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Geochemical Forms of Some Heavy Metals in the Sediment of Ala River, Akure, Nigeria

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Abstract

The total digestion method for determining the mobility and bioavailability of metals in sediments is not enough to fully evaluate the ecological impact of these heavy metals; hence the need for speciation is important by understanding its geochemical forms. Prior to the sequel extraction, certain parameters this includes determination of the sediment pH with the use of pH meter alongside its conductivity. The sequential extraction method involving was used to determine the distribution of heavy metals. The heavy metals studied are Iron, copper, zinc, lead, and cadmium from five distinct fractions prepared by the selection of five sampling area under study. The physicochemical parameters investigated for the fractions are classified as water soluble, exchangeable, carbonate, Fe-Mn oxide, organic and residual. The Fe-Mn oxide fraction has the highest amount in iron (42.9%), while exchangeable fraction has its highest amount in copper, zinc and lead were bound in non-residual fraction while residual has its highest amount in cadmium. The bioavailability of these metals can be related to the solubility of the geochemical forms of the metals. Therefore the mobility for these metals in the sediments are in decreasing order are; Iron > Lead > Zinc > Copper > Cadmium. The pH and electrical conductivity of these locations were found to range within the slightly acidic medium (5.26 – 6.02) and 30.5 – 53.0 µs/cm respectively. The values of the heavy metals from the result showed that Iron and lead was appreciably associated with the non-residual fractions in the sediments and thus, more potentially bio-available in comparison to other heavy metal studied. The residual fraction was discovered to consist of Copper, zinc, and Cd having average values of 73.2%, 67.6%, and 96%. However, Iron was found to bioavailable in the entire fraction with the highest% in Fe- Mn. It can be deduced that these metals (i.e. Copper and Zinc) possess low mobile fraction consequently, has a low potential risk for the aquatic life. Lead, on the other hand, has the highest portion in the mobile fraction and thus poses a high risk to aquatic environments.

1. Introduction

The need for reliable means to access the chemical forms of toxic and essential trace metals especially in natural water in our immediate environments are rising day by day. The total metal content of soils are useful for many geochemical applications but often, the speciation of these metals is more of an interest agriculturally in terms of what is biologically available [1]. Water, as well as air, can receive a largenumber of pollutants, but beside ability of self-cleaning, some pollutants among which are also heavy metals lead to modification of water quality to the level that it becomes useless for many purposes. The toxicity, bioavailability,

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andmobility of metals are related to their species [2].

Heavy metals refer to stable metals of density greater than $5 gcm^{-3}$. They take part in biogeochemical cycles and are not permanently fixed in soils; therefore, assessment of their distribution in soils is a key problem in many environmental studies [3]. Heavy metals are included in soil minerals as well as bound to different phases of soil particles by a variety of mechanisms, mainly absorption, ion exchange, co – precipitation and compexation.

It is observed that heavy metals pass through biogeochemical processes with different retention time in different parts of the atmosphere. They do not decompose but have the ability to bioaccumulate, because they are being retained in plants, animals, and nature in general. They are an extremely heterogeneous group of elements in terms of biological and ecological effects [4]. Speciation analysis is the determination of the different physico-chemical forms of a pollutant which together comprises its total concentration in a given sample or the determination of the distribution of an individual chemical element among different groups.

Sediments are vital components of aquatic ecosystems in which toxic metals accumulate through complex physical and chemical adsorption mechanism which depends on the nature of the sediment matrix and the properties of adsorbed compounds. Sediments are normally mixtures of several components including different mineral species as well as organic debris [5]. They are also known as the gateway for pollutants in a water system.

Speciation extraction procedures have been used to know the stability and strength to which the metals are bound in the sediment matrix [6], the degree of contamination of the sediments and the mobility of heavy metals across the food chain.

This research utilizes speciation technique in the extraction of heavy metals in Ala river sediments with the objective of investigating the abundance of some chemical forms and potential risk to the aquatic system.
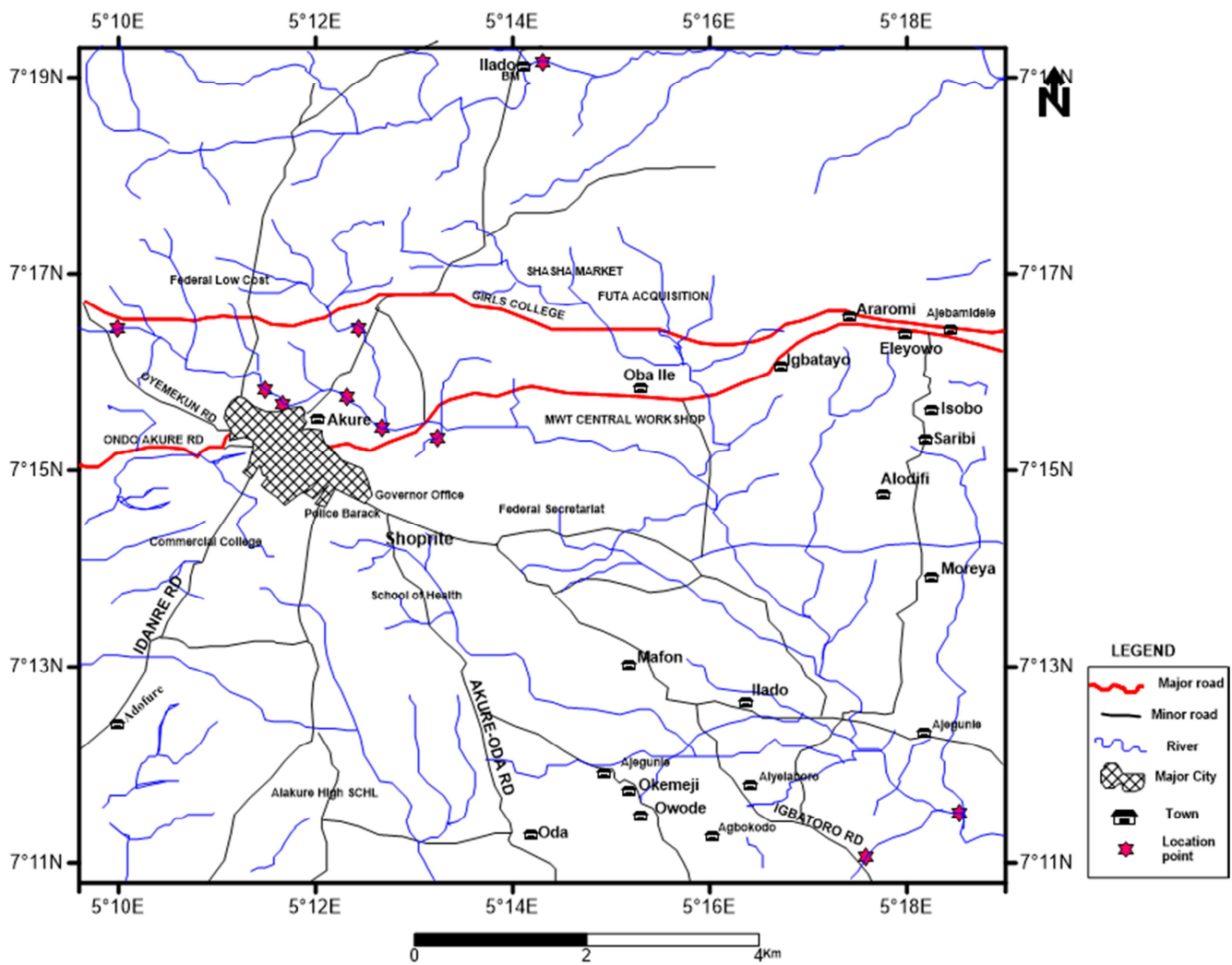

Figure 1. Map of the study area showing the sampling sites.

2. Materials and Methods

2.1. Sampling Sites

Five sampling areas were chosen at different locations in Akure which are Ehin-Ala, Okeijebu, Fiwasaye, Alagbaka, Araromi represented by Location A, B, C, D, and E respectively. All located in Akure, Ondo State, Nigeria. Table 1 shows the latitude and longitude of each location. Samples were collected during the dry season.

Table 1. The latitude and longitude of the selected locations.

| LOCATION	LATITUDE	LONGITUDE
A	07°11. 51N	005°18.53E
B	07°16. 44N	005°12. 31E
C	07°15. 33N	005° 13. 23E
D	07°15. 43N	005° 12. 67E
E	07°15. 67N	005° 11. 67E

All glass wares used (conical flask, beakers, measuring cylinder, volumetric flask, and watch glass) were washed with liquid detergent, rinsed with tap water and then soaked in 5% HNO_3 solution for a minimum of 24 h followed rinsing with distilled water before use.

Triplicate samples of the bottom sediment for each location were collected with sterilized hand tower. The sediment samples for each location were made into composite representative samples and were stored in clean polythene bags already washed with distilled water. The samples were air dried over an inert surface (drying took about a week for proper drying of the samples) after which the samples were sieved using a 2 mm mesh pore size to get rid of the pebbles and large particles.

2.2. Determination of Sediment pH

The soil pH was determined using pH meter according to [7] and the mixture was left for about 30 minutes. The soil pH was determined using pH meter according to [7] and the mixture was left for about 30 minutes. The pH meter was first calibrated with pH 4 buffers and pH 10 buffers before dipping the pH meter electrode in the soil solution, and then the readings were taken.
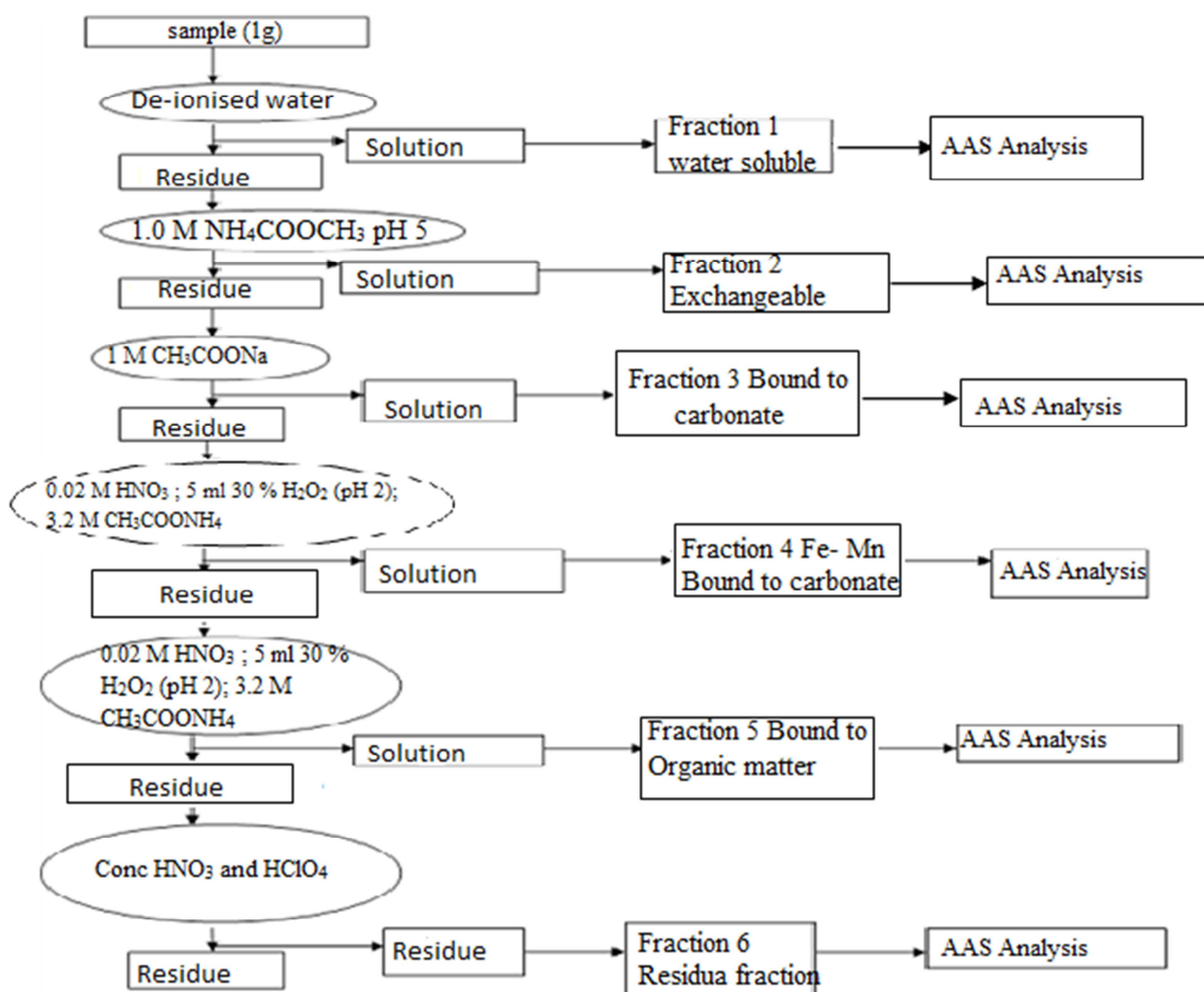
Figure 2. Schematic diagram of a sequential extraction procedure by [8] Akinnawo et al., 2016.

2.3. Determination of Conductivity

The ratio of soil to water used for this test was similar to that of soil pH (i.e soil: water = 1:2) [7]. The mixture was also left for about 30 minutes, and then the electrode of the conductivity metre was dipped in the soil solution for the readings to be taken. (For reliable and accurate readings, the electrode was rinsed and mopped with a clean tissue after every reading taken).

2.4. Sequential Procedure

The sequential extraction procedure was carried out through the modified method of [8] to extract metals from the sediments except that water soluble component was included. The samples were subjected to a six stage sequential procedure to extract and partition iron, copper, zinc, cadmium and lead into water soluble, exchangeable, bound to carbonate, bound to Fe-Mn oxides, bound to organic matter and residual fractions. One gram of each soil sample was weighed and extractions were made through steps in Figure 2. Distilled water was used to wash the residues following subsequent extraction in order to ensure selective dissolutions and to prevent possible interphase mixing between the extractants.

2.5. Data Analysis

The results of replicate readings were pooled and expressed as a mean ± standard deviation.

One way analysis of variance was used to analyze the results and Duncan's New Multiple

Range Test was used for the post hoc [9]. Statistical package for Social Science (SPSS) 18.0 for Windows was used for the analysis.

3. Results and Discussions

Table 2 shows the results of the physicochemical parameters of the surface sediment of Alariver

Table 2. Physico- chemical Parameters of the Sediment of Ala River.

Locations	P^H	Electrical Conductivity (EC)
A	6.02	53.0
B	5.93	37.0
C	5.26	30.5
D	5.64	50.4
E	5.47	32.7

Table 3. Iron concentration (mg/kg) in sediment Fraction.

Fractions	A	B	C	D	E
Water soluble	Bdl	2.50 ± 0.07	25.50 ± 0.71	8.250 ± 2.33	bdl
Exchangeable	15.75 ± 0.45	305.50 ± 1.41	29.95 ±0.18	258.50 ± 2.93	563.75 ± 7.50
Carbonate	18.00 ± 0.21	Bdl	13.75 ± 0.25	10.25 ± 0.01	66.50 ± 1.74
Fe-Mn oxides	1528.50 ± 32.09	7034.50 ± 51.93	4382.00 ± 77.10	3929.50 ± 39.25	1895.00 ± 18.55
Organic	1294.25 ± 11.83	681.50 ± 6.21	924.00 ± 16.73	425.00 ± 2.86	902.50 ± 9.64
Residual	1816.50 ± 23.06	4599.00 ± 37.29	2251.00 ± 4.62	1089.75 ± 2.37	3728.50 ± 36.82
Sum of fractions	4673 ± 67.6	12623 ± 97	7626 ±100	5721±50	7156±74
Non-residual%	61.1	63.6	70.5	80.9	47.9
Mobility factor%	0.71	2.45	0.90	4.84	8.80

bdl= below detection limit.

Table 4. Copper concentration (mg/kg) in sediment Fraction.

Fractions	A	B	C	D	E
Water soluble	0.50 ± 0.01	Bdl	0.50 ± NS	0.50 ± NS	2.5 ± 0.07
Exchangeable	2.50 ± 0.01	25.50 ± 0.69	1.00 ± 0.01	1.25 ± 0.01	4.25 ± 0.01
Carbonate	bdl	0.50 ± 0.01	0.25 ± 0.01	0.25 ± 0.01	2.75 ± 0.06
Fe-Mn oxides	bdl	1.00 ± 0.03	5.75 ± 0.13	1.50 ± 0.01	3.75 ± 0.06
Organic	1.25 ± 0.01	2.00 ± 0.01	2.75 ± 0.06	0.50 ±NS	7.50 ± 0.07
Residual	75.00 ± 1.04	19.50 ± 0.19	75.00 ± 1.02	95.00 ± 0.01	19.00 ± 0.17
Sum of fractions	79.25 ± 1.07	48.5 ± 0.93	85.25 ± 1.2	99.00 ± 0.04	39.75 ± 0.44
Non-residual%	5.36	59.79	12.02	4.04	52.20
Mobility factor%	3.79	53.61	2.05	2.02	23.90

bdl= below detection limit; NS= not significant but not zero

Table 5. Zinc concentration (mg/kg) in sediment Fraction.

Fractions	A	B	C	D	E
Water soluble	0.25 ±0.01	Bdl	0.50 ± 0.01	bdl	0.25 ± 0.01
Exchangeable	15.75 ± 0.01	21.50 ± 0.23	19.25 ± 0.02	25.00 ± 0.07	42.25 ± 0.87
Carbonate	3.75 ± 0.05	2.75 ± 0.02	4.25 ± 0.02	3.50 ± 0.04	9.75 ± 0.05
Fe-Mn oxides	6.00 ± 0.04	10.25 ± 0.05	17.25 ± 0.04	12.25 ± 0.02	7.25 ± 0.05
Organic	11.25 ± 0.05	8.25 ± 0.04	16.60 ± 0.11	8.25 ± 0.04	10.00 ± 0.06
Residual	237.00 ± 2.59	242.00 ± 2.97	533.00 ± 7.37	69.00 ± 0.52	19.50 ± 0.06

Fractions	A	B	C	D	E
Sum of fractions	274.00 ± 2.8	284.75 ± 3.3	590.85 ± 7.6	118.00 ± 0.69	89.00 ± 1.1
Non-residual%	13.50	15.01	9.79	41.53	78.09
Mobility factor%	7.21	8.52	4.06	24.15	58.71

bdl= below detection limit.

Table 6. Cadmium concentration (mg/kg) in sediment Fraction.

Fractions	A	B	C	D	E
Water soluble	bdl	Bdl	bdl	bdl	bdl
Exchangeable	bdl	Bdl	0.05±NS	bdl	bdl
Carbonate	bdl	Bdl	0.25 ±0.13	bdl	bdl
Fe-Mn oxides	bdl	Bdl	0.28± 0.23	bdl	bdl
Organic	bdl	Bdl	0.03 ± 0.025	bdl	bdl
Residual	2.50±1.50	3.00 ±2.00	3.00 ± 0.00	2.50 ± 0.50	1.00 ± 0.00
Sum of fractions	2.50 ± 1.50	3.00 ±2.00	3.60± 0.39	2.50 ± 0.50	1.00 ± 0.00
Non-residual%	0.00	0.00	16.67	0.00	0.00
Mobility factor%	0.00	0.00	8.33	0.00	0.00

bdl= below detection limit. NS= not significant but not zero

Table 7. Lead concentration (mg/kg) in sediment Fraction.

Fractions	A	B	C	D	E
Water soluble	bdl	Bdl	bdl	bdl	bdl
Exchangeable	bdl	37.78±14.73	bdl	239.25±23.3	bdl
Carbonate	bdl	Bdl	bdl	bdl	bdl
Fe-Mn oxides	bdl	Bdl	5.25 ± 5.25	bdl	6.75±0.6
Organic	bdl	Bdl	bdl	bdl	bdl
Residual	bdl	Bdl	bdl	bdl	bdl
Sum of fractions	bdl	37.78±14.73	5.25 ±5.25	239.25 ±23.3	6.75 ± 0.6
Non-residual%	0.00	100	0.00	100	0.00
Mobility factor%	0.00	100	0.00	100	0.00

bdl= below detection limit

3.1. Physicochemical Parameters of Sediment of Ala River

The pH of the tested samples ranges from 5.26 to 6.02 with the highest pH at location A (pH =6.02 and lowest at location C (pH =5.26). The result shows that the sediments are in slightly acidic condition. This might due to active microbial decomposition of drowned vegetation and other organic matter or detritus deposited at the bottom of the river. These values were within those obtained by some researcher in other areas of environmental concern. [10, 8]

Several studies have shown that availability of heavy metals is pH dependent [11], most of the pH values of the study areas indicate high metal uptake by plants since heavy metals are generally more mobile at pH<7 [12]. This work was slightly lower work carried out by [13, 14] where the pH values were between 6.2 – 6.6 and 6.2 - 6.7 respectively. Soils are referred to as being acidic, neutral, or alkaline (basic), depending on their pH values on a scale of 0 to 14. A pH of 7.0 is neutral; less than 7.0 is acidic, and greater than 7.0 is alkaline [15]. The pH has both direct and indirect effects on other variables of the environment. For example, the proportion of total ammonia nitrogen existing in the toxic, un-ionized form (NH_3) increases as the pH increases. This is obvious for the P^H of the soil samples considered for the various locations. This might be as a result of detritus deposit at the river [13]. The acidity of the soil might come from Al^{3+} and H^+ ions which occurs when Al^{3+} reacts with water H_2O to form $AlOH^{2+}$ and $Al(OH)^{2+}$ releasing extra H^+ ion.

Conductivity is a measure of the ability of a material to transmit (conduct) an electrical charge. Electrical conductivity, however, has its highest value of 53.0μs/cm recorded for location A and its least value of 30.5 μs/cm in location C with the mean value of 40.7 μS/cm. The highest value was recorded in location A, the agricultural area, while the lowest value was recorded in location C (Table 2). The application of this emerges from the increasing conductivity, which rises from sand to silt and clay having the highest conductivity. Consequently, conductivity (measured at low frequencies) correlates strongly with soil grain size and texture [16]. In addition to its ability to identify variations in soil texture, electrical conductivity has proven to relate closely to other soil properties that can influence a field's productivity, discussed in the following sections below. Organic carbon accumulates in the poorly drained soils that have higher clay contents [17]. Others factors include salinity, Cation exchange capacity etc.

Conductivity and pH are positively correlated. A linear

relationship between conductivity and pH was observed in the sediment of the Ala river. The sediment in location C was most acidic (low pH) and had the lowest conductivity value, while sediment in location A had the highest pH value recorded and the highest conductivity.

3.2. The concentration of Metals in Each Defined Geochemical Fractions of Five Sediments Samples

3.2.1. Iron

The distribution of iron in the sediment of Ala river from the Table 3 shows that the Fe-Mn oxide in each of the locations is extremely high with location B having the highest value of 55.7% and location A having the lowest percentage value of 26.5%. The value of Fe-Mn is high compared to the organic that is extremely low. This finding is similar to the report of [18] who reported that sulphide and carbonate were the largest fractions which amounted to 40 to 45% and 20 to 25%, respectively. [19] report was different from the findings of this study. They reported the predominant contribution of immobilized (46%) and fraction bound to organic matter (40%) in Goreckielake [13]., while the contribution of the fraction in the form of oxides was much smaller. Findings of [20] on the sediment of the 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 [21] reported that iron occurred predominantly in an immobilised fraction, but a fraction of oxide bound was twice as much smaller. Findings of [20] on the sediment of the 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 [22] 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 [23] Korfali and Jurdi in their study of Qaraaoun reservoir reported that iron speciation is dominated by the residual fraction with a mean percentage of 53 and ranging between 43% and 60%. [21] Kwapulinski and Wiechula reported that iron occurred predominantly in an immobilized fraction, but a fraction of oxide bound was twice as much. The percentage of total Iron associated with different geochemical fractions in the five soil samples follows the order below: Fe-Mn oxide > Residual > Organic > Exchangeable > carbonate > water soluble.

3.2.2. Copper

The distribution of Cu in the sediment of Ala river is as shown in Table 4 with the highest concentration of metals in the residual fraction and this cut across all the locations. The highest% of Cu was higher in locations A, C, and D with 94.6%, 87.9%, and 95.9 respectively. The only location that shows a small amount of Cu concentration in all fractions is locations B and E with 40.25% and 47.8% respectively.

(Table 4). The percentage value of B and E is in agreement with the work done by Olajire and Turki where the Cu level associated with residual was 47% and 40.4% respectively. Exchangeable has the highest value of copper which is 10% at location E, after which organic follows with a percentage of 18.9% at location E, then, Fe-Mn oxide with 6.7% at location C (Table 4 above) [6, 24]. The percentage of total copper associated with different geochemical fractions in the five soil samples follows the order below:

Residual > Exchangeable > Organic > Fe-Mn oxide > water soluble > carbonate. The% of Cu in some of the locations were in agreement with the report of [18] Sobczynski and Siepak (2001) that recorded the highest amount of copper in immobilised fraction (83%) in Goreckielake [13].

3.2.3. Zinc

Zinc concentrations are mostly found in the residual fraction like copper. The majority of the zinc was associated with the residual fractions with 90.2% in a location in Table 5 above and this wide range of residual fraction percentage shows that its degree of pollution to the environment is very low [25]. For the Zinc metal its residual has higher than other considered parameters the progression of the reducing residual are location C > B > A > D and E. The percentage of total Zinc associated with different geochemical fractions in the five soil samples follows the order below: Residual > Exchangeable > Organic > Fe-Mn oxide > carbonate > water soluble.

3.2.4. Cadmium

Cadmium level is apparently low considerably the fact that many considered parameters are below the detection limit. The distribution of Cd in the sediment of Ala river is as shown in Table 6 with the highest concentration of metals in the residual 100% in location B and C respectively. The appreciablevalue was recorded basically for all parameters considered for Cd. This result was in agreement with the work done by Olajire and Turki 2007 where the Cd level associated with residual was 47% and 40.4% respectively [6, 24]. The% of Cd in sediment is as follow: Residual > Organic= Fe-Mn= carbonate > Exchangeable > water soluble

3.2.5. Lead

The lead was also observed to have similar characteristics to Cd in that majority of the considered parameters were below the detection limit and for location B and D the exchangeable is 100% and Fe- Mn in location C were 100% respectively. The % of Cd in sediment is as follow: Exchangeable > Residual > Fe-Mn Organic = carbonate= water soluble

3.3. The Mobility of Iron, Copper, Zinc, Cadmium, and Lead

The mobility of metals in the soil sediments can be evaluated on

the basis of the absolute and relative content of fractions weakly bound to soil components [6]. Relative index of mobility of metals was calculated as a mobility factor (MF) developed by [26] Salbu *et al.,* 1988, using the following equation: (Key: F1 =Water soluble, F2 = Exchangeable, F3 = Carbonate, F4 =Fe-Mn oxides, F5 = Organic, F6 = residual fraction)

$$\text{Mobility Factor} = \frac{(F1+F2+F3)}{(F1+F2+F3+F4+F5+F6)} \qquad (1)$$

This index describes the potential mobility of the metals [26]. The mobility factor (MF) for all metals ranges from 0.7% to 59%. Copper happened to be the element with lowest mobility factor, with a lead having the highest value followed by iron and zinc. The lower MF for Cu in this work was in agreement with the work of [6] Olajire et al, 2002 on Nigeria industrial soil having the mobility factor value for Cu as the least. The low MF values in soil /sediment is an indication of the high stability of heavy metals in soil /sediment [6] (Olajire et al, 2002). The high mobility factor values in these sediments are a sign of high labiality and biological availability of heavy metals in soils [27-29].

4. Conclusion

The sequential extraction results showed that Iron and lead was significantly associated with the non-residual fractions in the sediments compared to other studied metals which indicated that these metals were potentially more bio-available than other metals analysed. Copper, zinc, and Cd were found mainly in the residual fraction in most soils having average values of 73.2%, 67.6%, and 96%. Iron was found to bioavailable in all the fraction with the highest% in Fe- Mn. It can be deduced that these metals (i.e Copper and Zinc) have their lowest portion in the mobile fraction and thus they are of low risk for the aquatic environments while lead has the highest portion in the mobile fraction and thus pose a high risk to aquatic environments. Zinc speciation pattern shows no risk for the aquatic environment at almost all sites with the exception in location E. The overall order of contamination of the sediments was Lead > Iron > Zinc > Copper > Cadmium

Acknowledgements

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