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Fractionation of Copper in Soils Around Waste Dump site in Kaduna Municipality, Nigeria

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Abstract: Generation of waste is increasing rapidly with increase in population, urbanization and industrialization. The indiscriminate dumping waste may cause serious environmental pollution. Copper among the other heavy metals was found as toxic accumulation at dumping sites. The bio-availability of copper (Cu) from soil could be estimated by a variety of chemical extraction procedures differing in nature and concentration of extractants, the sample weight and the time of extraction. The present study compared two different methods namely single and sequential extraction. Concentrated nitric acid (HNO_3) and 0.01 mol/L acetic acid (CH_3 COOH) were used as the single extractants. Whereas deionized water and varying strength of acids and alkali were used for sequential extraction of copper fractions. The total copper content ranged from 248 to 24700 mg kg^{-1} soil around the dump site. About 49 to 88% of the total copper was extracted using concentrated nitric acid. The results revealed that even strong acid HNO_3 is unable to release the cupper tightly bound to the soil matrix. This particular method with microwave digestion is commonly used for the estimation of anthropogenic pollution. On the other hand, the lowest copper yield was obtained using the acetic acid as the single extraction agent. In this case the concentrations were below 0.16% of the total Cu contents an amount that is generally referred as bio-available to plants.

Key words: Bio-availability, extraction methods, humic acid, tightly bound, anthropogenic.

Copper which is one of the essential plant nutrient element can have a detrimental effect on health hazard when it enters into food chain in excess than necessary. A little amount of copper is sufficient to satisfy crop requirement. However, municipal dumpsites are the potential copper sources mainly found in the refuse that are mainly used as manure in municipal agriculture.

Copper can be released from the soil by different extraction procedures. The least tightly bound water soluble fraction is obtained by the simple extraction using deionized water (Rodrigues *et al*., 2010). It gives an estimate of Cu present in soil pore water. This fraction of Cu is usually not in the form of the water-soluble ionic species but as species bound to dissolved organic water (Biester and Scholz, 1998). The use of diluted CH_3COOH as an extractant is a mild extraction procedures similar to use of $CaCl_2$ solution (Novozamsky *et al*., 1993).

The extraction solutions based on the chelating agent such as EDTA or DTPA represent yet another more efficient possibility. These agents are able to displace metals from insoluble organic or organometallic complexes in addition to those adsorbed on inorganic soil components. The other species of Cu fractions bound on iron sulphides, manganese hydroxides and carbonates, and Cu bound to the minerals can be obtained by acids, e.g. HCL (Lachler *et al.,* 1997). In soil Cu can be bound very tightly to the sulphur forming insoluble CuS (Boszke *et al.,* 2009). This fragment of Cu can be obtained either by aqua regia extraction in a microwave oven or using the saturated Na_2S solution from the residue remaining after the extraction procedures (Revis *et al.,* 1989). The concentration of $Na_2S_2O_3$ influences the extraction efficiency and has been studied in detail by Issaro *et al*. (2010).

The amount of Cu, which is not firmly bound to the silicate matrix of soil, is often obtained by using HNO_3 as an extraction agent (Reis *et al.,* 2010). The Cu concentration in these extracts enables an estimation of the Cu from anthropogenic sources. In some cases, concentrated nitric acid combined with HCl or H_2SO_4 is employed for total Cu

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content determination. It could also be used in sequential extraction procedures to obtain elemental Cu (Bloom *et al.,* 2006). Sequential extractions are suitable methods for the Cu speciation analysis of solid samples. However, there is no universal sequential extraction for the individual Cu fraction determination.

Materials and Methods

Collection and analysis of soil samples

Kaduna municipality was demarcated for sample locations. The soil samples were collected from Kakuri industrial waste disposal from ten sites. Sample were taken from the top layer (0-20 cm), air-dried, sieved < 2 mm and kept at 5°C for 5 weeks.

The soils were characterized for pH ($CaCl_2$) (Novozamsky *et al.,* 1993), organic matter content (Sims and Haby, 1971) and cation exchange capacity (ISO, 1994). Total content of sulphur was determined using x-ray fluorescence spectrometry. Total Cu was determined by atomic absorption spectrophotometer.

Extraction of copper fractions in soil

Single extraction chemical extractants having varying strength of HNO_3, $Na_2S_2O_3$, EDTA and CH_3COOH were used to determine the mobile and static phases of Cu element in soils. For determination of potentially mobilizable fractions, 0.25 g of each soil sample was decomposed in 5 ml of concentrated HNO_3. The mixture was digested at 280°C for 75 minutes using microwave digestion system. The digested samples were filtered using repeated washing of deionized water to final volume of 50 ml sodium thiosulfate extraction. Similarly for specific ion fractions following chemical extractants were used as described.

i. $Na_2S_2O_3$ extractant: Dissolve 1.0 g soil in 10 ml of 0.01 M solution of $Na_2S_2O_3$ and incubated overnight at ambient temperature.
ii. EDTA extractant: Dissolve 1.0 g soil in 10 ml 0.05 M EDTA solution (pH 7.0) and shaken for 1 h.
iii. 0.5 g of the sample was added to 10 ml of 0.1/mol/l solution of CH_3COOH and shaken overnight.
iv. Acetic acid extractant: Dissolve 0.5 g soil in 10 ml 0.1 M solution of CH_3COOH and shaken for overnight.

All the extractants were centrifuged for 10 minutes at 3000 rpm, supernatant were decantated and the Cu content in all the samples was determined using atomic absorption spectrophotometer.

Sequential extraction

This was designed by modifying the procedure in 50 ml centrifuge tubes by other authors (Blooms *et al.,* 2006; Boszke *et al.,* 2009). The 0.1 g weight of each soil sample was leached in 50 ml centrifuge tubes using 10 ml of chloroform, then shaken for 3 h and centrifuged. This stage was considered as F_0 and the residual soil obtained after the extraction was used for subsequent extraction. The solid/liquid ratio was kept uniform for all chemical extractants used in sequential extraction. The extraction procedures were performed on the bulk samples using following steps sequentially:

All the extractants were separated from a solid phase by centrifugation for 10 minutes at 4000 rpm and the supernatant was used for estimation of Cu content in respective fractions. The extraction agents of each single step were used as blank samples and the Cu content in all the extracts was determined by AAS.

F_1; Cu leachable in water	:	The residual soil obtained from F_0 as described above were dissolved with deionized water and the supernatant after the centrifugation was used for estimation of Cu content dissolved in
F_2; Cu leachable under acidic condition	:	The residual soil obtained from F_1 were dissolved with 0.5 MHCL and the supernatant was used for estimation of Cu content soluble in dilute acids.
F_3; Cu bound to humic substances	:	The residual soil obtained in F_2 was dissolved in 0.2 M KOH solution and the supernatant was used for estimation of Cu content soluble in alkaline.
F_4; Cu bound to complexes	:	The residual soil obtained in F_3 was dissolved and extracted using 50% HNO_3 solution and the supernatant was used for estimation of Cu content bound to soil matrix.
F_5; Residual copper	:	Finally the residual soil was digested for estimation of residual soil Cu content.

Results and Discussion

Soil characteristics

The soils are neutral in soil reaction (av. pH 7.18 with high cation exchange capacity (av. 131.7 mmol kg^{-1} soil), oxidizable carbon (1.2 to 3.4%) and sulphur (0.28 to 0.56%) content in the vicinity of dumpsite of Kaduna muncipility.

Characterization of different copper fractions

A wide variation was observed in total Cu content (248 to 24700 mg kg^{-1}) in soil around Kaduna dumpsite. More than fifty per cent of the total Cu content was extracted by concentrated nitric acid followed by sodium thiosulphate and EDTA and least in acetic acid extractants.

Single extraction

Generally, the extractant HNO_3 recovered more than 50% of the total Cu content in 1 to 8 sampling sites. However, the soil samples from most contaminated sites i.e. site no 9 and 10 about 70 to 90% of the total Cu content were recovered by using concentrated HNO_3 extractant. Similarly, the yield of Cu content extractor using sodium thiosulphate were also relatively higher for sample site (9 and 10) as compared to other sites indicating presence of more unstabilized Cu fraction at these two sites than others. The average values of copper in these samples was approximately 20% of the total. In other samples, the content of copper ranged from 1.2% to 3.5%. Therefore, it might be inferred that in places with high anthropogenic contamination, the presence of copper species bound to sulphur is higher than in less contaminated samples. In the case of the most contaminated site, the rate of extractable copper using $Na_2S_2O_3$ corresponds with the results reported by Issaro *et al*. (2010). They showed that the extraction yield of $Na_2S_2O_3$ usually reaches 50% of Cu obtained by HNO_3 extraction from soils with high Cu levels.

Further, using chelating EDTA the values of extractable Cu ranged between 0.5% and 2% of the total Cu content, in all the experimental samples. These results correspond to those reported by Subires-Munoz *et al*. (2011), who obtained by this type of extraction approximately 20% of the total Cu content. This variability suggests that the amount of copper which might serve as a source of plant uptake is similar both in more and less contaminated places. Incidentally results obtained by extraction with a solution of CH_3COOH simulates natural conditions of soil solution. The yields of CH_3COOH were below 15% and confirmed no significant difference. The low availability therefore seems to indicate that copper is strongly bound to sulphide phases and or to insoluble clay minerals and organic matter in the sample as also reported by Rodrigues *et al.,* 2010.

Sequential extraction

Copper content extracted using sequential extraction (step F_1 to F_5) are presented in Table 2. The sum of the amount removed by each extraction was in good agreement with the total amount obtained, except in soil samples where higher degree of Cu contamination was observed. In general, values obtained in sequential extraction ranged from 75% and 100% of the total Cu content at different sites. First extraction representing the total content of organo-copper components (F_1) was below the quantification limit (2 mg kg^{-1}) in all the sample.

Table 1. Total and extractable contents (mg kg^{-1}) of copper after single extraction utilizing different extractants

Sample site	Total	HNO_3	$Na_2S_2O_3$	EDTA	CH_3COOH
1	1069	568	14.20	7.92	0.69
2	248	141	8.06	2.89	0.46
3	424	208	7.84	6.17	0.28
4	413	247	9.24	7.41	0.56
5	540	284	11.40	7.61	0.41
6	2114	1211	61.40	8.41	0.84
7	446	217	14.10	3.46	0.41
8	561	301	7.41	2.81	0.81
9	24700	21114	64.11	592.00	12.40
10	11426	10011	34.66	66.40	9.10

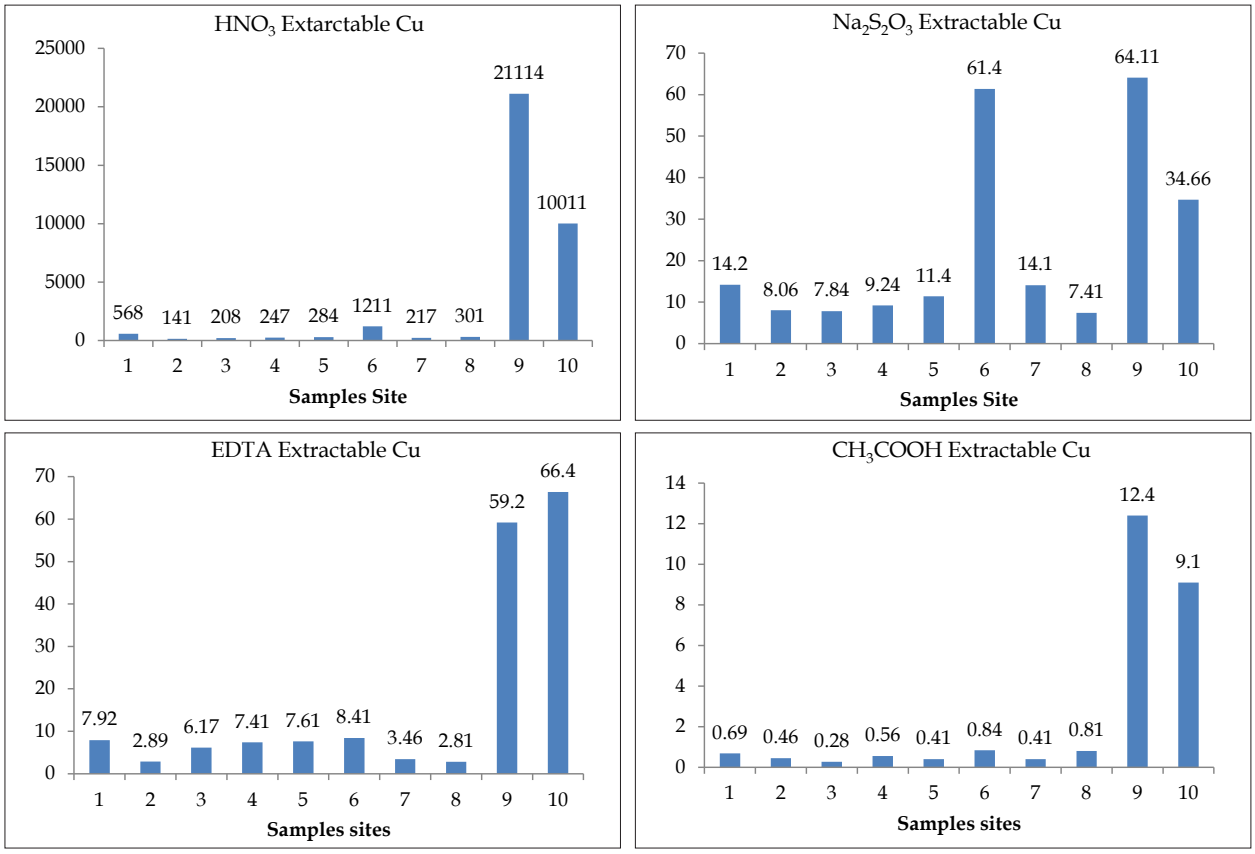

Fig. 1. Relative proposition of Cu content among different sampling sites using different chemical extractants.

The F_1 and F_2 generally considered as mobile fractions were also very low in the majority of the samples. The Cu fraction leachable in water was detectable in the samples (9 and 10) having higher degree of total Cu content.

Less than 8.1% Cu leachable under acidic conditions was recovered at most contaminated sampling sites. The Cu species extracted in F_3 and considered as mobile phase of Cu fractions were generally higher and ranged from 18 to 30%. The Cu species bound to organic matter were regarded as stronger complexes and thus have limited mobility (Liu *et al.*, 2006).

On the contrary, the per cent content of samples 9 and 10 were approximately 9% and differences among the amount of mobile and semi mobile fractions were relatively low. The highest Cu content was found in the case of non-mobile fraction (i.e. HNO_3 extractable fraction). The content of Cu in solid residue after the sequential extraction was less than 12% in majority of the soil samples. However, it was relatively more in highly contaminated samples (sample 9 and 10). In the majority of the samples, which originated from the surroundings of the dumpsite, less than 2% of the total Cu content was found as mobile fraction. The lowest Cu was found using the acetic acid extraction which is the amount generally called biologically available copper to plants (Quevauviller *et al.*, 1993). Conversely

Table 2. Various Cu fraction (mg kg^{-1}) extracted using sequential extraction procedure

Samples site	F_1	F_2	F_3	F_4	F_5
1	ND	ND	260	510	140
2	ND	ND	80	130	20
3	ND	ND	140	240	50
4	ND	ND	141	246	40
5	ND	ND	160	311	35
6	ND	40	36	1300	200
7	ND	ND	86	260	28
8	ND	1400	130	340	70
9	380	540	2600	18111	4400
10	190	ND	980	3900	3100

*Data below the quantification limit (2 mg kg^{-1}) shown as not detected "ND", F_1: Deionized extractable Cu, F_2: HCl extractable Cu, F_3: KOH extractable Cu, F_4: HNO_3 extractable Cu, F_5: Residual Cu.

elemental Cu and Cu complexes were found in the highest amount and the proportion of these fractions ranged between approximately 50% and 70%, respectively.

Conclusion

Wide variability was observed in total Cu content as well as their availability potential around the dumpsite depending on origin and physio-chemical parameters of the soil. A very less fraction of Cu (<2%) was recovered as mobile fraction. The present study is specific to dumpsite of Kaduna, therefore the outcome should not be taken as general characteristics for Cu fraction impacted due to anthropogenically contaminated sites.

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