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# Chemical Speciation and Potential Mobility of some Metals of Selected Farmland in Kogi State, North Central Nigeria

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## ABSTRACT

The contamination of agricultural soils with heavy metals is of concern because if the soil is contaminated, the metals can be transferred to food crops. The availability of these metals to food crops depends on the forms in which they are present in the soils. In this study, sequential extraction technique was applied to assess the exchangeable, carbonate-bound, Fe-Mn oxide bound, organic bound and residual fractions in the topsoil of farmlands in Kogi State, North Central Nigeria. Proportions in non-residual soil phases were 82.6 % Cd, 48.6 % Co, 72.5 % Cu, 73.2 % Ni, 41.9 % Pb, and 84.3 % Zn. Lead (Pb) and cobalt (Co) showed the highest phase of 58.1% and 51.4 %, respectively in the residual phase. The low concentration of lead in the non-residual fraction (41.9 %) and the highly mobile exchangeable phase and pH sensitive carbonate phase is an indication that there is no increase in anthropogenic input of Pb into the environment. Cadmium, zinc and nickel are most abundant in exchangeable fraction and this can be of concern especially cadmium.

**Keywords**: Heavy metals, Metal speciation, Farmlands, Food crops, Metal uptake

## INTRODUCTION

The speciation of an element is the chemical form(s) that it takes in solution. Some researchers suggest that free metal ion is the most toxic form of metals (Reddy *et al*., 1995; Sauve *et al*., 1997). Free metal activity in a wide variety of soils and with a variety of metals correlates well with factors such as organic matter and pH, suggesting that it is a good measure of plant available metal (Reddy *et al*., 1995; Sauve *et al*., 1997). Research carried out with plants, especially in solution culture, has supported the free metal ion hypothesis (Sparks, 1984; Bell *et al*., 1991; Ibekwe *et al*., 1998). It has earlier been suggested that not all metal in solution was available to plants. Subsequent work with other researchers has further supported this theory (Alva *et al*., 1986; Menzies *et al*., 1994).

The "free ion as the bioavailable species" theory has often been assumed in the literature so there is need to do thorough research to justify the hypothesis (Parker and Pedler, 1997). Work with chelates and organic acids has revealed that metals complexed with organic compounds are readily available compared to the free-ion activity (Bell *et al*., 1991; Laurie *et al*., 1991a; Laurie *et al*., 1991b; Srivastava and Appenroth, 1995; Parker *et al*., 2001). A research work done with Cd in both soil and solution culture revealed that Cl complexed Cd is also available to plants (Smolders and McLaughlin, 1996; Smolders *et al*., 1998). In contrast, research with *Kandelia candel* (mangrove) has suggested that NaCl reduces Zn and Cu toxicity (Chiu *et al*., 1995) but from the experimental design, this could just as easily indicate competition between $Na^+$ and $Zn^{2+}$ or $Cu^{2+}$ for uptake, or a positive effect of NaCl on growth in this halophytic species. Research work carried out by Lexmond and van der Vorm (1981) has shown that the toxicity of Cu in plant responses cannot be explained by the $Cu^{2+}$ ion alone. Parker and Pedler (1997) conducted computer simulations of various nutrient systems and found that while the free ion activity is generally a good measure of plant available metal, there are certain situations outside the bounds of the model.

The potential mobility of a metal assessment can be performed by the addition of the results of the exchangeable phase, carbonate phase, oxide and organic phase of that metal (Huang *et al*., 2007). The exchangeable phase offers the mobile and bioavailable heavy metal fraction. This is the phase in which the heavy metals can easily be released into the environment. The presence of heavy metals in this phase is hazardous because metals available in this form can easily be taken up by plants from the soil. Studies have revealed that the level of metals in soil and forms in which they are in the soil determines how they are taken up by food crops. Kogi State is a major food-producing state, especially in cassava and yam. Knowledge of the forms of metals in agricultural farmland is therefore very important in order to know the type of crops to be cultivated as regard hyper accumulator. However, there is a paucity of data in this regard. This study, therefore, focused on the forms of metals in Kogi State farmland.

## MATERIALS AND METHODS

All chemicals used were of reagent grade and pure deionized water was used throughout the experimentation. All plastic ware were soaked in 10% $HNO_3$. Procedural blanks preparation of standard solutions from a stock solution of 1000 ppm (Merck, Germany), clean laboratory environment, calibration of the Buck 200A Atomic Absorption spectrophotometer (AAS) using prepared standards and the analysis of calibrated standards after 10 samples to ensure that the instrument remain calibrated and to ensure it is performing optimally.

### Sample Collection

Soil samples were obtained at depths of 0-15 cm in each farm to make 320 composite samples. Composite sample each of topsoil (0-15cm) was collected. Samples were collected within an area of 10 m by 10 m with auger sampler to make a composite. The collected soil samples were air-dried, ground and sieved through a plastic sieve of 2 mm mesh size. The sieve soils were stored at ambient temperature in polyethylene bags until analysis time. The soils samples were collected from sampling locations (table 1) quarterly (3 months) within two years across the three senatorial districts of Kogi State, North Central Nigeria.

**Table 1**: Sampling site and coordinates

| SAMPLING SITE | GPS | | VEGETATION |
|---|---|---|---|
| | **LATITUDE** | **LONGITUDE** | |
| **Ofoke** | 07$^0$ 24' 9.5" N | 06$^0$ 46' 34.2" E | Typical of rainforest and Guinea savannah |
| **Ajaokuta** | 07$^0$ 31' 40.6" N | 06$^0$ 40' 24.8" E | It lies within the savannah belt, |
| **Macks** | 07$^0$ 42' 07.4" N | 06$^0$ 27' 39.2" E | It lies within the savannah belt, an area characterized by tall trees and grasses |
| **Idah** | 07$^0$ 08' 46.0" N | 06$^0$ 46' 09.7" E | Wooded savannah, rain and mangrove forest |
| **Ibaji** | 07$^0$ 03' 47.8" N | 06$^0$ 44' 10.9" E | Wooded savannah, and rain and mangrove forest |
| **Ejule** | 07$^0$ 22' 04.7" N | 07$^0$ 06 46.4" E | Typical of rainforest and Guinea savannah |
| **Ankpa** | 07$^0$ 22' 46.4" N | 07$^0$ 37' 54.2" E | Guinea savannah |
| **Anyigba** | 07$^0$ 29' 01.4" N | 07$^0$ 10' 43.2" E | Typical of rainforest and Guinea savannah |
| **Lokoja** | 07$^0$ 48' 07.4" N | 06$^0$ 41' 05.1" E | It lies within the savannah belt. |

### Metal Speciation Study

The sequential extraction procedure by Tessier *et al.* (1979) as described by European Community Bureau of Reference (BCR) was used (Rauret *et al.*, 1999; Cappuyns *et al.*, 2007; Passos *et al.*, 2010). The chemical partitioning of heavy metals allows distinguishing five fractions representing the following chemical phases: exchangeable metals, bound to carbonates, bound to Fe–Mn oxides, bound to sulphides and organic matter, and residual fraction. The procedure was carried out using 1 g of sieved dry soil sample.

### The Exchangeable Phase (Step 1)

The samples were extracted at room temperature (28 ºC) for 1 h with 8 mL of 1 M $MgCl_2$ (pH 7) with continuous stirring. The extracts were centrifuged for 30 min to achieve good separation. The supernatant was removed with a pipette and used for metal measurement and the solid residues from this step 1 were washed and used for step 2 extraction.

### The Carbonate Phase (Step 2)

The washed residue from step 1 was leached at room temperature with 8 mL of 1M NaOAc (adjusted to pH 5 with HOAc) for 6 h with continuous stirring. The pH was controlled after 3 h and adjusted to pH 5 with HOAc at room temperature, centrifuged. The supernatant was collected and the solid residue from step 2 was washed and used for step 3 extraction.

### The Oxide Phase (Step 3)

The residue from step 2 was extracted with 20 mL of 0.04 M $NH_2OH.HCl$ in 25 % HOAc (v/v) for 6 h at 96 °C in a water bath with occasional stirring. The supernatant was subjected to metal analysis and the solid residue from step 3 was washed and used for step 4.

### The Organic Phase (Step 4)

To the solid residue from step 3 was added 3 mL of 0.02 M $HNO_3$ and 5 mL of $H_2O_2$ 30% (adjusted to pH 2 with $HNO_3$). The mixture was heated to 85 °C and occasionally stirred. After 2 h, 3 mL of 30% $H_2O_2$ was added once more (adjusted to pH 2 with $HNO_3$). The temperature and the occasional stirring were maintained for another 3 hours. After cooling, 5 mL of 3.2 M $NH_4OAc$ (in 20% $HNO_3$ (v/v)) and 4 mL of deionized water was added and the mixture was agitated continuously for 30 min. The supernatant was subjected to metal analysis and the solid residue from step 4 was washed and used in step five.

### Residual Fraction (Step 5)

The residue from step 4 was digested with 7 mL of $HNO_3$ (65%) and 7 mL of HF (40%). The liquid was evaporated and after that, it was dissolved again with 2 mL of $HNO_3$, 2 mL of HCl and 10 mL deionized water with low temperatures. The samples were diluted to 50 mL with deionized water. The supernatant was subjected to metal analysis.

After each step, 5 mL of each extract was centrifuged for 30 minutes to achieve good separation. The supernatant was removed with a pipette. The residue was washed with 8 mL of deionized water and the solution centrifuged. After another 30 min of centrifugation, the supernatant was removed with a pipette and added to the first supernatant. The mixture of both solutions was diluted to 20 mL with deionized water using a 20 mL standard flask and used for analysis.

### Index of Geoaccumulation

The Index of geo-accumulation as described by Muller (1969) for the determination of levels of metals contaminants in soil (Banat *et al.*, 2005) was calculated using the equation

$$\text{Geoaccumulation index } (I_{geo}) = \log_2\left[\frac{C_n}{1.5 \times B_n}\right]$$

where $C_n$ is the measured concentration of the examined metal in the soil, and $B_n$ is the background concentration or reference value of the metal *n*. Factor 1.5 represents possible variations in background values for a given metal in the environment as well as very small anthropogenic influences.

## RESULTS AND DISCUSSIONS

### Speciation of Metals in Soil

Table 2 shows speciation of metals in soil. The results showed that the proportion in non-residual soil phases was 41.9 % Pb, 48.7 % Co, 72.5 % Cu, 73.2 % Ni, 82.6 % Cd and 84.3 %

Zn. Cadmium, zinc and nickel are most abundant in exchangeable fraction. This means that these metals are more mobile in this environment than other metals that are most abundant in the remaining four geochemical phases. The presence of these metals in the highly mobile exchangeable phase and pH-sensitive carbonate-bound fractions than in residual or organic-bound fraction makes the metal even more bioavailable in the soil. It, therefore, means that such metal can easily be taken up by food crops. The high exchangeability of Cd has been explained by the low adsorptive constant of the complex formed with organic matter (Ramos *et al.,* 1994). The result also shows that Cu is most abundant (41.8%) in the fraction bound to organics. This is due to the ability of copper to easily complex with organic matter because of its high degree of formation of organic-Cu compounds (Huang *et al*., 2007). The abundance of copper in the residual fraction was 27.5%. The bio-available (non-residual) fraction of lead is 41.9% while the residual fraction has the largest percentage (58.1) of lead. This result is different from those of similar works done elsewhere by other workers (Levy *et al*., 1992; Ip *et al*., 2007) and they reported that Pb has the highest concentration in the ferrous-manganese oxide bound fraction. Onianwa (2001) has also reported high Pb abundance in this phase. The low concentration (41.9%) of lead in the non-residual fraction and the highly mobile exchangeable phase and pH sensitive carbonate phase shows no increase in anthropogenic input of Pb into the environment. Therefore, Pb cannot be easily released to other environmental components such as crops since the highly mobile exchangeable phase (3.1%) is very low. The low percentage abundances exhibited by the metals in the oxidizable phase (organic-bound phase) (except Cu) could be attributed to the level of organic matter load in the soil. Many of the metals determined show low abundances in the carbonate bound phase, except Ni (21.2%) and Cd (15.59%) which show relatively high percentage abundances. Lead and cobalt showed the highest phase (58.1% and 51.4%, respectively) in the residual phase. This result agrees with that of Ramirez *et al*. (2005) who reported that Pb is mostly associated with the residual phase.

Sum of concentrations of metals in different geochemical phases can be used to express the potential mobility of metals. Adding up the results of the exchangeable phase, carbonate phase, oxide and organic phase of a particular metal can be used to assess the potential mobility of metal (Huang *et al*., 2007). The exchangeable phase represents the mobile and bioavailable heavy metal fraction. In this phase, the heavy metals can easily be released into the environment. The presence of heavy metals in this phase where they can be taken up by plants from the soils is hazardous to the ecosystem. In this study, Cd, Ni, and Zn had high fractions in the exchangeable phase and therefore could be highly mobile and available to plants. Despite this high concentration, the observed levels do not pose a serious risk since the overall concentrations of metals determined in the soil are within regulated limits (Emurotu and Onianwa, 2017).

**Table 2:** Fractional concentration of metals (%) in geochemical phases of selected soil samples

| PHASES | Cu | Zn | Pb | Cd | Ni | Co |
|---|---|---|---|---|---|---|
| **Exchangeable** | 3.50 | 37.0 | 3.10 | 41.5 | 35.3 | 6.90 |
| **Carbonate- bound** | 4.60 | 9.80 | 8.60 | 15.9 | 21.2 | 10.1 |
| **Fe-Mn oxide bound** | 24.6 | 24.5 | 10.7 | 14.6 | 8.1 | 12.4 |
| **Organic bound** | 41.8 | 13.0 | 19.5 | 11.0 | 8.6 | 19.2 |
| **Residual** | 27.5 | 15.7 | 58.1 | 17.4 | 26.8 | 51.4 |

## Pollution Index of Metal in Farmland Soil

### Geoaccumulation index

Geoaccumulation index ($I_{geo}$) rating is presented in Table 3 and $I_{geo}$ comparison with other countries is presented in Table 4. The content accepted as background concentration is multiplied in each case by a factor (1.5) to account for natural fluctuations of a given metal in the environment and as well as small anthropogenic influences (Loska and Wiechula, 2003). Geoaccumulation index ($I_{geo}$) rating indicated that all topsoil (0-15 cm) analysed belong to the unpolluted class (<0) except lead (Ajaokuta), Co (Ibaji) and Zn (Lokoja) with Igeo value of 0.48, 0.49 and 0.63, respectively that fall within the category of class 1 of slightly polluted. Cadmium showed $I_{geo}$ of <0 for all samples indicating that all soil samples were practically uncontaminated by Cd. This suggests that Cd input in the soil is associated with the parent material that formed the soil or other natural or small anthropogenic non-point sources. Overall, average Igeo value for agricultural soils indicated unpolluted agricultural soils. A similar result of unpolluted agricultural soils using Geoaccumulation index has been reported for Bukuru and Barkin Ladi council area of Plateau State, North Central Nigeria (Orisakwe *et al*., 2017). Also, the results of this study are similar to unpolluted agricultural soils reported for some farms in FCT Abuja, North Central Nigeria (Eze *et al*., 2018). Geoaccumulation index of heavy metals in agricultural soil was compared with other countries (Table 3). This study results compared well with values obtained in China and Bangladesh but significantly different from the results obtained in Greece. The variation may be due to the level of heavy metals pollution that exists in agricultural soils in Greece. As reported by Nikolaidis *et al*. (2010), the value for Greece agricultural soils vary from moderately polluted to strongly polluted especially with cadmium (Cd) as given in Table 3.

**Table 3:** Geoaccumulation index ($I_{geo}$) of heavy metals in topsoil samples of farmland

| Sample site | Cd | Co | Cu | Ni | Pb | Zn |
|---|---|---|---|---|---|---|
| **Ofoke** | -0.41 | -0.03 | 0.28 | -0.17 | 0.01 | 0.08 |
| **Ankpa** | -0.46 | 0.12 | -0.86 | 0.10 | -0.15 | -0.02 |
| **Ajaokuta** | -0.57 | 0.03 | 0.19 | 0.03 | 0.48 | 0.11 |
| **Macks** | -0.62 | 0.38 | 0.26 | 0.16 | 0.36 | 0.11 |
| **Ibaji** | -0.63 | 0.49 | 0.30 | 0.17 | 0.26 | 0.19 |
| **Idah** | -0.03 | -0.15 | -0.22 | -0.30 | -0.16 | 0.22 |
| **Ejule** | -0.31 | 0.34 | 0.15 | 0.25 | 0.29 | 0.55 |
| **Anyigba** | -0.29 | 0.35 | -0.02 | 0.003 | 0.28 | 0.02 |
| **Lokoja** | -0.68 | 0.13 | 0.14 | 0.42 | 0.14 | 0.63 |

**$I_{geo}$ classification**: $I_{geo} \leq 0$, class 0, unpolluted; $0 \leq I_{geo} \leq 1$, class 1, from unpolluted to slightly polluted, $1 < I_{geo} \leq 2$, class 2, moderately polluted; $2 < I_{geo} \leq 3$, class 3, from moderately polluted to strongly polluted; $3 < I_{geo} \leq 4$, strongly polluted; $4 < I_{geo} \leq 5$, class 5, from strongly to extremely polluted, $I_{geo} > 5$, class 6, extremely polluted.

**Table 4**: Geoaccumulation index of heavy metals in agricultural soil compared with other countries

| | Cd | Pb | Cu | Co | Ni | Zn |
|---|---|---|---|---|---|---|
| This study (mean) | -0.44 | 0.17 | 0.02 | 0.18 | 0.07 | 0.21 |
| China[a] | 1.08 | -0.04 | -0.07 | - | -0.38 | 0.06 |
| Greece[b] | 5.1 | 2.6 | 1.33 | - | - | 2.27 |
| Bangladesh[c] | 0.28 | 0.13 | 0.28 | - | 0.12 | 0.13 |

a. Wei and Yang, 2010; b. Nikolaidis *et al*., 2010; c. Rahman *et al*., 2012

## CONCLUSION

Chemical speciation of Cd, Ni and Zn were similar but different from that of Pb, Cu, and Co. The mean exchangeable concentration of Cd, Ni and Zn were higher compared to other fractions. The availability of Cd in this fraction is of concern because of its potential mobility in the soil environment and its uptake by food crops.

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