ENRICHMENT AND CHEMICAL FRACTIONATION OF COPPER AND MANGANESE IN SOILS OF ABUJA STREETS

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Abstract
Copper and Manganese contents and their chemical forms in the surface soils of the Abuja Streets were investigated to quantitatively assess their contamination, mobility, and potential bioavailability. Thirty surface soils samples were collected and analyzed for total contents and chemical forms of Cu and Mn. The results revealed that the total contents of Cu and Mn in the soils ranged from 4.93 to 9.67 mg/kg and 23.67 to 85.33 mg/kg respectively. The Enrichment Factors of Cu and Mn in some soils were lower than 1.0 with the exception of Ayingba Street, Aminu Kano, Lagos Street, Landoke Boleuvard, and Tafawa Balewa Streets where EFs were more than 1 for Mn, indicating that Mn has anthropogenic origin. Less than 2% and more than 60% of total Cu and Mn contents in the soil at most sampling sites were associated with the exchangeable fraction and residual fraction, respectively, showing their low mobility and bioavailability. The major sink for anthropogenic Cu was organic matter and Carbonates, while for Mn was carbonate and reducible phase.

Keywords: enrichment, fractionation, heavy metal, soil sediment

Introduction
Metal pollution has become a global environmental problem because of their toxicity and threat to human life and environment. Heavy metals are non-biodegradable and therefore have long life in the soil thus predicating far reaching effects on the biological system including soil micro-organism and other soil biota (Ram *et al*., 2000) causing functional disturbance in other environmental components.

As trace elements Cu and Mn are essential to maintain the metabolism of the human body, but at higher concentration they can lead to poisoning (Merritt and Erich, 2003). Health effects from exposure to Mn and Cu include neurological disorder, gastrointestinal disorder that could lead to stomach ache, nausea, vomiting and diarrhea, mobility dysfunction, liver damage and cancer (ATSDR, 2002; Centenol, 2006; Nordberg and Cherian, 2005). For risk assessments related to metal toxicity, more insight is required concerning the competitive binding of copper and manganese ions to biotic surfaces (Nordberg and Cherian, 2005).

Both natural processes and anthropogenic activities are responsible for introducing these trace metals into the terrestrial systems (Nriagu and Pacyna, 1988), through industrial activities such as mining, smelting, processing, recycling and unsanitary disposal of waste. Trace metals are not readily removed by natural degradation processes; thus, they may become enriched in soils over time (Amore *et al*, 2006). Therefore, anthropogenic trace metal pollution of soils is a critical area of growing concern worldwide. On the other hand, it is generally recognized that the particular behavior of trace metals in the environment is determined by their specific physicochemical forms rather than by their total concentration (Amore *et al*, 2006). Soil consist of several geochemical phases, mainly carbonates, sulfide, organic matter, iron and manganese oxides and clays, which act as scavengers of trace metals in the environment (Tessier et al, 1987). Hence, Selectively Sequential Dissolution (SSD) methods have been developed to determine the quantity and proportion of metal forms present in soils (McLaren and Crawford, 1973; Tessier et al., 1987; Han and Banin, 1995). Whereas SSD method is still subject to a broad controversy on non selectivity of extractants, redistribution of metals among various phases during extraction, and sampling differences (Amore et al, 2006), it is still widely employed to investigate mobility and bioavailability of trace metals in soils.

The objective of this research was to investigate the pollution, mobility, and potential bioavailability of Cu and Mn in the surface soils of Abuja streets, the Federal Capital of Nigeria.

Materials and Methods

Sample Collection and Pretreatment

In dry season, surface soil samples (about 0–15 cm depth) were taken at 30 sites from ten busy streets in Abuja, Federal Capital Territory, namely: Ademola Adetokumbo, Lagos, Gimbia, Aminu Kano, Tafawa Balewa, Moshood Abiola, Kashim Ibrahim, Landoke Boulevard, Ayangba, and Ahmadu Bello Streets, using plastic spoon. At each sampling site, soil samples from four different locations were taken, mixed together to make a composite and then transferred to acid-washed plastic bags. All soil samples were air-dried for one week in the laboratory, homogenized crushed and passed through 2 and 0.5 mm mesh for physicochemical properties and heavy metals analyzed respectively and stored in plastic bottles.

Laboratory Analyses

The content of organic matter (OM) in the samples was determined using Walkley-Black method. The particle size was determined by Hydrometer Method and clay content of less than 2 μm in particle size was calculated. Electrical conductivity and pH of the samples were determined using Electrical Conductivity meter and electrometric method respectively. In order to evaluate mobility and potential bioavailability, chemical forms of Cu and Mn in the soil samples were analyzed using a Selectively Sequential Dissolution (SSD) method developed by Han and Banin (1995). The chemical forms were operationally fractioned into five phases: (1) Exchangeable fraction (EXC); (2) Bound to carbonate minerals (CARB); (3) bound to oxides or reducible fraction (RUD); (4) Bound to organic matter (OM); and (5) Residual fraction (RES).

Calculation of Enrichment Factor (EF) and Statistical Analysis

The extent of soil contamination was assessed by Enrichment Factor (EF), which generally can differentiate anthropogenic trace metals from naturally occurring trace metals (Morillo et al., 2004; Adamo et al., 2005). To identify anomalous metal content, geochemical normalization of the heavy metals data to a conservative element is common. The EF is calculated by:

$$EF = \frac{CM/CFe}{BCM/BCFe}$$

Where CM and CFe are the metal M and Fe contents in the soil samples, respectively; BCM and BCFe are the background contents of metal M and Fe.

Results and Discussion

The soil under study had a coarse to fine texture, with mean clay content of 25.72 % (Table 1). The mean organic matter content is 1.81%. The soils of the streets generally contained less than 2% of organic matter which is an indication that the soils accepted relatively low organic pollutant load, resulting in low OM content in the soils (Feng and Bai, 2003). A content range value of element of mineral matrix (Cu) was 4.93– 9.67 mg/kg, while the elemental content of Mn was 23.67 – 85.33 mg/ kg. This showed the variation of mineral composition of the soil. The very high values of Mn contents at Moshood Abiola, Tafawa Balewa, Landoke Boulevard, Ademola Adetokunbo and Anyigba Street might be due to post depositional migration to surface soils which sometimes account for its high concentration (Tack and Verloo, 1998).

Table 1: Mean and Range Values of the Physical and Chemical properties of the studied soils

	Mean	Std. Deviation	Minimum	Median	Maximum
pH	7.44	0.18	7.14	7.43	7.87
Electrical Conductivity (msM^{-1})	300.03	208.41	108.00	178.00	997.00
% Organic Matter	1.81	0.93	0.31	1.64	3.87
% clay	25.72	4.67	21.92	23.92	39.82
% Silt	8.40	3.48	2.56	8.56	14.56
% Sand	65.87	5.10	47.52	67.52	73.52

Table 2: Total Content of Cu and Mn in the studied soils in mg/kg

Street name	Cu	Mn
Moshood Abiola	5.23	77.67
Ademola Adetokunbo	9.67	50.00
Ahmadu Bello	5.17	47.00
Anyigba Street	7.63	55.33
Aminu Kano	6.80	42.73
Gimbia Street	4.93	30.67
Lagos Street	6.23	45.00
Landoke Boulevard	8.10	55.73
Ibrahim Kashim	7.27	23.67
Tafawa Balewa	6.07	85.33

The contents of Mn in the soils were significantly correlated to pH and Electrical Conductivity of the soils (Table 3). Soil pH is one of the critical factors influencing the metal distribution in soils (Aloupi and Angelidis, 2001; Huang and Lin, 2003; Chimuka *et al*, 2005). Soil pH measurement is a predictor of various chemical activities within the soil. According to Van (1999) the level of Mn in the soil is primarily controlled by exchangeable Mn in response to pH changes. Multiple factors such as water potential, bulk density, time of measurement, cementing agent, salinity, exchangeable ions e.t.c contributes to soil electrical conductivity variability (Harstock *et al*, 2000). Positive correlation between EC and Mn might be due to increase levels of exchangeable Mn ions in the soil.

Table 3: Pearson correlation among selected physicochemical properties and elemental content in studied soils

		pH	EC	Org. Matter	Clay	Cu	Mn
pH	Correlation	1					
	Sig. (2-tailed)						
	N	30					
Ec	Correlation	-.533**	1				
	Sig. (2-tailed)	0.002					
	N	30	30				
Org. Matter	Correlation	-0.236	0.357	1			
	Sig. (2-tailed)	0.21	0.052				
	N	30	30	30			
Silt+Clay	Correlation	-0.093	0.059	-0.083	1		
	Sig. (2-tailed)	0.624	0.757	0.664			
	N	30	30	30	30		
Cu	Correlation	0.119	-0.068	-0.036	0.104	1	
	Sig. (2-tailed)	0.531	0.72	0.85	0.584		
	N	30	30	30	30	30	
Mn	Correlation	.445*	.481**	-0.009	0.16	-0.242	1
	Sig. (2-tailed)	0.014	0.007	0.961	0.399	0.198	
	N	30	30	30	30	30	30

** *Correlation is significant at the 0.01 level (2-tailed).*
* *Correlation is significant at the 0.05 level (2-tailed).*

The Chemical Fraction of Heavy Metals in the Soils

The perceptual distribution of Cu is as shown in Figure 1. The distribution of copper in the exchangeable fraction was limited, ranging from 3- 7%. The greatest percentage of copper was associated with carbonate fraction (Avg.33%) and residual fraction (Avg.42.2%). This shows that the contents of the most labile or mobile Cu in the soil was low, while the most stable contents of Cu was high (Yinghong *et al,* 2009). Copper in the organic fraction is low in all streets with exception of Ademola Adetokunbo, Moshood Abiola, Ibrahim Kashim and Aminu Kano.

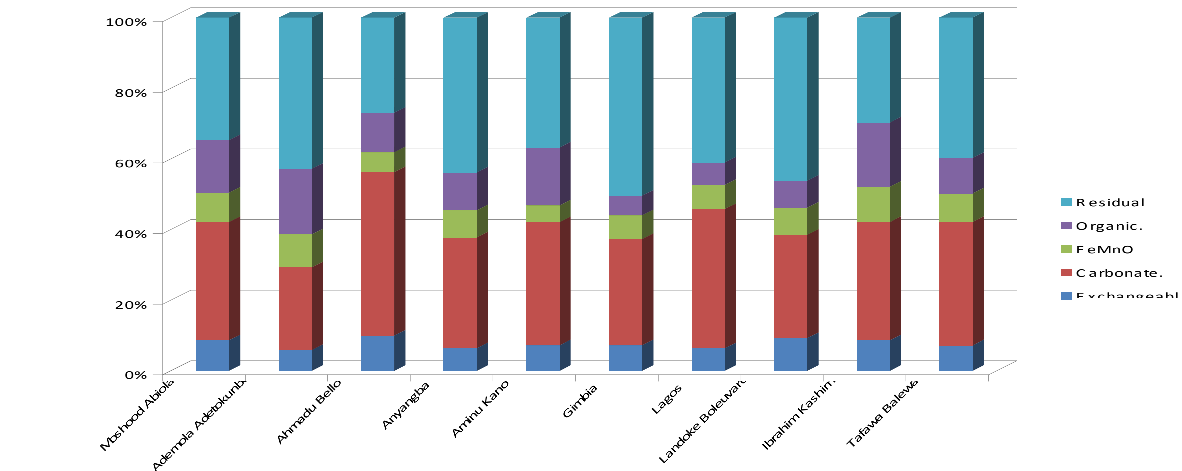

Figure 2: Chemical Fractionation of Cu in Abuja Street Soils

The association of Copper with organic fraction in these four streets may be due to the formation of stability constants of organic Cu complexes (Vuduc Loi *et al,* 2003).The preference of copper for organic fraction in the soil can be attributed to high organic matter content of the soil (Kabala and Singh 2001). Generally, organic matter fixes Cu very strongly (Blume and Br¨umer, 1987). Fe- Mn oxide fraction (Avg. 7.4 %) is also low when compared to other fractions but contained a significant portion of total Cu in Ademola Adetokunbo and Ibrahim Kashim way. The distribution pattern of copper among different fractions in the soils is mostly controlled by the mineral composition of soils and the anthropogenic wastes introduced to the study area via domestic discharges (Adachi & Tainosho, 2004). On the average, percentage of Cu associated with different geochemical fractions in the soil samples from the ten streets were in the following order; residual> carbonate> organic> Fe Mn Oxide> exchangeable.

Manganese was mostly concentrated in the residual fraction (Figure 2) except in Gimbia Street and Ibrahim Kashim way where concentrations in residual fraction were below 40%, which is an indication that the Mn has low environmental availability and is poorly affected by human activities in the study area (Maria *et al*, 2006).The oxide bounded fraction was the next most Mn containing fraction (Avg: 25.8%) among the non residual fractions of the soils. All the soil samples also had significant amounts of Mn in the carbonate fraction. The percentage of Mn in the exchangeable fraction is low (Avg: 6.2%) in all the streets except Aminu Kano way and Gimbia Streets. According to Tack *et al* (1998), Mn exhibit post depositional migration in surface soil and sediment which sometimes account for its low availability in the mobile fraction. The high percentage of Mn in Aminu Kano way and Gimbia Street does not necessarily indicate an anthropogenic contamination since it has preferential association with mobile fractions of soil and sediment as reported by Maria et al (2006). The low percentage of Mn (Avg: 3.4%) in organic fractions, revealed that the Mn is not readily adsorbed by the organic molecules. In general the association of Mn in the soils was in the order: residual> Fe- Mn oxide> carbonate> Exchangeable> Organic. The transition element (Mn) existed in a more stable forms in Abuja streets soil as relatively immobile species in silicate and primary minerals.

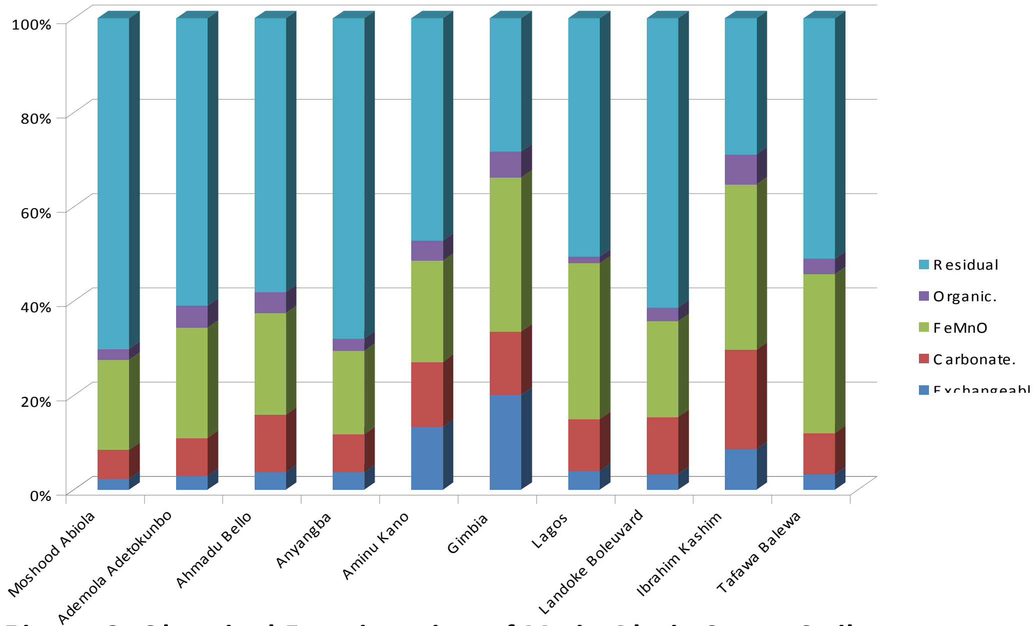

Figure 3: Chemical Fractionation of Mn in Abuja Street Soil

Evaluation of Soil Pollution

The absolute content of heavy metals in the soils may not directly show their contamination level because the quantitative evaluation of heavy metal contamination is based on the comparison with their background contents. In this study, Fe was used as a conservative normalizing element to conduct the geochemical normalization of heavy metal data, assuming

Fe and heavy metals have a uniform flux from their sources to sink (Eq. 1) The Enrichment Factors (EF) for most sites were lower than 1.0, indicating a predominantly natural origins for Cu and Mn. According to Lu *et al* (2005), Enrichment Factor (EF) values around 1.0 and below serve to indicate that the element is primarily from lithogenic sources. EFs suggested that the soils at the streets might be moderately contaminated by Mn, while at Landoke Boulevard soil was not or minimally contaminated. On the other hand, the soils at the streets were not contaminated by Cu.

Table 5: Enrichment Factor of Cu and Mn in Soils of Abuja Street

Street name	Cu	Mn
Moshood Abiola	0.1	0.2
Ademola Adetokunbo	0.2	0.8
Ahmadu Bello	0.04	0.9
Anyigba Street	0.1	1.3
Aminu Kano	0.1	1.5
Gimbia Street	0.04	0.6
Lagos Street	0.1	1.5
Landoke Boulevard	0.1	1.9
Ibrahim Kashim	0.01	0.4
Tafawa Balewa	0.1	3.4

Conclusions

Noting that EFs were less than 1 at most sampling sites with the exception of some streets (Ayingba Street, Aminu Kano Street, Lagos Street, Landoke Boleuvard and Tafawa Balewa Street) of the Abuja city where EFs were more than 1 for Mn is an indication that the metal has anthropogenic origin. The total content of Mn in the soil was significantly correlated to clay, pH, and Ec contents. Sequential extraction revealed that Cu and Mn contents in the most soil samples were mainly bounded in the residual fraction and were insignificantly associated with the exchangeable fraction, showing their low mobility and bioavailability. The major sink for anthropogenic Cu were carbonates and organic matter, while the major sink for anthropogenic Mn was the easily reducible phase dominated by Mn and amorphous Fe oxyhydroxides. Hence, anthropogenic Cu and Mn have relatively low potential mobility and bioavailability.

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