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# Research Article
# Chemical Speciation and Potential Mobility of Some Toxic Metals in Tropical Agricultural Soil

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## Abstract
The knowledge of chemical forms of association of toxic metals is important in understanding metal mobility and the potential risk of metal contamination in the soil. This study determined distribution, availability and mobility of Mn, Fe, Ni, Zn and Pb in the soil samples from arable and plantation plots of a farm settlement in South-Western, Nigeria. Heavy metals in the representative soil samples collected were sequentially extracted into seven fractions and concentration of the extracted metals was determined using Atomic Absorption Spectrophotometer (AAS). The range of heavy metals extracted from each of the seven soil fractions in percentages are as follows; soluble exchangeable (0.50-1.80), surface adsorbed (0.80-5.10), organic matter (3.30-17.9), Mn oxide (6.00-27.9), poor crystalline Fe oxide (10.3-25.4), crystalline Fe oxide (14.6-28.5) and residual (21.3-53.1). Available metals in the studied soils ranges between 6.47-10.9, 241-481, 1.34-2.39, 12.9-24.1 and 1.04-2.37 for Mn, Fe, Ni, Zn and Pb, respectively, while mobility factors of all the metals studied were $\leq$0.257. In the two agro-ecosystems (oil palm and arable), levels of heavy metals in available forms do not differ significantly in both seasons. Though, majority of the extracted toxic metals are found in oxides and the residual fractions and as such, may not pose environmental risk considering their general relatively low availability and mobility factors. Nevertheless, soils from this study area should be effectively managed to prevent release of occluded heavy metals into the available form for plant uptake.

Key words: Bio-availability, sequential extraction, mobility, tropical soil, heavy metals

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Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

## INTRODUCTION

The concentration of heavy metal's solution in the soil, their form of association with other soluble species and the ability of the soil to release them from the solid-phase to the soil solution determine the mobility, bioavailability and the potential toxicity of metals in the soil (Huang *et al*., 2005). The knowledge of the chemical forms in which those metals are associated reveals the metals behaviour, their mobility and bioavailability within the environment (Rieuwerts, 2007; Romic, 2012). The bioavailable concentration of heavy metals is a key factor affecting its uptake and accumulation in plants (Li *et al*., 2014). The simplest way to identify the forms in which heavy metals are found in soil is the use of sequential extraction, whereby, components loosely held in the soil are extracted first, followed by those that are more tightly bonded. When changes occur in the oxidation status of soils and sediments, transformations of metals between their soluble and insoluble chemical forms may occur. This affects the mobility and plant availability of those metals (Ogunfowokan *et al*., 2013). This information about the movement of heavy metals in the soil is essential in order to evaluate the potential risk of metal contamination and the feasibility of its remediation in the soil. It is therefore important for the agronomist to be able to identify the heavy metals in the soil at both the available and unavailable forms so that he could be guided in managing the soil in such a way to prevent plant toxicity. However, there is paucity of data in respect to trace metal behaviour in tropical soils (Bertoncini *et al*., 2005; Udom *et al.,* 2004) and most especially on the status of heavy metals pollution in the Nigerian farm settlements (Oyekunle *et al*., 2011). Therefore, it becomes pertinent to study the levels of heavy metals in the agricultural soils in Nigeria before high level of toxicity arises.

Different types of sequential extraction procedures have been used for this purpose, but the most widely used sequential extraction procedure is the Tessier scheme, which was originally developed for fluvial bottom sediments for temperate region. In the Tessier *et al*. (1979) method, the single reagent (0.04 M $NH_2OH/HCl$ in 25% (v/v) HOAc) used to extract metals attached to Fe-Mn oxide as a single fraction may be insufficient for our purpose. Tropical soils have been found to contain appreciable amount of Fe-Mn oxide minerals, which can retain substantial amounts of metals. Therefore, this study adopted Silveira's method of extraction formulated for tropical soils. Apart from separating the Fe-Mn oxide fractions in the soil, Silveira's method also separate heavy metals bound to non-crystalline Fe-oxides and crystalline Fe-oxide fractions. This method extracts more metals attached to Fe-Mn oxide that is released in reducing condition, which affect the heavy metal mobility in the soil (Silveira *et al*., 2002; Yu *et al*., 2004).

This study therefore, adopts Silveira *et al*. (2006) method of sequential extraction to extract Zn, Pb, Ni, Fe and Mn in arable and oil palm soil samples collected from a major farm settlement in tropical region of Nigeria. The five heavy metals were chosen because of their importance in agro-ecosystems as micronutrients (Fe, Zn, Ni and Mn) and toxicity (Pb).

## MATERIALS AND METHODS

The study area was located in Ogun state, South-west Nigeria, while the sampling site was Ago iwoye farm settlement in Ijebu North local government area. The farm settlement is one of the farm settlements established in the Western region of Nigeria in the early 60's and it is within latitude 03°49'02" and 03°50'20.1" and longitude 06°55'56.6" and 06°56'41.2". The area had a bimodal rainfall, with peaks between June-July and September-October. The most common cultivation in the area is arable crops (cassava and maize) and oil palm. Farmers here indiscriminately apply agrochemicals (fertilizer, herbicides and germicides) on their farm land to improve crop-yields without taking cognizance of their implications.

**Sampling:** Sampling site was Ago Iwoye farm settlement in Ijebu North local government area, South-west, Nigeria. Sampling was conducted in two climatic seasons between 2010 and 2012, from arable farml and andoil palm plantation. One hundred and eight soil samples were collected from 0-15 cm soil depth using hand trowel and Geographical Position System (GPS) into well labeled polythene bags. Figure 1 showed the sampling points on the study area.

**Laboratory analysis:** All soil samples in well labelled polythene bags were transported to the laboratory, where they were air-dried for two weeks at ambient temperature and sieved to 2 mm for heavy metal analysis. Final sample selection from the dried bulk was done using coning and quartering method (Fifield and Kealey, 1990).

Sequential extraction was carried out in duplicate, using 1 g of air-dried soils. Soil samples were placed in 50 mL polycarbonate centrifuge tubes, mixed in a stepwise fashion with various reagents and the suspensions equilibrated as described in Table 1.

After each equilibration, the solution and solid phase were separated by centrifugation at 1225 g for 10 min and between each successive extractant, the solid residues

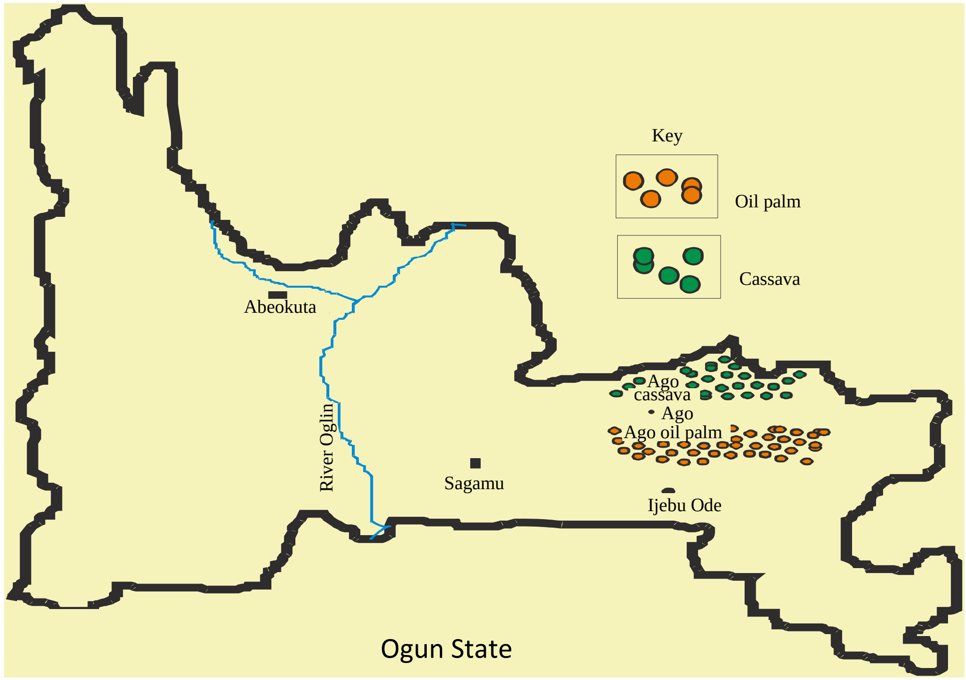


Fig. 1: Map of Ogun state showing the sampling areas at Ago Iwoye farm settlement in Ijebu-north local government

Table 1: Sequential extraction procedure for heavy metals in tropical soils

| Fractions | Solutions | Equilibrium conditions |
|---|---|---|
| Soluble-exchangeable | 15 mL 0.1 M $CaCl_2$ | 2 h, room temperature |
| Surface adsorbed | 30 mL 1 M NaOAC (pH 5) | 5 h, room temperature |
| Organic matter | 5 mL NaOCl (pH 8.5) | 30 min, 90-95°C |
| Mn oxides | 30 mL 0.05 M $NH_2OH/HCl$ (pH 2) | 30 min, room temperature |
| Poor crystalline Fe oxides | 30 mL 0.2 M oxalic acid+0.2 M $NH_4$ oxalate (pH 3) | 2 h, dark |
| Crystalline Fe oxides | 40 mL 6 M HCl | 24 h, room temperature |
| Residual | $HNO_3$-HCl digestion (3050 b) | |

were suspended in 5 mL of 0.1 M NaCl, shake by hand and centrifuged to displace extracting solution remaining from the previous step and the supernatant was added to the former extractant. This step was carried out to reduce sample dispersion and to minimize re-adsorption of the metal. The supernatants were filtered through a 0.45 µm membrane and the solid residues were preserved for the subsequent extractions (Silveira *et al*., 2006). The concentration of Pb, Fe, Zn, Mn and Ni in the various extracts was determined by atomic absorption spectroscopy using Buck Model 205 flame atomic absorption spectrophotometer.

The pseudo total contents of metals (Pb, Fe, Zn, Mn and Ni) were carried out by direct dissolution of the soil samples using acid mixture. About10 mL of a very efficient acid mixture (nitric ($HNO_3$), sulphuric ($H_2SO_4$) and perchloric ($HClO_4$) acid) in a volume ratio of 3:1:1 was used to sufficiently complete the dissolution of 1g of each sample (Barman *et al*., 2000; Twyman, 2005). Metal determinations in the filtrate of the digested soil samples were performed by atomic absorption spectroscopy.

**Quality assurance:** Calibrations were performed with standard solutions prepared in aliquots of sample blanks. The metal content extracted was compared with the sum of metal contents obtained from each fraction of the sequential extraction procedure. A good recovery (the sum of the amount of metals removed in each step was divided by total metal) is within 100±10%.

**Statistical data analysis:** Both descriptive and inferential statistical analyses were used to interpret the data in this study using the SPSS computer software package 17.0 for window evaluation version.

## RESULTS AND DISCUSSION

Result of total Mn, Fe, Zn, Pb and Ni in arable (cassava and maize) and perennial (oil palm) soils in Ago-Iwoye farm settlement were presented in Table 2, while that of sequential extraction of these heavy metals using Silveria method were presented in percentages in Fig. 2.

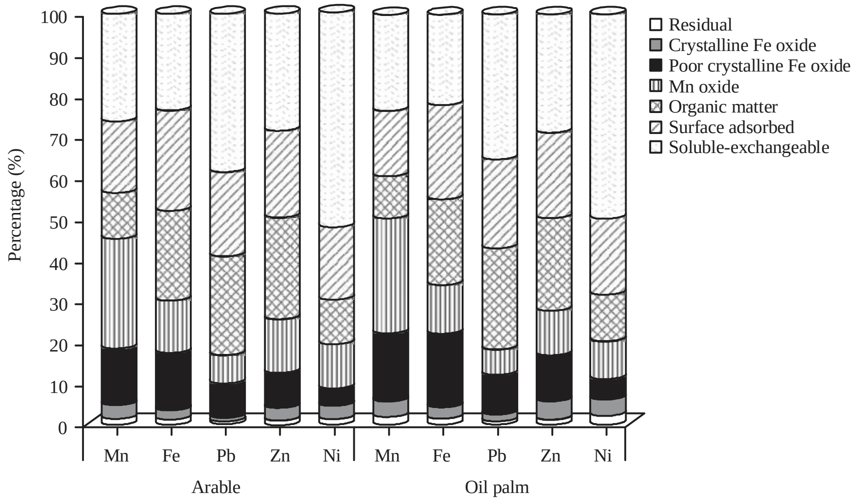


Fig. 2: Percentage of heavy metals extracted from soil fractions in Ago Iwoye farm settlement

Table 2: Levels of total heavy metals in arable (cassava and maize) and perennial (oil palm plantation) soils (mg kg$^{-1}$) from Ago-Iwoye farm settlement

| Season | Land use | Manganese | Iron | Lead | Zinc | Nickel |
|---|---|---|---|---|---|---|
| Dry | Arable | 36.6±4.2 | 1498±119.2 | 9.41±2.73 | 86.7±17.2 | 15.2±2.7 |
| | Oil palm | 48.2±8.6 | 2243±272.4 | 22.5±2.4 | 166.2±25.9 | 25.9±5.9 |
| Rainy | Arable | 30.0±5.6 | 1405±131.1 | 8.25±2.09 | 79.2±12.7 | 13.5±2.2 |
| | Oil palm | 48.6±4.4 | 2164±286.8 | 19.5±3.9 | 141.7±24.1 | 21.8±5.1 |

*M: Mean value, S: Standard Deviation

**Result of total heavy metals in the soil:** The total level of Mn, Pb, Fe, Zn and Ni was obtained in the mean range of 30.0-48.6, 8.25-22.5, 1405-2243, 86.7-166.2 and 13.5-25.9 mg kg$^{-1}$, respectively (Table 2). The prmissible level of Mn, Pb and Ni in the soil is between 100-300, 15-25 and 15-30 mg kg$^{-1}$, respectively (USEPA., 1997). The levels of all the metals determined were significantly lower ($p<0.05$) than the permissible levels.

Therefore, may pose no environmental risk despite long period of farming. However, the mean level of these metals differs significantly ($p<0.05$) between the arable and the oil palm plantations: Level in oil palm soils is significantly higher than the level in arable soils. This may be due to the fact that crop plantations are often grown with high level agrochemical (pesticides, herbicides and inorganic fertilizers), which pollutes the soil, the rate of nutrient and heavy metals decline under annual cropping systems are often much higher than that under perennial crops because loss through leaching and soil erosion is smaller in perennial crops plantation than under annual crops (Hartemink, 2005). Also, tree crops grow the whole year and plant nutrients are recycled by their deep roots, whereas, in annual cropping there may be periods when there is no crop.

The result also showed that levels of all the heavy metals determined in dry season were higher than that in rainy season (though not significant at $p = 0.05$) with oil palm soil samples having the highest. High precipitation, leaching, erosion and plant uptake may account for the reduction in heavy metal levels in the rainy season.

**Heavy metals partition among the soil geochemical fractions:** All the heavy metals determined in this study were found in the seven geo-chemical fractions. The Fe-oxide fractions contain a significant amount of all the metals analysed. Heavy metals (Mn, Fe, Pb and Zn) fractionated in Fe-oxide fractions (crystalline and non-crystalline) have the highest percentage i.e., for rainy season (arable soil: Fe (38.0), Pb (43.9), Zn (52.4), Mn (30.3) and oil palm soil: Fe (46.3), Mn (44.6) and Zn (46.4) and in dry season (arable soil: Fe (41.6), Pb (48.1), Zn (50.9) Mn (30.3) and oil palm soil: Fe (44.0), Pb (46.1), Zn (43.3) and Mn (28.7). In the dry season for oil palm soil, Mn (27.9) has the highest percentage in Mn-oxide fraction. The Ni has the highest percentage (>50.0%) in the residual fraction for both of the land use (Fig. 2).

This corroborates the findings of Fagbote and Olanipekun (2010), who reported that highest amount of Fe and Zn were found in crystalline Fe oxide fraction and both crystalline Fe oxide and amorphous iron oxide fractions, respectively, while Abollino *et al.* (2002) reported that highest amount of Mn was found in Mn oxide fraction. The highest amount of heavy metals found in Fe-Mn oxide form may be due to the chemical composition of the parent rock of tropical soils rich in Fe-Mn minerals. The association of higher concentration of metals with these fractions is caused by adsorption of these metals by the Fe-Mn mineral surface (Zakir *et al*., 2008).

High percentage abundance of metals in the Fe-Mn oxide phase has been reported to be influenced by the high concentration of Fe-Mn minerals in the soil (Etim and Adie, 2012) and may limit the mobility and bioavailability of heavy metals attached to these minerals.

Nevertheless, metals in Fe and Mn oxides fractions can be relatively more sensitive to environmental changes unlike metals in residual fraction, which are often unreactive with respect to metal dynamics scale (Horsfall and Spiff, 2005; Ma and Rao, 1997; Akinyemi *et al*., 2012). Precipitation and oxidation reactions control the availability of Fe and Mn in soils because they are present in appreciable quantities in tropical soils. Metals associated with oxide minerals are likely to be released in reducing conditions because; relatively small changes in Rh toward reducing conditions would cause reduction of Fe and Mn oxide species leading to dissolution of associated metals (Zakir *et al*., 2008).

Soil redox potential, changes in soil pH and organic matter can also cause a significant increase in soluble Fe and Mn concentrations, which consequently lead to more metals redistributed to available forms (Yu *et al*., 2004; Dabrowska, 2012) and consequently, lead to metal mobility. The percentage of metals extracted in residual fraction generally follows this trend: Ni>Pb>Mn>Fe>Zn. This agrees with the work of Ramirez *et al.* (2005), who reported that Cd, Mn, Ni and Pb were mostly associated with the residual phase. The residual fraction of Ni was by far the most important fraction for nickel. This result is consistent with the results of many researchers, who found the greatest percentage of nickel in the residual fraction (Osakwe, 2010; Iwegbue, 2011; Ololade *et al*., 2015).

**Available and mobility factors of the metals in soil:** Mobility of a metal is a measure of its bio-availability. Mobility of a metal is measured by how much of it is present in the first three geochemical fractions (the bio-available form), relative to how much of the metal is present in all the seven fractions. It measures the relative amount of the metal weakly bound to the soil components (Kabala and Singh, 2001; Adamma *et al*., 2014).

Available heavy metals in the studied site follows this trend; Pb<Ni<Mn<Zn<Fe, while mobility factors of these metals in soil follow this trend; Ni<Pb<Zn<Fe<Mn (Table 3).

The Mobility Factor (MF) varied in individual soils and among metals (Osakwe, 2010). Low Mobility Factor (MF) may be interpreted as evidence of relatively low reactivity, low lability and low biological availability of heavy metals (Ma and Rao, 1997; Kabala and Singh, 2001; Oluwatosin *et al.,* 2008) as evident in all the sampled soils. Metals under study are more mobile in rainy season compare to dry season. Reduction in pH, high precipitation (rainfall) and increase degradation of organic matter in rainy season may account for high MF indexes and high levels of heavy metals recorded in available forms in rainy season (Table 3). The fact that higher levels of the metals extracted were found in oxide and residual fractions, which are not readily mobile may account for the low MF values of the studied soils since, mobility and bioavailability of metals are usually controlled by organic matter and oxides, which act as principal adsorbents (McBride, 1995; Ajala *et al*., 2014).

Higher levels of heavy metals found in available forms in arable soils may be due to the fact that arable farms are more frequently mechanized compared to oil palm plantation. Ploughing and harrowing expose the soil from rhizosphere to top surface and bury organic matter into the soil. Organic matter which contain humus, humic acid and fulvin with high chelating characteristic provide more binding surfaces for heavy metals adsorption. Heavy metals that are attached to these organic constituent may becomes available because most of them are water soluble. Ploughing and harrowing also increases aeration thereby increasing oxygen content in the soil which increases vertical water movement and anaerobiosis is reduced. Mechanization also increases exposure to sunlight and accelerates photo-redox reactions, which facilitates release of metals attached to Iron and manganese mineral fractions in the soil. Degradation of organic matter under oxidizing conditions can lead to release of soluble trace metals bound to this component (Rao *et al*., 2008; Zakir *et al*., 2008).

As metals are lost with crops during harvest in arable soils, vacuum are created in the soil solution, redistribution from the other soil fractions is initiated in other to maintain equilibrium in the soil.

Though, the amount of Fe in available form in rainy season in both seasons is high, its MF factor is low, meaning that less Fe is mobile in the soil and may not be readily transferred to the plant. The Ni has the lowest mobility in both arable and oil palm soils. This may be due to the fact that more Ni is occluded in the residual fraction, which is not mobile in the soil. Lower level of Pb in available form and low mobility in the soil may corroborate the notion that lead is immobile in soil and when released to soil; it is normally converted from soluble lead compounds to relatively insoluble sulfate or phosphate derivatives (Fadiran *et al*., 2014). It also forms complexes with organic matter and clay minerals, which limits its mobility.

Table 3: Seasonal variation in available and mobility factor of heavy metals in Ago-Iwoye farm settlement

| | | Arable | | Oil palm | |
|---|---|---|---|---|---|
| | Heavey metals | Dry Mean±SD | Rainy Mean±SD | Dry Mean±SD | Rainy Mean±SD |
| Available | Mn | 9.08±2.76 | 10.9±1.8 | 6.47±0.70 | 7.73±1.63 |
| | Fe | 386±93 | 481±88 | 241±31 | 281±25 |
| | Pb | 2.28±0.49 | 2.37±0.46 | 1.04±0.34 | 1.15±0.33 |
| | Zn | 20.3±3.5 | 24.1±2.8 | 12.9±3.7 | 15.7±3.3 |
| | Ni | 2.34±0.91 | 2.39±0.50 | 1.48±0.39 | 1.34±0.18 |
| Mobility factor | Mn | 0.186±0.025 | 0.223±0.017 | 0.178±0.001 | 0.257±0.006 |
| | Fe | 0.173±0.024 | 0.222±0.012 | 0.165±0.005 | 0.202±0.001 |
| | Pb | 0.101±0.010 | 0.121±0.003 | 0.110±0.005 | 0.138±0.005 |
| | Zn | 0.127±0.004 | 0.172±0.009 | 0.148±0.016 | 0.197±0.010 |
| | Ni | 0.088±0.014 | 0.110±0.003 | 0.097±0.009 | 0.100±0.003 |

The difference in the amount of all the heavy metals under study in available form is insignificant at $p = 0.05$ except for Fe which is higher, Mn: Manganese, Fe: Iron, Pb: Lead, Zn: Zinc, Ni: Nickd

## CONCLUSION

The chemical distribution of the metals studied revealed the geochemical nature of heavy metals and their probable association with different chemical forms in arable and oil palm soils in Ago-Iwoye farm settlement. Speciation using Silveria method clearly showed that more metals were attached to the Fe and Mn oxide fractions compared to residual fractions and these metals can be released under reducing condition into plant available forms. The present study indicated that the metals under study do not pose environmental risk considering their general relatively low mobility factor and that their total levels fall between the permissible levels in the soil. It is recommended that soils from this study area should be effectively managed to prevent release of occluded heavy metals into bio-available form.

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