CHEMICAL SPECIATION OF Zn, Pb, Fe and Mn IN SOIL SAMPLES FROM THE VICINITY OF A KAOLIN MILLING PLANT IN ALKALERI, BAUCHI STATE NIGERIA

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ABSTRACT

This work is aimed at speciatiating some heavy metals in soil samples from the vicinity of a Kaolin milling plant. Soil samples analyzed in this research work were collected from twelve sampling sites from the vicinity of a Kaolin milling plants. Sample speciation analysis was carried out using method proposed by Tessier et al. as adopted by Omuku et al. with some modification. Elemental determination of manganese, iron, zinc and lead in the various speciation fractions were carried out using atomic absorption spectrometry (AAS) at various wavelengths. The result showed the distributions of heavy metals in various fractions as follows: Mn (F4,F2<F3<F5<F1) with concentration range in mg/kg between 1.00 – 5.50 and percentage range between 7.8 – 42.9%. Fe (F2<F1<F4<F3<F5) with concentration range in mg/kg between 11.7 – 110.8 and percentage range between 6.0 – 56.8%.Zn (F1<F4<F5<F3<F2) with concentration range in mg/kg between 0.0 – 2.5 and percentage range between 0 – 48.4%. Pb (F4<F5<F3<F1<F2) with concentration range in mg/kg between 4.00 – 14.67 and percentage range between 8.8 – 32.2%.Mn, Zn and Pb were seen to be highly mobile since they were mostly found in the fractions characterized by high mobility while Fe predominantly existed at the residual fraction.

Keywords: Speciation, Heavy metals, AAS, Soil, Kaolin, milling plant

INTRODUCTION

Soils may be contaminated by the accumulation of heavy metals and metalloids through emissions from the rapidly growing industrial areas, mine tailings, disposal of high metal wastes, leaded gasoline and paints, land application of fertilizers, animal manures, sewage sludge, pesticides and atmospheric deposition[1]. The distribution, accumulation, bioavailability, biodegradability, and toxicity of elements depend not only on their concentrations, but also on their physicochemical association with the surrounding[2]. The determination of

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concentration of metals in their various oxidation state and molecular forms is known as speciation. Speciation is necessary because the environmental and biological effect of these pollutants depend on their oxidation state as well as their chemical form[2]. In some cases, one form of a metal can be toxic and the other form may not be, and may even be essential for normal functioning of living organisms. In soils and sediments, elements of interest exist in several different forms and are associated with a range of components. It is generally recognized that information about the physicochemical forms of the elements is required for understanding their environmental behaviour (mobility, pathways, and bioavailability). The determination of speciation is useful in defining geochemical distributions of aqueous species, selecting unit operation processes such as adsorption or precipitation and modeling the effects of various physical and chemical scenarios encountered in practice[3]. Metal complexes can increase the tendency for metal precipitation, sequentially reducing the toxicity of the metal[3].

Chemical forms of iron, zinc, and manganese in cultivated soils around cement factory in Gombe state Nigeria was determined by wufem[4] using the method of Tessier *et al*[5] and Elsokkary[6] as adopted by Elsokkary *et al*[7]. The metal species were classified into six fractions namely exchangeable, carbonate, manganese oxide, iron-manganese oxide, organic/sulphide and residual. Wuana[8] also determine the chemical speciation of heavy metals in a spiked soil in the vicinity of Benue industrial layout and the assessment of uptake by maize using a modified method of Tessier[5]. Here, a six-stage sequential extraction procedure described by Kabala and Singh[9] namely water soluble, exchangeable, carbornate-bond, oxide bound, organic-bond and residual were carried out.

This work is therefore aimed at determining the speciation of some heavy metals in soil samples from the vicinity of the milling plant.

MATERIALS AND METHODS

Soil samples collection

Sampling was carried out using standard method[10]. A stainless steel auger capable of retrieving a cylindrical plug of soil was used for soil collection. Soil samples analyzed in this research work were collected from the

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vicinity of Kaolin milling plants. Samples were collected from twelve sampling sites (Figures 1a and b) where the surface was free of plant material and debris. Samples were taken from surface till the depth of 30 cm. Samples were placed in plastic bags sealed and labeled for transport and storage. In the laboratory, the samples were air-dried, mechanically ground, and sieved to obtain <2 mm fraction. About 10 g subsamples were drawn from each sample to obtain the representative samples.
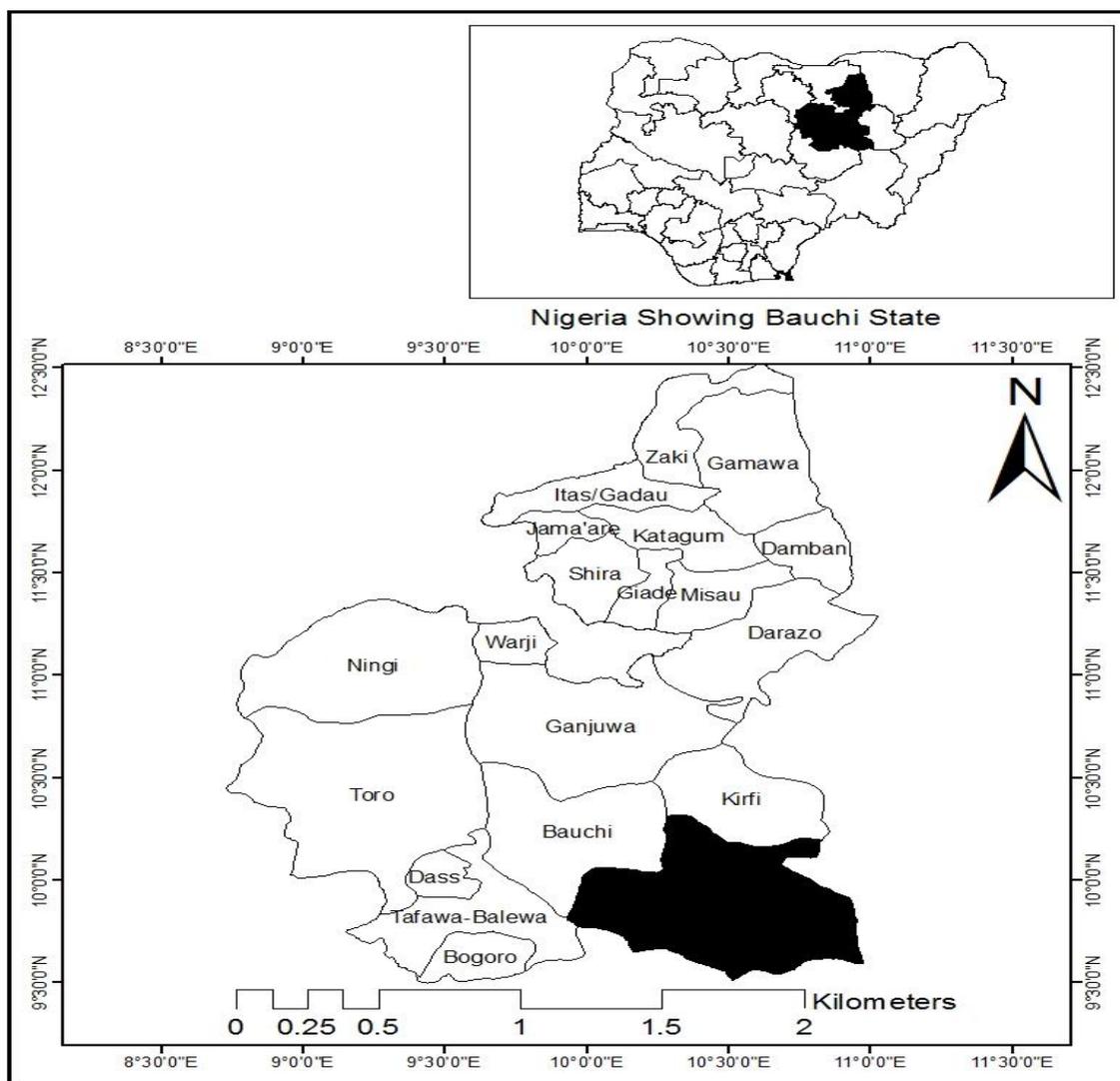

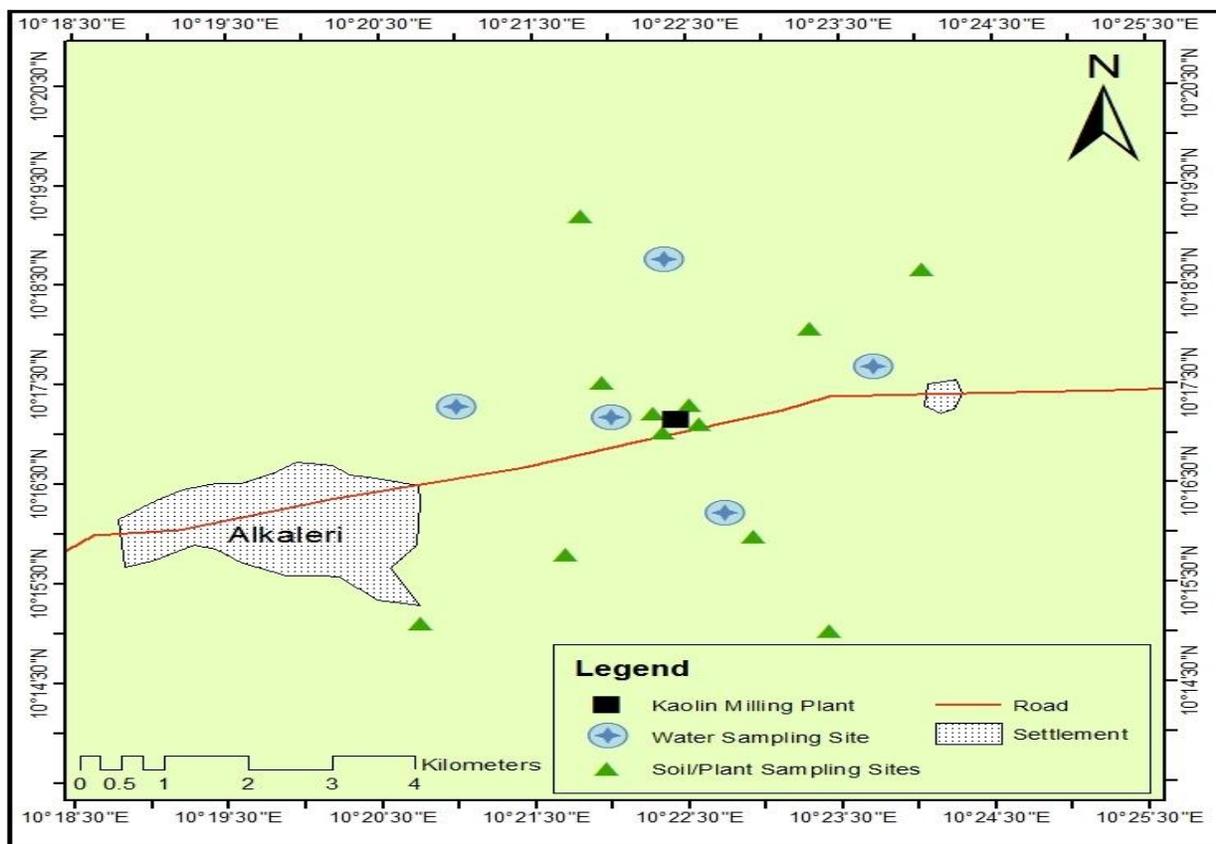**Figure 1a: Map of Bauchi State showing Alkaleri Local Government Area**

Figure 1b: Map of study area showing sampling sites

Sample preparation

The method proposed by Tessier *et al.*[5] as adopted by Omuku *et al.*[11] with some modification was used in the sample preparation for speciation analysis as follows.

Fraction 1 (F1): Exchangeable: This fraction indicate the capacity the soil to adsorb/desorb heavy metals in relation to changes in the ionic composition of the soil. 1.0 g finely divided soil sample was extracted at room temperature for 1 h with 8 cm^3 of sodium acetate (NaOAc at pH 8.2) with continuous agitation.

Fraction 2 (F2): Bound to carbonates: This fraction gives the heavy metals associated with carbonates and may vary with pH. The soil residue from fraction 1 (F1) was extracted with 8 cm^3 of 1.0 M sodium acetate solution (adjusted to pH 5 with acetic acid) for 5 hours using shaking device.

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Fraction 3 (F3): Bound to iron and manganese oxide (Fe-Mn Oxide Bound): This fraction indicates heavy metals, scavenged by iron and manganese oxides and is sensitive to redox potential variation. The residue from fraction 2 (F2) was extracted with 20 cm^3 of 0.04 M NH$_2$OH.HCl in 25% (v/v) acetic acid for 6 h at 96 ^{O}C with occasional agitation.

Fraction 4 (F4): Bound to organic matter: This fraction emphasizes heavy metals bound to various forms of organic matter that can be released under oxidizing conditions. The soil fraction from fraction 3 (F3) was mixed with 3 cm^3 of 0.02 M HNO$_3$ and 5 cm^3 of 30% H$_2$O$_2$ adjusted to pH 2 with HNO$_3$ and heated for 2 h at 85 ^{o}C with intermittent agitation. Another 3 cm^3 portion of 30% H$_2$O$_2$ was added and the mixture adjusted to pH 2 with conc. HNO$_3$ and heated at 85 ^{o}C for 5 h intermittent agitation. On cooling, 5 cm^3 of 3.2 M CH$_3$CONH$_2$ in 20% (v/v) acetic acid was added to the mixture and agitated for 30 mins.

Fraction 5 (F5): Residual fraction (metal structurally bound in silicates) this fraction indicating the metals occluded in primary and secondary minerals which are rarely released to the environment under natural conditions. The residue fraction (F4) from step 4 was digested with 5 cm^3 of mixture HCl and HNO$_3$ in 3:1 ratio (Aquaregia) and 1 cm^3 of perchloric acid and diluted to 50 cm^3. The mixture was heated at 150 ^{O}C for 3 h.

Elemental Determination
Elemental determination of manganese, iron, zinc and lead in the various speciation fractions were carried out using atomic absorption spectrometry (AAS) at various wavelengths.

RESULTS AND DISCUSSIONS

Table 1 show the concentration in mg/kg and percentage, figures 2 – 5 showthe relative distributions of manganese, iron, zinc and lead in five fractions of sequential extraction of the metals in soil sample within the vicinity of the Kaolin milling plant.

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Table 1: Concentration in mg/kg and percentage of heavy metals in fractions of soil samples in the vicinity of a Kaolin milling plant

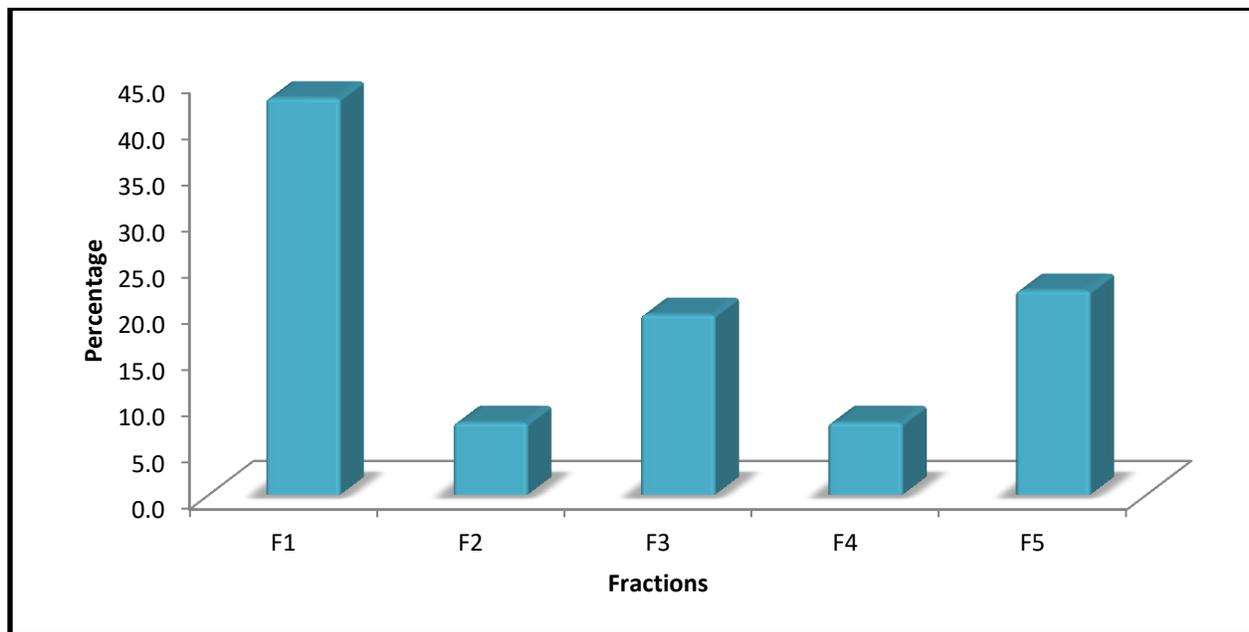| Fraction	Concentration (mg/kg)					Percentage			
	Zn	Pb	Fe	Mn		Zn	Pb	Fe	Mn
F1	0.00	14.67	12.5	5.50		0.0	32.2	6.4	42.9
F2	2.50	14.33	11.7	1.00		48.4	31.5	6.0	7.8
F3	1.50	8.33	43.3	2.50		29.0	18.3	22.2	19.5
F4	0.50	4.00	16.7	1.00		9.7	8.8	8.5	7.8
F5	0.67	4.17	110.8	2.83		12.9	9.2	56.8	22.1

Figure 2: Relative distribution of Mn in five fractions of soil sample within the vicinity of the Kaolin milling plant
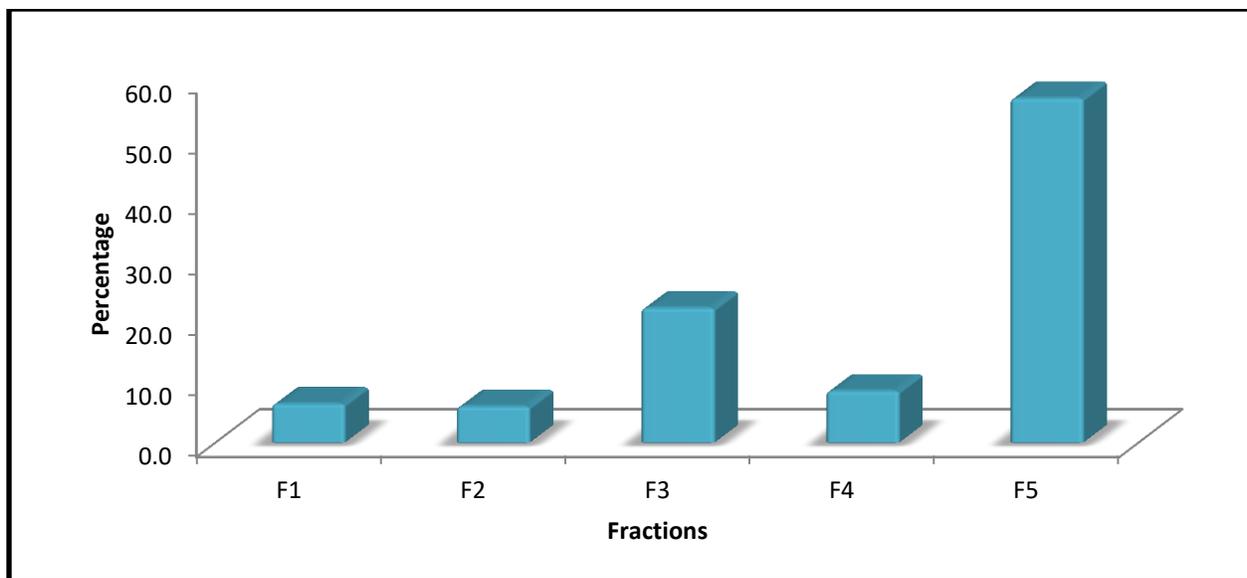
Figure 3: Relative distribution of Fe in five fractions of soil sample within the vicinity of the Kaolin milling plant
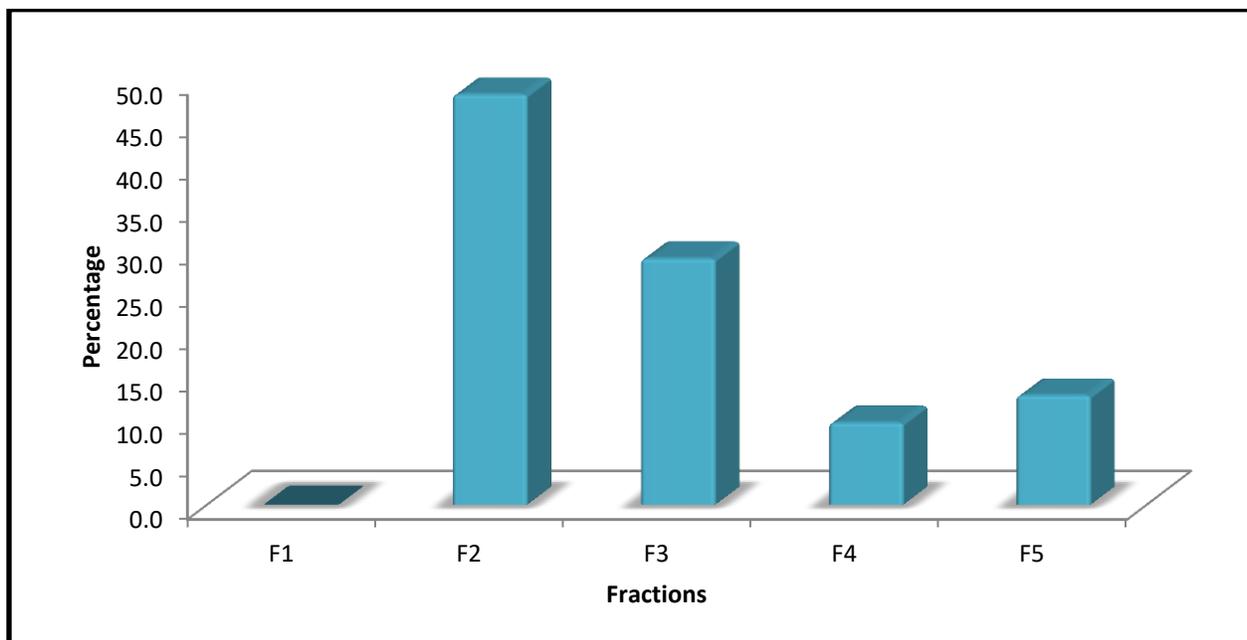

Figure 4: Relative distribution of Zn in five fractions of soil sample within the vicinity of the Kaolin milling plant
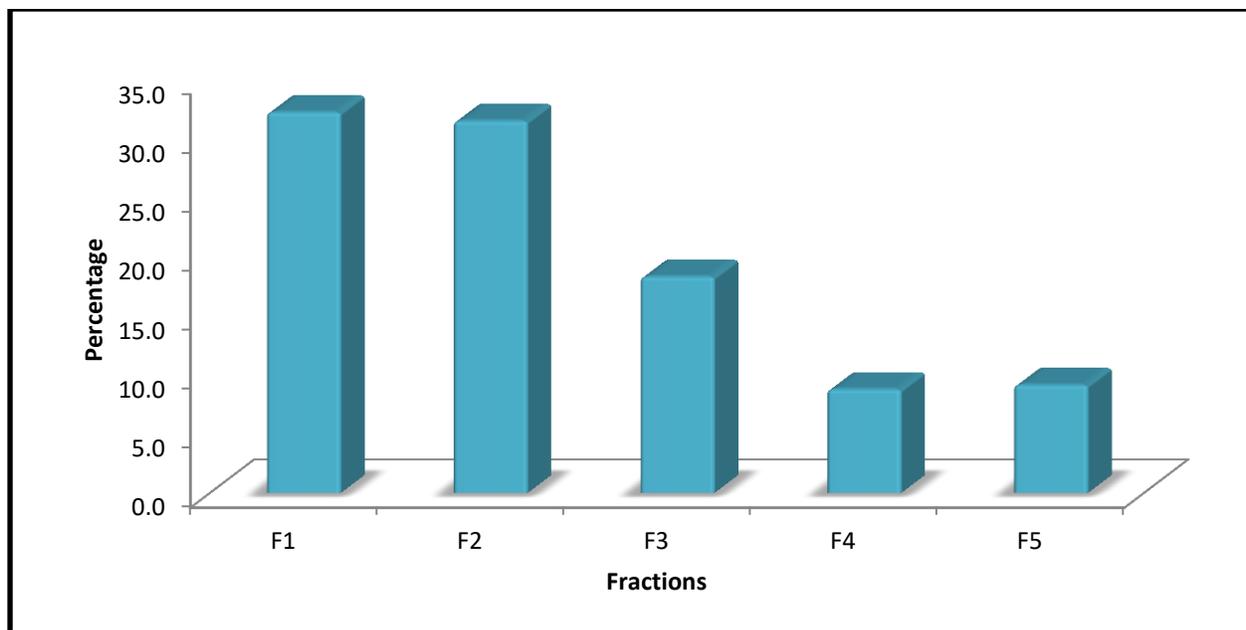
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Figure 5: Relative distribution of Pb in five fractions of soil sample within the vicinity of the Kaolin milling plant

Figure 2 showed relative distribution of Mn in five fractions (F1-F5) of soil samples within the vicinity of Kaolin milling Plant. The concentration of Mn is highest in F1 (exchangeable fraction) with 5.50 mg/kg (42.9%) followed by F3 (Fe-Mn oxide bound) with 2.50 mg/kg (19.5%), then the residue fraction (F5) has 2.83 mg/kg (22.1%) and the least were F2 (Bound to carbonate) and F4 (Bound to organic matter) having 1.0 mg/kg each (7.8%). The relative abundance of Mn in the fraction is the order F1>F3>F5>F2,F4. Manganese showed highest level of dominance in the exchangeable fraction F1 with 42.9 % of the

total fraction in the exchangeable. This indicates Mn presence in the sample may be in the +2 state since this fraction shows the capacity of soil to adsorb/desorb heavy metals in relation to changes in the ionic composition of soil[12]. Redox state has a large affect on Mn speciation and solubility in the soil solution[13,14,15,16]. Manganese (II) is the most soluble form of Mn and so under reducing conditions higher concentrations of Mn^{2+} will be present in the soil solution[17,16]. Hence, reducing soil conditions, such as flooding and soil compaction, tend to increase the availability of soil Mn and enhance toxicity[18,16].

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Figure 3 showed relative distribution of Fe in five fractions (F1-F5) of soil samples within the vicinity of Kaolin milling plant. The concentration of Fe is highest in F5 (residue fraction) with 110.8 mg/kg (56.8%) followed by F3 (Fe-Mn oxide bound) with 43.30 mg/kg (22.2%), then F4 (bound to organic matter) with 16.7 mg/kg (8.5%), F1 (exchangeable fraction) with 12.50 mg/kg (6.4%) and F2 (bound to carbonate) with 11.7 mg/kg (6.0%). The relative concentration of Fe in the fraction is the order F5>F3>F4>F1<F2.Fe highest concentration was determined in the residue fraction (F5). The residue fraction contains 56.8% of the total concentration of Fe in the sample. This is in agreement with AbdulAziz *et al.*[19] whose study showed that aluminium, chromium, iron and nickel occurred predominantly in the residual fraction thus showed low mobility. The presence of metals in the residual fraction may reflect the natural process of coagulation in soil[20,19].

Figure 4 showed relative distribution of Zn in five fractions (F1-F5) of soil samples within the vicinity of Kaolin milling plant. The concentration of Zn is highest in F2 (bound to carbonate) with 2.50 mg/kg (48.4%) followed by F3 (Fe-Mn oxide bound) with 1.50 mg/kg (29.0%), then the residue fraction (F5) has 0.67 mg/kg (12.9%), F4 (bound to organic matter) having 0.5 mg/kg (9.7%) and F1 (exchangeable fraction). The relative concentration of Zn in the fraction is the order F2>F3>F5>F2<F1.Zn was predominantly found in the bound to carbonate fraction F2 with 48.4%. This indicates more of the Zn in the sample was associated with carbonates and may vary with pH. Both Mn and Zn bioavailability are strongly affected by soil pH[21,22,23,16]. As soil pH decreases, Mn and Zn must compete with the extra H^+ and Al^{3+} for positions on the exchange sites, solubility of Mn and Zn increases in the soil solution and a greater proportion is present as highly available free metal ions in the soil solution[25,26,27,28,16]. This increases the concentrations of Mn and Zn in the directly bioavailable fraction, i.e. the soil solution[29,16]. Pb was predominant in the F1 and F2 fractions. The F1 fraction has 32.2% and the F2 has 31.5%. This indicates the readily bioavailability of Pb in the soil sample to plant since greater percentage of Pb are in the fractions with high mobility.

Figure 5 shows relative distribution of Pb in five fractions (F1-F5) of soil samples within the vicinity of Kaolin milling plant. The

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concentration of Pb is highest in F1 (exchangeable fraction) with 14.67 mg/kg (32.2%) followed by F2 (bound to carbonate) with 14.33 mg/kg (31.5%) then F3 (Fe-Mn oxide bound) with 18.30 mg/kg (18.3%), then the residue fraction (F5) with 4.17 mg/kg (9.2%) and F4 (bound to organic matter) having 4.0 mg/kg each (8.8%). The relative abundance of Pb in the fraction is the order F1>F2>F3>F5<F4. Zn was predominantly found in the bound to carbonate fraction F2 with 48.4%. This indicates more of the Zn in the sample was associated with carbonates and may vary with pH. Both Mn and Zn bioavailability are strongly affected by soil pH[21,22,23,16]. As soil pH decreases, Mn and Zn must compete with the extra H^+ and Al^{3+} for positions on the exchange sites, solubility of Mn and Zn increases in the soil solution and a greater proportion is present as highly available free metal ions in the soil solution[24,25,26,27,28,16]. This increases the concentrations of Mn and Zn in the directly bioavailable fraction, i.e., the soil solution[29,16]. Pb was predominant in the F1 and F2 fractions. The F1 fraction has 32.2% and the F2 has 31.5%. This indicates the readily bioavailability of Pb in the soil sample to plant since greater percentage of Pb are in the fractions with high mobility.

CONCLUSION

The speciation analysis of Mn, Zn, Fe and Pb showed the effect of different chemical forms of metals and chemical conditions such as pH on the solubility of heavy metals. Mn, Zn and Pb were seen to be highly mobile since they were mostly found in the fractions characterized by high mobility while Fe predominantly existed at the residual fraction.

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