lead from Nigeria gasoline as anti-knock. In a similar way, the source of zinc might also be due to anthropogenic inputs, such as fertilizer and pesticides from agricultural activities taking place along the reservoir banks. Iron is the most abundant metals in all the sediments, because it is one of the most common elements in the earth's crust. The concentration of trace metals in the bottom sediment of Aiba reservoir was less when compared with other findings reported of major urban receiving water sediments in the world (Table 2). Due to the fact that total concentration of heavy metals is not sufficient to give information on the bioavailability and toxicity of heavy metals, mobility, bioavailability, and toxicity of heavy metals have correlations with their speciation (Huang et al., 2009). It is therefore necessary to pay a closer attention to the speciation study of these metals. Figures 3 to 7 present the distribution of trace metals in nine different fractions.

Manganese

The distribution of manganese in the sediment sample revealed that carbonate fraction (14%) and plant available fraction (14%) were predominant. The contribution of Mn-oxide and organic matter were very small (9%) (Figure 3). Sobczynski and Siepak (2001) reported that carbonate fraction was predominant in sediment from Goreckie lake, while organic matter fraction contained only 6.1% of its total content. In a similar way, Sobczynski and Siepak (2001) reported a high percentage of carbonate fractions in river Seine reservoir. They concluded that in almost all cases, the smallest amount of manganese was in the form bound to organic matter. Loska et al. (2000) reported a much larger fraction of carbonate and sulphides (35 to 45%) and lower fraction in exchangeable and organically bound form in two locations in Rybnik reservoir. The association

Table 1. Physico-chemical parameters of bottom sediment of Aiba reservoir.

Location	pH	Conductivity (µS/cm)	Water absorbency (%)
Mean ± SD	6.44 ± 0.12	104 ± 5	54.66 ± 2.17
Range	6.2 - 6.6	50 -170	50 - 63.3

Table 2. The concentrations (µg/g) of Zn, Pb, and Cu in some urban receiving water sediments.

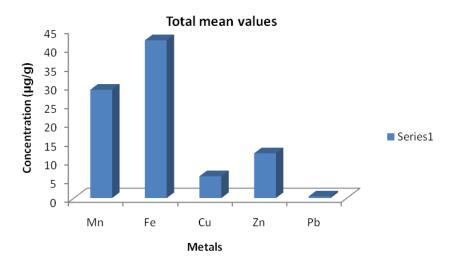| Metal	UK (Bryan, 1991)	USA (Frits, 1990)	Sweden (Chen and Morrison, 1992)	Singapore (Chen et al., 1995)	Present study (Aiba reservoir)
Zn	501	400	800	182	11.91
Pb	245	67	188	62	0.44
Cu	16	214	153	25	5.82

Figure 2. Mean total concentration of heavy metals in botton sediment of Aiba reservoir.
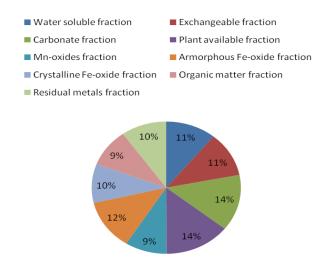

Figure 3. Distribution of Mn in surface water of Aiba reservoiur.

of Mn to the carbonate fraction is probably due to abundance of Mn in the earth crust, including soil (Tokalioglou et al., 2002).

Iron

The distribution of iron in the sediment of Aiba reservoir showed that the highest percentage of carbonate fraction (13%) and plant available fraction (13%), while the residual fraction was the lowest (8%) (Figure 4). This finding is similar to the report of Loska et al. (2000) who reported that sulphide and carbonate were the largest fractions which amounted to 40 to 45% and 20 to 25%, respectively. Sobczynski and Siepak (2001) report was different with the findings of this study. They reported predominant contribution of immobilised (46%) and fraction bound to organic matter (40%) in Goreckie lake, while contribution of the fraction in the form of oxides was
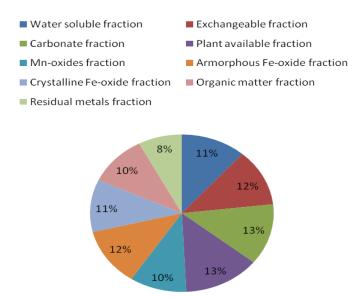
- Water soluble fraction
- Exchangeable fraction
- Carbonate fraction
- Plant available fraction
- Mn-oxides fraction
- Armorphous Fe-oxide fraction
- Crystalline Fe-oxide fraction
- Organic matter fraction
- Residual metals fraction

Figure 4. Distribution of Fe in surface water of Aiba reservoiur.

- Water soluble fraction
- Exchangeable fraction
- Carbonate fraction
- Plant available fraction
- Mn-oxides fraction
- Armorphous Fe-oxide fraction
- Crystalline Fe-oxide fraction
- Organic matter fraction
- Residual metals fraction

Figure 6. Distribution of Zn in surface water of Aiba reservoiur.

- Water soluble fraction
- Exchangeable fraction
- Carbonate fraction
- Plant available fraction
- Mn-oxides fraction
- Armorphous Fe-oxide fraction
- Crystalline Fe-oxide fraction
- Organic matter fraction
- Residual metals fraction

Figure 5. Distribution of Cu in surface water of Aiba reservoiur.

Pb

- Water soluble fraction
- Exchangeable fraction
- Carbonate fraction
- Plant available fraction
- Mn-oxides fraction
- Armorphous Fe-oxide fraction
- Crystalline Fe-oxide fraction
- Organic matter fraction
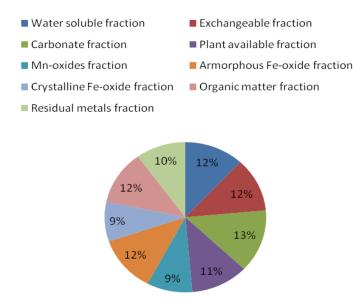- Residual metals fraction

Figure 7. Distribution of Pb in surface water of Aiba reservoiur.

much smaller. Findings of Welte et al. (1983) on the sediment of water reservoir in Orly on the river Siene showed that hydrated oxides of iron and manganese were predominant over the fraction bound to organic matter. Chen et al. (1995) in their study of sediment of a tropical reservoir reported that approximately 56% of Fe and Al were incorporated in the organic and sulphide phase. Korfali and Jurdi (2010) in their study of Qaraaoun reservoir reported that iron speciation is dominated by the residual fraction with mean percentage of 53 and ranging between 43 and 60%. Kwapulinski and Wiechula (1993) reported that iron occurred predominantly in immobilised fraction, but fraction of oxide bound were twice as much
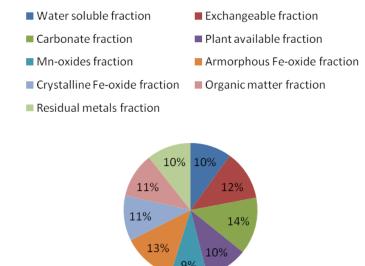
as iron as that bound with organic matter.

Copper

The distribution of copper in bottom sediment of Aiba reservoir is as shown in Figure 5 with the highest fraction in carbonate bound (13%) and the lowest were Mn-oxides fraction (9%) and crystalline Fe-oxide fraction (9%), respectively. This finding is contrary with the report of Sobczynski and Siepak (2001) that recorded the highest amount of copper in immobilised fraction (83%) in Goreckie lake. Further, they reported that all samples

taken from all Wielkopolski National Park lakes showed that the amount of copper were in the organic bound fraction. Loska et al. (2000) in their study concluded that there was an increase in the content of copper in the adsorbed and organically bound forms during aeration, and a decrease in the content of copper in the forms of carbonates and sulphides. Wufem et al. (2007) reported the highest percentage of copper in the exchangeable fraction (31.42%) in the bottom sediment of Gubi dam.

Zinc

The distribution of zinc showed that the highest distribution was found to be in the carbonate fraction (14%), followed by amorphous Fe-oxide fraction with 13%. In much smaller amount, it occurred in the form bound to Mn-oxide (9%) (Figure 6). This finding is in disagreement with the report of Sobczynski and Siepak (2001) that reported the highest fraction in the form bound to hydrated iron and manganese oxides (58%), while the lowest fraction was carbonate fraction (16%). Wufem et al. (2007) reported the highest percentage of zinc with the carbonate fraction (24.73%) in the bottom sediment of Gubi dam. Korfali and Jurdi (2010) reported high percentage speciation of zinc in the organic and sulphide fraction of the sediment. Loska et al. (2000) reported that zinc was characterised by an increase in the form of sulphides, while the content of the exchangeable and organically bound forms decreased. Lim and Kiu (1994) concluded that irrespective of the sampling sites, the speciation pattern of zinc indicates that more than 50% of the metal was associated with the moderately reducible and easily reducible fractions. The co-precipitation with carbonate minerals is of importance for a number of metals such as cadmium and zinc (Frostner and Wittmann, 1983; Alloway, 1995). The high content of carbonate fraction in the sediment of this reservoir might be due to carbonate rocks exposed to the reservoir especially in locations 2 and 5. These rocks mainly include bituminous limestone, limestone, chalky marl, and quaternary terrace deposits.

Lead

The distribution of lead showed that the highest distribution were found in exchangeable fraction (14%) and amorphous Fe-oxide fraction (14%), while the plant available, Mn-oxide fraction and residual fractions were the least with contribution of 9% each. Welte et al. (1983) in their study of the bottom sediment from the drinking water reservoir of Orly on the river Seine discovered that lead was mostly in the forms bound to hydrated iron and manganese while the least amount of lead was in the fraction bound to organic matter and it practically did not occur in the exchangeable fraction. Korfali and Jurdi

(2010) reported high percentage speciation of lead in the organic and sulphide fraction.

Speciation pattern (fractions 1 to 9) based on sampling sites

The speciation patterns of trace metals in the bottom sediment of Aiba reservoir based on the different sampling sites are as shown in Figure 8 (1 to 9). This figure presents the concentration of the metal species among the different sampling locations. In all the fractions, iron is predominantly high followed by manganese, Zinc and copper, while lead is the lowest. The concentrations of lead in all the fractions were almost similar. With respect to water soluble fraction, manganese and iron are conspicously high in locations 2, 3 and 5, while zinc is higher in location 4. The concentration of Cu and Pb are almost similar in all locations.

The exchangeable fraction showed the highest concentration of Mn and Fe in locations 2 and 5. The concentrations of Cu is almost similar in all the locations, while the concentrations of zinc were higher in locations 4 and 5. Metal bound to carbonate showed that location 5 has the highest concentrations of manganese, iron and zinc, followed by location 2, while the concentrations of copper were almost similar for all locations. Plant available fraction showed the highest concentration of manganese and iron in location 3 followed by location 1. The highest concentration of zinc was recorded in location 1, while the concentrations of copper were almost similar in all locations.

The trend in manganese-oxide fraction showed that the highest concentration of manganese and iron occurred in location 5. Copper was extremly low in location 2, while the concentration of zinc were almost the same in all the locations.

The concentrations of manganese and iron were high in location 3 followed by location 1 for armorphous iron-oxide fraction. The concentration of copper were almost similar in all the locations. The highest concentration of zinc occured in location 4. The crystalline iron-oxide fraction showed that concentrations of manganese, iron and zinc were higher in locations 1, 2, and 4. Copper was extermly low in location 1. In the same way lead was extremely low in location 1.

In nearly all the metals, locations 2 and 5 recorded the largest concentration in organic matter, fraction iron is exceptionally high in locations 2 and 5. The residual fraction showed that manganese was very high in locations 1, 2, and 5, while iron was very high in locations 2, 3, and 5. Copper was high in locations 1 and 3, but low in location 2.

The environmental impact of the nine speciation phases depends upon the ease of remobilization. The exchangeable and adsorptive, bound to carbonate and reducible phases are the most dangerous (Horsfall et al.,
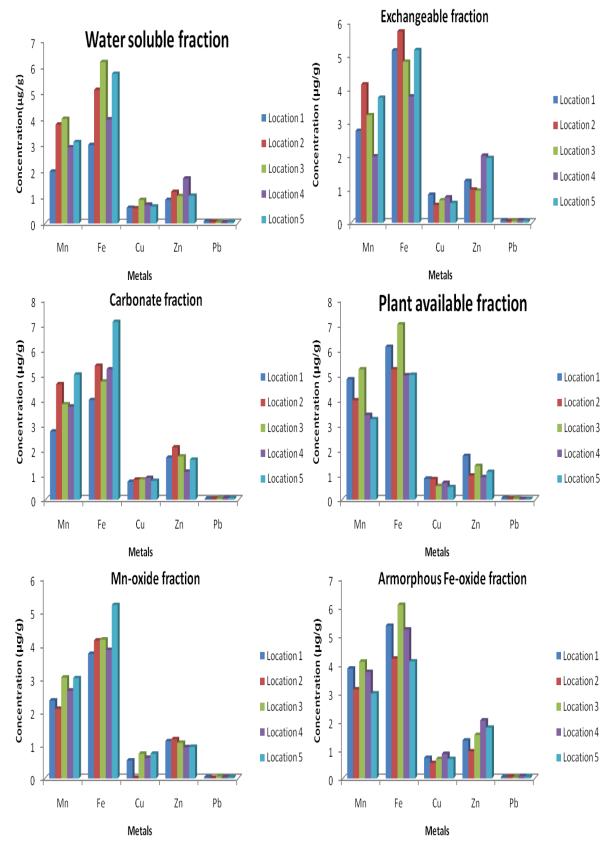
Figure 8. Speciation pattern (fractions 1 to 9) based on sampling location: water soluble (F1), exchangeable (F2), carbonate fraction (F3), plant available fraction (F4), Mn-oxide fraction (F5), amorphous Fe-oxide fraction (F6), crystalline Fe-oxide fraction (F7), organic matter fraction (F8), and residual metals fraction (F9).
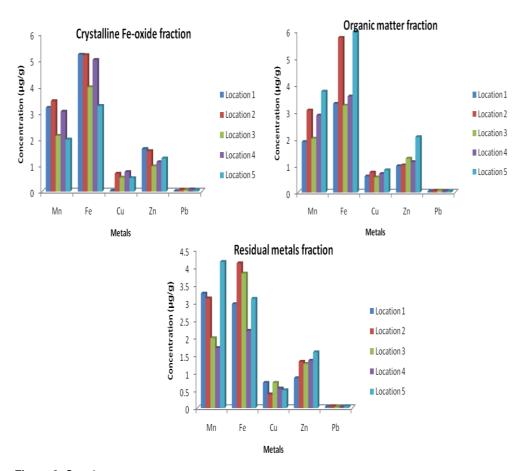
Figure 8. Contd.

Table 3. Pearson correlation matrix of the analysed parameters.

Metal	Mn	Fe	Cu	Zn	Pb	pH	Conductivity	Water Absorbency
Mn	1	-	-	-	-	-	-	-
Fe	0.784**	1	-	-	-	-	-	-
Cu	0.251**	0.216*	1	-	-	-	-	-
Zn	0.300**	0.197*	0.097	1	-	-	-	-
Pb	0.089	0.100	0.324**	0.112	1	-	-	-
pH	-0.822	-0.789	-0.554	-0.662	0.417	1	-	-
Conductivity	-0.852	-0.848	0.087	-0.591	0.221	0.726	1	-
Water absorbency	-0.760	-0.763	-0.386	-0.889*	0.794	0.821	0.444	1

**Correlation is significant at the 0.01 level (2-tailed); *Correlation is significant at 0.05 level (2-tailed).

1999). Figure 8 revealed that the metals considered in this study have different pollluting capabilities. Iron and manganese might be vulnerable, since both appear most in the exchangeable fraction in percentages. Further, the association of these metals being distributed in the iron/manganese-oxide, residual and oxidizable phase are in excellent agreement with metal speciation studies of sediments from other rivers and reservoirs (Calmano and Forstner, 1983). Metals bound in these different fractions will behave differently in the sedimentary and dia-magnetic environment, and therefore have different potential for remobilization and for uptake by biota (Fytianos and Lonrantou, 2003).

The matrix of linear relationship coefficient is shown in Table 3. The correlation value (r) shows a wide range in sediment from -0.889 between water absorbency per-centage and zinc, to 0.821 between pH and water absor-bency (Table 3). This suggest that different geochemical

factors influence their concentrations. The following metal associations can be deduced from Table 3: manganese is strongly positively corrrelated with iron, copper, and zinc at $P < 0.01$. Iron is positively correlated with copper and zinc at $P < 0.05$. Copper is strongly positively correlated with lead at $P < 0.01$. Zinc is negatively correlated with water absorbency at $P < 0.05$, this shows that both were not of the same source. The positive correlation between these metals shows that there was an association or interaction of these metals in the study area, and on the other hand, that these metals might have similar sources of input into the dust-soil environment, according to Miller and Miller (2000), a strong correlation between two variables or metals may be an occurrence of strong dependence of both variables on the same causal factor. This suggested that sources of the trace metals are essentially anthropogenic

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