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Geochemical Speciation of Toxic Metals in Paddy Soils along Ogbesse River, Southwest Nigeria

A. J. Adewumi [1*] and A. E. Lawal[2]

[1]Department of Geological Sciences, Achievers University, Owo, Ondo State, Nigeria

[2]Department of Geology, Ahamadu Bello University, Zaria, Kaduna State, Nigeria

*E-mail: adewumiadeniyi27@yahoo.com

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ABSTRACT

The sole purpose of the present study was to investigate the geochemical speciation of toxic metals and to assess the association and bioavailability of certain metals (Zn, Cd, Cu, Pb, Fe and Mn) in paddy soils around Ogbesse River, Ondo State, Southwest Nigeria. For this study, a total of six paddy soils were collected across the study area (2 upstream; 2 mid-streams, 2 downstream). After collection, the samples were air dried in the laboratory and physical parameters such as pH, organic matter content (OMC), and particle size distribution (PSD) were measured. Trace metals were analyzed using Atomic Absorption Spectrophotometer (AAS). Geochemical fractionation was carried out using the Tessier method. All statistical analysis was carried out using SPSS version 21. The Tessier method of sequential extraction was selected for this study. Results showed that pH is between 5.82 and 6.69 while OMC was between 2.17 and 3.08. The concentration of Zn, Cd, Cu, Pb, Fe and Mn in the paddy soil samples were between 4.87 mg/kg to 6.91 mg/kg, 0.11 mg/kg to 0.24 mg/kg, 0.48 mg/kg to 1.09 mg/kg, 0.97 mg/kg to 2.02 mg/kg, 365.65 mg/kg to 609.16 mg/kg and 30.17 mg/kg and 42.23 mg/kg respectively. The fractionation of metals in the samples showed that major portions were associated with the residual fraction, followed by Fe–Mn oxide, organic matter, exchangeable, carbonate respectively. The significant positive correlation with pH in soils of the area indicates an increasing tendency of sorption with increasing pH. The higher concentration of Fe in the Fe–Mn oxides fractions indicates that Fe–Mn oxides act as a natural sink for the metal. Metal factor (MF) showed that metals in the soils have low mobility and may not pose any toxicological effects in humans.

KEYWORDS: Chemical fractionation; Ogbesse River; Paddy soils; Heavy metals

1. Introduction

Soils are made up of debris, inorganic or organic loads which are assorted when it comes to their physicochemical and biological properties (Namiesnik and Rabajczyk, 2010; Laniyan and Adewumi, 2020; Adewumi and Laniyan, 2020a). Potentially toxic metals are related with various soil constituents in diverse ways, and these relationships decide their mobility and availability (Namiesnik and Rabajczyk, 2010; Alagarsamy, 2009; Al-Mercy *et al.* 2002). Water soluble and exchangeable forms are more moveable and available to plants, while metals incorporated into crystalline lattices of clays appear relatively inactive (Adewumi *et al.* 2020b). The other forms like carbonate bound, occlusion in Fe, Mn and Al oxides, or complexes with organic matter and Fe-Mn oxides have been found to be the most important in soil and might be the components, which influence the medium to long term effect on lability and bioavailability of metals (Namiesnik and Rabajczyk, 2010; Berthling *et al.* 2006; Badawy *et al.* 2002).

Recently, research on the speciation or chemical forms of toxic metals in paddy soils using sequential methods have grown (Namiesnik and Rabajczyk, 2010; Alagarsamy, 2009; Berthling *et al.* 2006; Badawy *et al.* 2002; Al-Mercey *et al.* 2002). This is because they give insights on metal association to soil components and the extent to which they are attached to the matrix (Cenci and Martin, 2004). Several extraction methods have been described in the literature (Tessier *et al.*, 1979; Ure *et al.*, 1993; Howard and Vandenbrink, 1999). The procedure of Tessier *et al.* (1979) is one of the most thoroughly researched and widely used methods to assess the probable chemical relationships of metals in sediments and soils. In this method, metal availability is studied through five major geochemical forms: (i) exchangeable phase; (ii) bound to carbonate phase; (iii) bound to Fe–Mn oxides; (iv) bound to organic matter, and (v) residual metal phase. The limitations of chemical extraction methods have also been addressed (Rauret *et al.*, 1999). The limitations include technical difficulties associated with selective dissolution and complete recovery of trace metal from chemical phases in soil and sediments (Cidu and Frau, 2009; Coupland *et al.* 2004). Therefore, the chemical forms of heavy metals from the sequential extraction methods are operationally defined phases only (Namiesnik and Rabajczyk, 2010; Alagarsamy, 2009).

Paddy rice is a common grain consumed by Nigerians. Ayede-Ogbesse is one of the major paddy field in Ondo state, with paddy rice grown on 600 hectares of land in the area. Metals accumulated in the soils are mobilized and enter into the plants which in turn determine the amount of nutrient available for the growth of the crop. Therefore, there is a necessity to know the extent of metal mobility in the soils to uncover the potential impact it will have on the crop. The aim of the present study was to investigate the geochemical speciation of toxic metals and to assess the association and bioavailability of certain metals, viz., Zn, Cd, Cu, Pb, Fe and Mn in paddy soils of Ayede-Ogbesse, Southwest Nigeria.

2. Materials and Methods

2.1 Study Area and Sampling

The study is Ayede-Ogbesse which is located in Akure North local government area of Ondo state. It is located on latitude and longitude with an average elevation of (Figure 1). The main river passing through this area is the Ogbesse River which is perennial in nature and runs from north to south and originated from Ekiti state. The area is intersected by the Akure-Owo-Benin expressway. The major occupations of people in this area are farming and business. The area is located on the basement complex terrain of Nigeria and is underlain by the granite gneiss (Adewumi *et al.* 2017).For this study, a total of six paddy soils were collected across the study area (2 upstream; 2 mid-stream, 2 downstream). Samples were collected using an uncontaminated plastic scoop (Adewumi and Laniyan, 2020a) from the topsoil layer (up to 15cm) in March 2018. All samples were properly placed in a well labeled ziplock bags and were transported to the laboratory for further analysis.

2.2 Sample Preparation and Analysis

All soil samples were air dried for five days in the laboratory at room temperature. The dried samples were grounded using agate mortar. Fine particles to below 100 mesh size were utilized for subsequent analysis. The soil pH was measured at the laboratory with the help of a Digital pH meter. Organic matter content was determined by the Walkley Black Method Namiesnik and Rabajczyk (2010). Total metals were estimated following the procedure of Namiesnik and Rabajczyk (2010) by Atomic Absorption Spectrophotometer (AAS) with a Perkin-Elmer Model-2380instrument at Sustainable agrotech laboratory in Akure, Ondo State, Nigeria. Metals analyzed were. Significant correlation coefficients between various pairs of soil components under study were determined using bivariate correlation using SPSS version 21. The results thus obtained were used to uncover the interrelationship between them at the existing physicochemical conditions of the soil system under study.

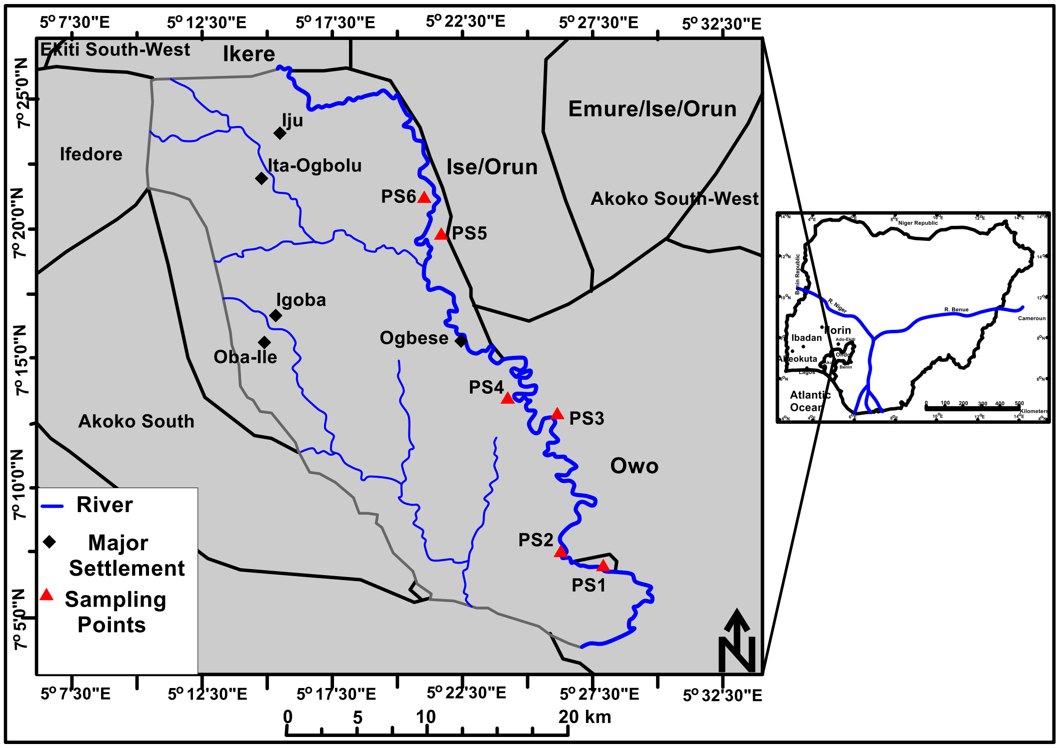

Figure 1: Location map of the study area showing the sampling points

2.3 Trace Metal Fractionation

The procedure of Tessier *et al.* (1979; 1985) was selected for this study. In this method heavy metals are separated into five operationally defined fractions: exchangeable (F1), bound to carbonate (F2), bound to Fe-Mn oxide (F3), bound to organic matter (F4) and residual fraction (F5). One gram of each soil sample was weighed and extractions were carried out following steps F1 to F5 by centrifugation at 10,000rpm placing the sample in polypropylene centrifuge tube at the Geological Laboratory of Achievers University, Owo, Ondo State, Nigeria.

(a) **F1: Exchangeable metals:** The sediment samples was extracted for 1 hour with 8 mL of 1M $MgCl_2$ at pH7.0 at room temperature;

(b) **F2: Metals bound to carbonate:** The residue from (a) was leached with 1M sodium acetate (NaOHc) adjusted to pH 5.0 with acetic acid (HoAc) for 5hours;

(c) **F3: Metals bound to Fe-Mn oxide:** The residue from (b) was extracted at 960^{o}C for 6 hour with 0.04M $NH_2OH.HCl$ in 25% (v/v) HoAc;

(d) **F4: Metals bound to organic matter:** The residue from (c) was extracted at 850^{o}C for 5 hour with 30% H_2O_2 adjusted to pH 2.0 with HNO_3 and then at room temperature with 3.2M NH_4OAc in 20% (v/v) HNO_3;

(e) **F5: Residual metals:** The residue from (e) was digested with a mixture of concentrated hydroflouric, nitric and perchloric acids.

Percentage recoveries of metals in paddy soils of the area were calculated using equation 1 following the method used by Qayyum *et al.* (2016).

$$Recovery = \frac{\Sigma_{sequential\ extraction\ procedure}}{Single\ digestion\ with\ strong\ acids} \times 100 \quad (Equation\ 1)$$

The mobility factor (MF) of metals in sud samples may be calculated on the basis of percentage absolute and relative content of fractions weakly bound to soil components and it is calculated using equation 2 as used by Qayyum *et al.* (2016)

$$MF = \frac{F_1 + F_2}{F_1 + F_2 + \cdots + F_n} \times 100 (Equation\ 2)$$

where MF is the mobility factor and F1, F2 and Fn are the first, second and nth fractions, respectively.

4. Results and Discussions

4.1 Results

1. Soil Properties

The physical properties of paddy soils in Ogbese area is presented in Figure 2. In sample PS1, the pH was 5.82 while the organic matter content (OMC) was 2.39. The percentage sand, silt and clay were 70%, 20% and 10% respectively. In PS2, the pH and OMC were 6.31 and 2.53 each while the percentage sand, silt and clay in the samples were 63%, 26%, and 11% respectively. The pH and OMC in PS3 were 6.02 and 2.87 respectively while the percentage sand, silt and clay in the samples were 72%, 18%, and 10% respectively. In PS4, the pH and OMC were 5.97 and 3.08 each while the percentage sand, silt and clay in the samples were 70%, 21%, and 19% respectively. In PS5, the pH was 6.48 while the OMC was 2.17 and the percentage sand, silt and clay in the samples were 68%, 20%, and 12% each. In PS4, the pH and OMC were 6.69 and 2.66 each while the percentage sand, silt and clay in the samples were 62%, 27%, and 11% respectively (Figure 2).

2. Total concentrations of heavy metals

The total concentration of toxic metals in paddy soils of Ogbesse area is presented in Table 1. The minimum value of Mn is 30.17 mg/kg while the maximum value is 42.23 mg/kg with an average of 35.62 mg/kg. In this area, the distribution of Mn is in the order: PS5 > PS1 > PS3>PS4 > PS4> PS6. For Fe, the minimum value is 365.65 mg/kg while the maximum is 609.16 mg/kg with an average of 428.75 mg/kg (Table 1). The distribution of Fe is in the following order: PS6 > PS5 > PS3 > PS1 > PS2 > PS4. The minimum concentration of Cu in paddy soil of the area is 0.48 mg/kg while the maximum concentration is 1.09 mg/kg and a mean value of 0.48 mg/kg. The distribution of Cu is in the order: PS4 > PS3 > PS5 > PS1 > PS2 > PS6. The minimum concentration of Zn in soils of the area is 5.59 mg/kg while the maximum concentration is 6.91mg/kg with an average of 5.28 mg/kg. The distribution of Zn is in the order: PS5 > PS3 > PS2 > PS1 > PS4 > PS6. The minimum concentration of Pb in the paddy soil is 1.04 mg/kg while the maximum concentration is 2.02 mg/kg with an average value of 1.46 mg/kg. The distribution of Pb in paddy soils of the area is in the order: PS5 > PS2 > PS4> PS3 > PS1 > PS6. The minimum amount of Cd in soils of the area is 0.11 mg/kg while the maximum value is 0.24 mg/kg with a mean value of 0.16 mg/kg. The concentration of Cd is in the following order: PS1 > PS4 > PS2 > PS5 > PS3 > PS6. The concentration of potentially toxic metals in the paddy soils of this area were lower compared to the USEPA (2002) standard for metals in agricultural soils (Table 1).

3. Geochemical speciation of toxic metals

The geochemical concentrations and percentages of toxic metals in different fractions (exchangeable, Fe-Mn, oxidizable, carbonate and residual) are presented in Table 2 and Figure 3. For PS1, the concentrations of Fe in the geochemical fractions were in the following order: residual > Fe-Mn > carbonate > exchangeable > oxidizable with percentage recovery of 92.21%while the concentrations of Mn were in the following order: residual > Fe-Mn > oxidizable > exchangeable > carbonate with percentage recovery of 91.14%. The amount of Zn in this fraction was in the following order: Residual >Fe-Mn> carbonate > oxidizable > exchangeable with percentage

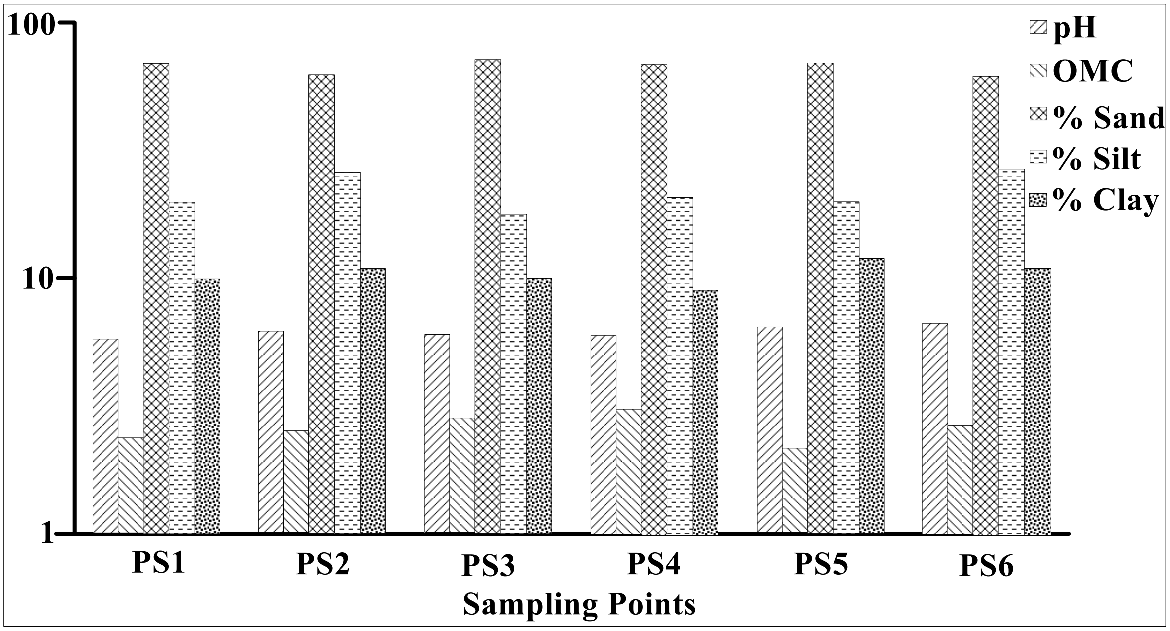

Figure 2: Physical properties of paddy soils around Ogbese River

Table 1: Total toxic metal in soils of Ayede-Ogbese paddy field

	Zn mg/kg	**Cd mg/kg**	**Cu mg/kg**	**Pb mg/kg**	**Fe mg/kg**	**Mn mg/kg**
PS1	6.58	0.11	0.98	1.04	405.96	39.11
PS2	4.87	0.14	0.98	1.83	371.29	30.17
PS3	6.91	0.19	0.61	1.41	408.16	36.89
PS4	4.89	0.11	0.48	1.51	365.65	33.23
PS5	6.08	0.18	0.67	2.02	412.29	42.23
PS6	5.59	0.24	1.09	0.97	609.16	32.11
Minimum	5.59	0.11	0.48	1.04	365.65	30.17
Maximum	6.91	0.24	1.09	2.02	609.16	42.23
Average	5.28	0.16	0.80	1.46	428.75	35.62
USEPA (2002)	1100.00	0.48	270.00	200.00	-	-

recovery of 98.91%. The amount of Cd in this fraction was in the following order: Fe-Mn> residual > exchangeable > carbonate >oxidizable with percentage recovery of 90.09%. The available Cu in this fraction were in the following order: residual >Fe-Mn>carbonate >exchangeable >oxidizable with percentage recovery of 97.44%. The available Pb in this portion were in the following order: residual > Fe-Mn> carbonate >oxidizable> exchangeable with percentage recovery of 92.21%. In this sample, the mobility factor (MF) for Zn, Cd, Cu, Pb, Fe and Mn were 33.61%, 67.04%, 36.96%, 34.44%, 36.21% and 37.97% respectively (Figure 4).

In PS2, fractionation of Zn were in the order: Residual > Fe-Mn> carbonate >oxidizable> exchangeable with percentage recovery of 99.27% while Cd were in the following order: Fe-Mn> residual > carbonate >exchangeable >oxidizable with 91.85% and 90.09% recoveries, while the amount of Pb and Cu in the fractions were in the following order: residual>Fe-Mn > oxidizable > carbonate > exchangeable with recoveries of 96.89% and 93.94% each. The amount of Fe in the fractions was in the following order: residual > Fe-Mn>carbonate>oxidizable> exchangeable with recovery of 92.77%. The concentration of Mn in the sample was in the order: Fe-Mn>residual > carbonate > exchangeable >oxidizable> with a recovery of 94.78%. In this sample, the mobility factor (MF) for Zn, Cd, Cu, Pb, Fe and Mn were 22.10%, 42.11%, 33.01%, 37.53%, 32.37% and 43.51% respectively (Figure 3).

For PS3, the concentration of Zn, Cd, Cu, Pb and Mn concentration in the fractions were in the order: residual > Fe-Mn>carbonate>oxidizable> exchangeable with percentage recoveries of 98.26%, 83.40%, 90.26%, 92.07% and 94.47% each while the amount of Fe in the sample was in the order: Fe-Mn>residual >oxidizable>carbonate>exchangeable with percentage recoveries of 95.11%.In this sample, the mobility factor (MF) for Zn, Cd, Cu, Pb, Fe and Mn were 31.52%, 34.07%, 35.10%, 33.02%, 45.00% and 47.32% respectively (Figure 3).

For PS4, the availability of Cd and Pbin the fractions were in the order: residual > Fe-Mn> carbonate > oxidizable > exchangeable with percentage recoveries of 92.63% and 94.74% each while the amount of Zn was in the order: residual > Fe-Mn>oxidizable> exchangeable > carbonate with percentage recovery of 98.74%. The amount of Cu was in the order: residual > Fe-Mn>oxidizable> carbonate > exchangeable with percentage recovery of 90.09% respectively. Fe in the fractions were in the following order: Fe-Mn> residual > oxidizable > carbonate > exchangeable with percentage recovery of 91.09% while Mn in the fractions were in the following order: Fe-Mn> residual > carbonate >oxidizable> exchangeable with percentage recovery of 94.47%.In this sample, the mobility factor (MF) for Zn, Cd, Cu, Pb, Fe and Mn were 30.05%, 30.25%, 34.05%, 28.82%, 44.86% and 47.32% respectively (Figure 3).

For PS5, the concentration of Zn, Cd, Cu, Pb and Mn concentration in the fractions were in the order: residual > Fe-Mn> carbonate >oxidizable> exchangeable with percentage recoveries of 98.83%, 92.63%, 90.67%, 97.43% and 94.92% each while the amount of Fe in the sample was in the order: Fe-Mn> residual > carbonate >oxidizable> exchangeable with percentage recovery of 94.92%.In this sample, the mobility factor (MF) for Zn, Cd, Cu, Pb, Fe and Mn were 32.28%, 32.18%, 32.04%, 32.62%, 48.01% and 45.00% respectively (Figure 3). For PS6, the amount of Cu, Pb and Mn in the fractions were in the order: residual >Fe-Mn>carbonate >oxidizable> exchangeable with percentage recoveries of 90.07%, 90.72% and 90.77% each while the amount of Zn was in the order: residual > Fe-Mn> carbonate > exchangeable >oxidizable with percentage recovery of 98.91%. The concentration of Cd in fractions of the sample were: residual >carbonate >Fe-Mn>oxidizable> exchangeable with percentage recoveries of 90.31% while that of Fe is in the order: Fe-Mn> residual > carbonate >oxidizable> exchangeable with percentage recoveries of 90.72%.In this sample, the mobility factor (MF) for Zn, Cd, Cu, Pb, Fe and Mn were 37.73%, 19.16%, 67.98%, 30.08%, 42.00% and 44.13% respectively (Figure 3).

4.2 Discussions

The geochemical properties of trace metals and their chemical forms can be confirmed using geochemical speciation (Kotoky *et al.* 2003). The metals mobile in the exchangeable (F1) and carbonate (F2) fractions are known to be weakly associated and may be at equilibrium with the aqueous phase thus increasing their bioavailability (Balasoiu *et al.* 2001; Li *et al.* 2001). However, metals in the residual fraction (F5) are not mobile under normal conditions (Balasoiu *et al.* 2001; Li *et al.* 2001). The Fe–Mn oxide (F3) and organic fractions (F4) provide a sink or reservoir for heavy metals (Li *et al.* 2000). The hydrous Mn-oxide fraction exhibits more isomorphic substitution than amorphous Fe-oxide and shows greater conditional equilibrium constants for the heavy metals than Fe-oxide (Li *et al.* 2000). The fractionation of Mn showed that a major portion is associated with the residual fraction (F5), followed by Fe–Mn oxide (F3), organic matter, (F5) exchangeable, (F4), carbonate. This in consonance with results obtained from similar study carried out by (Li *et al.* 2000; Balasoiu *et al.* 2001; Li *et al.* 2001). Mn had positive correlation with pH (r=0.715) while it showed weak but positive relationship with organic matter content (r=0.249). Mn showed negative relationship with Pb (r=0.728) (Table 3). The significant positive correlation with pH indicates an increasing tendency of sorption with increasing pH. Mn was more prominent in the Fe-Mn fractions (Table 3). The higher amount of the metal in the Fe-Mn oxide is due to the formation of stable complex (Jones and Turkie, 1997).

Association of Pb with Fe (r=0.519) and Mn(r=0.728) oxides fraction is also supported by their positive correlation (Table 3). In the case of organic matter content Pb shows significant positive correlation (r =0.579). The higher concentration of lead in the Fe-Mn oxide is due to the formation of stable complex (Jones and Turkie, 1997). The lower amount of Pb in the exchangeable fraction suggests low bioavailability but slightly higher concentration in the carbonate fraction indicates a challenge to the ecosystem as carbonates may dissolve readily with a change in soil characteristics (Namiesnik and Rabajczyk, 2010).The higher concentration of Fe in the Fe–Mn oxides fractions indicates that Fe–Mn oxides act as a natural sink for the metal (Namiesnik and Rabajczyk, 2010).

There is a positive correlation between Cu and OMC (r=0.571) (Table 3). This may be adduced to the fact that in moderate to highly organic soils, Cu is present in less mobile and less available forms to soil organisms and plants, the soluble and exchangeable metals (labile fraction) usually being considered as most hazardous (Li *et al.* 2000). The higher presence of Cu with the residual fraction indicates its low bioavailability (Namiesnik and Rabajczyk, 2010). Association of copper with different fractions is observed as residual > Fe-Mn oxides > organic > carbonate> exchangeable. Copper is strongly sorbed by hydrous Fe-Mn oxides, clay minerals and organic matter (Namiesnik and Rabajczyk 2010; Li *et al.* 2000). Due to high affinity of copper for soil colloids, copper is rated a low-mobility element in near neutral soils (Li *et al.* 2000). Sorption is possibly the most important controlling mechanism determining the association and mobility of copper under the existing physicochemical conditions. Many studies demonstrated that the sorption of copper on hydrous Fe–Mn oxides is due to co-precipitation of copper in the Fe–Mn oxide lattice (Li *et al.* 2000). However, the organic matter fraction [F4] contains a significant amount (15-20%) of copper in PS2, PS3, PS4 and PS6. Copper is preferentially retained on organic matter by complexation rather than by ion exchange (Balasoiu, 2001). This might be associated with the local geochemical behaviour of soil (Alagarsamy, 2009). The strong positive effect can be related with the fact that, copper easily forms complexes with organic matter due to the high stability constant of organic-Cu compounds (Al-Mercy *et al.* 2002). Organic material exhibits a high degree of selectivity for divalent ions and the probable order of binding strength for metals onto organic matter is copper> lead>zinc (Kotoky *et al.* 2003). Thus, the organically bound form is an important phase for copper in the soil (Kotoky *et al.* 2003). The carrier effect is more pronounced in the case of copper organic complexes compared to free copper (Cu^{2+}) ions available within the system (Cenci and Martin, 2004). Organically complexed copper (Cu^{2+}) is bound more tightly than any other divalent transition metal; lability of these complexes is rather low, limiting bioavailability. Probably this is the reason why farmers have been able to apply large amounts of copper salts to organic soils over time without causing toxicity to crops (Kotoky *et al.* 2003). The higher amount of Cu in the residual fraction [F5] is suggestive of non-availability to biotic community. The lower concentrations in exchangeable (1.3–2.1%) and carbonate fractions (1.1–1.8%) are also indicative of a low bioavailability. The geochemical fractionation revealed that residual fraction dominated the Zn distribution in the soil, which ranges from 32 to 50% in all the samples.

Similar results for distribution of Zn were also reported by other researchers (Li *et al.*, 2000; Li *et al.*, 2001). As evident from the study the non-residual Zn is likely to be retained in order as: Fe–Mn oxides > organic fraction > carbonate > exchangeable. Zinc (Zn) had a positive and strong relationships with organic matter content (r=0.613)(Table 3). The enrichment of total zinc up to 5% is reported to be bound in the humic acid fraction of the soil (Bodek *et al.*, 1988). The high content of zinc in the organic matter fraction is due to its scavenging effect. The present finding can be corroborated with the studies of Tessier *et al*. (1980) and Namiesnik and Rabajczyk 2010). Fe–Mn oxides seem to play a major role in zinc accumulation in the profile, as precipitation and co-precipitation products.

Table 2: Geochemical fractions of metals in paddy soils of the study area

	Fraction	**Zn (mg/kg)**	**Cd (mg/kg)**	**Cu (mg/kg)**	**Pb (mg/kg)**	**Fe (mg/kg)**	**Mn (mg/kg)**
PS1	Exchangeable	0.14	0.09	0.65	0.56	10.82	9.26
	Fe-Mn	1.89	0.52	1.12	1.93	32.77	15.28
	Oxidizable	0.17	0.02	0.46	0.72	10.62	13.29
	Carbonate	1.50	0.06	0.73	1.37	25.25	7.65
	Residual	2.34	0.22	1.83	2.65	40.95	19.15
	Total Fractions	6.04	0.91	4.79	7.23	120.41	64.63
	Pseudo Total	6.41	1.01	4.916	8.248	130.58	70.91
	%Recovery	**98.91**	**90.09**	**97.44**	**87.66**	**92.21**	**91.14**
PS2	Exchangeable	0.11	0.21	0.28	0.55	9.20	6.00
	Fe-Mn	0.88	0.67	1.06	1.66	20.01	18.01
	Oxidizable	0.16	0.25	0.72	0.71	9.20	4.08
	Carbonate	0.70	0.35	0.59	0.59	15.15	11.74
	Residual	2.63	0.61	1.41	2.38	36.68	15.36
	Total Fractions	4.48	2.09	4.06	5.89	90.24	55.19
	Pseudo Total	4.87	2.32	4.19	6.27	97.27	58.23
	%Recovery	**99.27**	**90.09**	**96.89**	**93.94**	**92.77**	**94.78**
PS3	Exchangeable	0.27	0.07	2.68	0.67	27.97	5.67
	Fe-Mn	1.87	0.71	8.38	2.09	129.36	26.64
	Oxidizable	0.49	0.21	3.36	1.42	59.44	7.33
	Carbonate	0.98	0.32	3.69	1.59	38.46	8.66
	Residual	3.18	0.98	13.40	2.59	94.4	19.98
	Total Fractions	6.79	2.26	31.51	8.36	349.63	68.28
	Pseudo Total	6.84	2.71	34.91	9.08	367.59	72.28
	%Recovery	**98.26**	**83.40**	**90.26**	**92.07**	**95.11**	**94.47**
PS4	Exchangeable	0.54	0.07	2.85	0.29	35.79	5.67
	Fe-Mn	0.89	0.55	10.31	1.37	206.76	26.64
	Oxidizable	0.68	0.19	5.70	0.63	75.55	7.33
	Carbonate	0.55	0.29	3.78	1.08	51.69	8.66
	Residual	2.10	0.95	16.02	2.39	170.97	19.98
	Total Fractions	4.76	2.01	38.66	5.76	540.76	68.28
	Pseudo Total	4.82	2.17	42.91	6.08	593.59	72.28
	%Recovery	**98.76**	**92.63**	**90.09**	**94.74**	**91.09**	**94.47**
P5	Exchangeable	0.72	0.10	2.99	0.30	37.07	4.95
	Fe-Mn	1.22	0.64	6.57	1.06	160.61	39.59
	Oxidizable	0.92	0.16	3.58	0.39	61.77	9.90
	Carbonate	0.98	0.28	5.07	0.51	45.30	13.20
	Residual	2.17	1.12	11.63	1.91	107.07	31.34
	Total Fractions	5.94	2.01	29.84	4.17	411.82	98.98
	Pseudo Total	6.01	2.17	32.91	4.28	423.59	104.28
	%Recovery	**98.83**	**92.63**	**90.67**	**97.43**	**97.22**	**94.92**
P6	Exchangeable	0.39	0.05	4.24	0.51	21.10	4.08
	Fe-Mn	1.67	0.45	4.08	2.01	67.52	18.86
	Oxidizable	0.21	0.18	2.06	0.92	25.32	6.63
	Carbonate	1.11	0.63	1.04	1.26	35.87	8.65
	Residual	2.08	1.30	0.82	3.68	61.19	13.77
	Total Fractions	5.46	2.61	12.24	8.38	211.00	51.99
	Pseudo Total	5.52	2.89	13.59	8.79	232.59	57.28
	%Recovery	**98.91**	**90.31**	**90.07**	**95.34**	**90.72**	**90.77**

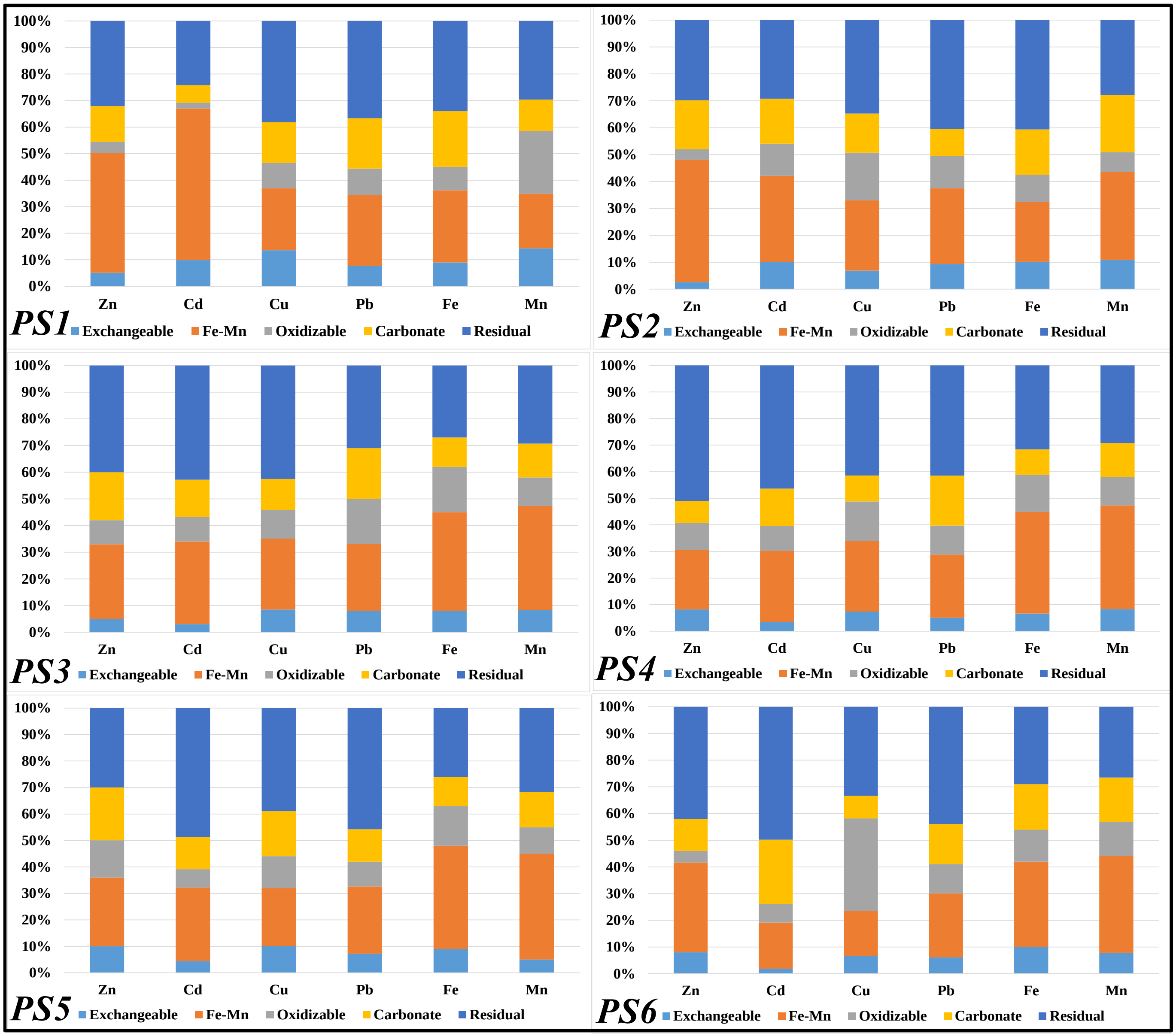

Figure 3: Percentage geochemical fractions of metals in paddy soils of Ogbese area

Zinc has positive and strong relationships with Fe and Mn in paddy soils of this area (Zn/Fe, r=0.893; Zn/Mn, r=0.710)(Table 3).The association of zinc with Fe–Mn oxides in soil has been widely recognized (Jones and Turkie, 1997). The sorption of zinc in soil and sediments strongly imparts its mobility in the environment (Li *et al.*, 2000). For this reason, severe zinc contamination tends to be confined to the region of the source (Li *et al.*, 2000). Hydrous Fe and Mn oxides, clay minerals, carbonate minerals, and, to a lesser extent, organic matter has been noted as sorbents that control the behaviour of zinc in soil. A minor amount is also associated with exchangeable [F1] and carbonate fractions [F2]. Lower concentration in the exchangeable fraction indicates low bioavailability (Kotoky *et al.* 2003). Association of Cd is observed as maximum in residual fraction. The association of Cd with the different fractions was observed in the following order: residual > Fe–Mn oxides > organic > carbonate > exchangeable. Cadmium has a strong and positive other trace metals (Table 3). The higher relationship of Cd with the organic matter contents is also manifested by the positive correlation coefficients. Mobility factors indicated that Zn and Pb have least mobility compared to other metals (Figure 4). This assertion is supported by previously studies such as that of Kotoky *et al.* (2003) and Ogundiran and Osibanjo (2009). However, Cd has lower mobility factor in uncontaminated paddy soils when compared to those reported in soils affected by hazardous waste by Ogundiran and Osibanjo (2009). Copper (Cu), Fe and Mn also showed similar trend. This showed that metals in paddy soils of the area may not pose impactful toxicological effects (He *et al.*, 2005).

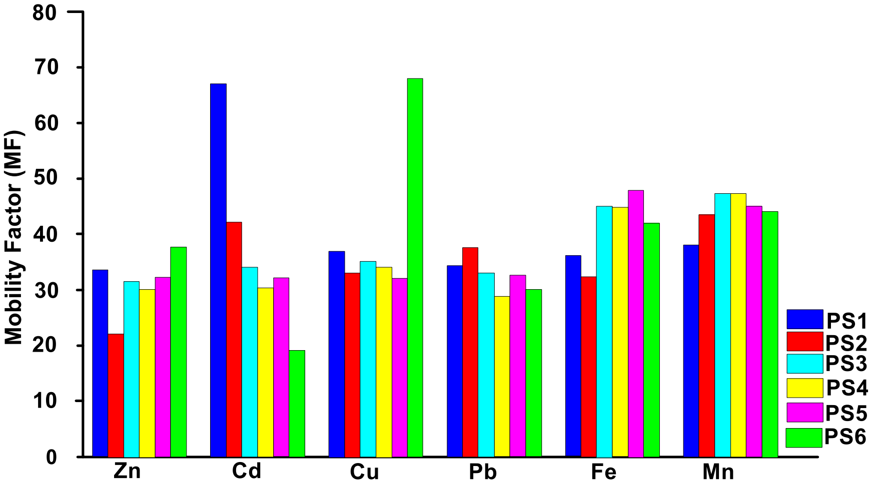

Figure 4: Mobility factor of heavy metals in paddy soils

Table 3: Bivariate correlation between physicochemical parameters in the paddy soil

	Zn	Cd	Cu	Pb	Fe	Mn	pH	OMC	%Sand	%Silt	%Clay
Zn	1										
Cd	**0.683**	1									
Cu	**0.937**	**0.578**	1								
Pb	**0.580**	**0.744**	0.374	1							
Fe	**0.893**	**0.820**	**0.570**	**0.519**	1						
Mn	**0.710**	**0.928**	**0.561**	**0.728**	**0.726**	**1**					
pH	**0.576**	**0.790**	**0.433**	**0.757**	**0.690**	**0.715**	1				
OMC	**0.613**	**0.858**	**0.571**	**0.579**	**0.908**	0.249	**0.527**	1			
%Sand	**0.580**	0.388	**-0.730**	**0.972**	**-0.410**	**0.590**	**-0.790**	**0.636**	1		
%Silt	**-0.670**	**0.518**	**0.700**	**0.784**	**0.540**	**-0.750**	**0.670**	**0.935**	**-0.970**	1	
%Clay	**0.910**	**0.540**	0.425	0.396	**0.533**	**0.770**	**0.596**	**-0.810**	**-0.540**	0.310	1

5. Conclusions

Sequential extraction of trace metals in this study uncovered the geochemical nature of Zn, Cd, Cu, Pb, Fe and Mn, and their possible relationships with different chemical forms in paddy soils along the Ogbesse River, Ondo State. The study revealed that the concentration of trace meals in paddy soils of the area were lesser than the internationally acceptable limits for agricultural soils. The study also looked at the impact of soil physicochemical properties on the retention and partitioning of six trace metals. Metals in the paddy soils are mainly related with the residual and Fe–Mn oxides fractions. The Fe–Mn oxides and organic matter fractions easily form complexes and may provide a sink for heavy metals. The acidic nature of the soils possibly restricts the concentration of the metals in carbonate and exchangeable fractions. It is evident from the study that the soil characteristics played a significant role in defining the chemical forms of the metals within the system. The present study indicates that the metals under study do not pose environmental risks under the existing physicochemical environment. The study showed that metals in the soils have low mobility which may not portend intense toxicological effects in humans. However, since paddy rice is a commonly ingested grain in the area, there is a need for continuous monitoring of toxic metals in paddy soils in the area. This will go a long way to prevent outbreak of diseases that are associated with the ingestion of contaminated agricultural produce.

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