

Chemical Fractionation of Trace Metals in Sewage Water – Irrigated Soils

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Received 7 June 2009;

Revised 29 Sep. 2010;

Accepted 10 Oct. 2010

ABSTRACT: The bioavailability of trace metals, their biological uptake and ecotoxicological effect on soil biota can be better understood in terms of their chemical fractionation. The present study examined the mobility and availability of Cd, Cu, Ni, Pb and Zn in sewage water – irrigated soils using sequential extraction technique as a basis for predicting metal uptake by plants. The residual fraction was the most abundant pool for all the five metals examined. A significant amount (2.7 – 70.2%) of all the five metals was also present in the potentially available fraction: - nonresidual fraction. The result further indicated that the contamination of Cd and Ni in these soils was not as severe as Pb, Cu and Zn. Assuming that mobility and bioavailability of these metals are related to their liability and geochemical forms, and that they decrease in the order of extraction sequence. The apparent mobility and potential bioavailability for these five metals in the soils were: - Pb> Zn> Cu> Ni> Cd.

Key word: Fractionation, Sewage water, Soils, Bioavailability, trace metals, Mobility

INTRODUCTION

Vegetable production at Fadama (flood plains) lands along river banks or/and other water ways in northern states of Nigeria using wastewater for irrigation during dry season is one of the economic enterprises, which is contributing tremendously to the general economic well being of the farmers in the region. Northern states of Nigeria are characterized by a tropical climate with two distinct seasons; a rainy season (May – October) and a dry/harmattan season (November – April). Based on this, fresh water is not sufficient to meet the water requirements of vegetable crops during dry season. To sustain irrigated agriculture, one option is the use of contaminated water for irrigation. Untreated wastewater irrigation on urban and sub-urban lands has long been practiced in several parts of the world due to its high contents of plant nutrients and due to lack of infrastructure and facilities for safe disposal. The urban agricultural soils of northern states of Nigeria are often irrigated with municipal sewage water for growing vegetables (Chiroma *et al.*, 2003; Audu and Lawal, 2005). This sewage water may constitute of dangerous toxic materials, inorganic compounds and organic materials. Repeated direct discharges of these unwanted toxic materials in excess on sewage water – irrigated soils bring the failure of self – cleaning mechanism of the soil environmental compartments. In assessing the environmental quality of contaminated soil, the prediction of mobility and bioavailability of

metals is very important, since deposition of trace metals in agricultural soil may become detrimental to plant growth or to the consumers of the harvested vegetable crops, which depends upon the chemical form of metals present in the soils (Ma and Rao, 1997; Nasrabadi *et al.*, 2010; Taghinia hejazi *et al.*, 2010; Vasanthavigar *et al.*, 2009). The form in which trace metals exist in soil is very important to the environmental chemists as well as others because of the close relation between toxicity and fractionation. It is not just enough to raise alarm that a soil is heavily polluted by certain trace metals without knowing the quantity that is readily mobilizable and bioavailable. In addition, measurement of the total concentration of metals provides inadequate information to allow us to assess the bioavailability or toxicity of metals. An evaluation of total metals levels following a strong acid digestion of the soil may be useful as a global index contamination, but it provides little indication of their bioavailability, mobility and reactivity in trace metal contaminated soils (Ma and Rao, 1997). The investigation of chemical fractionation of metals in soil may help to assess the bioavailable metals fractions and the possibility of mobilization of these metals in soil. Chemical fractionation was defined (Templeton *et al.*, 2000) as the process of classification of an analyte or a group of analytes from a certain sample according to physical (e.g., size, solubility) or chemical (e.g., bonding, reactivity) properties.

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Recently, interest in determining the chemical form of metals in environmental samples has increased. The interest has arisen largely because of the awareness that it is the chemical forms, rather than metal itself, that plays an important role in the transfer of metals along the water-soil – plant – animal – human chain (Rattan *et al.*, 2005).

Before we can evaluate how trace metals affect the biological populations and what environmental risks they pose, the fate of such trace metals must be known. Knowingly, accumulation, mechanisms in sediments and soils can be classified into five categories: (i) Water soluble and exchangeable, (ii) bound to carbonate phases, (iii) bound to reducible phases (Fe and Mn oxides), (iv) bound to organic matter and sulfides, and (v) bound to silicates and detrital materials (Solomons and Forstner, 1980). Trace metals present in these categories have different remobilization behaviors under changing environmental conditions (Forstner, 1985). Geochemical forms of trace metals in soils affect their solubility which directly influences their bioavailability (Xian, 1987). Therefore, determining total content of trace metals is insufficient to assess the environmental impact of contaminated soils and sediments (Solomons and Forstner, 1980), because it is the chemical forms that determine metals behaviors in the environment and its remobilization ability.

Conceptually, to study metal mobility and availability in soils, the solid materials can be partitioned into specific fractions, which can be extracted selectively by using appropriate reagents. Numerous extraction schemes for soils and sediments have been described in the literature (Tessier *et al.*, 1979; Shuman, 1985). The use of sequential extraction, although more time consuming, furnishes detailed information about the origin, mode of occurrence, biological and physicochemical availability, mobilization and transport of metals (Rattan *et al.*, 2005). The selective extraction scheme used here is based on operationally defined fractions:- water soluble, exchangeable, Oxidizable (bound to organic matter), acid soluble (bound to carbonate), reducible bound to oxides and hydroxides and residual (bound to silicates and detritus materials) to investigate the chemical fractionation of selected metals (Cd, Cu, Ni, Pb and Zn) in soils irrigated with sewage water and evaluate the effect of total metal concentration on metal partitioning into different fractions. The fractionation of metals into these defined fractions is based on the believe that metals in the soil environmental compartments could be remobilized into soils solution due to these – changes in the acidity, changes in solution ionic strength, changes in the redox potential and the formation of complexes.

MATERIALS & METHOD

This study was carried out with the aim to ascertain the chemical partitioning of Cd, Cu, Ni, Pb and Zn in agricultural soils repeatedly irrigated with sewage water. For this purpose ten suitable sites were selected in Zaria metropolis, Nigeria. The surface (0 – 10cm depth) soil samples were collected from these sites where sewage irrigation is being practiced on agricultural land. During the sampling, the selected sampling sites were subdivided into grids of 20 x 20m and samples taken from the centre of each grid, 10 soil samples were collected from each site. To obtain composite samples of each site, bulking method was employed to harmonize the samples. A conning and quartering method was applied repeatedly to reduce the sample volume of each site (Jackson, 1958). Each representative site sample was prepared by mixing one sample with the other replicates from different grids of the same site to overcome spatial variability. The soil samples were air – dried, ground, and sieved mechanically using 2mm sieve. They were then stored in polythene bags at room temperature. The soil pH and electrical conductivity (EC) were measured in air – dried samples (1:10 w/v) using digital pH and conductivity meter. Organic matter content was determined by loss on ignition, Exchangeable cations were extracted by 1.0mol/dm³ CH₃COONH₄ and subsequently determined by AES and AAS for Na, K and Ca, Mg, respectively (Agbenin, 1995). Textural analysis based on the proportions of different particle size was also carried out. The textural classification was in accordance with the international systems of textural classification (Allen, 1974).

The quality assurance for soil sample was conducted as described by Awofolu *et al.*, (2005) through spiking experiment to evaluate the digestion process and the effectiveness of AAS machine. A chemical analysis protocol through multi-element standard solution was applied. Soil samples were digested in accordance with the procedure used by Francis (2004). One gram of finely ground dried soil samples were mixed with 20cm³ (1:1) HCl/HNO₃ acid mixtures and the content was heated until dryness. The residue was extracted using 2 mol/dm³ HCl and brought to 50cm³ with distilled water, which was used for direct aspiration into an air – acetylene flame of AAS machine (Shimazu model AA 650) to obtain a metal profile of the soils. Prior to the sample analysis, the AAS was calibrated and standardized by using relevant primary standards (prepared with AR grade chemicals). Triplicate digestion and analysis of the samples together with blank were carried out.

The procedure of Tessier *et al.* (1979) was selected for this study that is designed to separate trace metals

into six operationally defined fractions: - water soluble, exchangeable, acid soluble, oxidizable, reducible and residual fractions. One gram of each of the three sub-samples (Triplicate) of soil was weighed into a 40mL polycarbonate centrifuge tube and the following fractions obtained.

1. Water soluble: Each sample was extracted with 15mL of deionized water for 2 hours.

2. Exchangeable: Residue from 1 was shaken at room temperature with 16mL of 1 mol/dm³ Mg (NO₃)₂ at pH 7.0 for 1 hour, centrifuged and supernatant decanted and made up to 40mL with distilled water prior to analysis.

3. Oxidizable (bound to organic): residue from 2 + H₂O₂ 8.8 mol/dm³ + 6mL HNO₃ 0.02mol/dm³ was shaken for 5 + 1 hour at 98°C. 10mL CH₃COONH₄ 3.5 mol/dm³ was added as an extracting agent, centrifuged and supernatant decanted and made up to 40mL with distilled water prior to analysis.

4. Acid soluble (bound to carbonate): 25mL of 0.05 mol/dm³ Na₂ EDTA was added to the residue from 3, shaken for 6 hours and centrifuged. The supernatant was decanted and made up to 40mL with distilled water prior to analysis.

5. Reducible (bound to Fe/Mn oxides and hydroxides): residue from 4 + 17mL NH₂OH.HCl 0.1mol/dm³ + 17mL CH₃COONH₄ 3.5mol/dm³ was shaken for 4+1 hour at 98°C. The residue was extracted with 10mL CH₃COONH₄ 3.5 mol/dm³ shaken for 1 hour, centrifuged, the supernatant was decanted and made up to 40mL with distilled water prior to analysis.

6. Residual (bound to silicates and detritus materials): residue from 5 was digested using aqua – regia/hydrofluoric acid (HCl/HNO₃/HF) (0.35:12 w/v soil/solution ratio) in acid digestion Teflon cup. It was dried to ash for 2 hour and evaporated to dryness. The residue was diluted to 40mL with distilled water prior to analysis.

After each successive extraction, the samples were centrifuge at 4500 rpm for 15 minutes (Legret *et al.*, 1988). The supernatant was removed with pipette and filtered with Whatman No. 42 filter paper. The residue was washed with deionized water followed by vigorous hand shaking and then followed by 15 minutes of centrifugation before next extraction. The volume of rinsed water was kept to minimum to avoid excessive solubilization of solid materials. Finally, the extracts collected were analyzed using AAS to determine the concentration of Cd, Cu, Ni, Pb and Zn metals in each of the aforementioned fractions.

RESULTS & DISCUSSION

The validity of the digestion procedures used for soil samples treatment and the precision and accuracy of the AAS analysis were tested by spiking experiment.

The mean percentage recoveries of metals used to spike the soil sample are presented in Table 1. The mean percentage recoveries from spiked soil sample for metals ranged from 86.4±0.4 to 96.2±0.2, which is similar to the 86 – 98% range reported for the same metals in similar matrix by Awofolu *et al.* (2005). Therefore, the reproducibility of the methods and the precision and accuracy of the AAS machine were adjudged reliable.

Table 1. Means % recoveries (± SD) of metal standard added to pre-digested soil sample*

| Metals | Spiked Conc. (mg/L) | % recoveries |
|--------|---------------------|--------------|
| Zn | 2.0 | 96.2±0.2 |
| Ni | 2.0 | 91.6±0.3 |
| Cu | 2.0 | 89.8±0.5 |
| Pb | 0.5 | 86.4±0.4 |
| Cd | 0.5 | 93.8±0.4 |

* Values are mean of triplicate analyses, SD is the standard deviation.

Selected physicochemical characteristics of soil samples are tabulated in Table 2. The result indicated that the pH values for the soils varied from 5.83 to 7.32. This suggested that the studied soils were slightly acidic to slightly alkaline in nature. The electrical conductivity (EC) of the soils was found to be between 0.38 to 0.66dmS/m. The high values of conductivity of the soils may be attributes to the secondary addition of soluble salts as a result of irrigation with sewage water, from which more ions got into the soils. In fact, studies have shown that sewage water-irrigated soils become enriched with soluble salts from sewage water when used for irrigation (Ibrahim *et al.*, 1992). The typical amount of organic matter in soil varies from < 1% in ordinary soils to 90% in mineral soils (Rodojevic and Bashkin, 1999). Therefore, the values obtained in this work were within this range and the relevance of organic matter to this study is its influence on mobility and flux of trace metals in the soils. The normal range of organic matter found signified that the trace metals in the soils would be available since trace metals are known to form complexes with organic matter which influence their availability (Sauve *et al.*, 1998).

The result for the cation exchange capacity (CEC) which was determined by the sum of cations in 1.0 mol/dm³ varied from 17.6 to 28.4 cmol/kg. Calcium was the dominant exchangeable base (13.14 to 20.92 cmol/kg) in all the samples. It is clear from the results obtained that the exchangeable base K⁺, Na⁺, Mg²⁺ and Ca²⁺ followed the trend as Ca²⁺ > Mg²⁺ > K⁺ > Na⁺. This may be due to the influence of the type water used for irrigating the soils, as it was earlier reported

that sewage water of municipal origin contained appreciable amount of major plant nutrients and possibly, supplied additional nutrients to sewage water – irrigated soils (Rajesh *et al.*, 2004). The result obtained is in accordance with the result obtained by Mapanda *et al.* (2005) in a similar study. However, in contrast, Abdel – Hady (2007) reported a different trend of which the exchangeable bases were in the following order: $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$. Thus, sewage water irrigation has influence on the quality/property of soil. The particle size method for textural analysis revealed that the soil texture was loam to silt loam across the sampling sites. From this classification, it could therefore be deduced that the soil of the study sites have high potential of leaching trace metals due to their low clay contents, which could easily penetrate into the subsurface layer of the soils. As such, this further indicated that the soil solutions of the study sites might be enriched with trace metals, thus making them available for plant uptake.

The results of total metal contents of soil samples are presented in Table 3. The total concentration of Zn varied from 117.2 ± 5.4 to 296.8 ± 9.8 mg/kg, while Ni concentration ranged from 62.3 ± 5.1 to 143.4 ± 5.7 mg/kg and Cu level was from 76.8 ± 3.7 to 204.7 ± 10.4 mg/kg. The Pb and Cd levels ranged from 29.8 ± 5.4 to 83.4 ± 4.6 mg/kg and 8.5 ± 2.3 to 46.6 ± 4.3 mg/kg, respectively. All the soil samples showed maximum Zn concentration followed by Cu concentration. The Cd concentration was found to be the least as compared to other metals in all the soil samples. The predominance of Zn in the soils may be attributed to the stabilization of Zn oxides in the soils, as it was reported that Zn oxides in soils have high stability constant (Ma and Rao, 1997), while in the case of Cd may be due to weak adsorption nature of Cd in the soils (Mido and Satake, 2003).

The average values of the metals analysed in this investigation were lower than the metal levels (Pb, 128.12; Zn, 768.21; Cu, 234.40 and Ni, 319.42 mg/kg) reported by Rattan *et al.* (2005) for sewage water – irrigated soils in India, but high than the values (Pb, 2 – 15; Cu, 0.5 – 2.0 and Cd, 0.1 – 0.25 mg/kg) reported by Dike *et al.* (2005) for Jakara river bank soils also irrigated with wastewater during dry seasons. In the same vein, the soil mean metal levels obtained in this work were above the recommend permissible limits in soils by EU (1986), except for Zn and Pb. Although the maximum concentrations of Zn and Pb fell within the range of standard, it was found that their concentrations in the surface soils were higher than the natural concentration, 25 and 0.5 mg/kg, respectively (Ward, 1995). This suggested that the soils accumulated the trace metals excessively. Therefore, in general, the soils studied were truly contaminated with the five metals analyzed,

which may be due to water sources that were used for irrigating the soils. Also, an evaluation of total metal levels in the soils may be useful as an index of contaminations, but it provides little or no indication of their bioavailability, mobility and reactivity in soils. As such, investigation of fractionation of metals became imperative, with which to help to assess the bioavailability and the possibility of mobilization of these metals in the soils studied.

Soil has long been regarded as a repository for society's wastes. Gradually mobilized by biogeochemical processes and thus, soils contaminants can pollute/contaminate water supplies and impact food chains. Trace metals, such as Cd, Cu, Ni, Pb and Zn, are all potential soil pollutants/contaminants. Soils consist of heterogeneous mixtures of organic and inorganic solid components as well as a variety of soluble substances. Therefore, metal distribution among specific forms varies widely based upon the metal's chemical properties and soil characteristics (Soon and Bates, 1982). Thus, it is important to evaluate the availability and mobility of trace metals to establish environmental guidelines for potential toxic hazards and to understand chemical behavior and fate of trace metal contaminants in soils (Davies, 1980).

The sequential extraction used in this study is useful to indirectly assess the potential mobility and bioavailability of trace metals in the soils. The six chemical fractions are operationally defined by an extraction sequence that follows the order of decreasing solubility (Xian, 1989; Soon and Bates, 1982). Assuming that bioavailability is related solubility, then metal bioavailability decreases in the order: water soluble > exchangeable > acid soluble > reducible > oxidizable > residual. This order is just a generalization and offers only qualitative information about metals bioavailability. Based on the above information, we can further assume that metals in the nonresidual fractions are more bioavailable than metals associated with residual fraction. The nonresidual fraction is the sum of all fractions except the residual fraction.

The distribution patterns of the studied metals in various fractions were found to be as follows:-
 Zn: residual > reducible > acid soluble > exchangeable > oxidizable > water Soluble
 Ni: residual > exchangeable > reducible > acid soluble > oxidizable > water soluble
 Cu: residual > oxidizable > acid soluble > reducible > exchangeable > water soluble
 Pb: residual > reducible > acid soluble > oxidizable > exchangeable > water soluble
 Cd: residual > exchangeable > reducible > acid soluble > oxidizable > water soluble.

Table 2. Selected physicochemical properties of the sewage water – irrigated soil (mean \pm SD, n = 3)

| Properties | pH | Electrical conduct. (dS/m) | Organic matter % | Textural class | CEC (Cmol/kg) | Ex-Na ⁺ Cmol./kg | Ex-K ⁺ Cmol/kg | Ex-Mg ²⁺ Cmol/kg | Ex-Ca ²⁺ Cmol/kg |
|------------|-----------------|----------------------------|------------------|----------------|------------------|-----------------------------|---------------------------|-----------------------------|-----------------------------|
| Soil A | 6.72 \pm 0.19 | 0.39 \pm 0.07 | 4.55 \pm 1.53 | Loam | 25.43 \pm 5.92 | 0.26 \pm 0.07 | 1.26 \pm 0.31 | 5.45 \pm 1.06 | 18.48 \pm 3.12 |
| Soil B | 6.31 \pm 0.23 | 0.51 \pm 0.04 | 5.14 \pm 2.03 | Loam | 26.15 \pm 4.64 | 0.39 \pm 0.05 | 0.99 \pm 0.08 | 6.56 \pm 2.11 | 18.21 \pm 4.09 |
| Soil C | 6.44 \pm 0.18 | 0.37 \pm 0.12 | 7.07 \pm 1.83 | Loam | 24.06 \pm 6.24 | 0.18 \pm 0.03 | 1.03 \pm 0.60 | 3.69 \pm 1.84 | 19.16 \pm 6.02 |
| Soil D | 6.78 \pm 0.35 | 0.43 \pm 0.26 | 8.28 \pm 2.51 | Loam | 20.72 \pm 4.17 | 0.48 \pm 0.19 | 2.01 \pm 0.16 | 5.09 \pm 2.04 | 13.14 \pm 5.17 |
| Soil E | 6.83 \pm 0.82 | 0.49 \pm 0.09 | 7.45 \pm 2.26 | Loam | 19.62 \pm 6.86 | 0.22 \pm 0.03 | 0.76 \pm 0.28 | 4.81 \pm 1.83 | 13.83 \pm 4.62 |
| Soil F | 7.25 \pm 0.68 | 0.59 \pm 0.17 | 4.89 \pm 1.52 | Loam | 29.98 \pm 7.04 | 0.78 \pm 0.22 | 1.52 \pm 0.03 | 6.76 \pm 2.16 | 20.92 \pm 8.26 |
| Soil G | 6.94 \pm 0.20 | 0.38 \pm 0.05 | 8.04 \pm 1.34 | Silt loam | 24.17 \pm 5.38 | 0.24 \pm 0.04 | 0.32 \pm 0.08 | 6.25 \pm 1.59 | 17.36 \pm 4.08 |
| Soil H | 5.83 \pm 0.42 | 0.66 \pm 0.22 | 9.82 \pm 2.81 | Silt Loam | 21.79 \pm 3.84 | 0.33 \pm 0.06 | 2.23 \pm 0.09 | 4.09 \pm 0.98 | 15.14 \pm 3.62 |
| Soil I | 6.11 \pm 0.18 | 0.40 \pm 0.03 | 6.76 \pm 1.73 | Silt Loam | 26.11 \pm 3.96 | 0.51 \pm 0.12 | 1.59 \pm 0.35 | 6.76 \pm 2.16 | 17.25 \pm 4.81 |
| Soil J | 7.32 \pm 0.12 | 0.62 \pm 0.06 | 10.21 \pm 2.08 | Silt Loam | 22.08 \pm 4.17 | 0.61 \pm 0.08 | 0.88 \pm 0.11 | 4.55 \pm 1.88 | 16.04 \pm 5.03 |

All data reported as a mean with SD (mean \pm SD) of triplicate determinations

Table 3. Total metal contents in sewage water – irrigated soils (means \pm SD, n = 3)

| Metals | Zn | Ni | Cu | Pb | Cd |
|---------------------|-----------------|-----------------|------------------|----------------|----------------|
| Soil A | 217.8 \pm 4.6 | 103.1 \pm 8.2 | 121.2 \pm 5.6 | 72.6 \pm 7.2 | 25.7 \pm 3.6 |
| Soil B | 223.6 \pm 6.2 | 137.9 \pm 6.4 | 167.8 \pm 9.3 | 44.6 \pm 4.3 | 12.4 \pm 2.1 |
| Soil C | 148.3 \pm 7.3 | 68.9 \pm 4.4 | 143.5 \pm 8.2 | 29.8 \pm 3.2 | 17.4 \pm 2.2 |
| Soil D | 183.5 \pm 6.6 | 86.2 \pm 5.3 | 176.4 \pm 5.9 | 48.7 \pm 3.7 | 35.4 \pm 3.2 |
| Soil E | 162.5 \pm 4.6 | 143.4 \pm 5.7 | 84.5 \pm 4.2 | 36.4 \pm 2.8 | 46.6 \pm 4.3 |
| Soil F | 214.5 \pm 8.6 | 98.6 \pm 4.6 | 76.8 \pm 3.7 | 83.4 \pm 4.6 | 8.5 \pm 2.3 |
| Soil G | 296.8 \pm 9.4 | 76.7 \pm 5.5 | 133.8 \pm 6.4 | 68.5 \pm 4.6 | 44.6 \pm 4.1 |
| Soil H | 117.2 \pm 5.4 | 134.4 \pm 6.2 | 204.7 \pm 10.4 | 39.2 \pm 5.7 | 11.2 \pm 1.8 |
| Soil I | 156.1 \pm 7.4 | 62.3 \pm 5.1 | 127.3 \pm 5.3 | 40.8 \pm 4.2 | 28.8 \pm 2.7 |
| Soil J | 132.6 \pm 4.8 | 83.9 \pm 4.3 | 116.9 \pm 7.8 | 30.3 \pm 2.6 | 10.7 \pm 2.2 |
| Range | 117.8-296.8 | 62.3-143.4 | 76.8-204.7 | 29.8-83.4 | 8.5-44.6 |
| E U and Ewers limit | 150-300 | 30-75 | 50-140 | 50-100 | 1-3 |

Source: European Commission, 1986 and Ewers, 1991.

The difference in distribution patterns can be inclined towards possible mobilization of the metals. The greater percentage of Zn in the residual fraction (54.2 – 97.3%) likely indicated the greater tendency of Zinc to become unavailable in the soils. This is because the residual fraction represented metals that are largely embedded in sedimentary matrix of the soils and may not be available for remobilization except under very harsh conditions (Ma and Rao, 1997). Similar result was reported for soils from tailing dumps (Jordao and Nickless, 1989). The reducible fraction amongst the non residual fractions contained the highest concentration of Zn in almost all the samples, followed by the acid soluble and then the exchangeable fraction. The highest amount of Zn in the reducible may be attributed to the high stability of Zn oxides, (Ma and Rao, 1997). Several other researchers such as Ramos et al. (1994) and Xian (1989) have also found Zn associated with the reducible fraction. Xian (1989) found that the sum of the exchangeable and acid soluble fractions was strongly correlated with Zn uptake by cabbage. Therefore, the sum of Zn in the exchangeable and acid soluble fractions in this study was significant in some soils and thus, Zn content in some of these soils may be available for plant uptake (Table 4).

Table 5 present the result of six steps sequential extraction of Ni for each sampling site of the sewage water – irrigated soils. The majority of the Ni concentration was in the residual fraction (29.8 – 91.8%). The exchangeable was the second most concentrated fraction followed by the reducible and then the acid soluble fraction. The reducible fraction was also important for nonresidual fractions in the soils. This may be due to the ability of Fe²⁺ and Fe³⁺ species to scavenge metals from soil solution that would normally not precipitate (Asagba et al., 2007). The significant amount of Ni also found in the acid soluble fraction may be due to co-precipitation of the metal into carbonates of these soils. A similar result was reported

by Asagba et al. (2007). The appreciable percentage of Ni in the nonresidual fraction in the majority of the soils suggested the mobility and bioavailability of Ni. Metals present in the exchangeable fraction are usually thought to be readily available for plant uptake (Xian, 1989), because exchangeable fraction of soils consists of metal species found in soil solution. Therefore, in general, Ni was found relatively mobile and bioavailable in the majority of the soils.

Most of the Cu was associated in the residual fraction (Table 6). The range of residual fraction varied from 55.8-90.7%. The highest percentage of Cu was found in oxidizable fraction amongst the nonresidual portion. The major association of Cu with oxidizable fraction in these soils may be attributed to the high formation constant of organic – Cu complexes (Stumm and Morgan, 1981). The acid soluble fraction was the next important fraction for these soils. This result is consistent with that of Harrison (1981) who found significant amount of Cu associated with oxidizable and acid soluble fractions. The poor presence of Cu in the exchangeable and water soluble fraction may be as a result of high stability of Cu in the Cu – organic complexes, immobility caused by the carbonates through the provision of adsorbing/nucleating surface (Ramos et al., 1994) and Fe/Mn oxides scavenging effect, since the Cu concentration in the nonresidual portion was in these fractions.

Lead was predominantly in the residual fraction (Table 7). The amount of Pb in the residual fraction varied from 50.6 – 67.8%. The highest Pb content found in the residual fraction in this study is in agreement with the finding of Osakwe and Egharevba (2008) and Asagba et al. (2007). Amongst the non residual fractions, reducible and acid soluble fractions were found the highest. Some researchers have also found Pb to be highly associated with reducible form (Ramos et al., 1994). The high percentage of Pb in the reducible form may be due to ability of Fe/Mn oxides to scavenge

Table 4. The chemical fractionation of Zn metal in the contaminated soil sample (Mean \pm SD, mg/kg dry weight)

| Fractions | Water soluble phase | exchangeable phase | oxidizable phase (Bound to organic) | Acid soluble phase (Bound to carbonate) | Reducible phase (Bound to oxides) | Residual phase (Bound to silicates) | Non-residual phase | Total extractable (ΣT) |
|-----------|---------------------|--------------------|-------------------------------------|---|-----------------------------------|-------------------------------------|--------------------|----------------------------------|
| SS A | 1.2+0.080.5% | 22.1 \pm 3.69.5% | 2.6 \pm 0.91.1% | 10.7 \pm 2.84.6% | 25.6 \pm 3.310.9% | 170.6 \pm 6.173.3% | 62.2 26.7% | 232.8 |
| SS B | 0.2+0.010.1% | 5.7+1.62.4% | 4.3+1.21.8% | 19.8+2.68.4% | 27.9+3.411.8% | 178.3+5.775.5% | 57.9 24.5% | 236.2 |
| SS C | 0.8+0.30.5% | 17.1+2.510.9% | 2.0+0.71.3% | 11.8+2.87.5% | 14.0+2.68.9% | 111.5+6.370.9% | 45.8 29.1% | 157.3 |
| SS D | 0.5+0.090.2% | 9.9+2.15.5% | 12.2+2.86.8% | 25.0+3.713.9% | 31.8+4.117.7% | 100.2+5.955.8% | 79.3 44.2% | 179.5 |
| SS E | 0.5+0.20.2% | 5.8 \pm 1.33.7% | 11.3+1.97.2% | 14.7+2.39.4% | 23.8+2.715.2% | 100.8+6.264.3% | 55.9 35.7% | 156.7 |
| SS F | 0.2+0.0.40.1% | 0.7+0.30.3% | 0.7+0.30.3% | 1.1+0.60.5% | 3.3+1.11.5% | 215.8+8.497.3% | 6.0 2.7% | 212.8 |
| SS F | 1.8+0.80.6% | 20.3+2.46.7% | 21.2+2.77.0% | 20.6+3.6.8% | 46.6+4.215.4% | 192.0+5.963.5% | 110.4 36.5% | 302.4 |
| SS H | 0.3+0.080.2% | 1.9+0.71.9% | 0.5+0.20.4% | 1.2+0.90.9% | 12.3+2.69.6% | 111.9+4.887.0% | 16.7 13.0% | 128.6 |
| SS I | 0.8+0.30.5% | 2.8+1.01.7% | 2.3+0.71.4% | 41.1+4.224.9% | 28.5+3.217.3% | 89.3+4.454.2% | 75.5 45.8% | 164.9 |
| SS J | 1.2+0.30.8% | 3.0+1.22.1% | 8.2+2.25.7% | 26.9+3.418.6% | 15.0+2.410.4% | 90.2+4.962.4% | 54.4 37.6% | 144.6 |

Table 5. The chemical fractionation of Ni metal in the contaminated soil sample (Mean \pm SD, mg/kg dry weight)

| Fractions | Water soluble phase | exchangeable phase | oxidizable phase (Bound to organic) | Acid soluble phase (Bound to carbonate) | Reducible phase (Bound to oxides) | Residual phase (Bound to silicates) | Non - residual phase | Total extractable (Σ T) |
|-----------|---------------------|---------------------|-------------------------------------|---|-----------------------------------|-------------------------------------|----------------------|---------------------------------|
| SS A | | | 1.3 \pm 0.51.1% | 1.5 \pm 0.61.3% | 2.7 \pm 0.82.3% | 107.8 \pm 6.8 | 10.9 | 118.6 |
| SS B | 0.9 \pm 0.09 0.8% | 4.3 \pm 1.13.6% | 1.9 \pm 0.61.3% | 2.6 \pm 0.81.8% | 3.6 \pm 1.02.5% | 90.9% | 9.1% | 143.5 |
| SS C | 1.4 \pm 0.51.0% | 2.1 \pm 1.03.4% | 0.7 \pm 0.21.0% | 0.8 \pm 0.31.2% | 1.2 \pm 0.71.8% | 89.3% | 10.7% | 65.7 |
| SS D | 0.5 \pm 0.080.8% | 29.2 \pm 3.130.0% | 2.5 \pm 0.92.6% | 21.2 \pm 4.221.8% | 14.5 \pm 2.814.9% | 29.0 \pm 3.7 | 68.3 | 97.3 |
| SS E | 0.9 \pm 0.20.9% | 41.2 \pm 4.629.7% | 2.5 \pm 1.11.8% | 22.5 \pm 4.116.2 | 15.7 \pm 2.611.3% | 29.8% | 70.2% | 138.6 |
| SS F | 0.6 \pm 0.10.4% | 3.3 \pm 1.05.7% | 6.6 \pm 2.17.5% | 3.0 \pm 0.93.4% | 11.6 \pm 3.313.2% | 56.3 \pm 3.5 | 82.3 | 83.2 |
| SS G | 1.1 \pm 0.31.2% | 3.9 \pm 1.74.7% | 1.1 \pm 0.71.3% | 2.1 \pm 0.82.5% | 2.9 \pm 1.23.4% | 40.6% | 59.4% | 83.9 |
| SS H | 0.8 \pm 0.090.9% | 3.3 \pm 1.12.2% | 6.1 \pm 1.84.1% | 14.6 \pm 2.89.8% | 22.6 \pm 3.715.2% | 62.6 \pm 5.7 | 25.6 | 148.6 |
| SS I | 0.9 \pm 0.20.6% | 2.6 \pm 0.93.5% | 3.5 \pm 1.24.7% | 9.3 \pm 2.612.4% | 14.8 \pm 2.819.8% | 71.0% | 29.0% | 74.8 |
| SS J | 1.2 \pm 0.71.6% | 3.7 \pm 1.73.8% | 5.9 \pm 2.26.1% | 9.4 \pm 2.49.7% | 14.4 \pm 2.714.9% | 73.2 \pm 4.3 | 10.7 | 96.4 |
| | 0.9 \pm 0.10.9% | | | | | 87.2% | 12.8% | |
| | | | | | | 101.2 \pm 4.8 | 47.4 | |
| | | | | | | 68.1% | 31.9% | |
| | | | | | | 43.4 \pm 3.9 | 31.4 | |
| | | | | | | 58.0% | 42.0% | |
| | | | | | | 62.3 \pm 4.8 | 34.1 | |
| | | | | | | 4.6% | 35.4% | |

Table 6. The chemical fractionation of Cu metal in the contaminated soil sample (Mean ± SD, mg/kg dry weight)

| Fractions | Water soluble phase | exchangeable phase | oxidizable phase (Bound to organic) | Acid soluble phase (Bound to carbonate) | Reducible phase (Bound to oxides) | Residual phase (Bound to silicates) | Non - residual phase | Total extractable (ΣT) |
|-----------|---------------------|--------------------|-------------------------------------|---|-----------------------------------|-------------------------------------|----------------------|------------------------|
| SS A | 1.1±0.20.8% | 1.6±0.81.2% | 11.1±3.18.4% | 7.4±2.75.6% | 6.0±2.34.5% | 105.3±5.379.5% | 27.1 20.5% | 132.4 |
| SS B | 2.0±0.91.3% | 3.7±1.02.4% | 17.6±3.211.3% | 15.1±2.39.7% | 10.7±2.46.9% | 106.5±4.968.4% | 49.2 31.6% | 155.7 |
| SS C | 1.2±0.10.8% | 2.6±0.81.9% | 8.8±2.66.4% | 7.1±2.25.1% | 6.5±2.14.7% | 111.9±4.781.0% | 26.3 19.0% | 138.2 |
| SS D | 1.5±0.30.8% | 4.3±1.22.3% | 27.9±2.615.0% | 20.9±3.411.2% | 20.3±3.210.9% | 111.5±3.859.8% | 74.9 40.2.2% | 186.5 |
| SS E | 0.9±0.30.9% | 3.2±1.13.3% | 17.0±1.617.3% | 11.9±2.512.1% | 8.4±1.48.5% | 56.9±2.757.9% | 41.4 42.1% | 98.3 |
| SS F | 0.7±0.20.8% | 1.3±0.81.4% | 2.9±0.83.2% | 2.5±0.92.7% | 2.0±0.72.2% | 82.3±4.189.7% | 95. 10.3% | 91.8 |
| SS G | 1.6±0.20.5% | 2.7±0.82.1% | 16.7±2.413.0% | 13.3±2.910.3% | 20.6±3.116.0% | 74.8±4.258.1% | 54.0 41.9% | 128.8 |
| SS H | 1.2±0.70.6% | 6.3±1.83.1% | 5.3±1.22.6% | 2.4±1.01.2% | 3.6±1.81.8% | 183.6±6.290.7% | 18.8 9.3% | 202.4 |
| SS I | 1.9±0.81.4% | 5.6±1.44.1% | 13.6±2.310.0% | 18.7±2.613.8% | 20.2±3.414.9% | 75.7±2.755.8.8% | 59.9 44.2% | 135.6 |
| SS J | 1.4±0.61.1% | 3.4±0.92.8% | 9.3±1.37.6 | 5.9±1.54.8% | 4.1±1.43.3% | 98.7±4.480.4% | 24.1 19.6% | 122.8 |

metals from the soil solution that would normally not precipitate (Asagba *et al.*, 2007). However, small amount of Pb content was also found in the oxidizable fraction. Exchangeable and water soluble fraction of Pb were found in a very small percentage and not even detected in the soil A, B, C, E, G and J (detection limit was 0.05mg/L). This suggested that Pb in these soils may not be bioavailable because the exchangeable and water soluble fractions consist of metals species found in the soil solution. They are the most labile and may easily be absorbed into the plant matrix or leached into the ground water sources (Asagba *et al.*, 2007). Overall, upon all the ten soils studied were contaminated with Pb and may be available once the amount of the metal is significantly increased in the nonresidual forms.

Table 8 shows the result of the distribution of Cd amongst the six fractions. The Cd concentration was chiefly concentrated in the residual fraction. The amount of Cd in the residual fraction ranged from 30.2 – 96.5%. More than 83% of the total Cd in all the soils excluding soil B, D and E was associated with residual fraction. The Cd concentration in soil B, D and E was mostly concentrated in the residua phase. Among the nonresidual fraction of these soils, exchangeable was the highest, followed by the reducible and then the acid soluble fraction. This suggested that Cd in these three soils was potentially bioavailable for plant uptake (Xian, 1989; Asagba *et al.*, 2007). These findings are in

agreement with the earlier observations of Harrison (1981), Ma and Rao (1997) and Kuo et al. (1983). However, in soil J, no Cd was detected in the reducible, acid soluble and oxidizable fractions of this soil (detection limit was 0.03 mg/L). In overall, the average Cd distribution amongst the soils, the residual fraction was the most abundant pool in almost all the soils studies.

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**Table 7. The chemical fractionation of Pb metal in the contaminated soil sample
(Mean \pm SD, mg/kg dry weight)**

| Fractions | Water soluble phase | exchangeable phase | oxidizable phase (Bound to organic) | Acid soluble phase (Bound to carbonate) | Reducible phase (Bound to oxides) | Residual phase (Bound to silicates) | Non - residual phase | Total extractable (ΣT) |
|-----------|------------------------|-----------------------|-------------------------------------|---|-----------------------------------|-------------------------------------|----------------------|----------------------------------|
| SS A | 0.6 \pm 0.09 0.8% | BDL | 5.4 \pm 1.1 6.9% | 6.7 \pm 1.3 8.6% | 25.9 \pm 2.9 33.1% | 39.6 \pm 3.2 50.6% | 38.7 49.4% | 78.3 |
| SS B | BDL | 0.7+0.3 1.3% | 3.3 + 0.8 6.4% | 6.0+1.4 11.6% | 11.3+2.0 21.8% | 30.5+3.4 58.9% | 21.2 41.1% | 51.7 |
| SS C | BDL | 1.1+ 0.5 2.9% | 2.4 + 0.7 6.7% | 3.8+1.0 10.5% | 6.3+1.5 17.3% | 22.8+2.7 62.6% | 13.6 37.4% | 37.4 |
| SS D | 0.3 \pm 0.0 0.6% | 2.0 \pm 0.5 3.4% | 3.7 \pm 0.8 6.5% | 5.9 \pm 1.4 10.2% | 8.9 \pm 2.1 15.4% | 36.7 \pm 3.6 63.9% | 20.8 36.1% | 57.5 |
| SS E | BDL | BDL | 1.4+0.6 3.2% | 4.8+1.3 10.8% | 13.1+2.4 29.3% | 25.3+2.6 56.7% | 19.3 43.3% | 44.6 |
| SS F | 0.8+0.2 0.9% | 2.3+ 0.6 2.6% | 4.6+1.4 5.2% | 7.7+1.1 8.8% | 12.9+2.2 14.7% | 59.5+4.2 67.8% | 28.3 32.2% | 87.8 |
| SS G | BDL | BDL | 3.3+0.8 4.4% | 8.9+1.7 12.1% | 17.3+2.7 23.4% | 44.4+3.8 60.1% | 29.5 39.9% | 73.9 |
| SS H | 0.3 \pm 0.03 0.7% | 0.7+0.3 1.6% | 1.4 \pm 0.8 3.1% | 4.3 \pm 1.3 9.4% | 8.3 \pm 1.3 18.3% | 30.4 \pm 3.3 66.9% | 15.0 33.1% | 45.4 |
| SS I | 0.2+0.0 0.4% | 0.6 + 0.3 1.2% | 2.3+0.6 4.6% | 6.1+1.1 12.4% | 10.0+2.4 20.3% | 30.0+2.8 61.1% | 19.1 38.9% | 49.1 |
| SS J | BDL | BDL | 1.0+0.3 2.8% | 3.1+0.8 8.4% | 8.4+2.2 22.7% | 24.6+2.3 66.6% | 12.6 33.9% | 37.2 |

BDL - Below detection limit for Pb, the detection limit for Pb was 0.05mg/l

Table 8. The chemical fractionation of Cd metal in the contaminated soil sample (Mean ± SD, mg/kg dry weight)

| Fractions | Water soluble phase | exchangeable phase | oxidizable phase (Bound to organic) | Acid soluble phase (Bound to carbonate) | Reducible phase (Bound to oxides) | Residual phase (Bound to silicates) | Non - residual phase | Total extractable (ΣT) |
|-----------|---------------------|--------------------|-------------------------------------|---|-----------------------------------|-------------------------------------|----------------------|------------------------|
| SSA | 0.3±0.5 1.2% | 2.2±0.8 7.7% | 0.5±0.2 1.6% | 0.6±0.4 2.2% | 1.0±0.06 3.4% | 23.5±3.8 83.5% | 4.5 16.5% | 28.2 |
| SSB | 0.2±0.04 1.1% | 3.7±1.2 25.5% | 0.3±0.02 2.1% | 2.2±0.8 15.3% | 1.7±0.7 11.6% | 6.5±2.1 44.4% | 8.1 55.6% | 14.6 |
| SSC | 0.3±0.01 1.4% | 0.7±0.4 3.8% | 0.3±0.01 1.8% | 0.5±0.2 2.4% | 0.5±0.1 2.7% | 17.0±3.2 87.9% | 2.3 12.1% | 19.3 |
| SSD | 0.3±0.05 0.9% | 11.5±1.8 29.6% | 1.0±0.4 2.6% | 8.4±2.1 21.8% | 5.8±1.2 14.9% | 11.7±2.9 30.2% | 27.0 69.8% | 38.7 |
| SSE | 0.2±0.06 0.5% | 12.6±3.1 29.7% | 0.8±0.5 1.8% | 6.9±1.8 16.2% | 44.8±1.6 11.3% | 17.2±3.4 40.5% | 25.2 59.5% | 42.4 |
| SSF | 0.1±0.0 0.9% | 0.3±0.06 2.0% | 0.2±0.04 1.2% | 0.2±0.04 1.5% | 0.3±0.06 1.8% | 12.9±3.2 92.6% | 1.0 7.4% | 13.9 |
| SSG | 0.4±0.1 0.8% | 1.3±0.6 2.9% | 0.6±0.2 1.3% | 0.7±0.3 1.5% | 1.2±0.5 2.6% | 43.3±4.7 90.5% | 4.5 9.5% | 47.8 |
| SSH | 0.1±0.0 0.8% | 0.4±0.03 2.7% | 0.2±0.07 1.2% | 0.3±0.06 1.8% | 0.3±0.03 2.2% | 13.0±2.7 91.3% | 1.2 8.7% | 14.2 |
| SSI | 0.1±0.0 0.5% | 0.5±0.1 1.9% | 0.2±0.03 0.7% | 0.3±0.04 1.2% | 0.4±0.1 1.5% | 24.8±3.8 94.2% | 1.5 5.8% | 26.3 |
| SSJ | 0.1±0.0 0.8% | 0.3±0.04 2.7% | BDL | BDL | BDL | 9.5±2.9 96.5% | 0.3 3.5% | 9.8 |

BDL - Below detection limit for Cd, the detection limit for Cd was 0.03 mg/l

CONCLUSION

This work indicated that irrigation with sewage water increased the total levels of metals in the soils studied, but are mostly found in the more resistant fraction (less soluble form). A sequential extraction procedure was used to fractionate Cd, Cu, Ni Pb and Zn present in ten sewage water – irrigated soils. Different geochemical fractions were operationally defined by an extraction sequence that generally follows the order of decreasing solubility. The residual fraction was the most abundant pool for all the metals in the soils examined. However, in most of the soils, a significant percentage of total metals was associated with nonresidual fractions, which could possible be leached or absorbed by plants. Significant amount of Pb, Zn, Cu and Ni were associated with the nonresidual fractions in the soils studied, which indicated that these metals were potentially bioavailable. In the case of Cd, only three out of these soils were fully saturated with nonresidual fractions. Overall, the order of contamination was Pb> Zn> Cu> Ni> Cd. Among the ten soils tested, soil A, B, D, E, G and I were the most contaminated with the five metals examined.

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