Geochemical Fractions of Copper in Agricultural Soils of an Alfisol Origin at the University of Ibadan

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Abstract

The content and distribution of copper forms in a selected farmland of metamorphic rock parent material origin soils was studied. The aim was to observe differences in the total content and distribution of copper forms in these soils; with a view to using this information to predict if the natural, non-contaminated levels of copper in these soils could cause toxicity to ground water and plants. Five samples were collected from three soil profiles at the Teaching and Research farm plot along Parry road, University of Ibadan. Total copper content in soils were extracted using aqua regia solution while a five-step sequential extraction procedure was used to determine its different geochemical fractions. Atomic Absorption Spectrophotometer (AAS) was then used to determine the concentration in extracted copper samples. The lowest proportion of copper in the analyzed soils occurred in the exchangeable form (0.01-0.07%) followed by the solution form (0.18-1.80%) at 0-15, 15-32, 32-60, 60-84 and 84-160 cm depth. The highest proportion of copper was bound to organic matter (15.86-74.22%) followed by the residual phase (4.34-56.02%). The contribution of each form of copper to total copper content followed a reducing trend with organic matter bound > residual > iron-manganese oxides bound > carbonate bound > solution > exchangeable. Soil pH and exchangeable bases were observed to have the most profound influences on copper in the soils. The copper form bound to oxides of manganese and iron was the most significant contributor to the observed variations in total copper. It is therefore concluded that total copper content is influenced by soil properties.

Keywords: Copper, Depth, Geochemical fractions, Sequential extractions, Toxicity.

Introduction

Bioavailability and mobility of heavy metals in sediments and soils largely depend on the mineralogical and chemical forms (Baeyens *et al*., 2003 and Fijalkowski *et al.*, 2012). Heavy metal pollution affects all facets of the environment but their impact is long lasting in soils due to the relatively strong absorption of many metals to humic and clay colloids in soil (Alloway and Arye, 1994). Fractions, mobility and bioavailability of heavy metals in soils rather than the total concentration is an indication of their bioavailability. For this reason, sequential extraction procedures are commonly applied because they provide information on the fractionation/speciation in the different lattices of the solid sample which serves as a good compromise to give information on environmental contamination risk (Margui *et al*., 2004; Nadaska *et al.*, 2009). Since the early 1980s and 1990s sequential extraction methodology has been developed to determine speciation of metals in sediments (Tessier *et al*., 1979; Coetzee, 1993) due to the fact that the total concentration often does not

accurately represent their characteristics and toxicity, it is helpful to evaluate the individual fractions of the metals to fully understand their actual and potential environmental effects (Tessier *et al*., 1979). Heavy metal pollution in agricultural land is a serious and widely spread environmental problem due to the persistent and non- biodegradable properties of these contaminants (Yuan *et al*., 2004). Copper is required in small concentrations (5-20 mg/kg) in plant tissue for normal growth. Tissue concentrations of < 4 mg/kg are generally considered deficient, while > 20 mg/kg can be toxic to plants. Copper plays an important role in plant enzymes and enzyme systems. Copper deficiencies can affect photosynthesis, respiration, carbohydrate distribution, nitrogen metabolism, cell wall metabolism, water relations, seed production and disease resistance.

Since metals can adsorb to the soil, runoff into rivers or lakes or leach into the groundwater (Mulligan *et al*., 2001), it is important to study the soil mechanisms involved in their retention and solubility. The sequential extraction procedures allow scientists to understand them since the chosen extractions attempt to minimize solubilization of other soil fractions even if none of them are completely specific (Mulligan *et al*., 2001). The objective of this study was to determine the forms of copper in the selected soils of the parent material (Granite Gneiss) at different depths.

Materials and Methods

Description of the study area
The study was conducted at the University of Ibadan (latitudes 07°9' and 07°11'N and longitudes 3°51' and 3°52'E; about 190 m to 210 m above sea level), Nigeria. According to Durotoye (1972), three major metamorphic parent rocks; Granite Gneiss, Biotite Gneiss and Quartz Schists underlie the University of Ibadan. The selected area of study was an oil palm plantation at the Teaching and Research farm along Parry road, University of Ibadan.

Sample collection and preparation
A total of five soil profile samples were collected from the oil palm plantation at the Teaching and Research farm along Parry road, University of Ibadan. Soil samples were obtained using a soil auger at five depth ranges of 0-15 and 15-32, 32-60, 60-84 and 84-160 cm in order to determine the influence of organic matter amongst others, on copper abundance, mobility and availability. Samples were air dried, crushed with mortar and pestle to break up the clods and enable the soil pass through a 2 mm sieve for particle size distribution and routine analysis. For the determination of organic carbon, total nitrogen and copper speciation, the soil was further passed through a 0.5 mm sieve.

Laboratory analysis
The chemical parameters analyzed include: Organic Carbon (C), soil pH (H_2O), Total Nitrogen (N), available Phosphorus (P), Exchangeable Bases [Magnesium (Mg), Calcium (Ca), Potassium (K) and Sodium (Na)], Exchangeable Acidity (H^+), Extractible Micronutrients [Manganese (Mn), Zinc (Zn), Iron (Fe), Copper (Cu)], Effective Cation Exchange Capacity (ECEC), Percentage Base Saturation according to Udo and Ogunwale (1986). The particle size distribution of the soil was determined using the method described by Gee and Or (2002).

Analytical methods used for determining the forms of copper in the soils

The extraction scheme used for fractions of copper in the experimental soil used were based on six operationally defined fractions as described by Salbu and Oughton, (1998). This method is a modification of the conventional sequential extraction procedure for fractions of metals in soil and sediments (Tessier *et al.*, 1979). One gramme of soil sample was weighed and placed in a 100 ml polypropylene bottle. The sequential extractions into six fractions are as described below;

Solution copper

Ten ml of distilled water was added to the soil sample in the polypropylene bottle and the mixture was shaken for one hour. The mixture was then centrifuged for 15 min at 1500 rpm. The supernatant was then filtered into another polypropylene bottle to determine copper concentration in the filtrate using Atomic absorption spectrophotometer (AAS). While the residue (i) was used for the next extraction.

Exchangeable copper

Eight ml of sodium acetate solution (1M NaOAc, pH 8.2) was added to the residue from (i) at room temperature and agitated for 2 hours. Then, the mixture was centrifuged at 1500 rpm for 15 min. The supernatant was filtered into another bottle for copper analysis and the residue (ii) used for the next extraction.

Copper bound to carbonates

The residue from (ii) was leached at room temperature with 8 ml of 1M sodium acetate (NaOAc) adjusted to pH 5.0 with acetic acid (HOAc). Continuous shaking was maintained for 1 hour. The mixtures were centrifuged at 1500 rpm for 15 mins. Then the supernatant was filtered and measured for copper content

using the Atomic absorption spectrophotometer (AAS), leaving the residue (iii) for the next step.

Copper bound to manganese-iron oxides

To the residue from (iii) 20 ml of 0.3M sodium dithionite ($Na_2S_2O_4$+ 0.175M Na-citrate + 0.025M citric acid, as prescribed by (Anderson and Jenne, 1970) was added at $96 \pm 3^{\circ}C$ with occasional shaking. These mixture were centrifuged as in step (ii) above and the supernatant was filtered then copper content measured with the AAS. The residue (iv) was used for the next extraction.

Copper bound to organic matter

Three ml of $0.02M$ HNO_3 and 5 ml of 30% H_2O_2 adjusted to pH 2 with HNO_3, was added to the residue from (iv). The mixture was heated to $85 \pm 2^{\circ}C$ for 2 hours with occasional shaking. Three ml aliquot of 30% H_2O_2 (pH 2 with HNO_3) was then added to the mixture and the sample was heated again to $85 \pm 2^{\circ}C$ for 3 hrs with intermittent shaking. After cooling, 5 ml of 3.2M NH_4OAc in 20% (v/v) HNO_3 was added and the sample was diluted with 20 ml and agitated continuously for 30 minutes. Ammonium acetate (NH_4OAc) was added to prevent adsorption of extracted metals to the oxidized soil. The mixtures were centrifuged at 1500 rpm for 15 min then the supernatant was filtered and copper content was analysed as previously described.

Residual copper

The residue from (v) was digested with a 5:1 mixture of hydrofluoric and perchloric acids. The soil was first digested in a platinum crucible with a solution of concentrated $HClO_4$ (2 ml) and HF (10 ml) to near dryness; subsequently a second addition of $HClO_4$ (1 ml) and HF (10 ml) was made and again the

mixture was evaporated to near dryness. Finally, $HClO_4$ (1 ml) alone was added and the sample was evaporated until the appearance of white fumes. The residue was dissolved in 12N HCl and diluted with 25 ml. The resulting solution was then analyzed by atomic absorption spectrophotometer for copper metal using the standard addition technique (Tessier *et al*., 1979).

Determination of mobility factor

Mobility of metals in soil was assessed on the basis of absolute and relative content of fractions weakly bound to soil components. The relative index of metal mobility was calculated as a mobility factor according to (Kabala and Singh, 2001) and on the basis of the following equation.

$$\text{Mobility Factor} = \frac{(F1)+(F2)+(F3)}{(F1)+(F2)+(F3)+(F4)+(F5)+(F6)} \times 100$$

Where F1 = water soluble fraction; F2 = exchangeable fraction; F3 = carbonate bound fraction; F4 = Fe - Mn oxides-bound fraction; F5 = organic matter bound fraction and F6 = Residual fraction.

Statistical Analysis

The data generated were subjected to correlation and stepwise regression analyses using the Genstat statistical package (Buysse *et al*., 2004).

Results

Chemical properties of the soils and textural classes

The clay silt and sand content ranged from 154-454 g/kg, 80-140 g/kg and 446-706 g/kg respectively. The textural classes observed were sandy loam on the uppermost and last horizons, sandy clay loam on the second and fifth horizons while sandy clay occupied the middle horizon as shown in Table 1. The soil pH ranged from neutral to slightly alkaline (6.9-7.3), organic carbon was low at all depths (5.82-9.56 g/kg) except at 0-15 cm where it was very high (25.76 g/kg), total nitrogen was moderately high ranging from (3.02-4.37 g/kg), available phosphorus (Bray-1-P) mg/kg was very low ranging from (0.04-0.11 mg/kg) while very low amounts of exchangeable potassium were observed at all depths (0.14-0.20 cmol/kg) except at 84-160 cm depth where low (0.23 cmol/kg K) amounts was observed . The total exchangeable bases (TEB) ranged from 6.07-10.36 cmol/kg, the exchangeable acidity (EA) ranged from 0.30-0.70 cmol/kg and the ECEC ranged from 6.57-11.06 cmol/kg. ECEC less than 16 cmol/kg as shown in Table 2.

Copper fractions in soil collected from the study site

Copper bound to the residual had the highest value at depth 15-32 cm closely followed by

Table 1: Particle size distribution and textural classes of the soil

Soil Depth	Clay	Silt	Sand	Textural Class
(cm)		(g/kg)		
0-15	154	140	706	Sandy Loam
15-32	294	80	626	Sandy Clay Loam
32-60	454	100	446	Sandy Clay
60-84	314	140	546	Sandy Clay Loam
84-160	174	180	646	Sandy Loam

depth 84-160 cm. Total copper values ranged from 49.93-146.83 mg/kg with solution copper ranging from 0.15-0.91 mg/kg, exchangeable copper ranged from 0.08-0.48 mg/kg, carbonate-bound copper ranged from 0.72-3.20 mg/kg, organic matter-bound copper ranged from 8.00-96.60mg/kg, manganese and iron oxides-bound copper ranged from 9.91-29.25 mg/kg and residual copper ranged from 5.65-28.25 mg/kg (Table 3). There was no consistent increase or decrease in any of the fractions either up or down the profile. However, total copper increased steadily from 0-15 cm to 84-160 cm depth. Solution copper contributed 0.30-1.80% of the total copper, exchangeable copper contributed 0.05-0.89%, carbonate-bound copper contributed 1.11-6.35%, and organic matter-bound copper contributed 15.86-

74.22%, manganese and iron oxide-bound copper as shown in Table 3.

Mobility factor of Copper in the experimental soils

Mobility factor observed ranged from 1.3-8.5%. No consistent pattern of increase or decrease in mobility factor was observed either up or down the profile as shown in Table 4 Solution copper contributed 11.8-24.3% of the total mobility factor, exchangeable copper contributed 3.3-31.5% and carbonate-bound copper contributed 56.7-74.9% of the total mobility factor as shown in Table 4. Carbonate bound copper had the highest contribution to the mobility of copper in study area and the least was recorded for exchangeable copper fractions.

Table 2: Chemical properties of the soils samples collected from the oil palm plantation of the Teaching and Research Farm University of Ibadan

| Depth (cm) | Ph | Organic Carbon (%) | Total N (%) | Avail. P (mg/kg) | Exchangeable Bases (cmol/kg) | | | | | ECEC | %Base Sat. | Micronutrients (mg/kg) | | | |
					Ca	Mg	K	Na	Acidity			Mn	Fe	Cu	Zn
0-15	7.3	2.58	0.47	0.09	4.31	1.37	0.18	1.83	0.40	8.09	95.1	278	131	43.0	10.3
15-32	7.1	0.96	0.34	0.11	2.06	1.17	0.14	2.70	0.50	6.57	92.4	108	185	43.7	4.9
32-60	7.0	0.58	0.33	0.05	3.51	1.37	0.17	2.65	0.30	8.00	96.3	81.9	270	22.8	2.4
60-84	7.0	0.71	0.37	0.04	2.86	3.94	0.20	2.91	0.50	10.42	95.2	77.9	263	25.3	2.9
84-160	6.9	0.79	0.30	0.07	4.34	2.35	0.23	3.44	0.70	11.06	93.7	63.9	251	29.6	3.2

Avail P = Available phosphorus, ECEC = Effective cation exchange capacity Total N = Total Nitrogen.

Table 3: Copper fractions (mg/kg) in the experimental soil samples collected from the oil palm plantation of the Teaching and Research Farm University of Ibadan

Soil Depth (cm)	Solution	Exchangeable	Carbonate bound	Organic matter bound	Mn-Fe oxides bound	Residual	Total
0-15	0.15	0.40	0.72	19.40	9.96	19.30	49.93
15-32	0.91	0.16	3.20	8.00	9.91	28.25	50.43
32-60	0.41	0.48	1.52	25.40	10.66	15.25	53.72
60-84	0.44	0.08	1.44	96.60	25.94	5.65	130.15
84-160	0.59	0.08	1.76	93.00	29.25	22.15	146.83

Table 4: Mobility factor of copper (mg/kg) from the soil samples collected at different depths from the oil plantation at the Teaching and Research Farm University of Ibadan

Soil Depth (cm)	Solution Cu	Exchangeable Cu	Carbonate bound Cu	Total Cu	Mobility Factor (%)
0-15	0.15	0.40	0.72	49.93	2.5
15-32	0.91	0.16	3.20	50.43	8.5
32-60	0.41	0.48	1.52	53.72	4.5
60-84	0.44	0.08	1.44	130.15	1.3
84-160	0.59	0.08	1.76	146.83	1.5

Correlation between copper forms in the soil and some soil properties

Significant correlations were obtained between oxidizable copper fraction and total copper ($r = 1.00$, $P<0.01$); organic matter and oxidizable fractions, organic matter and total copper ($r = 0.974$, $P<0.01$); carbonate fractions and pH ($r = -0.922$, $P < 0.01$). Non-significant correlation were observed between the solution fractions and the exchangeable fractions of copper($r = 0.541$) also between organic matter and the residual fractions of copper ($r = -0.571$); Copper in the exchangeable and oxidizable fractions ($r = -0.757$); exchangeable and total fractions ($r = 0.760$); Exchangeable copper fractions and organic matter ($r= 0.668$); Carbonate and residual fractions of copper (-0.560). Carbonate fractions and organic matter ($r= -0.565$); Carbonate fractions and manganese ($r = -0.621$); carbonate copper fractions and copper concentration in soil ($r = -0.595$); Oxidizable copper fractions and iron ($r= 0.568$).

Table 5: Correlation between copper forms and some soil properties of soil collected from the oil plantation at the Teaching and Research Farm University of Ibadan

	SOL	EXC	CAR	OM	OX	RES	TOT	pH	ORGC	Mn	Fe	Cu	Zn
SOL		-.541	.213	-.032	.074	.425	.080	.069	-.437	-.421	.174	.260	-.385
EXC			-.170	-.668	-.757	.006	-.760	.130	.347	.430	-.250	.007	.336
CAR				-.255	-.099	.560	-.097	-.922**	-.565	-.621	.072	-.595	-.408
OM					.974**	-.571	.974**	.014	-.295	-.353	.595	-.274	-.411
OX						-.375	1.000**	-.117	-.361	-.445	.568	-.304	-.449
RES							-.373	-.339	.010	-.054	-.448	.169	.150
TOT								-.116	-.364	-.447	.569	-.302	-.452
PH									.602	.674	-.254	.821*	.490
ORGC										.986**	-.837*	.736	.982**
Mn											-.802	.757	.960**
Fe												-.667	-.925**
Cu													.723
Zn													

*Significant at 5% level   ** Significant at 1% level
SOL= Solution copper fractions, EXC= Exchangeable copper fractions, CAR= Carbonate copper fractions, OM= Organic matter copper fractions.   OX= Oxidisable copper fractions, RES= Residual Copper fraction, TOT= Total copper fractions   ORGC= Organic Carbon

Discussion

The textural classes of the study areas were mainly sandy loam which is a major characteristic of soil that are derived from basement complex according to Murdoch *et al*. (1976). Sandy soil do not hold nutrients because of their texture and therefore may not have enough basic cations that are essential for plant growth. The pH of the soils in different horizons were slightly alkaline, which is ideal for growing arable crops. Nitrogen in the soil at all depth is high according to the classification of soil fertility classes by Agboola and Ayodele (1985) which recorded that any Nitrogen value in southwestern soils >0.20% is high. The high N is a reflection of the high organic carbon of the soil at all depths. Furthermore high organic carbon may be due to high organic matter accumulated over the years which corroborates with the findings of Ogunkunle and Eghaghara (1992) and Ogeh and Ogwurike (2006). The low exchangeable Potassium, acidity, available P, and ECEC values indicated the dominance of low activity clays and the texture of the soil (Hassan *et al*., 2011 and Yakubu *et al*., 2011).

However, available phosphorus of the soil at different depths were below the critical value of P in soils from that region as described by Agboola and Ayodele (1985). Micronutrients (Zn, Cu, Mg and Fe) in this soil are above the critical value recorded for soils in south-western Nigeria by Agboola and Ayodele (1985).

This study showed high proportion of copper in the inaccessible forms (manganese-iron oxide bound form, organic matter bound form and residual form at higher depth (32-160 cm). The high proportion of copper in the residual fraction as well as other low accessible forms and the generally low levels of extractable copper were an indication that the soils were not polluted by copper as reported by (Christine *et al*., 1994). Copper had been reported to be tightly bound to compounds in soil organic matter, and much of copper in soil solution is also associated with organic matter rather than other micronutrients; and thus, are generally unavailable to plants (Marthur and Levesque, 1983; He *et al*., 2006). However copper bound to the residual fractions had the highest value at depth 15-32 cm closely followed by depth 84-160 cm. This same observation was as earlier been reported by Mescouto *et al.* (2011). This is an indication that the availability of copper in this soil depend on the organic matter, manganese –iron oxide form and residual. However, a number of previous studies on soils and sediments (Rauret *et al*., 1991; Ure *et al*., 1993; Thomas *et al*., 1994) reported extractable copper to be mainly associated with the oxidizable phase, where it was likely to occur as organically complexed metal species through reactions with COOH groups and phenolic OH. The low mobility factor of copper in the solution and exchangeable fractions across the different depth is an indication that the concentration of copper in the carbonate organic matter fractions and residual is high.

Carbonate content, soil pH, organic matter, CEC and clay content were predominant factor in copper adsorption in soil as described by Raikhy and Takkar (1981). The positive correlation of Cu and pH agreed with the findings of Saddiq *et al*., (2008) and Samndi *et al*., (2007). Soil pH is an important property controlling the bioavailability of Cu.

The significant (p=0.01) negative correlation (r=-0.957) between clay and sand contents showed that as clay content of the soil increases there is a corresponding decrease in the sandy content as well. A positive correlation between

soil organic carbon and copper and zinc suggest that these metals have a strong affinity for soil organic matter. Lu *et al*. (2003) reported similar findings that in non-urban soils a positive correlation was found between organic carbon and copper. Increase in exchangeable fraction which caused a decrease in organic matter, Fe and Mn oxide fractions and total copper in this study is attributed to the parent rock material.

There was no relationship between soil silt and total copper. Though, Ahmed and Soraya (2007) working on several metals reported that the sample with the highest percentage sand had the lowest total metal content while the sample with the highest finer particles had the highest total metal content thus suggesting a direct relationship between total metal content and the fraction percentages.

Conclusion

The sequential chemical analysis demonstrated diverse copper distribution in its total content, in sequenced fractions in each of the soil profiles investigated. This study showed that the contribution of each form of copper to total copper content followed the trend organic matter bound>residual> iron-manganese oxides bound> carbonate bound> solution> exchangeable. The highest proportion of copper in the analyzed soils occurred in the organic matter-bound fraction, followed by the residual phase. Solution copper was the second most significant contributor to variations in total copper. Carbonate-bound copper had the highest contribution to mobility factor. High proportion of the total copper were held in the inaccessible forms making toxicity impossible.

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