



## **Speciation of Heavy Metal (Cd and Pb) of some Dumpsites Soil in Lagos State, Nigeria Using Atomic Absorption Spectrophotometry**

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### **ABSTRACT**

*The speciation of metals in environmental samples is a serious factor in appraising the potential environmental impacts, before their disposal. The distribution and speciation pattern of toxic heavy metals in dumpsites soil samples collected randomly from three sites for a period of five weeks between the months of October and November, 2006 were subjected to stepwise sequential extraction method. The five step extraction procedure previously proposed by stone was used with modification to systematically study the speciation of cadmium and lead in dumpsite soil. The extracts were analyzed for heavy metal, using atomic absorption spectrophotometry (AAS). The concentrations of solubilized fraction profile for Cd and Pb in the solid samples were from 1.20 and 1.60, 3.00 and 7.20, 1.47 and 2.10 ( $\mu\text{g}/\text{kg}$ ): from Ojota, Oke-Afa and Solous respectively. Conversely, the unsolubilized fractions of Cd and Pb in the soil samples showed a profile of 8.40 Pb and 2.70  $\mu\text{g}/\text{kg}$  Cd for Ojota, 2.40 Pb and 1.90  $\mu\text{g}/\text{kg}$  Cd for Solous while 13.60  $\mu\text{g}/\text{kg}$  was obtained for Pb and Cd was not detected in Oke-Afa soil sample. The pH value ranged from 7.14 -7.68 with Ojota soil sample recording the highest value of 7.68 while the moisture content value of the soil samples ranged from 17.35-47.36% respectively.*

**Keyword:** Bioaccumulation, sequential extraction, speciation, dumpsites, Heavy metal, soil.

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### **INTRODUCTION**

In recent years, concerns over the possible health and ecological effects of the accumulation of heavy metals contaminants in the soil have prompted numerous surveys [1]. Metal bioaccumulation is a major route through which increased levels of the pollutants are transferred across food chain web creating public health problems wherever man is involved in the food chain [2]. Several reports have also confirmed that heavy metal can adversely affect metal and

neurological functions as well as induced impairment in endocrine and immune system [3] The presence of heavy metals such as Pb and Cd in the environment has been a source of worry to environmentalists, government agencies and health practitioners and this is mainly due to their health implications since they are non-essential metal and of no benefit to human [4-5]. The presence of these metals in the ecosystem has far reaching implication directly to the soil and indirectly to man. Data are available for soil from environment such as dumpsite, industrialized cities, highway roadsides, rural villages in old mining area and agricultural land for crops or grazing [6] The determination of total heavy metal content used previously does not provide useful information about the risks of bioavailability; it takes no account of the different chemical forms, the capacity for remobilization, the behavior of the metals in the environment and the association of the metal likely to result from wide variety of potential contaminants [7]. Sources such as sewage sludge application, industrial emission from smelters mining soils, particulate from car exhaust has been reported [8-10].

Heavy metals usually occur in soil at low concentration as a result of weathering and other pedogenic processes acting as the parent materials on which the soil develops. The natural occurrence of heavy metals varies between rock types and certain bed-rocks which provide exceptionally high metal concentration to overlying soils. Soils are clearly of enormous environmental importance, being the media that support virtually all plants life; hence their potential for environmental pollution requires attention [11-12].

While soils are important sinks for heavy metals, they can also release them into the ecosystem. It is therefore important to understand the content, chemistry and geology of heavy metals in soil as well as the chemical forms. However, the determination of specific chemical species or binding forms is difficult and often virtually impossible. For this reason, sequential extraction procedures are commonly applied because they provide information about the fractionation of metals in the different lattices of the solid sample, which is a good compromise method that gives information on the environmental contamination [13-14]. Polluted soils constitute major environmental problems and therefore are subjected to detailed risk assessment and management studies. In this paper, soil samples collected from three different dumping site located in Ojota, Oke Afa and Solous Lagos were examined to systematically study the speciation of cadmium and lead in dumpsite soil which allows a distinction to be made between residual metals (insoluble forms) and metal bound to organic matter, iron and manganese oxide, carbonate and exchangeable (soluble forms). This evaluation gives a relative distribution of Cd and Pb fraction in the soluble (bioavailable) and insoluble (non-bioavailable form) using AAS to assess their potential environmental impacts.

## MATERIALS AND METHODS

### Sampling

The soil samples were collected randomly from various places. After collection of the 5-8 individual samples from various points they were mixed together and one average was compiled for the analysis. The samples were collected once a week between the months of October and November 2006 from the three different sites:

The sampling sites were designated as A,B, and C for soil sample from Ojota, Oke-Afa (along Isolo road )and Solous dumpsite(along LASU Ojo road).The samples were collected with the aid of a soil auger which was screwed down and pulled out from the depth of 15 cm and stored in a polythene bag prior to analysis following the procedure of Adeniyi et al 2004.

The samples (2g each) were dried at 55 °C for 5 days to constant weight to remove moisture, ground in an acid-washed agate mortar to reduce particle size and stored in polyethylene containers. The extraction was carried out with an initial mass of 2.0 g oven dried sample. Metal contents were determined using 304 u/c Atomic Absorption Spectrometer.

The conventional method earlier reported [15-17] was followed for the sequential extraction.

- (i) Exchangeable About 2.0g from each samples were extracted at room temperature with 8 mL of 1M magnesium chloride with continuous agitation for 1 hours at pH 7.0
- (ii) Acid extractable: Residue from above step (i) was leached at room temperature with 8 mL of 1 M of sodium acetate (NaOAc) (pH 5 adjusted with HOAc) with continuous agitation for 2 h.
- (iii) Reducible: Residue from (ii) was extracted with 10 mL of 0.1 M hydroxylamine hydrochloride (NH<sub>2</sub>OH.HCl) in 25 % (v/v) HOAc agitated for 1h (bound to Fe-Mn Oxide, C)
- (iv) Oxidizable: To the residue from (iii) were added 3 mL of 0.02 M nitric acid (HNO<sub>3</sub>) and 5 mL at pH 2, heated at 85 °C for 1 h with continuous agitation for 5 h. and centrifuged.
- (v) Residual: Residue from (iv) was digested with 8 mL of aqua regia (HCl and HNO<sub>3</sub>, 3:1 v/v) and heated to dryness respectively.

About 30 mL of distilled water was added to the residue, warmed and allowed to cool and filtered with ashless whatman 40 filter paper. The resulting solutions were analyzed with flame atomic absorption spectrophotometry, Buck 304 u/c with air acetylene flame for determination of Pb and Cd respectively.

## RESULTS AND DISCUSSION

The result presented in Table 1 -3 shows Cd and Pb concentration in the extracts A – E of the samples. In general, the samples have higher concentration of Pb but relatively lower concentration of Cd. The soluble species are the arithmetic sum of fraction A-D while fraction E represents the insoluble species.

**Table 1 (A) concentration of solubilized and unsolubilized fraction of Cd and Pb in soil sample from Ojota dumpsite (µg/kg)**

Fraction	Cd	Pb
A	0.20	18.00
B	ND	4.20
C	1.00	ND
D	ND	ND
E	8.40	7.20
<b>Sf(A-D)</b>	<b>1.20</b>	<b>22.20</b>
<b>Usf(E)</b>	<b>8.40</b>	<b>7.20</b>

*Sf = solubilized fraction, ND = not detected, Usf = unsolubilized fraction*

**Table 2: (B) ( $\mu\text{g}/\text{kg}$ ) Concentration of solubilized and unsolubilized fraction of Cd and Pb in soil sample from Oke-Afa Dumpsite**

Fraction	Cd	Pb
A	1.37	1.37
B	1.50	5.80
C	1.40	ND
D	ND	ND
E	ND	13.60
<b>Sf(A-D)</b>	<b>4.27</b>	<b>7.17</b>
<b>Usf(E)</b>	<b>ND</b>	<b>13.60</b>

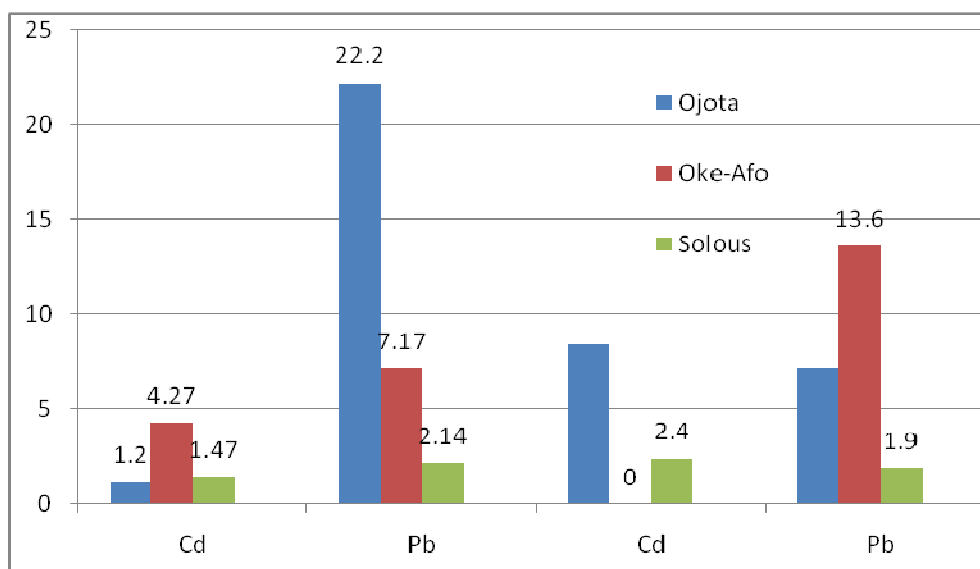
*Sf = solubilized fraction, ND = not detected, Usf = unsolubilized fraction*

**Table 3 (C) ( $\mu\text{g}/\text{kg}$ ) Concentration of solubilized and unsolubilized fraction of Cd and Pb in soil sample from Solous dumpsite**

Fraction	Cd	Pb
A	0.07	0.14
B	0.8	0.58
C	1.30	0.64
D	0.02	0.78
E	2.40	1.90
<b>Sf(A-D)</b>	<b>1.47</b>	<b>2.14</b>
<b>Usf(E)</b>	<b>2.40</b>	<b>1.90</b>

*Sf = solubilized fraction, Usf = Unsolubilized fraction*

**Figure 1. Bar chart showing the comparison of the concentration of solubilized and unsolubilized fraction of Cd and Pb from the three dumpsite**



Among the several groups of element present in dumpsite soil, heavy metals are certainly the most critical and at the same time the most contentious one as those responsible for pollution.

**Table 4**( $\mu\text{g}/\text{kg}$ ) Concentration of solubilized and unsolubilized fraction of Cd and Pb from the three dumpsites

Site	SF		USF	
	Cd	Pb	Cd	Pb
Ojota	1.20	22.20	8.40	7.20
Oke-Afa	4.27	7.17	ND	13.60
Solous	1.47	2.14	2.40	1.90

Cadmium concentration of  $1.00 \mu\text{g}/\text{Kg}$  and  $1.40 \mu\text{g}/\text{Kg}$  and  $1.30 \mu\text{g}/\text{Kg}$  respectively was obtained in the reducible fraction (bound to Fe and Mn oxides) as shown in Tables 1, 2 and 3 for Ojota and Oke Afa and Solous dumpsites which may be attributed to the diffusion mechanism of the metal [15][18] the result revealed that these metals can be released into the environment from this sites under extremely reducible condition. The obtained values for Cd are within normal range of  $0.1 - 7 \text{ mg}/\text{kg}$  reported [11, 19] for cadmium in soil. On the other hand it is advantageous when cadmium which is phytotoxic in the environment is found in the forms which are not easy or very difficult to activate. Conversely, lead was not detected in the reducible fraction from Ojota and Oke Afa dumpsites which may be attributed to low acidic strength and low extracting power of  $\text{NH}_2\text{OH}-\text{HCl}$  toward the soil from the two sampling sites. A smaller contribution of lead at reducible form was observed in Solous soil sample. The result suggested that this metal did not exist to a large extent as easily reducible species. Cadmium (Cd) and lead (Pb) were not detected in oxidizable fraction (Bound fraction to organic matter) as shown in Table 1 and 3 which may be attributed to incomplete oxidation of organic matter by acidified hydrogen peroxide despite the fact that oxidation with hydrogen peroxide was extensive. More efficient method such as use of mixture of sulphuric acid and perchloric acid exist but they usually suffer from lack of speciation in the sense that they may also effect a partial attack of silicate lattice. The exchangeable fraction of Cd and Pb was observed in all the samples from the three sampling site with highest concentration in Ojota sampling site which suggested that the leaching of the metals to the environment is possible from the studied samples sites. The predominant form of Pb available in the entire fraction is exchangeable fraction which was observed in Ojota dumpsite with highest fraction compared the two other dumpsites with smaller fraction which is followed by acid extractable fractions in Oke Afa dumpsites. The highest fraction of exchangeable Cd was noticed in Oke-Afa dumpsite soil compared to the other site which an indication that leaching of Cd to the environment from Oke Afa dumpsite is possible while acid extractable was not detected (table 2) . Based on the order of metal concentration of the sequential fraction of the reducible > exchangeable and, no acid extractable as well as oxidizable fractions was found for Cd in Ojota dumpsite soil while the order of sequential fraction for Oke Afa acid was extractable> reducible>exchangeable with no oxidizable fraction was detected for Cd. Solous dumpsite soil sample (table 3) exhibited the order of sequential fraction of reducible> acid extractable> exchangeable> oxidizable for Cd respectively. The presence of Cd in the exchangeable and acid extractable fractions of Solous dumpsite soil implied that Cd can cause environmental toxicity during mobility [20].

Figure 1 and Table 4 showed the trend of concentration of solubilized and unsolubilized fractions of the three dumpsites with lead having a higher concentration of solubilized fraction in all the three dumpsites than Cadmium. For instance in Ojota it was  $22.20 \mu\text{g}/\text{kg}$  as against  $1.20 \mu\text{g}/\text{kg}$ ; Oke-Afa  $7.14 \mu\text{g}/\text{kg}$  against  $4.27 \mu\text{g}/\text{kg}$  and Solous  $2.14 \mu\text{g}/\text{kg}$  against  $1.47 \mu\text{g}/\text{kg}$  respectively. The obtained result is in agreement with earlier report by Adeniyi *et al*, 2004 in which Pb has

been found to occur in higher concentration in soil. Furthermore, unsolubilized fraction of Cadmium was not detected in Oke-Afa dumpsite while the unsolubilized fraction of lead was 13.60 $\mu\text{g}/\text{kg}$  in the same dumpsite. These distribution patterns in metal speciation between solubilized and unsolubilized fractions in the sample agreed with the findings of Calace *et al.*, [21] in their metal speciation study. The level of lead (13.6 to  $\mu\text{g}/\text{kg}$ ) in Oke-Afa dumpsite may be taken as an indication of bioaccumulation of lead in the environment [22-23]. The mobility of metals in soils and sediment are affected by a variety of factors such as the type of interactive process in soil and the characteristics of the soil involved [24].

The study of metal distribution in this dumpsite soil may suffer inadequacies due to the errors that may occur during sample handling and analysis. However, the soluble component of lead (Pb) and cadmium (Cd) in the samples are of major concern since they are known to bioaccumulate as they journey through the environment and biological system [2,11,22,25].

Invertebrates are important links in the complex food web [26], lead and cadmium are not even required in small amounts by living organisms [27], hence their presence in living tissue are sources of concern [28].

There is also the need to pay more attention to the level of hygienic sourcing and handling of such soil when used for agricultural purposes [29]. However, the major accumulative phases are exchangeable carbonate bound, Fe-Mn oxide bound and organic matter bound. It should be noted that the soluble component of lead and cadmium in the soil samples are relatively low compared to permissible level [11]. Nevertheless, lead and cadmium are generally known to bioaccumulate in biological system over time.

## CONCLUSION

We assessed the speciation pattern of three dump site soil from Ojota, Oke Afa and Solous. Exchangeable fraction of Cd and Pb was observed in all the samples from the three sampling site with highest concentration in Ojota sampling site which suggested that the leaching of the metals to the environment is possible from the studied samples sites Lead had a higher concentration of solubilized fraction in all the three dumpsites than Cadmium. Therefore there is need to pay more attention to the level of hygienic sourcing and handling of such soil when used for agricultural purposes.

## REFERENCES

- [1] Gibson M.J and Farmer J.G. *Environ. Pollut.* **1986**, 11:117.
- [2] Ambedkar .G and Muniyan .M. *Advances in Applied Science Research*, **2011**, 2 (5):221.
- [3] Majolagbe A.O, Kasali A.A., Ghaniyu L.O. *Advances in Applied Science Research*, **2011**, 2(1) 289.
- [4] Adebayo K. S. and R. Odoh. *Advances in Applied Science Research*, **2011**, 2 (5):561.
- [5] Tyler T.G *Heavy Metals in soil biology and Biochemistry*, In: Paul and EA and Ladd J N (eds) *soil Biochemistry*, Marcel Dekker, New York **1981**, 33.
- [6] Bisson .M. Campbell P.G.C and Tessier. *Anal. Chem.*, **1979**, 51:844.
- [7] Adeniyi A.A. Okedeyi O.O, Idowu A.B. *Ghana J of Chem.* **2005**, 6:17.

- [8] Okoye, C. O. B., Ibeto C. N and Ihedioha, J. N. *Advances in Applied Science Research*, **2011**, 2 (3):63.
- [9] Hsu, J.H.; Lo, S.L. *Environ. Pollut.* **2001**, 114:119.
- [10] Serife T, Senol K and Gokhan .B. *Turk. J. Chem.* **2001**, 27:333.
- [11] G.O. Adewuyi, Ph.D.1; F.A. Dawodu, and N.N. Jibiri, S. *PJST.* **2010**, 11(1):616.
- [12] Dudka .S. Piotrowska M. Terelak .H. *Environ. Pollut.* **1996**, 94: 181.
- [13] Scancar J, Milacic R, Strazar M, Burica O. *Sci. Total. Environ.* **2000**, 250, no 1-3:9.
- [14] Pueyo, M.; Rauret, G.; Lück, D.; Yli-Halla, M.; Muntau, H.; Quevauviller, Ph.; Lopez-Sanchez, J.F. *J. Environ. Monitor.* **2001**, 3: 243.
- [15] Adeniyi A.A. Okedeyi O.O. *Pak. Journ.of Sci. & Ind. Res.* **2004**,47, (6) 430.
- [16] Stone .M. and Marsalek .J. *Trace Metal. Waters Air soil Poll.* **1996**, 87:147.
- [17] Tessier, A.; Campbell, P.G.C.; Bisson, M. *Anal. Chem.* **1979**, 51:844.
- [18] Backes, C.A.; McLaren, R.G.; Rate, A.W.; Swift, R.S. *Soil Sci. Soc. Am. J.* **1995**:59:778.
- [19] Bohn, H.L., McNeal, B.L., and O'Conor, G.A. *Soil Chemistry*. John Wiley and Sons: New York, NY **1979**. 272.
- [20] Karbassi, A.R.; Shankar, R. *Inter. J. Environ. Sci. Technol.* **2005**:1: 307.
- [21] Calace N. Petronio, B.M. Petronio, E and Pietroneis, M. *Toxicol. Environ. Chem.* **2000**, 76, 157.
- [22] Olowu R A, Ayejuyo, O O , Adejoro A A, G. O. Adewuyi G O, Osundiya , M. O. Onwordi C.T ., Yusuf K A and. Owolabi M.S. *E-J Chem.* **2010**, 7, (2):526.
- [23] Garate, A., Ramos .I. Manzanarus, M. Lukena J.J. B. *Environ. Contam. Tox.* **1993**, 50: 709.
- [24] Adeniyi A.A., Fashola .J. Ekanmem, O A. *Nig. J. .Rev. Sci.* **1993**, 1:65.
- [25] Van der Watt. H.V.H., Summer, M.E. and Cabreera M.L. *J. Environ. Qual.* **1994**, 23, 43.
- [26] Bartsch, M.R. W.G Rada, R.G .*Water, Air, soil poll*, **1999**, 190:277.
- [27] Techemitchin N.N., Villagra A. Techemitchin, A.N. *Environ. Toxic. Water.* **1998**, 13:43.
- [28] He Mr. Young, H and Oha. Y. *Toxicol. Environ. Chem.* **2000**, 76:137.
- [29] Adeniyi A.A. Adams T.M.O, Okedeyi O.O. Odoguwa O.O. *Fresen. Environ. Bull.* **2007**, 16:256.