

## **BIOAVAILABILITY AND POLLUTION ASSESSMENT OF SELECTED HEAVY METALS IN AGRICULTURAL SOIL IN IBESE, OGUN STATE, NIGERIA**

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### **ABSTRACT**

*The bioavailability of heavy metals (As, Ni, Cu, Pb and Zn) in rice fields' soil samples from Ibesse, Nigeria were carried out using Colorimetric method (for Arsenic) and Atomic Absorption Spectrophotometry (for other selected heavy metals). Soil properties including pH, Cation exchangeable capacity (CEC), soil particles and organic matter were determined using standard procedures. The pollution of the heavy metals was assessed with the geoaccumulation index model (Igeo). The pH range of the soil samples here determined was 5.1 - 6.6 while the percentage organic matters (%TOM) ranges 0.6 – 2.4. Sequential extraction was carried out to assess the environmental availability of these heavy metals in the studied soil. The most exchangeable metals with biota in the surrounding ecosystems in all the soil samples are **Ni** and **Pb**, followed by **Cu**. **Ni**, together with **As**, are mainly bound to carbonate fraction. Consequently, the exchangeability of heavy metals in the investigated soil samples decreases in the following order: Ni>Pb>Cu>As>Zn. Generally, the soil is not polluted with the heavy metals.*

**Keywords:** Heavy metals, bioavailability, sequential extraction, soil

## I. INTRODUCTION

The land is the main support of terrestrial biodiversity. Land is base for mountains, forests and plains. Upon the land is where we live (Taylor and Mclelland, 1995). Survival of man on land is based on three major factors: air, food and water. Oxygen, the main component of air for human respiration, is a byproduct of plant photosynthesis. Land is the support for plants. Larger percentages of human food are land based. Fertile soil remains an indispensable natural asset and the main factor of productive agricultural practices (NAP, 2019). Land and water are one complementary balance that sustains the mother earth.

High volumes of natural materials used by man are inorganic (metals) in form of ores. These ores are processed in the industries for the productions of various products of human demands, such as production of insecticides, herbicides and fertilizers (Adel et al., 2020). In the process, high concentrations of these metals are discharged into the environment in form of wastes, which then offset the natural elemental contents of the soil. Also, used products of these ores are metal residues, thrown in the soil. Soil is one big reservoir for all sorts of discharged substances. Other factors which erode the soil of its integrity include erosion and urbanization (Ali and Vinod, 2019) and geogenicity (Godwin et al., 2020).

The presence of toxic heavy metals in agricultural soil can interfere with the microbiological balance and reduces its fertility (Hazrat et al., 2019; Chuanyu et al., 2019). The anthropogenic presence of heavy metals in agricultural soils has been appraised as having direct deleterious effect on plants and the soil microbes (Anitha et al., 2015; Farah, 2018; Tatiana et al., 2018; Ahmadreza et al., 2019; Rim et al., 2019; Zhen et al., 2019; Liu et al., 2020). Heavy metals in the soil, however, are difficult to control due to the following features: concealment, accumulation, non-degradability, distribution in-homogeneity and regionality (Yuhu, 2019). The health of the ecosystem is threatened as a result of translocation and bioaccumulation characteristics of heavy metals (Deepmala et al., 2014; Qun et al., 2020). The main route of exposure to the heavy metals in agricultural soil is through food chain. Edible crops, like grains and vegetables, trans-locate and accumulate doses of heavy metals in proportions to heavy metals contents of the soils. Nonetheless the specie of crop is a factor of translocation and bioaccumulation. Herbivores that feed on heavy metal contaminated crops may be at the risk of heavy metal toxicity.

It is therefore necessary to determine, from time to time, the level of human exposure to these substances in the environment to prevent their unhealthy implications.

## II. METHODOLOGY

### A *Location Description*

The samples sites are located in Ibese land (6°58'19.79" N and 3°02'06.69" E), in Yewa South Local government, Ogun state, Nigeria. Ibese town hosts Ibese Dangote Cement plant and Ewekoro Cement factory. The town is one of the few that engage in rice in Nigeria. The farms are situated along a stream. The soils are water logged during the raining season and dry-caked dry season. Rice is mainly cultivated on the fields during dry season as well as dry season vegetable crops. Occasionally, fallowing is practiced. The fields are labeled: A, B, C and D.

### B *Soil Sampling*

The samples were collected in line with guidelines of appropriate procedures. Soil samples were randomly collected at depths of 0 – 15 cm and at 40 m intervals; and were placed in sealed polythene bags. The samples were air-dried, ground up and sieved with 4 mm mesh. Each sample was immediately placed in a polythene bag and tightly sealed.

### C Sample Analysis

Metal Speciation was done using Tessier et al. method (Tessier et al., 1979). The pH, the Cation Exchange Capacity (CEC), Hydrometer method for soil particle analysis and the %TOM were determined using Gupta method (Gupta, 2001). The Geoaccumulation index (Igeo) (Loska et al., 2004; Ali and Vinod, 2019; Jin et al., 2019) was employed in determining the pollution extent of the soils by the heavy metals:

$$I_{geo} = \log_2 \frac{HM_s}{\frac{3}{2} \times HM_b}$$

Where  $HM_s$  is heavy metals concentrations of the soil samples and  $HM_b$  is background heavy metals concentrations of the soil: As (15 ppm) (GB, 1995), and Zn (71 ppm), Ni (20 ppm), Cu (25 ppm), and Pb (20 ppm) (Taylor and Maclenan, 1995).

Table 1: Geoaccumulation Index

Igeo value	<0	0-1	1-2	2-3	3-4	4-5	≥5
Index	No pollution	Moderate pollution	Strong pollution	High pollution	Very high pollution	Severe pollution	Extreme pollution

## III. RESULTS AND DISCUSSION

### A Physicochemical Parameter

The results of the pH, the %TOM and the percentage Cation Exchangeable Capacity (% CEC) of the soil samples from the selected rice fields from Ibese, Ogun State, Nigeria, are presented in Table 2.

The pH range of the soil samples was slightly acidic: 5.1 – 6.6. This pH range indicates oxidizing condition of the soil and most metals are in ionizing states. Heavy metals are mostly mobile and bio-available under acidic conditions (Awokunmi et al., 2015). The CEC is a measure of soil chemical activity. The % CEC range as determined in the soil samples in this study is 0.90 – 2.00. The CEC is a measure of nutrient retention capacity of the soil. TOM is a measure of carbon-containing compounds in the soil. The % TOM range as determined in this study soil samples is 0.60 – 2.40. The TOM is directly proportional to the % CEC (Table 2).

### B. Sequential Extraction

#### Arsenic (As)

**Arsenic (As)** was present in all the fractions in almost equal proportions, except oxidizable fraction where it was least bonded (Figure 1). This may have to do with low organic matters of the soils. The highest proportion of **As** was found in carbonate-bound, exchangeable and residual fractions in the soil sample from fields A, B, C and D (21%) (Table 5). **As** proportion in reducing fraction is 20 % in all the fields. While in oxidizable fraction, it was in the range 17 – 18 % among all the fields. The result of Salman et al. (2018) agreed with the result of this work. Some researchers reported that **As** was mainly found in reducing fraction (Radim et al., 2010; FAO 2004; Nastja et al., 2008). Some reported that **As** was extracted from oxidizable fraction (Erika et al., 2005). However the types of soil studied were different.

## Nickel (Ni)

Figure 1(c) shows that Ni, from all the paddy soil samples, was strongly associated with the carbonate-bound fraction, followed by the exchangeable fraction. The highest part of Ni in the carbonate-bound fraction was determined in paddy soil samples from fields C(64 %), B(63 %) D(56 %) and A(42 %). The dominant part of Ni in the exchangeable fraction was determined in the paddy soil sample from field A(40 %) (Table 5). Cajuste et al., (2000) who studied entisol, the type of soil in this study, reported results that were in agreement with this study. However the reports of other researchers have it that Ni in calcaric cambisol, cambic podsol and mollic andosol was extracted from residual phase (Probst et al., 2003; Lena and Gade, 1997) and in vertisol was extracted from the oxidizable fraction (Fitamo et al., 2007).

Table 2: the Physicochemical parameters

Field	A	B	C	D
<b>pH</b>	5.5	5.1	6.2	6.6
<b>% TOM</b>	1.20	2.40	1.60	0.60
<b>% CEC (cmol/Kg)</b>	1.40	2.00	1.60	0.90
<b>%Clay</b>	5	5	3	2
<b>%Silt</b>	4	11	10	6
<b>%Sand</b>	91	84	87	92

## Copper (Cu)

**Cu** in all the soil samples (Fig. 1(b)) was almost entirely bounded to the exchangeable fraction and then oxidizable fraction. This was similar to what were reported by Erika et al., 2005 and Marquez et al., 2018. The highest concentration of **Cu** was extracted from exchangeable fraction from field D (with highest pH value and least TOM) soil sample (52 %) and the highest in oxidizable fraction was (33 %) from field A soil sample (Table 5). Field A is loamy sand with higher organic content than field D, which is sand. Some studies reported that Cu was extracted from oxidizable fraction (Nastja et al., 2008; Probst et al., 2003; Lena and Gade, 1997; Fitamo et al., 2007). Cajuste et al., (2000) reported that Cu was generally associated with reducing fraction, and then exchangeable and carbonate fractions.

## Lead (Pb)

A large part of Pb (Fig. 1(d)) was equally bound to the exchangeable and carbonate-bound fractions. The highest amount of Pb was found in the exchangeable fraction in the soil sample from field D (67%), followed by field C (42%). The highest share of Pb in the carbonate-bound fraction was found in the soil sample from field C (50%) (Table 5). The fields C and D are both sandy. Reports of some researchers agreed with our results here (Erika et al., 2005; Fitamo et al., 2007). In other reports Pb bound to residual fraction (Nastja et al., 2008; Cajuste et al., 2000).

## Zinc (Zn)

On the average, Zn is mainly extracted from the residual fractions (fig. 1(e)), followed by carbonate-bound fraction, and then exchangeable fraction, with the least in oxidizable fraction. The highest Zn level in the highest in the residual fraction was determined in field C soil

(87%), the highest in the carbonate-bound fraction occurs in field A soil (28%) while highest in the exchangeable fraction occurs in field B soil (23%) (Table 5). Nastja et al., (2008) reported that Zn was mainly associated with the reducible fraction. According to Probst et al., (2003), Zn was majorly extracted into oxidizable fraction; and into exchangeable fraction by Kai et al., (2018). Some researchers have reported similar results (Lena and Gade, 1997; Cajuste et al., 2000; Erika et al., 2005; Fitamo, 2007).

In this work, on the average, the most exchangeable elements with biota in the surrounding ecosystems in all the soil samples are **Ni** and **Pb**, followed by **Cu**. **Ni**, together with **Pb**, is mainly bound to carbonate fraction, and as such may mimic  $\text{Ca}^{2+}$  in the soil. Consequently, the exchangeability of heavy metals in the investigated soil samples decreases from  $\text{Ni} > \text{Pb} > \text{Cu} > \text{As} > \text{Zn}$ . This decreasing trend of heavy metals in sequential extraction fractions only follows the trend reported by Fitamo et al., (2007) for Entisol type of soil and Jin et al., (2019).

**Table 3: Soil Speciation**

Parameter	Field	Fraction(mg/kg)					
		F1	F2	F3	F4	F5	total
As	A	3.80	3.76	3.75	3.13	3.75	18.20
	B	2.27	2.19	2.23	1.91	2.23	10.83
	C	4.60	4.60	4.52	3.85	4.53	22.10
	D	5.23	5.44	5.15	4.50	5.16	25.50
Zn	A	BDL	12.90	6.20	6.20	20.00	45.30
	B	0.15	BDL	0.80	BDL	49.95	50.90
	C	0.90	5.55	0.20	BDL	43.35	50.00
	D	6.90	BDL	2.60	0.40	41.10	51.00
Ni	A	14.7	15.60	1.80	3.00	4.20	39.30
	B	5.70	16.65	BDL	2.20	3.40	27.94
	C	5.70	16.35	BDL	1.60	3.00	26.65
	D	6.00	14.40	BDL	2.20	4.60	27.20
Cu	A	2.85	3.60	2.40	6.40	2.00	17.25
	B	3.60	1.80	1.60	4.80	1.80	13.60
	C	5.55	2.55	1.60	3.80	5.40	18.90
	D	10.05	3.00	2.60	4.40	1.60	21.65
Pb	A	7.50	7.50	BDL	2.00	2.00	19.00
	B	7.50	7.50	4.00	BDL	4.00	23.00
	C	7.50	9.00	BDL	2.00	BDL	18.50
	D	6.00	1.50	BDL	2.00	BDL	9.50

F<sub>1</sub>= exchangeable metal fraction; F<sub>2</sub>= carbonate bond metal fraction; F<sub>3</sub>= Fe-Mn oxide bond fraction(reducing); F<sub>4</sub>= organic & sulfide bond metal fraction(oxidizing); F<sub>5</sub>= residual metal fraction.  
BDL- below detection limit

**Table 4: Igeo Values**

Field	A	B	C	D
Heavy metals				
As	-0.31 <sup>a</sup>	-1.05 <sup>a</sup>	-0.03 <sup>a</sup>	0.18 <sup>b</sup>
Zn	-1.23 <sup>a</sup>	-1.07 <sup>a</sup>	-1.09 <sup>a</sup>	-1.06 <sup>a</sup>
Ni	0.39 <sup>b</sup>	-0.10 <sup>a</sup>	-0.17 <sup>a</sup>	-0.14 <sup>a</sup>
Cu	-1.12 <sup>a</sup>	-1.46 <sup>a</sup>	-0.99 <sup>a</sup>	-0.79 <sup>a</sup>
Pb	-0.66 <sup>a</sup>	-0.38 <sup>a</sup>	-0.70 <sup>a</sup>	-1.66 <sup>a</sup>

**a- No pollution**

**b- moderate pollution (see Table 1)**

**Table 5: Heavy Metal-Fractions Comparison among Soil Samples (%)**

Field	Parameter	Fraction (%)				
		F1	F2	F3	F4	F5
A	As	21	21	20	17	21
	Zn	--	28	14	14	44
	Ni	40	42	4	6	8
	Cu	20	25	12	33	10
	Pb	42	42	--	8	8
B	As	21	20	20	18	21
	Zn	23	--	1	--	76
	Ni	21	63	--	6	10
	Cu	31	16	10	31	12
	Pb	36	36	14	--	14
C	As	21	21	20	17	21
	Zn	2	11	1	--	87
	Ni	22	64	--	5	9
	Cu	34	16	7	18	5
	Pb	42	50	--	8	--
D	As	21	21	20	18	20
	Zn	14	--	4	1	81
	Ni	24	56	--	6	14
	Cu	52	15	10	17	6
	Pb	67	16	--	17	--

F<sub>1</sub>= exchangeable metal fraction; F<sub>2</sub>= carbonate bond metal fraction; F<sub>3</sub>= Fe-Mn oxide bond fraction(reducing); F<sub>4</sub>= organic & sulfide bond metal fraction(oxidizing); F<sub>5</sub>= residual metal fraction.

--- not determined



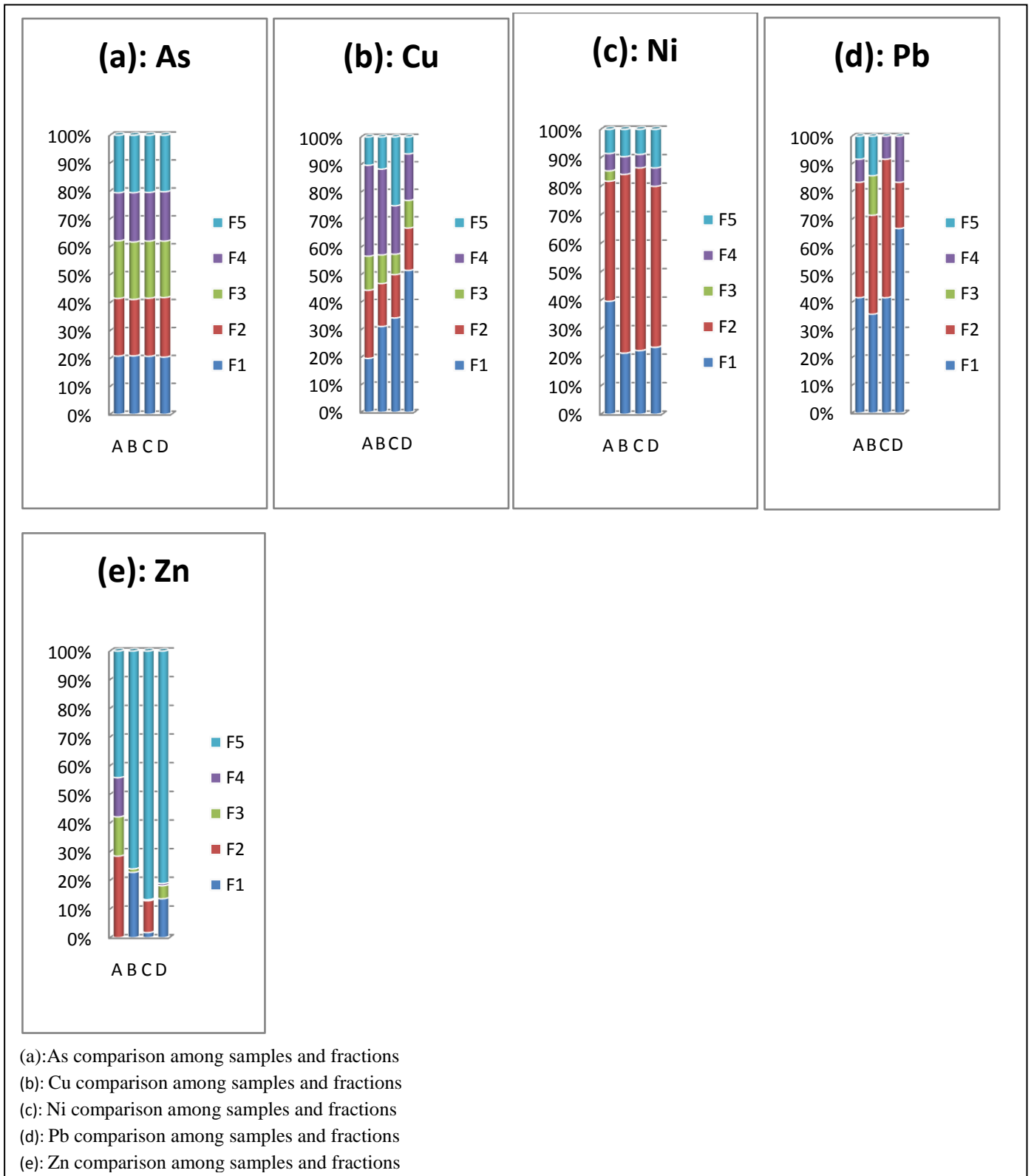


Fig. 1: heavy metals comparison among samples and fractions

**Table 6: Pearson Correlation Analysis (SPSS 20)**

Heavy Metal	Parameter	F1	F2	F3	F4	F5
<b>As</b>	pH	<b>0.965</b>	<b>0.972</b>	<b>0.963</b>	<b>0.975</b>	<b>0.964</b>
	%TOM	<b>-0.880</b>	<b>-0.890</b>	<b>-0.883</b>	<b>-0.881</b>	<b>-0.882</b>
	%CEC	<b>-0.870</b>	<b>-0.886</b>	<b>-0.872</b>	<b>-0.879</b>	<b>-0.871</b>
	%Clay	<b>-0.872</b>	<b>-0.887</b>	<b>-0.870</b>	<b>-0.894</b>	<b>-0.871</b>
	%Silt	-0.448	-0.448	-0.453	-0.431	-0.451
	%Sand	<b>0.754</b>	<b>0.760</b>	<b>0.758</b>	<b>0.748</b>	<b>0.756</b>
<b>Zn</b>	pH	<b>0.804</b>	-0.208	-0.137	-0.304	0.058
	%TOM	<b>-0.748</b>	-0.173	-0.486	-0.275	0.478
	%CEC	<b>-0.834</b>	-0.033	-0.409	-0.167	0.366
	%Clay	<b>-0.846</b>	0.435	0.333	<b>0.515</b>	-0.292
	%Silt	-0.292	<b>-0.592</b>	<b>-0.925</b>	<b>-0.795</b>	<b>0.880</b>
	%Sand	<b>0.605</b>	0.353	<b>0.691</b>	<b>0.501</b>	<b>-0.668</b>
<b>Ni</b>	pH	-0.324	<b>-0.701</b>	-0.345	-0.421	0.324
	%TOM	-0.248	<b>0.938</b>	-0.221	-0.223	<b>-0.774</b>
	%CEC	-0.139	<b>0.971*</b>	-0.109	-0.171	<b>-0.798</b>
	%Clay	<b>0.535</b>	<b>0.632</b>	<b>0.556</b>	<b>0.561</b>	-0.243
	%Silt	<b>-0.777</b>	<b>0.725</b>	<b>-0.757</b>	<b>-0.764</b>	<b>-0.829</b>
	%Sand	0.477	<b>-0.904</b>	0.451	0.455	<b>0.840</b>
<b>Cu</b>	pH	<b>0.883</b>	0.346	0.441	<b>-0.537</b>	0.284
	%TOM	<b>-0.683</b>	<b>-0.790</b>	<b>-0.881</b>	-0.083	0.161
	%CEC	<b>-0.769</b>	<b>-0.702</b>	<b>-0.880</b>	-0.010	0.222
	%Clay	<b>-0.941</b>	-0.121	-0.317	<b>0.689</b>	-0.258
	%Silt	-0.128	<b>-0.952*</b>	<b>-0.911</b>	<b>-0.685</b>	0.430
	%Sand	0.496	<b>0.900</b>	<b>0.943</b>	0.332	-0.279
<b>Pb</b>	pH	<b>-0.740</b>	<b>-0.590</b>	<b>-0.740</b>	<b>0.740</b>	<b>-0.953*</b>
	%TOM	<b>0.751</b>	<b>0.707</b>	<b>0.839</b>	<b>-0.839</b>	<b>0.761</b>
	%CEC	<b>0.838</b>	<b>0.797</b>	<b>0.765</b>	<b>-0.765</b>	<b>0.742</b>
	%Clay	<b>0.778</b>	<b>0.626</b>	<b>0.556</b>	<b>-0.556</b>	<b>0.870</b>
	%Silt	0.353	0.421	<b>0.656</b>	<b>-0.656</b>	0.290
	%Sand	<b>-0.631</b>	<b>-0.630</b>	<b>-0.812</b>	<b>0.812</b>	<b>-0.812</b>

\*Correlation is significant at the 0.05 level (2-tailed); results in bold were correlated

### Statistical Analysis

The Pearson correlation analysis was carried out on the sequential extraction results presented in Table 3 against the physicochemical parameters (Table 2). The pH and %sand were directly correlated with **As** in all the fractions (Table 6). The %TOM, %CEC and %Clay were all inversely correlated with **As** in all the fractions. The pH and %sand were positively correlated with Zn in F1 fraction (%sand also directly correlated in F3, F4 and inversely in F5); %TOM, %CEC and %Clay were inversely correlated with Zn in F1 (%clay also directly correlated in F4); while %silt was inversely correlated with Zn in the F2, F3 and F4 fractions and directly in F5 fraction. pH was inversely correlated with Ni in F2. %TOM and %CEC were directly correlated with the Ni in F2 and inversely in F5. %Clay was directly correlated with Ni F1, F2, F3 and F4. %silt was inversely correlated with Ni in F1, F3, F4, F5 and directly in F2. %sand was inversely correlated with Ni in F2 and directly in F5. pH was directly correlated Cu in F1 and inversely in F4. %TOM and %CEC were inversely correlated with Cu in F1, F2 and F3. %Clay was inversely correlated with Cu in F1 and directly in F4. %silt was inversely correlated with Cu in F2, F3 and F4; while %sand was correlated with Cu in F2 and F3. pH was inversely correlated with Pb in F1, F2, F3, F5 and directly in F4. %TOM, %CEC and %Clay were directly correlated with Pb in F1, F2, F3, F5 and inversely in F4. %silt was directly correlated with Pb in F3 and inversely in F4; while %sand was inversely correlated with Pb in F1, F2, F3, F5 and directly in F4.

### CONCLUSION

The sequential extraction results showed that **As** is prevalent in most of the fractions, except in oxidizing fraction. The most exchangeable, labile and available element for plant uptake and possible contamination of the surrounding ecosystem in all the paddy soil samples is **Ni**, closely followed by Pb and Cu. Ni is mainly bound to carbonate. **As** is also weakly bound to organic matter. The mobility potential of heavy metals in the investigated paddy soil samples decreases from **Ni>Pb>Cu>As>Zn**. The Igeo index results revealed that the soils are not polluted.

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