

Fractionation profile, mobility patterns and correlations of heavy metals in estuary sediments from olonkoro river, in tede catchment of western region, Nigeria



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ABSTRACT

This work was carried out to determine the concentrations, bioavailability and mobility of heavy metals in the sediments of Olonkoro River, Tede, Oyo State, Nigeria. The river sediments were sampled at ten selected locations and the samples were analyzed for some heavy metals to determine the concentration, speciation and distribution pattern of the metals. The sediments were obtained specifically at upstream, middle-stream and downstream of the river. In general, the total metal concentrations were in the order: Fe > Zn > Mn > Cu > Pb > Cd in sediment samples and for Tessier's sequential fractionation, manganese was found to be more in the exchangeable phase, Fe in the Residual, Zn in carbonate-bound metal while Pb was greater in the exchangeable form and Cu was found to be more concentrated in the organic phase. **Percent of bioavailable and non-bioavailable proportions of heavy metals for Mn, Fe, Cu, Zn, Pb, and Cd in the sediment samples varied between 12.92-87.08, 11.57-88.43, 0.29-99.71, 10.76-89.24, ND-100 and ND, respectively.** This clearly indicates that with the exception of Cu and Cd the metals are highly bioavailable leading to their having a higher impact on the target system, subsequently leading to contamination of the water. The high percent bioavailability is an indication of poor retention in the residual geochemical form partly due to saturation of the sediment (river). The pH value was found to be basic but within the WHO standards throughout all locations. The high percentage of Mn, Cd and Pb in the bioavailable forms suggested the need to keep close surveillance on these metals because of their high toxicity.

1. Introduction

Shortage of sufficient potable water has led many people to depend on rivers, not only for drinking, but also for other domestic, agricultural and industrial uses. The pollution status of rivers is, thus, of serious concern worth investigation and assessment. A major alarm has been raised over the discharges from industries within the location that the river could be polluted excessively. However, the need to assess the quality and suitability of pollutants becomes imperative. Heavy metals are serious pollutants due to their toxicity, persistence in natural conditions and ability to be incorporated into food chains (Szefer et al., 1997; Klavins et al., 2000; Armitage et al., 2007; Sakan et al., 2009).

Sediments of rivers are sinks for contaminants, such as heavy metals (Yusuf and Osibanjo, 2006; Okoro et al., 2014). Sediment may be regarded as being contaminated when the level of these pollutant (heavy metals) are found in it are higher than the recommended permissible limit (Agirtas and Kilicel, 1999). The contamination of aquatic systems by heavy metals, especially in sediments, has become one of the most challenging pollution issues owing to the toxicity, abundance, persistence, and subsequent bio-accumulation of these materials (Fatoki et al., 2012; Gielar et al., 2012; Varol and Sen, 2012).

Numerous studies, especially during the last decade, have demonstrated that marine sediments from industrialized coastal areas are greatly contaminated by heavy metals (Singh et al., 2007; Fernandes et al., 2011; Filgueiras et al., 2004; Okoro et al., 2013, 2014). Natural

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sources of these heavy metals can be traced to the biogeochemical processes, where their burden in sediment are continually on the increase through anthropogenic sources (Giwa et al., 2009).

Moreover, the total concentration of metals often does not accurately represent their characteristics and toxicity. In order to overcome these obstacles, it is helpful to evaluate the individual fractions of the sediment to which the metals are bound to fully understand their actual and potential environmental effects (Okoro et al., 2014; Tessier et al., 1979).

To date, studies on metal speciation in river sediments have been conducted in only a few villages and towns in Nigeria (Okoro et al., 2014). Data on metal speciation in Olonkoro river sediments are lacking. In this study, river sediments collected from Olonkoro River were analyzed using modified Tessier five-step sequential extraction procedure. This study aimed at the investigation of heavy metals (Mn, Fe, Cu, Zn, Pb, and Cd) fractionation profile *vis-à-vis* the mobility patterns. The correlations and binding behaviours of the heavy metals in the sediments was also evaluated using Pearson Correlation Coefficient (PCC).

2. Materials and methods

2.1. Description of study area

The study area is the Olonkoro River in the Atisbo Local Government Area of Oyo State and it is located between latitude 8°33'36"N and 3°28'30"E (Fig. 1). Table 1 shows location sites and description referenced with global positioning system (GPS). The typical tropical climate, consisting of the dry and rainy seasons is governed by the northeastern and southwestern winds which generally influence the climate of Nigeria. The river empties into a popular Ago-Are Dam used by two indigenous communities with a population of about one hundred and twenty thousand for domestic purposes. The main sources of pollution in the river catchments are socio-economically related (Shea butter production, cassava milling and agricultural activities). The natives also depend on the river for fishing and as a source of water for domestic purposes. They are also involved in commercial sand dredging. Some industrial concerns within the vicinity of the river catchments empty partially treated effluents into the river.

Table 1

Location sites and description referenced with global positioning system (GPS).

Sample Location	Coordinate	Activity	Depth
L1	N8 33.757 E3 26.710	Industry producing Shea butter	24 cm
L2	N8 33.762 E3 26.697	Industry producing Shea butter	25 cm
L3	N8 33.810 E3 26.630	Industry producing Shea butter	24 cm
L4	N8 33.908 E3 26.599	Industry producing Shea butter	26 cm
L5	N8 34.001 E3 26.536	Industry producing Shea butter	25 cm
L6	N8 34.015 E3 26.505	Industry producing Shea butter	23 cm
L7	N8 34.496 E3 26.480	Agricultural activities	23 cm
L8	N8 34.609 E3 26.334	Fetching for drinking	22 cm
L9	N8 34.809 E3 26.305	Agricultural activities	20 cm
L10	N8 34.926 E3 26.198	Fetching for drinking	25 cm

Domestic waste discharges and makeshift latrines are evident in the river banks.

2.2. Sampling and analytical procedure

Sediment samples that were used for metal determination were collected from ten different locations along the Olonkoro River. Surface sediments were collected at depths of 20–30 cm in the sediment core with a stainless-steel Ekman Grab Sampler (Table 1) following the standard procedure described by American Public Health Association. The content of the sampler was emptied into a black polyethylene bag at each location and later transferred to cooler boxes already containing ice packs and then transported to the laboratory for analysis. Plants, metals or plastics debris in the sediments were removed manually prior to chemical treatment. The sampler was inspected for possible cross-contamination and cleaned with ambient water for individual sample collection. The difference from one sampling point to another was approximately 100 m. The choice of locations was based on the ease of access to the River and the activities carried out along the River at such points. Heavy metal concentrations of the digested solutions were

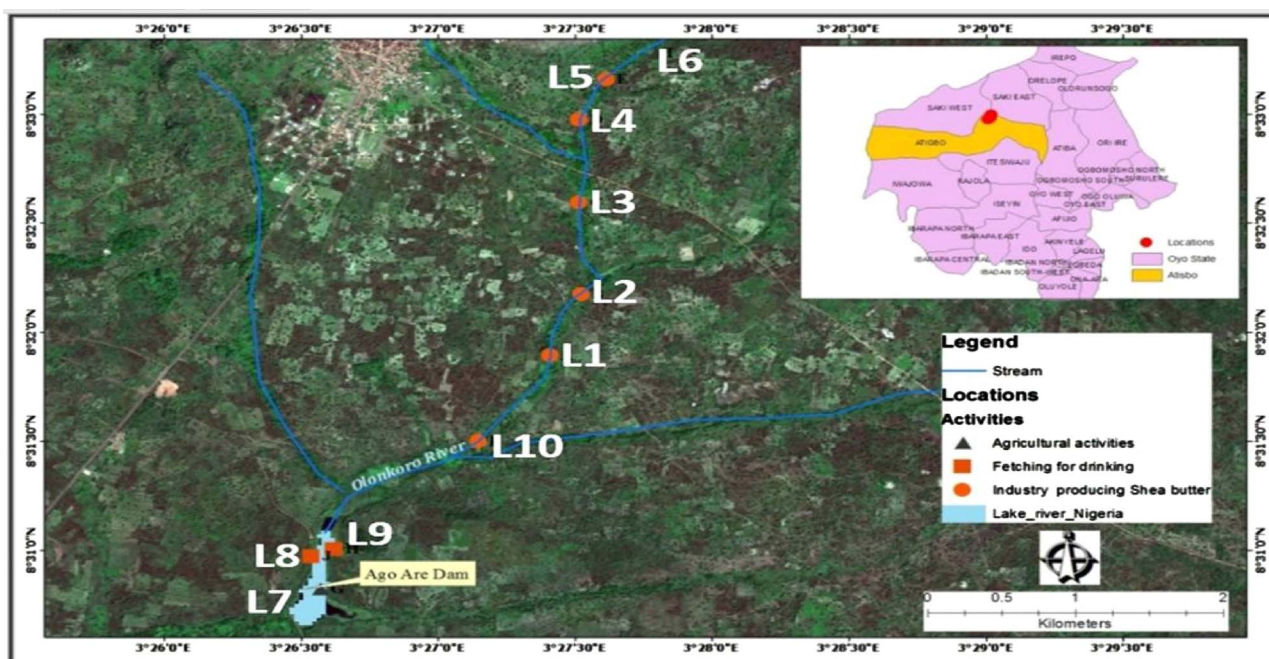


Fig. 1. Map showing the sampling locations and sampling points in Olonkoro River. Note: Cadmium was below detecting limit in all the locations (Table 3).

Table 2
Experimental conditions in a sequential extraction procedure.

S/N	Chemical fractions	Extraction conditions
1	Exchangeable fraction	8 ml of 1 M Sodium acetate at pH 8.2 at room temperature
2	Metals bound to carbonate	8 ml of 1 M sodium acetate (pH 5 with glacial acetic acid)
3	Metals bound to Fe-Mn oxides	8 ml of 0.1 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ (in 25% v/v acetic acid)
4	Metals bound to organic matter	3 ml of 0.02 M HNO_3 and 5 ml of 30% H_2O_2 adjusted to pH 2.0
5	Residual fraction	Acid digestion using HCl : HNO_3 aqua regia (7.5 ml HCl : 2.5 ml HNO_3)

Extraction time: The extraction was first carried for 40 mins and later 10 mins to rinse the residual samples in the extraction tube.

determined using Buck scientific model 210 VGP Atomic Absorption Spectrophotometer (AAS). Each sediment sample for metal determination was analyzed in triplicates and the relative standard deviation was found to be < 5%. The modified sequential extraction scheme of Tessier et al. (1979) was adopted to partition the heavy metals into five fractions given below (Okoro et al., 2014)

2.3. Sequential extraction procedures

Speciation experiments were performed using the modified Tessier method (Okoro et al., 2014; Horsfall et al., 1999). The main modifications included the use of 1 M sodium acetate instead of MgCl_2 , and centrifugation steps of 20 and 5 mins to get a clear supernatant clear solution. The extraction was applied to the fine particles with the amount of 1 g, and the experiments were conducted according to modified Tessier's sequential extraction conditions (Okoro et al., 2014; Horsfall et al., 1999). The method has been previously validated by the previous study carried out by Okoro et al., 2014. The extraction procedure was carried out in a centrifuge (Table 2).

2.4. Statistical analysis

Data collected was subjected to correlation analysis by SPSS PASW Statistics 20 to determine association as well as the differences in the concentration between different zones and also with one-way analysis of variance (ANOVA) to assess whether heavy metals varied significantly between location and distances from the river, possibilities less than 0.05 ($p < 0.05$) was considered statistically significant.

3. Results and discussion

3.1. Heavy metals fractionation and distribution

3.1.1. Total metal concentration in sediment samples of olonkoro river, tede, oyo state in terms of location and their seasonal variation

The result of the total metals contents showed that Iron has the highest average concentration while cadmium has the least concentration. In general, location L2, L5 and L7 recorded important concentrations for most of the heavy metals signifying that these sites were the most polluted of all the 10 locations sampled. Locations L2 and L5 stood out as the most polluted areas within the sites. Location 2 and 5 are the major areas where Shea butter, Cassava are being produced largely. Total metal concentration of sediment samples is illustrated in Fig. 2 for. The readings for Manganese showed the highest value of 1.78 mg/kg at location L8 and a minimum value of 0.72 mg/kg at location L6. The average concentration value was found to be above the WHO limits of 1.00 mg/kg thus suggesting its toxicity and potential mobility in the sediment sample. Manganese, like other lithophile elements, is relatively abundant with an average upper crustal abundance of 600 mg/kg and a bulk continental crust average of 1400 mg/kg (Taylor and

McLennan, 1995).

The readings for Manganese showed the highest value of 87.08 mg/kg at location L8 and a minimum value of 0.72 mg/kg at location 3 (Table 3). There is a slight variation in the value of Mn across the locations, showing high value concentration at locations L8 and L3. The average concentration value was found to be above the WHO limits of 1.00 mg/kg thus suggesting its toxicity and potential mobility in the sediment sample. The presence of manganese in high concentration in L8 and L3 can be as a result of the farm activities, Industrial effluent which involves the use of fertilizers and other chemicals and probably erosion of manganese containing soil. Manganese concentration above acceptable limits may cause objectionable and tenacious stains to laundry and plumbing fixtures (Okoro et al., 2012).

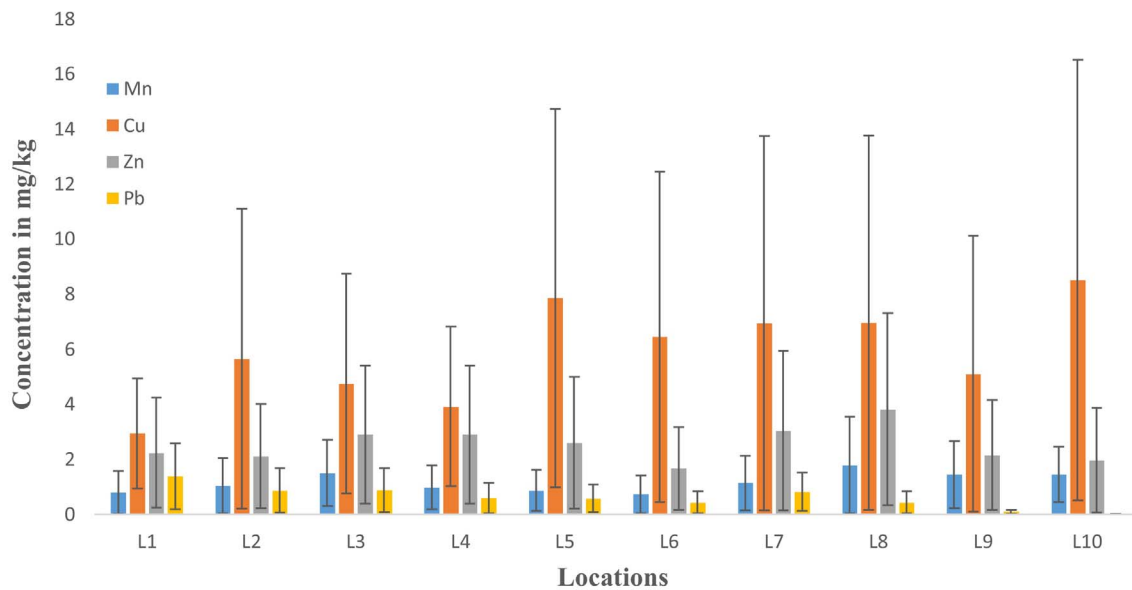
The concentrations recorded for Fe varied significantly across all locations. A very high significant variation was found in the concentration of iron (Table 4). The highest mean total concentration value was recorded at location L2 with 85.54 mg/kg, followed by location L5 77.41 mg/kg. The high value recorded in location L2, L5, L7 and L9 could be as a result of industrial activities taking place such as dumping of scraps and waste along the river bank, Shea butter production, cassava milling, geogenic influence etc. There was a significant increase down the river which could be as a result of runoff and introduction of different materials from different sources as the river flows. The concentration of iron was found to be above the MCL of WHO (2008), USEPA (2005) and FEPA (2003) (Table 4). The result from this study is similar to that of Oketola et al. (2006). Cu metal concentration was found to be high in location L10 with a value of 8.5 mg/kg and least in locations L1 with concentration value of 2.93 mg/kg. All the results obtained from this study were above the MCL of WHO (2008), USEPA (2005) and FEPA (2003) limit (Table 3). The concentrations of Zn ranged from 1.66–3.81 mg/kg (Fig. 2).

The concentrations of Zn were higher in the sediment at all the locations (Fig. 2). This could be as a result of Zn particles from suspended domestic wastes and roofs of houses close to the river and the runoff water coming into the river (Ideriah et al., 2012). Zinc concentration location L8 (3.81 mg/kg) was found to be the highest and the least concentration was recorded at L6 (1.66). The result obtained was similar to that reported by Ideriah et al., 2012. Zinc concentrations for all locations were found to be far above the limit of WHO (2008), USEPA (2005) and FEPA (2003) (Table 3). The concentrations of Pb ranged from 0.01–1.38 mg/kg (Fig. 2). The concentrations of Pb were found to be high in all the concentrations.

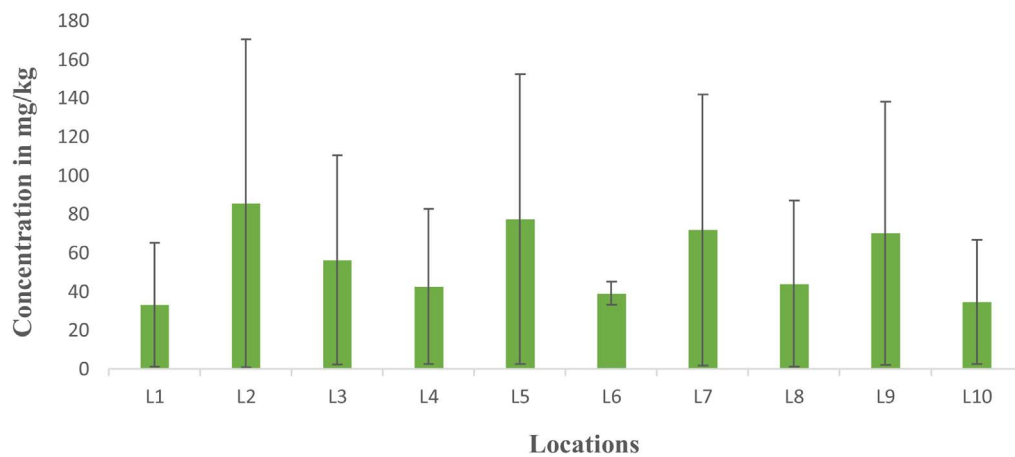
The presence of lead in high concentration level can be related to pollution from the dumpsite, agricultural and industrial activities around the area. The presence of lead at concentration above MCL of WHO (2008) (Table 3) can damage nervous connection (especially in young children) and cause blood and brain disorder. It is also a cumulative poison and a possible human carcinogen (Tslalom and Kiflom, 2015). Cadmium was below detecting limit in all the locations (Table 3). Cadmium is toxic at extremely low concentration. In humans, long term exposure results in renal dysfunction, characterized by tubular proteinurra. It can also cause kidney damage as well as produce acute health effects resulting from over exposure to high concentration (Orisakwe et al., 2006). In general, the distributions of metals across locations is shown in Fig. 4(a–j).

3.2. Percentage distribution of heavy metals in Olonkoro river sediment

Mean concentrations and standard deviation of some selected heavy metals in the different fractions of sediments from Olonkoro River, Tede, and Oyo State after sequential extraction are shown by the graphical representations illustrated in Fig. 3(a–e) and Tables 4–6. Major amount of manganese were found to be present in the exchangeable fractions and carbonate fractions with the least being in the organic fraction Tables 4–6 and Fig. 3a. The amount present in the exchangeable fraction constituted about 31.08% and 29.38% for the



a



b

Fig. 2. (a) Total metal concentrations for metals in sediments samples from Olonkoro River. (b) Total metal concentrations for iron in sediments samples from Olonkoro River.

Table 3

Total metal concentrations for metals in sediments samples from Olonkoro River.

Locations	Mn (mg/kg)	Fe(mg/kg)	Cu(mg/kg)	Zn(mg/kg)	Pb(mg/kg)	Cd(mg/kg)
L1	0.79 ± 0.77	33.07 ± 32.00	2.93 ± 2.00	2.23 ± 2.00	1.38 ± 1.20	–
L 2	1.04 ± 1.00	85.54 ± 84.75	5.64 ± 5.45	2.11 ± 1.90	0.86 ± 0.80	–
L 3	1.49 ± 1.20	56.19 ± 54.00	4.74 ± 4.00	2.89 ± 2.50	0.87 ± 0.80	–
L 4	0.98 ± 0.80	42.52 ± 40.00	3.91 ± 2.90	2.89 ± 2.50	0.59 ± 0.55	–
L 5	0.86 ± 0.75	77.41 ± 75.00	7.85 ± 6.87	2.59 ± 2.40	0.57 ± 0.50	–
L 6	0.72 ± 0.69	39.02 ± 36.00	6.45 ± 6.00	1.66 ± 1.50	0.43 ± 0.40	–
L 7	1.13 ± 1.00	71.78 ± 70.00	6.94 ± 6.80	3.03 ± 2.90	0.81 ± 0.70	–
L 8	1.78 ± 1.75	44.06 ± 43.00	6.95 ± 6.80	3.81 ± 3.50	0.43 ± 0.40	–
L 9	1.44 ± 1.22	70.02 ± 68.00	5.1 ± 5.00	2.15 ± 2.00	0.09 ± 0.07	–
L10	1.45 ± 1.00	34.52 ± 32.00	8.5 ± 8.00	1.96 ± 1.90	0.01 ± 0.001	–

carbonate fraction of total mass while that of the residual fraction constituted about 7.96% of the total mass. The high percentage of Mn in the exchangeable and carbonate fraction may be due to the abundance of Mn in the earth crust including sediment and most likely due to the similarity in ionic radii to that of Ca, which allows them to substitute for Ca in the carbonate phase (Pederson and Price, 1982; Zhang et al.,

1988 Zhang et al., 1988). This is in agreement with the literature as several authors had previously reported high concentrations for manganese, especially in exchangeable and carbonates fractions $F1 > F2 > F5 > F3 > F4$ (Adekola et al., 2010; Okoro et al., 2014; Abdus-Salam et al., 2011)

Greater amounts of Fe were found in the residual fractions and

Table 4

The mean metal content (mg/kg) for five step sequential extraction for location P1 to P4.

LOCATIONS	Fractions	Mn (mg/kg)	Fe(mg/kg)	Cu(mg/kg)	Zn(mg/kg)	Pb(mg/kg)	Cd(mg/kg)	Total metal
L1	F1	0.22 ± 0.12	6.29 ± 6.00	0.3 ± 0.10	0.8 ± 0.040	0.93 ± 0.90	–	8.54 ± 8.00
	F2	0.22 ± 0.15	5.02 ± 4.00	–	0.77 ± 0.50	0.22 ± 0.200	–	6.23 ± 6.00
	F3	0.08 ± 0.05	2.19 ± 2.00	–	0.22 ± 0.10	–	–	2.49 ± 2.00
	F4	0.03 ± 0.01	2.58 ± 2.20	2.58 ± 2.00	0.2 ± 0.10	0.23 ± 0.20	–	5.62 ± 5.00
	F5	0.24 ± 0.20	16.99 ± 15.00	0.05 ± 0.01	0.24 ± 0.20	–	–	17.52 ± 17.00
	Total metal	0.79 ± 0.65	33.07 ± 32.00	2.93 ± 2.07	2.23 ± 2.00	1.38 ± 1.20	–	
L2	F1	0.35 ± 0.20	25.84 ± 23.03	0.23 ±	0.23 ± 0.10	0.22 ± 0.10	–	26.87 ± 20.00
	F2	0.26 ± 0.15	23.91 ± 22.15	–	0.96 ± 0.15	0.4 ± 0.20	–	25.53 ± 23.12
	F3	0.17 ± 0.12	4.63 ± 4.02	0.3 ±	0.42 ± 0.40	–	–	5.52 ± 4.05
	F4	0.04 ± 0.02	5.02 ± 5.00	5.02 ±	0.23 ± 0.20	0.24 ± 0.10	–	10.55 ± 10.00
	F5	0.22 ± 0.10	26.14 ± 25.00	0.09 ±	0.27 ± 0.23	–	–	26.72 ± 25.00
	Total metal	1.04 ± 1.20	85.54 ± 80.00	5.64 ±	2.11 ± 2.10	0.86 ± 0.70	–	
L3	F1	0.48 ± 0.20	18.97 ± 15.00	0.23 ± 0.20	1.22 ± 1.10	0.29 ± 0.23	–	21.19 ± 20.00
	F2	0.57 ± 0.10	22.96 ± 20.00	–	0.91 ± 0.50	0.31 ± 0.25	–	24.75 ± 24.00
	F3	0.18 ± 0.10	2.17 ± 2.00	0.02 ± 0.10	0.3 ± 0.10	–	–	2.67 ± 2.00
	F4	0.04 ± 0.01	4.45 ± 3.00	4.45 ± 4.42	0.24 ± 0.20	0.27 ± 0.25	–	9.45 ± 9.00
	F5	0.22 ± 0.21	7.64 ± 7.50	0.04 ± 0.02	0.22 ± 0.15	–	–	8.12 ± 8.00
	Total metal	1.49 ± 1.20	56.19 ± 50.00	4.74 ± 4.70	2.89 ± 2.00	0.87 ± 0.80	–	
L4	F1	0.32 ± 0.20	2.42 ± 2.00	0.02 ± 0.01	0.21 ± 0.15	0.13 ± 0.10	–	3.1 ±
	F2	0.36 ± 0.10	2.27 ± 2.21	0.02 ± 0.00	2.04 ± 2.00	0.29 ± 0.20	–	4.98 ±
	F3	0.04 ± 0.02	2.38 ± 1.50	0.02 ± 0.01	0.22 ± 0.10	–	–	2.66 ±
	F4	0.02 ± 0.01	3.76 ± 3.50	3.76 ± 2.00	0.2 ± 0.10	0.17 ± 0.15	–	7.91 ±
	F5	0.24 ± 0.10	31.69 ± 30.00	0.09 ± 0.05	0.22 ± 0.15	–	–	32.24 ±
	Total metal	0.98 ± 0.95	42.52 ± 40.00	3.91 ± 3.00	2.89 ± 2.50	0.59 ± 0.20	–	

exchangeable fractions constituting 46.22% and 21% of the total mass respectively with the least value of 5.23% recorded in the Fe-Mn fractions Tables 4–6 and Fig. 3b, this is in agreement with Abdus-Salam and Oyede (2013). Fe is available in significant proportions in the five fractions with a good percentage also present in the residual phase. High values recorded could be attributed to wastewater from domestic activities around the Tede in addition to contribution from industrial activities. It may also be due to the specific sediment type at this location, which may contain a high percentage of clay particles. Clay particles in soils often contain iron as part of the clay mineral structure (Dumbleton and West, 1966).

In the case of Cu, a substantial amount was found in the organic fraction constituting about 94.51% of the total mass as shown in Tables 4–6 and Fig. 3c. The higher concentration of Cu in fraction 4 may be due to the weathering of rocks. The percentage distributions in the other fractions were found to be low suggesting Cu metal to be least strongly bioavailable in the sediment sample. Few speciation works have been done on Cu metals (AbulKashem et al., 2007; Fatoki and Awofolu, 2003). The order of zinc metal mobility in different fractions is F4 > F1 > F5 > F3 > F2.

Zinc metal was observed to have a high percent value in the carbonates fraction (44.94%) closely followed by the exchangeable fraction (22.87%) as in Tables 4–6 and Fig. 3d. Rubio et al. (2001) suggested that Zn is fixed mainly to the oxy-hydroxides during deposition. The high percentage of Zn in carbonates and the exchangeable fraction confirmed the known ability of this phase to scavenge Zn from the aqueous phase (Isuare et al., 2005). The fractionation results indicate that contamination due to Mn and Zn might pose a potential risk to the water column if the environmental conditions change. The order of zinc metal mobility in different fractions is F2 > F1 > F3 > F5 > F4.

Pb metal was found to have high percent values in the exchangeable and carbonate phases with an average percent value of 42.22% as shown in Tables 4–6 and Fig. 3e. This subsequently leads to the high bioavailability value of the metal leading to toxicity if not properly handled even though it was not detected in over 60% of the sediment samples making it to have no precise regular pattern. However, there was no unique pattern except that fractions bound to Fe-Mn and residual are associated with the least of Pb or not detected while the

exchangeable and carbonates fractions have the highest Pb in association with the geochemical fractions (Fatoki and Awofolu, 2003; Bhujr, 2007).

The order of Pb metal mobility in different fractions is F2 > F1 > F4 > F3 > F5. However, Cd was found to be below detecting levels, limiting all the fractions and suggesting that the sediment was not contaminated with cadmium Tables 4–6.

3.3. Bioavailability and mobility in relation to chemical speciation

Sequential extraction was used to determine the potential mobility and bioavailability of some selected heavy metals. Metal bioavailability factor was found to be $\frac{F1 + F2 + F3}{F1 + F2 + F3 + F4 + F5}$ and the non-bioavailable fractions to be $\frac{F4 + F5}{F1 + F2 + F3 + F4 + F5}$ (Fatoki and Awofolu, 2003). The bioavailable fractions for each metal was estimated to be within the range of: Mn (54.65–87.08), Fe (16.63–88.43) Cu (0.29–10.24), Zn (70.41–89.24), Cd (0–100) and Pb (53.49–83.61), respectively. These metals are classified as bioavailable groups on the basis of their relative mobility and toxicity to the sediment and eventually river water (Okoro et al., 2014).

The bioavailability level of each metal in the sediments for all locations is shown in Table 7. The percentage of Zinc shows a high bioavailability dominance of 89.245% closely followed up by Manganese with a percentage value of 87.08%, while that of lead was found to be 83.33%. Fe and Cu showed low bioavailability and was found to be dominant in the non-bioavailability. This shows that Zn, Mn and Pb metals are more mobile than the other three metals due to their high percentage bioavailability. High percentage of the Zn, Mn and Pb recorded in fractions 1–3 was due to the greater mobility as stated by some researchers (Okoro et al., 2014; Fatoki and Awofolu, 2003). High percentage bioavailability is an indication of poor retention in the residual geochemical form partly due to the old age of the river or saturation (Fatoki and Awofolu, 2003). In general, Mn metal alongside Pb metal was found to be highly bioavailable. Cu metal was found to be least bioavailable in the sediment sample for all locations. The study thus relates the presence of heavy metals that were bioavailable, highly mobile and thus toxic. This subsequently poses potential danger to the water making it unsafe for drinking. The impact of a metal in an



Fig. 3. (a–e) Percentage distribution of Metals in sediments of Olonkoro River in different fractions.

environment is determined by its ease of availability, the higher the level of bioavailability, the higher the impact on its target system (toxicity effect) (Fatoki and Awofolu, 2003).

Coefficient of Correlation (r) is a statistical test and was used to evaluate the strength and weakness relationship between metals in the

study. Significant correlations between the contaminants of Zn and Mn (0.537), could indicate the same or similar source input or similar enrichment mechanism (Nguyen et al., 2009) (Table 8), suggesting that the anthropogenic sources of these metals are closely related in the sediment from Olonkoro River.

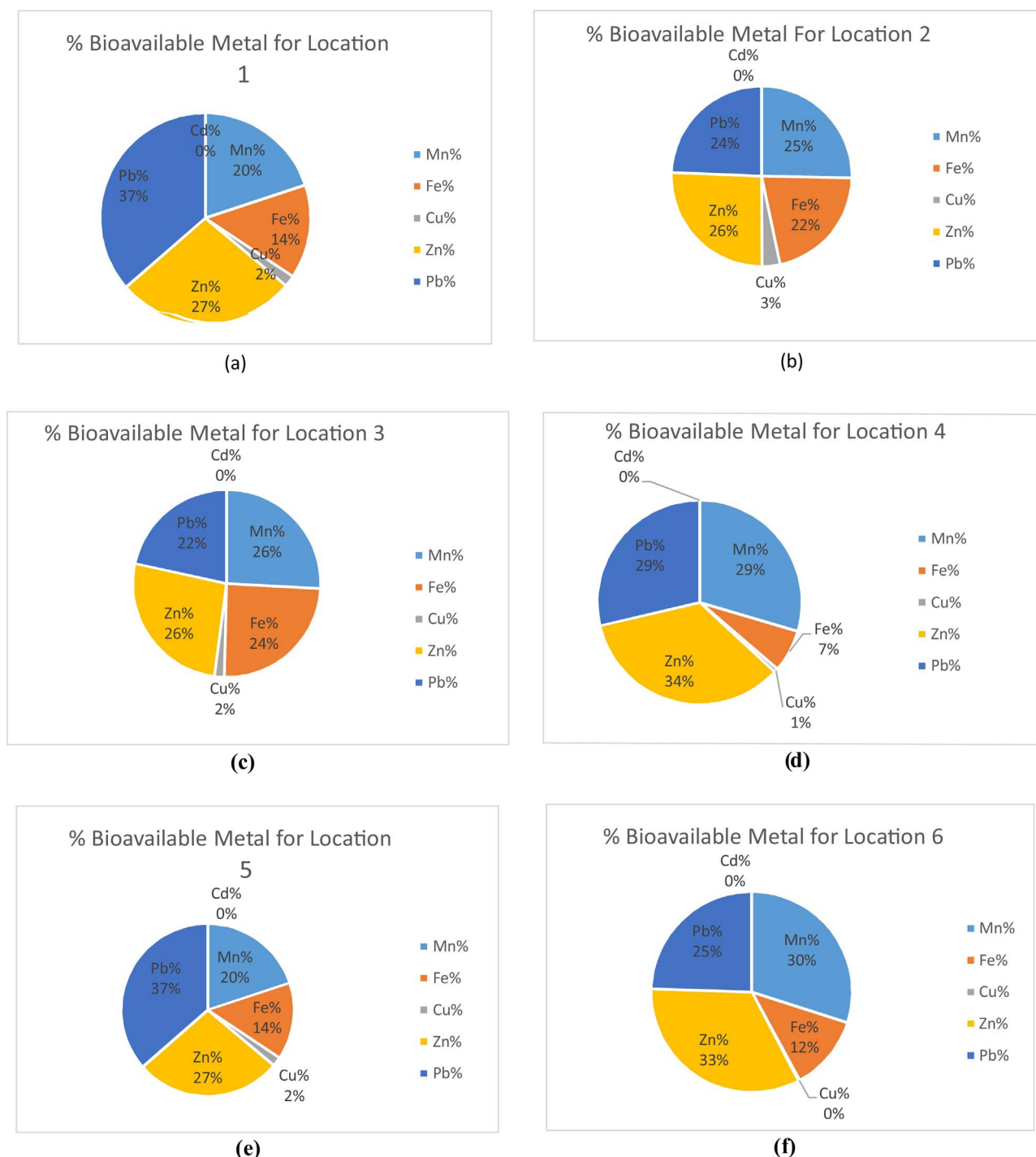


Fig. 4. (a–f) Percentage bioavailability of the metals in sediments samples in all locations across the Olonkoro River in%.

3.4. Conclusion

Sediment samples collected from Olonkoro River, Tede, and Oyo State at the time of sampling were found to be contaminated which also affected the water quality making it unfit for human consumption and other purposes without proper treatment. This is so because with the exception of Cd concentration, all other sediment quality parameters were above the WHO acceptable limits. High concentration levels of Pb, Fe, Zn, Cu and Mn alongside their potentially bioavailable nature in the sediments pose potential toxicity to the aquatic life and human health and this could be due to heavy metal contamination from industrial and domestic sources and other non-point sources that come from residen-

tial and industrial areas in and around the study area. It is thus recommended that Periodic and constant monitoring of Olonkoro River water and sediment samples is desirable to ensure that good quality standards are achieved. Maintenance and sanitation policies should be put in place for both inhabitants and visitors to avoid dumping of waste in the River Olonkoro catchment.

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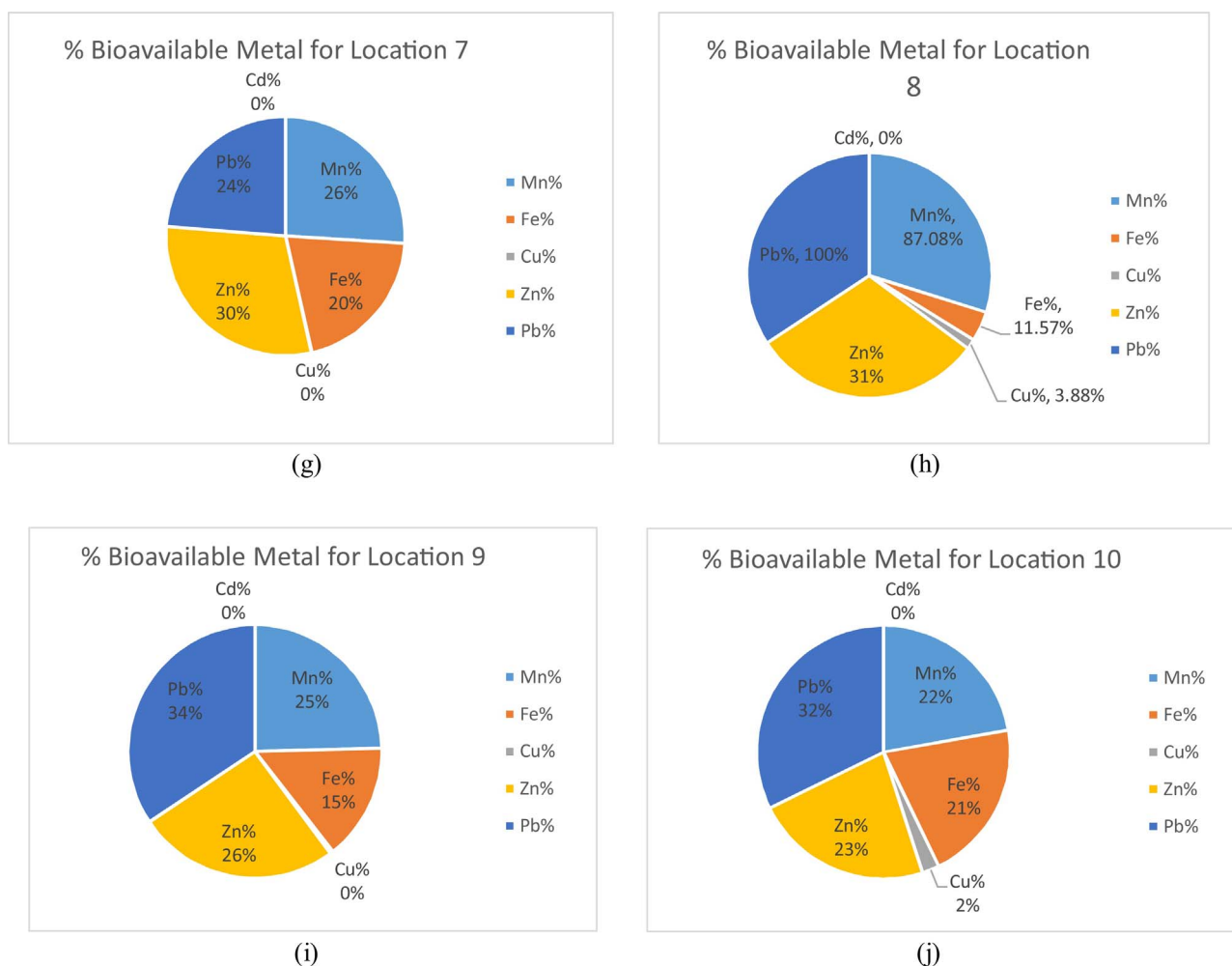


Fig. 4. (continued)

Table 5

The mean metal content (mg/kg) for five step sequential extraction for location P5.

L5	F1	0.21 ± 0.10	17.12 ± 15.00	0.06 ± 0.02	0.82 ± 0.50	0.24 ± 0.20	–	18.45 ± 10.00
	F2	0.22 ± 0.20	9.79 ± 9.00	0.02 ± 0.01	0.77 ± 0.60	0.33 ± 0.20	–	11.13 ± 10.00
	F3	0.09 ± 0.05	3.74 ± 3.50	0.3 ± 0.10	0.36 ± 0.25	–	–	4.49 ± 2.00
	F4	0.07 ± 0.03	7.29 ± 7.00	7.29 ± 6.50	0.26 ± 0.21	–	–	14.91 ± 12.00
	F5	0.27 ± 0.20	39.47 ± 35.00	0.18 ± 0.16	0.38 ± 0.30	–	–	40.3 ± 30.00
	Total metal	0.86 ± 0.50	77.41 ± 75.00	7.85 ± 7.0	2.59 ± 2.00	0.57 ± 0.10	–	–
L6	F1	0.21 ± 0.10	4.22 ± 4.00	0.03 ± 0.01	0.26 ± 0.21	0.22 ± 0.15	–	4.94 ± 3.50
	F2	0.22 ± 0.20	3.63 ± 3.50	–	0.68 ± 0.50	0.01 ± 0.00	–	4.54 ± 4.00
	F3	0.04 ± 0.01	2.45 ± 2.00	–	0.26 ± 0.20	–	–	2.75 ± 2.50
	F4	0.05 ± 0.01	6.36 ± 6.00	6.36 ± 0.02	0.22 ± 0.10	0.2 ± 0.15	–	13.19 ± 12.00
	F5	0.2 ± 0.00	22.36 ± 20.00	0.06 ± 0.02	0.24 ± 0.20	–	–	22.86 ± 20.00
	Total metal	0.72 ± 0.50	39.02 ± 30.01	6.45 ± 6.30	1.66 ± 1.60	0.43 ± 0.25	–	–
L7	F1	0.56 ± 0.20	19.07 ± 19.02	0.02 ± 0.01	0.24 ± 0.20	0.23 ± 0.14	–	20.12 ± 15.00
	F2	0.23 ± 0.10	18.86 ± 15.00	–	1.92 ± 1.00	0.32 ± 0.20	–	21.33 ± 20.00
	F3	0.05 ± 0.01	4.03 ± 2.00	–	0.42 ± 0.30	–	–	4.5 ± 3.0
	F4	0.05 ± 0.02	6.84 ± 3.00	6.84 ± 6.00	0.22 ± 0.20	0.26 ± 0.10	–	14.21 ± 12.00
	F5	0.24 ± 0.15	22.98 ± 22.00	0.08 ± 0.01	0.23 ± 0.15	–	–	23.53 ± 20.00
	Total metal	1.13 ± 1.10	71.78 ± 70.05	6.94 ± 6.20	3.03 ± 3.02	0.81 ± 0.50	–	–
L8	F1	0.47 ± 0.20	2.04 ± 1.02	0.07 ± 0.02	0.9 ± 0.50	0.21 ± 0.10	–	3.69 ± 3.00
	F2	0.59 ± 0.35	0.75 ± 0.65	0.2 ± 0.10	2.12 ± 2.00	0.22 ± 0.15	–	3.88 ± 3.20
	F3	0.26 ± 0.23	2.31 ± 2.00	–	0.38 ± 0.15	–	–	2.95 ± 2.00
	F4	0.23 ± 0.10	6.64 ± 6.40	6.64 ± 6.00	0.23 ± 0.20	–	–	13.74 ± 12.00
	F5	0.23 ± 0.12	32.32 ± 30.10	0.04 ± 0.02	0.18 ± 0.12	–	–	32.77 ± 30.00
	Total metal	1.78 ± 1.50	44.06 ± 40.00	6.95 ± 6.40	3.81 ± 2.50	0.43 ± 0.20	–	–

Table 6

The mean metal content (mg/kg) for five step sequential extraction for location P9 to P10.

L9	F1	0.44 ± 0.30	18.53 ± 10.00	0.04 ± 0.001	0.61 ± 0.55	0.08 ± 0.02	–	19.7 ± 15.00
	F2	0.35 ± 0.25	9.36 ± 9.00	–	0.65 ± 0.60	0.01 ± 0.00	–	10.37 ± 10.20
	F3	0.24 ± 0.20	2.32 ± 2.00	0.02 ± 0.01	0.35 ± 0.20	–	–	2.93 ± 2.00
	F4	0.19 ± 0.10	4.97 ± 4.50	4.97 ± 4.50	0.22 ± 0.15	–	–	10.35 ± 10.10
	F5	0.22 ± 0.15	34.84 ± 32.00	0.07 ± 0.02	0.32 ± 0.20	–	–	35.45 ± 32.02
	Total metal	1.44 ± 0.19	70.02 ± 69.00	5.1 ± 4.50	2.15 ± 2.00	0.09 ± 0.03	–	–
L10	F1	0.37 ± 0.12	1.9 ± 1.50	0.57 ± 0.30	0.5 ± 0.20	–	–	3.34 ± 2.00
	F2	0.41 ± 0.20	0.33 ± 0.20	–	0.56 ± 0.30	0.01 ± 0.00	–	1.31 ± 1.20
	F3	0.22 ± 0.10	2.74 ± 2.50	–	0.32 ± 0.20	–	–	3.28 ± 3.20
	F4	0.21 ± 0.10	7.86 ± 6.50	7.86 ± 7.50	0.25 ± 0.10	–	–	16.18 ± 16.00
	F5	0.24 ± 0.10	21.69 ± 20.00	0.07 ± 0.02	0.33 ± 0.25	–	–	22.33 ± 20.15
	Total metal	1.45 ± 1.20	34.52 ± 30.50	8.5 ± 8.00	1.96 ± 1.50	0.01 ± 0.00	–	–

Key: F1–Exchangeable metal fraction; F2–Carbonate-bound metal fraction; F3–Fe-Mn oxide metal fraction; F4–Organic and sulphide metal; F5–Residual metal fraction.

Table 7

The% Bioavailable and% Non-bioavailable proportions of heavy metals in the sediment.

LOCATIONS	Fraction	Mn	Fe	Cu	Zn	Pb	Cd
1	Bioavailable	65.82	40.82	10.24	80.27	83.33	–
	Non-bioavailable	34.38	59.18	89.76	19.73	16.67	–
2	Bioavailable	75	63.57	9.4	76.3	72.09	–
	Non-bioavailable	25	36.43	90.6	23.7	27.91	–
3	Bioavailable	82.55	78.48	5.27	84.08	68.97	–
	Non-bioavailable	17.45	21.52	94.73	15.92	31.03	–
4	Bioavailable	73.47	16.63	1.53	85.47	71.19	–
	Non-bioavailable	26.53	83.37	98.47	14.53	28.81	–
5	Bioavailable	54.65	39.59	4.84	75.29	100	–
	Non-bioavailable	45.35	60.4	95.16	24.71	–	–
6	Bioavailable	65.28	26.4	0.47	72.29	53.49	–
	Non-bioavailable	34.72	73.6	99.53	27.71	46.51	–
7	Bioavailable	74.34	58.46	0.29	85.15	67.9	–
	Non-bioavailable	25.66	41.54	99.71	14.85	32.1	–
8	Bioavailable	87.08	11.57	3.88	89.24	100	–
	Non-bioavailable	12.92	88.43	96.12	10.76	–	–
9	Bioavailable	71.53	43.14	1.18	74.88	100	–
	Non-bioavailable	28.47	56.86	98.82	25.12	–	–
10	Bioavailable	68.97	63.64	6.71	70.41	100	–
	Non-bioavailable	31.03	36.36	93.29	29.59	–	–

–: (Not Detected)

Table 8

Pearson's correlation coefficient among the selected heavy metals.

		Mn	Fe	Cu	Zn	Pb	Cd
Correlation	Mn	1.000	–0.027	0.255	0.537	–0.446	–
	Fe	–0.027	1.000	0.183	0.048	0.044	–
	Cu	0.255	0.183	1.000	0.019	–0.614	–
	Zn	0.537	0.048	0.019	1.000	0.136	–
	Pb	–0.446	0.044	–0.614	0.136	1.000	–
	Cd	–	–	–	–	–	1.000

Note: *is significant at p < 0.05.

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