

Chemical speciation and Distribution of heavy metals in soil of waste dump sites at various automobile mechanic workshops of South-south, Nigeria

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Abstract. Distribution and determination of chemical form of heavy metals in soil of automobile mechanic waste dump sites of South-South, Nigeria were investigated. Sequential extraction was used to fractionate heavy metals from the samples into five operationally defined groups; exchangeable fraction, fraction bound to carbonate, Fe/Mn oxide bound fraction, fraction bound to organic matter and residual fraction. Analysis of the metals was carried out by UNICAM SOLAAR 32 atomic absorption spectrophotometer. Zn (2.661; 1.831; 1.035 µg/g) was predominantly associated with Fe/Mn oxide for the Sites A, B and C respectively. The carbonate fraction of Pb represents more than 25% of the total Pb found in the soils. A major portion of Cu (1.716, 0.280, 0.082 µg/g) was associated with organic fractions for the three sites respectively, whereas Cd (0.293, 0.335, 0.305 µg/g) was associated with exchangeable for the three sites respectively. The results were interpreted in terms of the environmental mobility and bioavailability of the metals. However, Pb (96.658, 98.691 and 100 %) was more mobile and bioavailable compared to the other metals studied.

Keywords: Speciation, metals, sequential extraction, bioavailability

1 INTRODUCTION

Chemical speciation is an important aspect of environmental analysis and research. The bioavailability and toxicity of an element depends on its species, binding state, chemical form, environmental factors and soil properties like pH, organic matter content etc. heavy metals speciation is of great importance in recent years, since the toxicity of the metals differs dramatically with the wide range of its organic and inorganic chemical forms (Vahter and Concha, 2001; Thomas et al., 2001).

The metal ions in polluted soils are tied up as coordinate compounds by the naturally occurring ligands and chelating agents such as humic substances, sulfide, pesticide, and EDTA. These metal coordinate interactions would affect the biogeochemical pathways taken by the metal such as its bioavailability and toxicity to organisms, and adsorption/desorption reactions on suspended materials.

Jiang et al., 2004 reported that many soils are polluted with heavy metals due to the use of sludge or municipal compost, pesticides, fertilizers and emission from municipal waste incinerators, car exhaust, residues from metalliferous mines and smelting industries.

Heavy metal speciation, in this context is taken to mean the fraction of the total content in exchangeable (bound to exchangeable site of clay minerals), acid extractable (bound to carbonates and hydroxides), reducible (bound to Fe/Mn oxides), oxidizable (bound to organic matter/sulfides) and residual form (bound to clay minerals).

In this study, the distribution and chemical speciation of heavy metals (Pb, Cd, Zn and Cu) in soil of automobile mechanic waste dump sites in South-south, Nigeria were determined. The mobility factors were also determined.

2 MATERIAL AND METHODS

Sample collection and Preparation.

The soil samples were collected in March/April, 2011 from three different sampling points at 0 to 20 cm depth using soil auger in Rivers State, Nigeria. The samples were air dried and grounded to fairly uniform size and sieved with 2 mm sieve. The samples were stored in a clean polyethene bag and labeled A, B and C respectively. Where A, B, and C represents waste dump sites in automobile mechanic workshops at Diobu (Odu street), Rumuola, Choba (East-west road) respectively.

Heavy metal fractionation.

The conventional method developed by Tessier, et al., (1979) was followed for the sequential extraction. The sequential extraction process was accomplished in five steps.

Sequential extraction procedure:

Extractions were carried out on 1.0 g aliquots of soil and involved the five following steps (Tessier et al., 1979, Tessier et al., 1980):

1. Exchangeable fraction: the sample was placed in contact with a high ionic strength solution, in order to release the so-called exchangeable fraction of metal traces by altering the sorption-desorption superficial processes. In this step 8 ml of 1 N MgCl_2 were added to the sample and the suspension was shaken for 1 h.
2. Fraction bound to carbonates: the fraction of metal traces bound to carbonates, present in the sample, may be selectively labilised by varying the pH of the sample itself with a slightly acidic extraction solution. 8 ml of 1 M of CH_3COONa , plus CH_3COOH (pH 5) were added to the residue obtained from the first extraction, and the suspension was shaken for 5 h.
3. Fraction bound to iron and manganese oxides: this fraction may be labilised in anoxic reducing conditions. Therefore, 20 ml of 0.04 M $\text{NH}_2\text{OH}/\text{HCl}$ in 25% CH_3COOH were added to the residue and the suspension was shaken for 6 h at the temperature of $96 \pm 3^\circ\text{C}$.
4. Fraction bound to organic matter and to sulphides: this fraction can be released by treating the sample with an oxidising agent. 3 ml of 0.02 N HNO_3 and 5 ml of 30% H_2O_2 were added to the residue obtained from the third extraction, and the suspension was shaken for 5 h at the temperature of $85 \pm 2^\circ\text{C}$. After cooling, 5 ml of 3.2 M $\text{CH}_3\text{COONH}_4$ were added to the suspension, which was diluted to 20 ml with HPW and shaken for 30 min.

5. Residual fraction: it is the metal fraction present as scatter within the crystal lattice of the rocks and minerals that constitute the soil. It was calculated from the difference between the concentration of total metal and the sum of the first four fractions.

3 RESULTS AND DISCUSSION

Table 1. Cadmium speciation of soils of automobile mechanic waste dump sites

FRACTIONS	A (µg/g)	%fraction A	B (µg/g)	%fraction B	C (µg/g)	%fraction C
F1	0.293	62.473	0.335	57.858	0.305	59.687
F2	0.131	27.932	0.135	23.316	0.145	28.376
F3	0.028	5.97	0.085	14.68	0.061	11.937
F4	ND	0	0.019	3.282	ND	0
F5	0.017	3.625	0.005	0.864	ND	0
SUM	0.469	100	0.579	100	0.511	100

1=exchangeable, F2=carbonate bound, F3=Fe/Mn oxide bound, F4= bound to organic matter and sulphide, F5=residual fraction, ND=not detected, sampling sites (A, B, C).

Table 2. Copper speciation of soils of automobile mechanic waste dump sites

FRACTIONS	A (µg/g)	%fraction A	B (µg/g)	%fraction B	C (µg/g)	%fraction C
F1	0.061	1.778	0.004	0.582	0.082	19.759
F2	0.327	9.534	0.123	17.904	0.013	3.133
F3	0.436	12.711	0.081	11.790	0.016	3.855
F4	1.716	50.029	0.28	40.757	0.194	46.747
F5	0.89	25.948	0.199	28.967	0.11	26.506
SUM	3.430	100.000	0.687	100.000	0.415	100.000

F1=exchangeable, F2=carbonate bound, F3=Fe/Mn oxide bound, F4= bound to organic matter and sulphide, F5=residual fraction, ND=not detected, sampling sites (A, B, C).

Table 3. Lead speciation of soils of automobile mechanic waste dump sites

FRACTIONS	A (µg/g)	% A	B (µg/g)	% B	C (µg/g)	% C
F1	2.426	37.363	2.255	42.781	2.119	74.013
F2	0.209	3.219	0.647	12.275	0.521	18.198
F3	1.987	30.602	1.721	32.650	0.223	7.789
F4	1.654	25.474	0.579	10.985	ND	0.000
F5	0.217	3.342	0.069	1.309	ND	0.000
SUM	6.493	100.000	5.271	100.000	2.863	100.000

F1=exchangeable, F2=carbonate bound, F3=Fe/Mn oxide bound, F4= bound to organic matter and sulphide, F5=residual fraction, ND=not detected, sampling sites (A, B, C).

Table 4. Zinc speciation of soils of automobile mechanic waste dump sites

FRACTIONS	A (µg/g)	% A	B (µg/g)	% B	C (µg/g)	% C
F1	0.37	5.055	0.51	11.143	0.343	12.973
F2	1.777	24.279	0.731	15.971	0.384	14.523
F3	2.661	36.357	1.831	40.004	1.035	39.145
F4	1.79	24.457	1.179	25.759	0.696	26.324
F5	0.721	9.851	0.326	7.123	0.186	7.035
SUM	7.319	100.000	4.577	100.000	2.644	100.000

F1=exchangeable, F2=carbonate bound, F3=Fe/Mn oxide bound, F4= bound to organic matter and sulphide, F5=residual fraction, ND=not detected, sampling sites (A, B, C).

Table 5. Mobility factor (%), pH and Temperature for the metals studied.

SITES	MOBILITY FACTOR (%)					
	Cd	Cu	Pb	Zn	pH	Temp(°C)
A	96.375	74.052	96.658	90.149	8.34	26.4
B	99.136	71.033	98.691	92.877	8.14	26.4
C	100	73.494	100	92.965	6.67	26.6

The results obtained in table 1, showed that concentration of Cd ranged from 0.017 – 0.293 µg/g with mean value of 0.117 µg/g; 0.005 – 0.335 µg/g with mean value of 0.116 µg/g and 0.061 – 0.335 µg/g with mean value of 0.180 µg/g for sample A, B, and C respectively. The result reveals that Cd was extracted more at F1 and lower at F5 for all the samples with F4 not detected for sample A and C.

The concentration of Cu ranged from 0.061 – 1.716 µg/g with mean value of 0.686 µg/g; 0.004 – 0.280 µg/g with mean value of 0.137 µg/g and 0.013 – 0.194 µg/g with mean value 0.083 µg/g for sample A, B and C respectively (table 2.). Cu was extracted more at F4 in sample A, B and C while F1 was the least. However site A has higher concentration of Cu followed by C and B.

Lead has values ranging from 0.217 – 5.209 µg/g with mean value of 2.699 µg/g; 0.069 – 2.255 µg/g with a mean value of 1.054 µg/g and 0.223 – 2.119 µg/g with mean value 0.954 µg/g for site A, B and C respectively (table 3). The highest value of Pb was extracted at F2 for sample A and F1 for sample B and C.

Zinc concentration studied ranged from 0.370 – 2.661 µg/g with a mean value of 1.464 µg/g; 0.251 – 1.831 µg/g with a mean value of 0.864 µg/g and 0.186 – 1.035 µg/g with mean value of 0.529 µg/g for sample A, B and C respectively (table 4). From the results, it was observed that the concentration of the metals were higher at site A and lower in B and C. the low value may be attributed to lower anthropogenic activities around the studied area.

Heavy metal speciation:

The distribution of metals in the samples studied area generally followed the order below for the various metals; Cd: F1 > F2 > F3 > F5 > F4, Cu: F4 > F5 > F3 > F2 > F1, Pb: F1 > F3 > F4 > F5 > F2, Zn: F3 > F4 > F2 > F5 > F1; Cd: F1 > F2 > F3 > F4 > F5, Cu: F4 > F5 > F2 > F3 > F1, Pb: F1 > F3 > F2 > F4 > F5, Zn: F3 > F4 > F2 > F1 > F5 and Cd: F1 > F2 > F3, Cu: F4 > F5 > F1 > F3 > F2, Pb: F1 > F2 > F3, Zn: F3 > F4 > F2 > F1 > F5 for sample A, B and C respectively.

The study of the distribution of the metals revealed that all the metals are associated with different phase. Zn is mostly abundant bound (36.357%, 40.004% and 39.145%) to Iron and Manganese oxides for sample A, B and C respectively (table 4). Abundance of Zn in other fractions was low. Zn in this environment was more mobile than the metals that were mostly abundant in the Residual fraction. This is in agreement with Zerbe et al., (1999).and Fagbote and Olanipekun (2010). The residual phase represents metal largely embedded in the crystal lattice of the soil fraction and should not be available for remobilization except under very harsh considerations.

The results of sequential extraction in this study revealed that copper is mostly abundantly bound to organic matters; 50.02%, 40.76% and 46.75% for sample A, B and C respectively (table 2). Copper can easily complex with organic matters because of high formation of organic-Cu compounds (Haung et al., 2007). Heavy metals with high abundance in the phase bound to Organic matter are more available than heavy metals in the Residual fraction. The organic phase is relatively stable in nature but can be mobilized under strong oxidizing conditions due to degradation of organic matter (Tessier et al., 1979; Haung et al., 2007).

Cd and Pb are distributed more at the exchangeable phase in the entire sample with the fractions; 62.47%, 57.85% and 59.69%, Cd; 37.36, 42.78% and 74.01%, Pb for sample A, B and C respectively (table 1 and 3). High levels in the exchangeable, acid soluble and easily reducible fractions may indicate pollution from anthropogenic origin (Mesuere et al., 1991; Hung et al., 1993). These heavy metals, as shown in table 1 and 3 had the lowest abundance in the Residual fraction as follows: Cd – 3.6%, 0.86%, and 0%; Pb – 3.34%, 1.31% and 0% for A, B and C respectively. This did not agree with Ramrez et al. (2005) and Fagbote and Olanipekun (2010) who reported that Cd, Fe, Mn, Ni and Pb were mostly associated with the Residual phase. Metals present in the Residual fraction are a measure of the degree of environmental pollution. The higher the metals present in this fraction, the lower the degree of pollution and verse versa (Banat, 2001). In this study it was found that the percentage of Cd and Pb present in the residual fraction is the lowest which indicate that the samples are highly polluted with Cd and Pb.

Mobility of Cd, Cu, Pb, and Zn in the samples was assessed on the basis of absolute and relative content of fraction weakly bound to soil components (Kabala and Singh, 2001). The potential mobility of a metal can be assessed by adding up the results of the Exchangeable phase, Carbonate phase, Fe-Mn oxide phase and organic phase of that metal (Haung et al., 2007).The mobility factor gave value not higher than 75% (table 5) for Cu, which is signified high stability of Cu in the samples. The mobility factor of Pb increased from 96.658 % to 100%. This is as a result of relatively high liability and biological availability of Pb in the samples. High abundance of Zn bound to Iron and Manganese oxides accounts for the high potential mobility of Zn. Cu has the lowest potential mobility (71.033 to 74.052%) of all the heavy metals in all the metal, probably due to higher decomposition and decay of organic matter in the sample therefore, less formation of organic-Cu compounds.

The results of this study suggest that the mobility and availability of the metals are in the following order: Pb>Cd>Zn>Cu; Cd>Pb>Zn>Cu and Pb=Cd>Zn>Cu for A, B and C respectively. High Average Potential Mobility indicates high reduction in concentration soil.

4 CONCLUSION

The speciation of heavy metals with selective extracting agents gives additional information about the fundamental reactions governing the behaviors of the metals in the soils.

Anthropogenic inputs of Cd were primarily in the exchangeable and carbonate fractions. Inputs of Cu and Pb appeared on the Fe/Mn Oxides forms but predominantly in organic and carbonate fractions respectively. Zn was found in Fe/Mn oxides, organic and carbonate fractions. The distribution of the metals in the various fractions confirms differences in mobility. Of the metals studied, Cd appeared to be the most readily solubilized, thus, making the metal the most potentially bioavailable. This may posed a threat as Cd is transferred into the food chain from soil contaminated by cadmium.

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