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Relationship of Soil Properties to Fractionation and Mobility of Lead and Cadmium in Soil

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Abstract
The pollution level and mobility of Pb and Cd in soil from dumpsites along River Jakara, Kano have been studied in this research. Sequential method of extraction was used to assess the risks of Pb and Cd in contaminated soils, and to determine relationships among soil parameters and heavy metals soil fractionation. The concentration of Pb ranged from 3.41 to 172.00 mg/kg and Cd from 2.11 to 45.00 mg/kg. Regression analysis using linear and second order polynomial models indicated relationships between these metals contamination and some soil properties at P ≤0.05. A correlation between cation exchange capacity and organic matter content was anticipated. The result shows that the soils studied are contaminated with the metals. The speciation analysis revealed that the metals studied are very mobile and available for plant uptake.

Keywords: fractionation, dumpsite, mobility, regression, correlation, heavy metal

INTRODUCTION

Environment is a combination of all the external factors that influence the wellbeing of every living things. Some of these factors could be biological in nature; chemical origin or maybe physical or socio-cultural. The size of the world's population today has resulted in extensive dependence on technology to harness and improve the available natural resources, increase food production, produce more goods and services (Ebong *et al*., 2007). This has led to increased industrialization, which in turn is responsible for the various industrial wastes found in the environment. As a result of this industrial revolution, the use for heavy metals have increased which leads to increased anthropogenic emission into the environment (Tukura *et al*.,2007).The toxic effect of these metals in soils depends not just on the total amount, but also on their speciation, binding state, their properties, as well as environmental factors such as soil pH, organic matter etc (Lu *et al*., 2003).Odukoya *et al*. (2000) reported that refuse dumpsites soils contain various kinds and amounts of heavy metals, owing to the age, composition and location of the dumpsite. Both the soil and the vegetation found on and within the vicinity of these dumpsites will pose a serious threat to the wellbeing of the inhabitants of such areas. Further reports have revealed that these metals from dumpsites have the tendency to pileup and remain in the soil at environmentally dangerous levels (Ebong *et al*., 2007).Hence, human existence and the quality of life is threatened by the quality and the safety of food and drinking water we take (Lu *et al*., 2003).

Studies in countries like China, South Korea, and USA have revealed that water (Lin *et al*, 2007), Vegetables (Zheng *et al*; 2007), rice (Yang *et al*; 2006), and fish (Schmitt *et al*; 2007) often contain heavy metals derived from mining and smelting activities.

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The chemical state of the metal is indicative of the kind of processes it undergoes within a soil and consequently determines its movement and transport between different soil mixtures (Keepax *et al*., 2005). Organic matter and clay content are some of the most important soil characteristics affecting adsorption reactions (Bolan and Duraisamy, 2003). Metals like Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+} often get trapped within iron oxide structures, thereby restricting their movements in soil. The profound role played by the soil characteristics on the movements and availability of heavy metals in soil is well documented (Tukura *et al*., 2007).Soil pH, for example, is an essential parameter since the availability of soil metal is low if the soil pH is close to neutral. The cation exchange capacity (CEC) of the soil also influences the metal availability and mobility since the greater the CEC value the greater the retention of metals and the lower the mobility.

MATERIALS AND METHODS

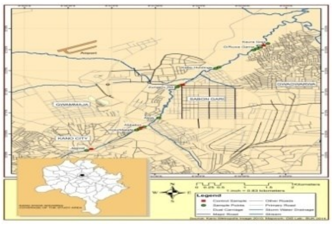
Samples for the research were collected from dumpsites along River Jakara in Kano metropolis. The dumpsite soil along this river is used extensively by farmers to grow vegetables along the river banks.

All samples were collected based on established analytical procedures and were stored in appropriate containers before analysis to avoid contamination.

To achieve the aim of the research, thirteen (13) soil samples were collected at thirteen (13) different dumpsites along River Jakara, Kano. From each location, four samples were obtained in a square area of 5m and composite samples made in the laboratory. Each of the composite soil samples was divided into two portions, air dried and grind to pass through a 2-mm sieve and stored in plastic bags at room temperature prior to laboratory analysis. One portion of the sieved sample was used for the determination of soil properties; while the remaining portion was used for the speciation scheme. All analysis was carried out in triplicates and the mean results reported.

To determine the Soil pH a 1:1 (v/v) ratio of soil and 0.01M $CaCl_2$ solution suspension was analysed. The soil samples were analysed for cation exchange capacity by the method described by Gillman and Sumpter, soil organic matter by Walkley- Black titration, the textural class of the soil was determined by hydrometer method, phosphate content by the method described by Udo *et al.,* (2009); total metal content of the soil by the method described by Nguyen *et al.,* (2010).

A modified method by Tessier *et al*., (1979) was used to estimate fractionations of Pb and Cd into six fractions. The fraction of the metals soluble in soil solution was obtained by leaching 1 g of air dried and sieved sample with 14 ml of distilled water for 1 hour. The exchangeable fraction s of the metals was obtained by also leaching the residual soil at room temperature for 1hour with 14.00 cm^3 1.00 M $MgCl_2$ at pH 7.0. Soil and extraction solution was thoroughly agitated using mechanical shaker throughout the extraction. The fraction bound to the carbonate was determined by extracting the residual at room temperature with 14.00 cm^3 1.00 M sodium acetate (NaOAc) at pH 5.0 (using acetic acid) for 5 hours. The fraction associated with the Fe-MnO was extracted with 20.00 cm^3 of 0.40 M $NH_2OH.HCl$ in 25% (v/v) acetic acid with agitation at 96^oC in a water bath for twelve hours. The fraction bound to the organic matter was obtained by oxidizing the residue soil with 3.00 cm^3 of 0.02 M HNO_3 and 5.00cm^3 of 30% (v/v) hydrogen peroxide, which has been adjusted to pH 2 .0 (with HNO_3). The mixture was heated to 85^oC in a water bath for 2 hours with occasional agitation and allowed to cool down. Another 3.00 cm^3 of 30% hydrogen peroxide, adjusted to pH 2.0 with HNO_3, was added. The mixture was again heated at 85^oC for 3 hours with occasional agitation and allowed to cool down. Then 5.00 cm^3 of 3.20 M ammonium acetate (NH_4OAC) in 20% (v/v) nitric acid (HNO_3) was added, followed by dilution to a final volume of 20.00 cm^3 with deionized water. Fraction bound to silicate materials was extracted by digesting the residue with a mixture of nitric acid and hydrochloric acid (*aqua regia*).



Map of the study area

RESULTS AND DISCUSSION

The values of the selected physico-chemical parameters of the soils differ considerably and are presented in Table 1. The pH values of the waste soils ranged from slightly acidic (6.2) to slightly above neutral (7.8). This result agrees well with the work of Dawaki *et al.*, (2015). The level of acidity (or alkalinity) in soils determines the nutrients availability for plant healthy growth and maintenance (Arias *et al.,* 2005). Hence being an important parameter in reactions taken place in the soil, the observed pH values in this research may have effects on the metal availability and their subsequent uptake by both plants and microorganisms.The content of soil organic matter was low (0.68 to 4.05%). These values are in good agreement with those reported in literature (Finzgar *et al.*, 2007; Uba *et al.*, 2008; Obasi *et al.*, 2012). It has been shown that treatment of contaminated soil using organic matter reduced heavy metal availability for plant absorption (Khan *et al.*, 2000).

The PO_4^{3-} and SO_4^{2-} contents of the refuse waste soils ranged from 22.96 mg/kg to 58.33 mg/kg, and 2.88 to 38.95 mg/kg respectively. This phosphate content of the soil may have drastic implications on metal bioavailability as a result of soluble salt formation. These results also compare very well with those reported by Finzgar *et al.*, 2007; Obasi *et al.*, 2012.The cation exchange capacity (CEC) of the waste soils range from 3.4 to 13.00 cmol/100g (Table 1). CEC of the soil decreases the mobility of nutrient cations through ion exchange mechanisms. (Yoo and James, 2002). Clay content of a soil is also an important factor that must be considered when assessing the degree of contamination of soil by heavy metals and their subsequent levels in plants tissues, because of the high potential of clay to bind the heavy metals in soil.Soils having high clay and organic matter contents, have high capacity to adsorb metals thereby restricting their movements in the soil (Sheoran *et al.*, 2009). All soils having high adsorption capacity for metal cations, (soils with high clay content), have the ability to sequester metallic elements (Nessner and Esposito, 2010). Going by the clay contents of the waste soil samples studied which ranged from 6.00 to 16.48%, it may have a profound effect on the metal distribution and mobility in the study area. The textural class of the soil samples was mainly sandy loam.

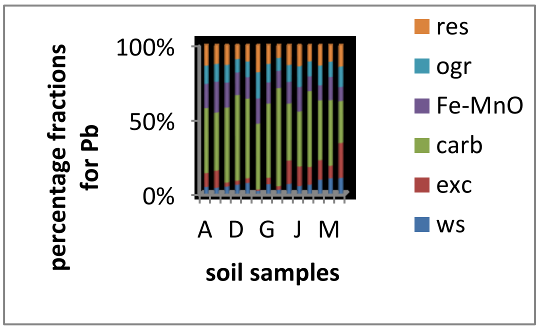
Table 1: soil properties

Samples	A	B	C	D	E	F	G	H	I	J	K	L	M	N
pH	7.10	6.20	7.10	7.80	6.80	6.60	6.80	6.60	7.10	6.80	7.20	6.60	6.20	6.60
OM(%)	3.37	4.06	2.89	3.16	1.24	2.89	1.58	4.30	1.38	3.65	2.13	0.48	2.41	1.67
Phos(ppm)	36.61	42.20	38.47	27.92	29.16	48.40	29.16	42.20	22.96	58.33	34.13	47.16	36.61	28.93
Clay (%)	12.48	12.24	14.40	14.38	12.44	14.48	16.28	14.54	16.49	12.88	16.58	12.99	1247	6.00
Silt(%)	12.62	18.56	12.64	16.56	0.70	14.72	6.96	6.56	16.16	12.58	12.46	4.54	10.57	16.00
Sand(%)	74.90	69.02	72.96	69.06	86.86	70.80	76.76	78.90	66.85	74.54	70.96	82.46	76.96	78.00
Texture	Sandy loam	Sandy loam	Sandy loam	Sandy loam	Sandy loam	Sandy loam	Loamy sand	Sandy loam	Sandy loam	Sandy loam	Sandy loam	Loamy sand	Sandy loam	Loamy sand
Pb (mg/kg)	126.22	135.50	120.40	140.00	123.00	145.00	137.20	114.32	150.10	172.00	141.41	115.20	120.10	3.41
Cd (mg/kg)	15.11	44.01	45.00	32.12	11.98	37.24	29.31	21.44	38.11	39.28	24.54	33.45	28.11	2.11
CEC(cmol/ 100g)	9.10	11.80	10.30	1.00	3.40	12.70	7.40	13.00	9.60	12.30	10.30	6.60	11.20	7.20
SO_4^{2-} (ppm)	27.26	35.35	30.86	32.96	10.19	38.05	22.17	38.95	28.76	36.85	30.86	19.77	33.56	3.65

A: Abattoir, B: Akija, C: koki/malafa2, D: koki/malafa1, E: kabo holdings2, F: JagwalG: Air port road1, H: Air port road2, I: Gidan ruwa3, J: Kaura goje, K: Kabo holdings1,L: Gidan ruwa2, M: Gidan ruwa1, N: Control.

Pb Fractionation and mobility

The mobility and availability of heavy metals in soils depend on how they distribute among the soil fractions, which in turn determine their probable behaviors in the soil (Maiz *et al.*, 2000). These metals are attached to the various solid particles of the fractions such as the carbonate, organic matter, oxides etc. The pattern of Pb distribution among the different soil fractions is shown in Figure 1. Total Pb concentration in the soils ranged from 3.41 to 172.00 mg/kg. All the soil samples were within the USEPA limit for Pb in soil of 30-300 mg/kg. The mean recovery of Pb after the extraction process was 94.85%. The highest fraction of the total Pb was associated with soil carbonate (28.27-65.94%) followed by Fe-MnO fraction (9.38-20.69%) then the residual fraction (8.63 – 18.24%). This trend in metal distribution in this study was in contrast to the findings of Finzgar *et al*., (2007), Obasi *et al*., (2012) who reported Pb to be more in the organic phase followed by carbonate and then residual. The association of metals with the exchangeable and extractable fractions (as in this study), signifies the probability of them becoming bioavailable due to solubility. According to Banat, (2001), the more the fraction of the metal bound to the residual fraction, the less the level of ollution. This shows that the soils studied in this research is likely to be polluted with Pb metal.



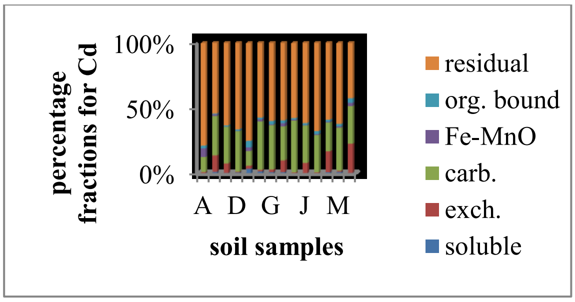


Figure 1: Percentage fractions for Pb Figure 2: Percentage fractions for Cd
Res – residual fraction, org – organic matter fraction, Fe-MnO – oxide fraction, carb- carbonate fraction, exc- exchangeable fraction, we- water soluble fraction
Cd Fractionation and mobility

Total Cd concentration in the soils varied between 2.11 and 45.00 mg/kg (Table 1). All soil samples exceeded the critical permissible concentration of 3.0 mg/kg for agricultural soils (USEPA, 1986; MAFF, 1992) except the control sample. This high concentration may be as a resultof dumping of cadmium containing substances like cadmium batteries and metals from residence and industries to these sites. The mean recovery of Cd after the extraction process was 90.78%. The residual Cd fraction (42.46 – 78.74%) and that bound to carbonate (11.36 – 39.73%) were the predominant fractions in the speciation process (Figure 2).This relatively high percentage of the total Cd in the carbonate fraction is indicative that Cd in these soils is likely to be more bioavailable for plants uptake. This result is in agreement with the findings of Gupta and Sinha, (2006); Achi *et al*., 2011. However, it is in contrast to that reported by Nguyen *et al*., (2010) who reported that the highest percentage of Cd was associated with the oxide fraction. Element bioavailability is an essential parameter when assessing the extent of phytotoxicity in plants as a result of metal uptake. Going by the preceding discussions, the Cd in this study is likely to cause phytotoxicity in the vegetables cultivated using soils from these dumpsites as manure.

Relationship Among Soil Properties and Metal Speciation.
It is an established fact that the speciation of heavy metals in soil is greatly influenced by the various soil characteristics. To ascertain which of the soil parameters actually affected the speciation of the metals, a regression model was applied to the experimental data gathered at p
≤ 0.05. The result showed no significant relationship between soil pH, clay content and CEC, however the presence of soil organic matter was strongly correlated with the soil CEC (P = 0.001, R^2 = 62.20.)

The total soil metal content had no significant correlations whatsoever with the soil pH and organic matter. While the percentage of metal bound to the soluble fractions was significant for Pb (p = 0.002, R^2 = 56.20), no such relationship existed for Cd. Significant correlation was also established between total metal content and proportions bound to exchangeable and carbonate fractions for both metals, such correlation only existed for Cd for fractions in Fe-MnO (p = 0.015, R^2 = 40.30)Furthermore, while the total cadmium content was correlated with fraction contained in organic fraction (p = 0.000, R^2 = 71.80), no such relationship was obtained for residual bound fraction for both metals.

A number of studies have established positive correlations between soil pH and the metal speciation (Carlon *et al*., 2004; Finzgar *et al*., 2007). No significant correlation was observed between the soil pH and the speciation of the metals in the current study. However, it should be noted that the soil pH values were all above ranges where metal solubility is appreciable.

Clay content was only significant as per the Cd in carbonate (p = 0.047, R^2 = 29.00) and Pb in exchangeable fractions (p = 0.018, R^2 =51.60). A highly positive correlations was observed for soil CEC and proportion of metals bound to the water soluble (p = 0.000, R^2 = 84.00) and organic matter fractions (p = 0.001, R^2 = 70.00). This means that the percentage Cd and Pb in the water soluble fraction were influenced by the soil CEC. However, all the metals showed no correlation between fraction the soil CEC and fractions bound to carbonate. This agrees with the reports by Janssen *et al.*, (1997), Francois *et al.*, (2004); Finzgar *et al.*, (2007).
Organic matter content was positively correlated with fractions of Pb bound to the water soluble and Fe-MnO fractions only. This relationship study shows that the soil parameters have varying relationships with the various fractions of the metals in the soil.

CONCLUSION
The heavy metal pollution levels of the soils from dumpsites along River Jakara have been assessed. The pH of the dumpsite soils was found to be slightly acidic to slightly basic in nature. The soils have low organic matter and clay contents as well as moderate cation exchange capacity. The metals were found to distribute themselves between different fractions of the soil in different amounts. Their mobility also varied from metal to metal.
The soil properties are believed to have immense influence on the partitioning of the metals among the soil fractions, but at $p \leq 0.05$, data gathered from soils from these dumpsites showed that only few of these parameters actually influenced the metal fractionation. This means that there might be other inherent factors within the soil in addition to the obvious parameters that govern metal speciation in soil.
Results obtained in the study also showed that the level of the heavy metals in the dumpsites was highly elevated compared to the control soils. The result also revealed that the studied metals are available for plant uptake in the soil and that lead was more mobile than cadmium. As a result, continued use of the dumpsite soil as organic manure for crops pose health risk to the consumers.

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