

Study of Some Metals Speciation in Bida Municipal Wastes by Sequential Extraction

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Abstract: Sequential extraction was applied to determine the chemical association of some heavy metals in municipal waste in Bida. The results of the study show that competition for the binding phase occurs, and oxidisable fraction was found to be more accessible to heavy metal than all other solid phases. Among the five heavy metals studied in these wastes, the mean of the amount of Pb bound to oxidizable fraction was the highest (102 mg/kg) and the lowest was Cu bound to the residual fraction (4.59 mg/kg). Loading plots obtained from the results of principal components analysis show the data point for Fe and Sn bound to exchangeable fraction clustered. It was observed that the municipal waste was not highly contaminated, with most metal concentrations below the permissible levels for the application to agricultural land as regulated by the US EPA.

Key words: Heavy metals, sequential extraction, speciation, sediment.

Introduction

Management of waste is one of the most important environmental problems today in Nigeria. As urban cities increase in population and become more industrialized, the volume and composition of wastes generated grow and change. This is especially significant for cities in Nigeria, where populations and economies are rapidly expanding, but the infrastructure necessary to manage the ensuing problems is inadequate. At present, infrastructure for waste treatment in Bida is either absent or of poor quality. Municipal and industrial waste treatment systems are insufficient. Industrial solid wastes are disposed together with municipal wastes at poorly designed dumpsites, allowing pollutants to leak into the groundwater and rivers. These dumps in these areas pose risks of contamination by heavy metal pollutants from anthropogenic sources.

In general, the absolute concentration of heavy metal ions in refuse sediment depends on the original metal content of the parent material, any juvenile input of the

metal and the ability of the refuse sediment to retain metals by absorption or precipitation mechanisms. Heavy metal ions in the refuse sediment are always portioned between the various solid phases present: organic matter, oxyhydroxides of iron, aluminium and manganese, carbonates and sulfides (Bolt and Van Riemsdijk, 1987; Gambrell, 1994). The combination of the retaining solid phase and the retention mechanism determines the bioavailability and potential toxicity of heavy metal ion (Ansari et al., 2004; Tessier et al., 1979). The relative importance of any solid phase for retaining a metal depends on the identity and concentration of the metal, the abundance of the solid phase and the controlling parameter of pH of the sediment and the interstitial water affect metal retention in several ways; development of pH dependant change at weakly acidic surface functional groups on organic and inorganic colloids determines the extent of ion exchange reaction (Bolt and Van Riemsdijk, 1987).

In order to assess the potential environmental impacts of materials contaminated with metals, the determination

of total trace and heavy metal content alone is insufficient, as it is the chemical forms (or species) of the metal in the matrix that determine its behaviour in the environment and its mobilization capacity (Gupta et al., 1996; Tisdell and Breslin, 1995; Tack and Verloo, 1993; Rauret et al., 1989; Cottenie and Verloo, 1984). Sequential extraction or metal speciation techniques provide more relevant information (Nathalie et al., 2000).

The Tessier scheme (Tessier et al., 1979) has been widely employed for metal fractionation in soils and sediments. Due to its extensive application on a variety of materials in the past, this method enables a comparison of metal mobility and reactivity between samples, which have similar total metal contents (D'Amore et al., 2005).

With the increasing use of technological products and poor disposal system, this research work has been undertaken to determine using single and sequential procedure, the speciation of copper (Cu), tin (Sn), lead (Pb), manganese (Mn) and iron (Fe) in refuse dump from Bida metropolis, Nigeria.

Materials and Methods

Sample and Sampling Preparation

Municipal solid wastes were collected between 0 and 20 cm depth at twenty-five locations using plastic containers. These waste samples were air-dried at less than 40°C, and were used for determining the mode of occurrence of metals using sequential extraction procedure. The less than 1 mm size fractions from both sets of samples were retained for analysis following gentle grinding to break up aggregates.

Total Metal Analysis

Total metals were determined in samples using an adaptation of an aqua regia digestion method. Duplicates of 1 g of each dried samples were predigested overnight in 15 ml of aqua regia; sample-acid mixture were then digested at 140°C until near dryness (ca. 5 hr). Digests were filtered (Whatman No. 42) into vials and diluted to known volume with deionized water.

The total and metal fractions from sequential extractions were assay using an atomic absorption spectrometer (Model PE-3100). The reported values are the average of these determinations. The relative standard deviation of these values lies within $\pm 5\%$.

Sequential Extraction

The extraction procedure used in this study is mainly based on the work of Tessier et al. (1979). These extractions were carried out as soon as possible following

sample collection, due to the possibility of metal phase changes resulting from sample storage and pretreatment (Förstner, 1993; Rapin et al., 1986). The procedure consisted of the following successive extraction steps:

1. *Exchangeable cations (EXC)*: 1 g of clay sample was extracted for 2 h at 20°C in 20 ml of 1 M ammonium acetate.
2. *Carbonatic fraction (CARB)*: The residue from step 1 was extracted for 24 h at 20°C in 40 ml of 1 M sodium acetate solution at pH 5.
3. *Oxidic fraction (OX)*: The residue from step 2 was extracted in the dark for 24 h at 20°C in 40 ml of 0.2 M ammonium oxalate/oxalic acid solution at pH 3.
4. *Organic fraction (ORG)*: The residue from step 3 was digested for 5 h at 85°C in 10 ml of 30% hydrogen peroxide and the 0.02 M nitric acid at pH 2. After cooling to 20°C, the samples were extracted with 25 ml of acidified ammonium acetate.
5. *Residual fraction (RES)*: The residue from step 4 was extracted with hydrochloric acid (7 ml) and nitric acid (21 ml) (aqua regia) for 2 h at 140°C.

The procedure, with the exception of step 5, was conducted in 50 ml polypropylene centrifuge tubes. The extracts were separated from the solid waste by centrifugation at 5000 rpm for 15 min. and subsequently filtered through 0.45 μm syringe filters. Between each extraction step, the solid waste residue was washed with 10 ml of deionised water. All treatments were carried out in triplicate and the reported values are the average of these determinations. The relative standard deviation of these values lies within $\pm 5\%$. The concentrations of copper (Cu), tin (Sn), lead (Pb), manganese (Mn) and iron (Fe) in the extraction solutions were determined by AAS.

Data Analysis

Principal components analysis was performed using SPSS 11 software.

Results and Discussion

Distribution of the Municipal Solid Waste Matrices and Heavy Metals

The mean, minimum, maximum and standard deviations of the amount of five heavy metals bound to municipal waste matrices are summarized in Table 1. The mean of the exchangeable, acid extractable, reduceable, oxidisable and residual fractions are 33.02, 42.46, 43.67, 48.27 and

20.95 mg/kg respectively. This result indicates that oxidisable fraction provided more binding sites for heavy metals than other phases and that competition for the binding phase occurs for acid exchangeable, reduceable and oxidisable since their mean concentrations are within the same range. As could be seen from Table 2, it is generally observed that the sum of the five metal fractions obtained from the sequential extraction procedure was higher than the total metal contents following total acid digestion. This difference was particularly pronounced for all the heavy metals. This had also been observed by Paré et al. (1999); Scheckel and Ryan (2004) and may be due to incomplete digestion with the mixed acid compared to the slow and increasingly stronger attack by the reagents of the sequential extraction. It was also observed that the standard deviation of most binding phases of the five heavy metals were fairly high; the standard deviations for Cu and Pb bound to exchangeable and residual phases were even higher than their respective means. This implies that the spatial distribution of each

heavy metal bound to the waste matrices varies remarkably with different sampling sites.

Table 1: Summary Results of the Municipal Waste Matrices

	<i>Minimum</i>	<i>Maximum</i>	<i>Mean</i>	<i>Std. deviation</i>
Exchangeable	2.9	135	33.02	31.46
Acid extractable	1.4	152	42.46	45.56
Reduceable	2.9	152	43.67	42.84
Oxidisable	4.3	188	48.27	44.96
Residual	2.43	148.04	20.95	28.34

Among the five heavy metals studied in these wastes, the mean of the amount of Pb bound to oxidizable or organic fraction was the highest (102 mg/kg). The mean of the amount of Mn (64.00 mg/kg) was the next in this oxidisable fraction. Mn bound to acid extractable is the second highest (68.20 mg/kg) to lead. However the lowest binding phase was noted for Cu bound to the residual

Table 2: Summary of Values of Metal Fractions, Sums of Fractions and Total Heavy Metal Contents in Municipal Waste (mg/kg)

		<i>F1</i>	<i>F2</i>	<i>F3</i>	<i>F4</i>	<i>F5</i>	<i>Sum</i>	<i>Total</i>
Cu	Mean	10.52	5.12	4.86	25.44	4.59	50.53	47.14
	(% ^a)	20.82	10.86	9.62	53.97	9.08	100.00	
	Minimum	2.9	1.4	2.9	4.3	2.43		12.58
	Maximum	32.5	11.4	7.1	57.5	7.92		104.04
	Std. Deviation	12.51	4.23	1.6	20.68	2.51		21.44
Pb	Mean	42.20	68.20	84.30	102.49	50.04	347.23	155.54
	(% ^a)	12.15	19.64	24.28	29.52	14.41	100.00	
	Minimum	25	35	35.5	57	16.4		54.23
	Maximum	57.00	152.00	152.00	188.00	148.04		422.36
	Std. Deviation	12.38	49.22	56.68	52.01	55.13		156.5
Sn	Mean	80.90	42.00	42.50	34.00	19.94	219.34	67.01
	(% ^a)	36.88	19.15	19.38	15.50	29.76	100.00	
	Minimum	57.50	20.00	20.00	20.00	15.50		59.3
	Maximum	135.00	57.50	77.50	37.50	22.95		74.15
	Std. Deviation	31.81	15.85	24.94	7.83	2.85		11.84
Fe	Mean	8.00	10.00	14.00	15.40	4.74	52.14	18.92
	(% ^a)	15.34	19.18	26.85	29.54	9.09	100.00	
	Minimum	5.00	5.00	5.00	5.00	3.50		15.35
	Maximum	20.00	20.00	20.00	22.00	6.20		23.69
	Std. Deviation	6.71	7.07	8.22	6.58	1.31		8.45
Mn	Mean	23.50	87.00	72.70	64.00	25.46	272.66	92.72
	(% ^a)	8.62	31.91	26.66	23.47	9.34	100.00	
	Minimum	17.50	35.00	20.00	17.50	19.05		76.04
	Maximum	35.00	150.00	100.00	150.00	29.75		116.3
	Std. Deviation	8.40	57.84	31.69	51.50	4.16		21.38

F1= Exchangeable, F2 = Acid extractable, F3 = Reduceable, F4 = Oxidisable, F5 = Residual, ^aRatio percentage of each fraction to sum of total extraction, Sum = F1+F2+F3+F4+F5

fraction (4.59 mg/kg). Based on the ratio (expressed in percentage) of the binding amount to total extractable amount as seen in Table 1, Cu was easily bound to oxidisable or organic fraction (53.97% of the total extractable amount of Cu); Pb had high affinity for oxidizable or organic (29.52% of the total extractable amount of Pb) and reduceable (24.28% of the total extractable amount of Pb) fractions; Sn was majorly bound to exchangeable (36.88% of the total extractable amount of Sn) and reduceable (29.76% of the total extractable amount of Sn). The binding behaviour of Fe showed great affinity for reduceable (26.85% of the total extractable amount of Fe) and oxidizable or organic (29.54% of the total extractable amount of Fe) fractions; Mn had highest affinity for acid extractable (31.91% of the total extractable amount of Mn) followed by reduceable (26.66% of the total extractable amount of Mn) and then oxidisable or organic (23.47% of the total extractable amount of Mn) fractions. The binding behaviour of Cu, Pb, Fe and Mn with organic phase is similar to the results obtained by Hickey and Kittrick (1984); Boughriet et al. (1992); Calmano et al. (1993) and Juan and Sosa (1994). Kuang-chung yu et al. (2001) and D'Amore et al. (2005) also found that some heavy metals are mainly bound to organic matter contained in sediments matrices. This observed heavy metal affinity is contradictory to the findings of Nathalie et al. (2000) and Qiao and Ho (1997) who reported that metals in sludge are generally found in very stable, insoluble forms.

Correlation between Any Two Heavy Metal Binding Phases

A principal component analysis (PCA) was done to simplify the variables to only two principal factors for exploring the correlations between any two heavy metal binding fractions. Table 3 shows the cumulative variance of the five heavy metals bound to exchangeable, acid extractable, reduceable, oxidisable and residual sediment matrices depicted by factor 1 and factor 2 together that is 72.30, 94.35, 82.19, 81.39 and 87.01% respectively. This indicates that the two principal factors can be used to interpret properly the binding behaviour of the five heavy metals in association with the fine sediments phases.

Loading plots of factor 1 and factor 2 obtained from the results of PCA are shown in Figure 1. Figure 1 (a) shows that the data point for Fe and Sn bound to exchangeable fraction cluster together indicate that despite different sampling sites the binding behaviour of these two metals were in association in exchangeable fraction. By performing PCA and cluster analysis (CA), Tsai et al. (1998) obtained significant correlations

Table 3: Principal Component Analysis of the Heavy Metal Binding Fractions

<i>Phase</i>	<i>Factor</i>	<i>Eigenvalues</i>	<i>% of variance</i>	<i>Cumulative %</i>
Exchangeable	1	2.21	44.22	44.22
	2	1.40	28.08	72.30
Acid Extractable	1	3.32	66.31	66.31
	2	1.40	28.04	94.35
Reduceable	1	2.93	58.57	58.57
	2	1.18	23.62	82.19
Oxidisable	1	2.96	59.23	59.23
	2	1.11	22.16	81.39
Residual	1	3.14	62.85	62.85
	2	1.21	24.16	87.01

between Fe and Sn binding fractions. They claimed that the two metals might be discharged from the same pollution source. The data points for Pb, Mn and Cu were far from Fe and did not cluster implying that their correlation is insignificant in exchangeable fraction. It can be seen from Figure 1 (b, c, d, e) that there is no strong clustering together of any heavy metals. To interpret the significant correlations between any two heavy metal binding fractions, Tessier et al. (1985) also pointed out that under the same environmental conditions, the most important influential environmental factors are stability constants of heavy metal complexation reaction within the waste and the source of the input of heavy metal into the waste.

Municipal Waste and Agricultural Land

It was observed that the municipal waste was not highly contaminated, and most metal concentrations are below the permissible levels for the application to agricultural land as regulated by the US EPA. Table 4 lists the 'high quality' pollutant concentration limits and annual pollutant loading rates promulgated by the US EPA (Walsh, 1995). If a sludge/waste meets these concentration limits, it can be applied to agricultural land provided that the application rate does not exceed the annual pollutant-loading rate.

Table 4: U.S. EPA Land Application Pollutant Limits (mg kg⁻¹)

<i>Metal</i>	<i>High quality pollution concentration limits</i>	<i>Ceiling concentration limits</i>
Cu	1,500	4,300
Zn	2,800	7,500
Mn	—	—
Ni	420	420
Pb	300	840

(Walsh, 1995)

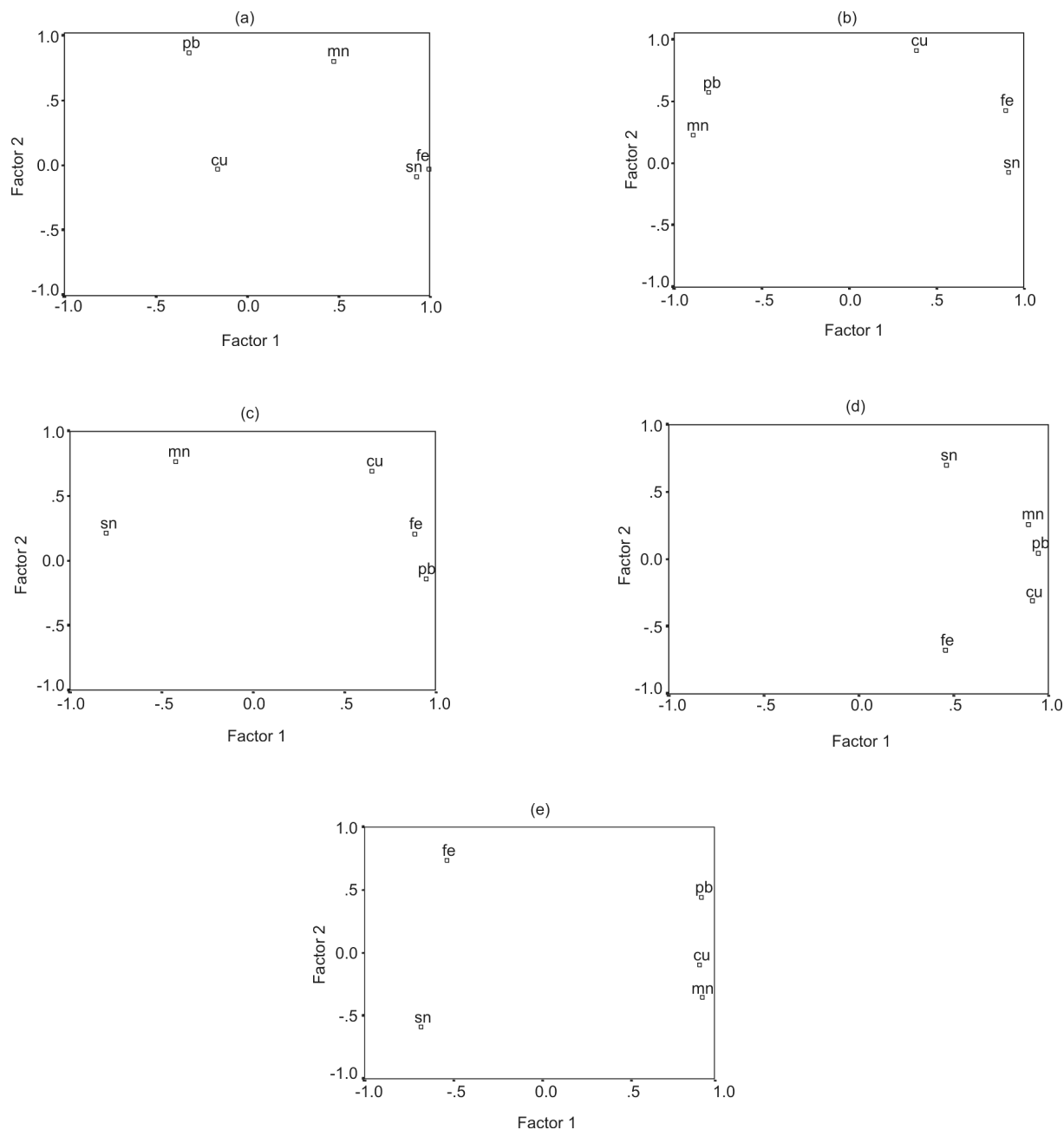


Figure 1: Loading plots of heavy metal binding fractions by PCA (a) bound to exchangeable (b) bound to acid extractable (c) bound to reduceable (d) bound to oxidisable (e) bound to residual.

Conclusion

By analyzing these sets of data obtained from the municipal waste, chemical fractionation suggested that most of the metals were in oxidisable form. In addition, mean total metal concentrations were not above limits for land application. For this reason, there is unlikely to be any significant impact on agricultural lands.

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