

Spatial Distribution and Bioavailability of Some Essential Trace Elements in Southern Ondo State Nigeria

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Abstract

The total elemental content of soil though may give abundance of element concentration but have been found not to be suitable for prediction of environmental bioavailability and toxicity by scientific community. Surface (0-30cm) and subsurface (60-90cm) soil profile in the Southern Ondo State Nigeria were investigated for spatial distribution, bioavailability and mobility of some essential trace elements (Cu, Fe, Mn, Zn). Their spatial distribution were very similar in both surface and subsurface soil environment indicating that similar geochemical factors may be responsible for their distribution. The North was composed of basement complex while the South was largely undifferentiated sedimentary rock. Higher concentrations of Cu, Fe, Mn and Zn were recorded in the North through the centre of study area to lower concentrations in the South. The spatial concentration of the trace elements may have been influenced by the nature of underlying bedrock type. Cu was potentially bioavailable in both surface and subsurface soil environment considering the fact that >50% of its total concentration were in the nonresidual fraction. Other trace elements were not bioavailable because >60% of their total concentrations were found in residual fractions. The relative risk assessment code of Cu (surface; subsurface) indicated progressive risk (MoF1, MoF2, MoF3) from low (2-10; 1-6) through medium (12-30; 10-21) to high risk (25-40; 21-35) in both surface and subsurface soil environment while Zn (surface) shows similar trend (1-5; 11-21; 22-35) only in the surface soil environment. Other elements show some level of risk to no risk. There is likelihood that Cu and/or Mn may be associated with anthropogenic sources.

Keyword: spatial distribution, bioavailability, mobility, trace elements, Nigeria

1. Introduction

Soil is a part of the ecosystem and it occupies a basic role for humans, because the survival of man is tied to the maintenance of its productivity (Gruhn *et al.*, 2003). Soil functions as a filtering, buffering, storage, and transformation system; thus it protects against the effects of element pollution (Blum *et al.*, 2006). Soil is effective in these functions only as long as the physical, chemical and its biological activities are preserved. Soil is the main source of trace elements for plants both as micronutrients and as pollutants (Kabata-Pendias & Mukherjee, 2007). It is also a direct source of these elements to humans due to soil ingestion affected by "pica-soil", geophagia, dust inhalation, and absorption through skin (Bisi-Johnson *et al.* 2010).

It has been assumed that the behavior of elements in soils and in consequence their bioavailability differ as to their origin (Zhang *et al.*, 2002). The element transfer from soil is a very complex process governed by several factors, both natural and affected by humans (Roivainen *et al.*, 2012). Soil processes (Retallack, 2001) and anthropogenic factors (Mirsal, 2008) are the major factors that control the behavior of elements in soil. Several recent reports have indicated that regardless of the forms of the anthropogenic elements, their availability to plants is significantly higher than those of natural origin (Kabata-Pendias & Mukherjee, 2007; Alloway, 2013).

Elements present in soils can be associated with several reactive components. Although total element concentrations may indicate the overall level of elements in soils, they provide no information regarding the chemical nature or potential mobility and bioavailability of a particular element (Vijver *et al.*, 2004; Jin *et al.*, 2005; Powell *et al.*, 2005). Sequential fractionation is a frequently used approach to evaluate element distribution

into different chemical forms present in a solid phase. Conceptually, sequential fractionation categorizes elements associated with chemically homogeneous fractions that, ultimately, affect element availability (Clemente *et al.*, 2008; Nobuntou *et al.*, 2010; Burt *et al.*, 2011; Cornejo-Ponce & Acarapi-Cartes, 2011). Although often criticized due to lack of specificity of extractants and possible readsorption of elements during extraction (Rao *et al.*, 2008). Sequential fractionation can provide useful information to predict the fate of heavy metal in the environment (Michalke, 2003; Michalke, 2009; Ajmone-Marson & Biasioli, 2010; Nannoni *et al.*, 2011; Luo *et al.*, 2012).

The mobility of heavy metals in soil samples can be evaluated by dividing the fractions that are weakly bound to soil components with all fractions (Kabala & Singh 2001). These are usually classified according to a risk assessment code (RAC) based on the strength of the bond between the element and the different geochemical fractions in soils and the ability of the elements to be released and enter into the food chain (Rodriguez *et al.*, 2010). The RAC expressed as a percentage, is defined by taking the ratio of the mobile fractions (water soluble and exchangeable fractions) to the total concentration of elements in the soil. However, Batjargal *et al.* (2010) has expressed that exchangeable and carbonate bound fractions are bioavailable and additionally, fraction bound to Fe/Mn oxides could be leached by weak acidic solution. Consequently, it is therefore necessary to assess the possible contribution of these potentially leachable pools of elements to bioavailable component and thus ascertain their risk in the environment.

Generally, the extent of anthropogenic contamination can be expressed using the enrichment index and it has been widely used by several authors in order to establish the degree of contamination by elements (Rubio *et al.*, 2000; Loska *et al.*, 2003; Ghrefat *et al.*, 2011; Ahiamadjie *et al.*, 2011; Likuku *et al.*, 2013). This index is usually computed by averaging the ratios of the concentrations of the measured element to the hazard criteria or to the soil quality guidelines for that element. It is notable that neither in Nigeria nor sub-Saharan Africa have soil quality guidelines been established. Thus, the determination of permissible levels of element concentration in soil and the application of such standards as used by other countries may not be easy as there could be varying lithography. Hence rather than expressing the enrichment index (equation 1) as an estimate of pollution, it can as well be used as an estimate of possible anthropogenic influences on the surface environment assuming that under normal conditions pedogenic process on the subsurface soil should give rise to surface soil.

$$TF_i = (X_i/X_{ref})/(Y_i/Y_{ref}) \quad (1)$$

where, X_i is concentration of the metal in bulk soil in surface environment, X_{ref} is the concentration of the T_i in bulk soil in surface environment, Y_i is the concentration of metal in subsurface environment, Y_{ref} is the concentration of the T_i in subsurface environment. Values >1.0 indicate accumulation of metals in soils due to anthropogenic sources while values of 1.0 and <1.0 show that enrichment of metals is not detectable and loss of metals due to pedogenic processes (Acosta *et al.*, 2011).

2. Materials and Methods

2.1 Sampling Description

Southern part of Ondo State lying between 6°15'N-5°10'E and 7°00'N-4°20'E, wherein lies the bitumen belt, was divided into regular grids of 12.5 X 12 sq. Km and in each of the grid, five points were sampled and pooled to represent a field composite sample (Figure 1). All samples were georeferenced using Geographic Positioning System (GPS). Each sample was air dried in the open laboratory, picked, disaggregated using mortar and pestle, sieved through 2mm nylon mesh (British Standard) and stored in poly propylene bottles prior to analysis (Patnaick, 2004).

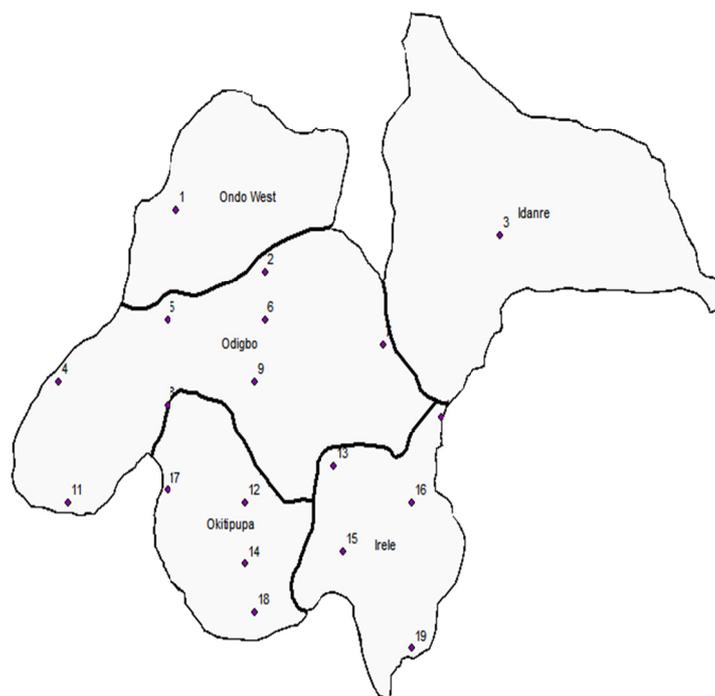


Figure 1. Map showing the geographically referenced sampling points

2.2 Determination of Total Fe, Zn, Cu and Mn Contents of Soil

200mg of air dried soil sample was weighed into an acid washed Teflon beaker and placed on a sand bath with mixtures of the following acids; 10 ml HF + 5 ml HClO₄ + 2.5 ml HCl + 2.5 ml HNO₃. The mixture was heated to almost dryness to dissolve the silica content of the soil sample. The resulting salt was dissolved in 20% aqua regia (HCl:HNO₃/1:3), filtered and made up to 10 ml in a standard volumetric flask (Zhang *et al*, 2008). Each digest was analysed using inductively coupled plasma-optical emission spectrophotometer (ICP-OES).

2.3 Selective Extraction Procedure

The following sequential extraction procedure was applied to 10g soil:

Stage 1: Soluble + Exchangeable: 10 g of air dried soil sample was leached at room temperature for 2 h with 40 ml of 1M MgCl₂ (pH=5) with continuous agitation,

Stage 2: Bound to Organic Matter: residue from stage 1 above was leached at room temperature with 30 ml 0.5M NaOH and agitated continuously for 16 h,

Stage 3: Precipitation of Carbonates: to the residue from stage 2 above was added 30 ml of 0.05MNa₂EDTA will be used to leach it at room temperature for 6 h,

Stage 4: Bound to Iron and Manganese: the residue from stage 3 above was extracted in darkness at room temperature for 4 h with 30 ml Oxalic acid-Oxalate, pH 3.0,

Stage 5: Precipitation of Sulphides: the residue from stage 4 above was digested with 50 ml 4M HNO₃ and the mixture heated on sand bath to 80±2°C for 16 h with occasional agitation,

Stage 6: Residue: Obtained by difference between the total content and the sum of the above five fractions (Figure 2).

Selective extractions were carried out in 50ml polypropylene centrifuge tubes with caps to minimize losses of solid material. Between each successive extraction, separation was performed by centrifuging at 6000rpm for 25 minutes. The resultant supernatant solution was decanted, filtered and made up to volume in a 50ml standard flask with distilled water. This solution was analysed for multi-elements while the next extractant was added the residue sample (Gimeno-Garcia *et al*, 1995). Between each step in the sequence, the residue was not washed with distilled water because washing may results in elements losses and therefore low recoveries of elements in a

given extraction step. To reduce the possible error, the equation suggested by Sposito *et al* (1982) was applied. This equation contains a correction for the amount of element in the solution entrained with the soil sample after the centrifugation that follows each extraction:

$$\mu\text{gextracted} = (CxM) - (C'xM') \quad (2)$$

Where C is the concentration ($\mu\text{g/g}$) of element in the extracted solution, C' is the concentration ($\mu\text{g/g}$) of element in the solution extracted in the preceding step of the sequence, M is the mass (g) of extractant used, M' is the mass (g) of solution carried over to the present extraction from the preceding one. Extracts were analysed using inductively coupled plasma-optical emission spectrophotometer (ICP-OES).

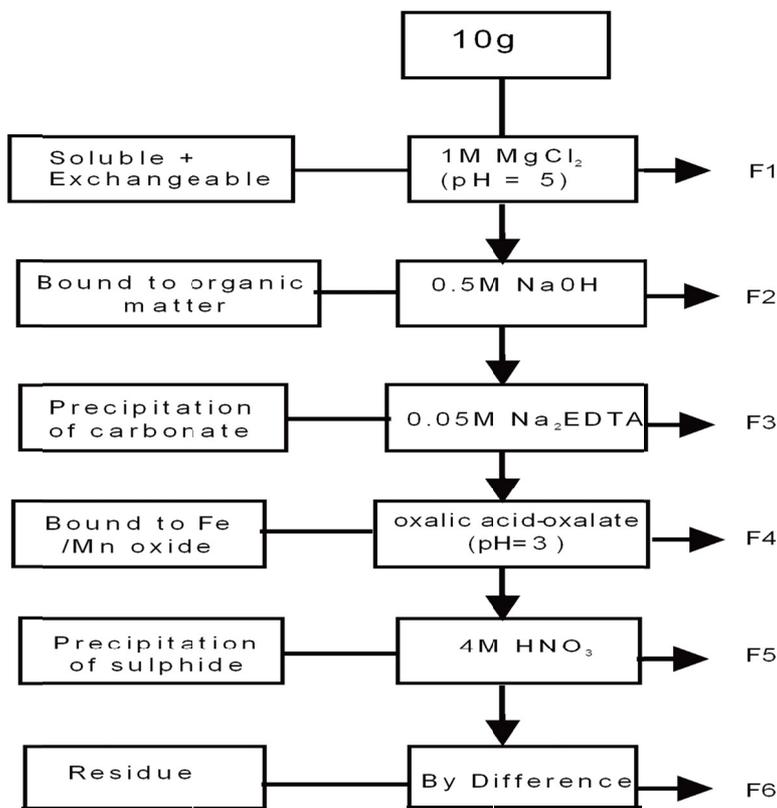


Figure 2. Flow chat for the sequential extraction procedure

3. Results and Discussion

3.1 Spatial Distribution of Cu, Fe, Mn and Zn

The surface environment have lower Cu concentrations in the NE through the centre towards the S axes of the study area while higher concentration was found along the E and NW, W and SW axes (Figure 3). Total Cu spatial distribution in the subsurface environment is similar to those of the surface environment (Figure 4). Consequently, it can be said that the same factor could be responsible for total Cu distribution in both the surface and subsurface environment. However, copper is higher in concentration in the surface than the subsurface environment. Spatial distribution map of total Fe concentration in both surface (Figure 5) and subsurface (Figure 6) environment indicated that higher total Fe concentration was found in the N while lower concentration was obtained in the S. This demarcation correlate with bedrock type; the N is of basement complex while the S is undifferentiated essentially sedimentary. The total Mn concentration spatial distribution map for surface environment shows that higher concentration of Mn were found in the N with NW having the highest while lower concentration spread to the S (Figure 7). Total Mn concentrations spatial distribution of subsurface is similar to that of surface environment in all respect with the subsurface environment having higher values of Mn concentration than the surface environment (Figure 8). Total Zn concentration in the surface environment is relatively higher from the N central through the centre of the study area to the S with highest concentration in the E (Figure 9). The spatial distribution of total Zn concentration in the subsurface environment is similar to the surface environment though higher values were obtained in the case of subsurface environment (Figure 10).

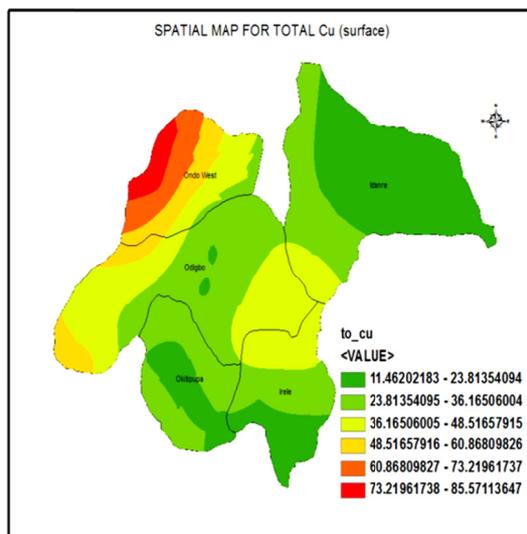


Figure 3. Spatial distribution map of total copper for surface soil

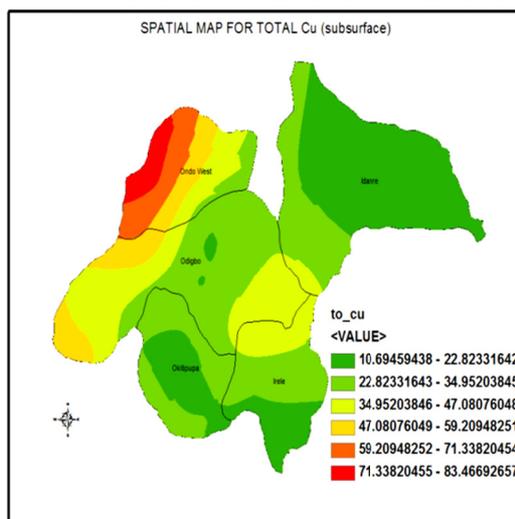


Figure 4. Spatial distribution map of total copper for subsurface soil

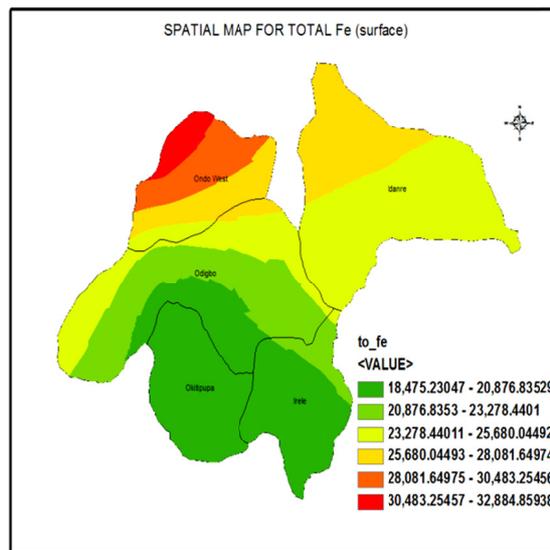


Figure 5. Spatial distribution map of total iron for surface soil

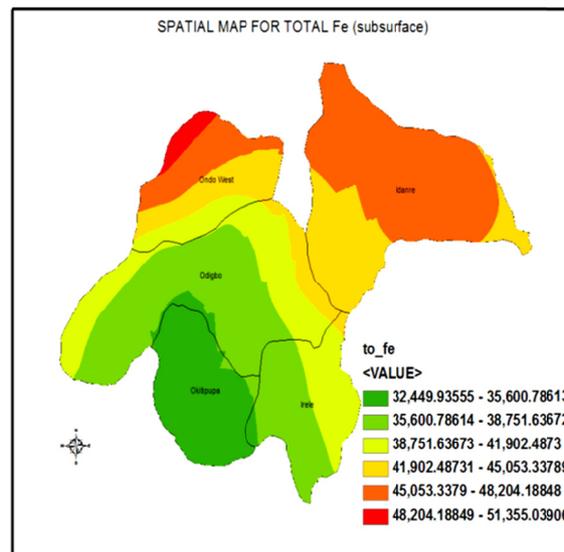


Figure 6. Spatial distribution map of total iron for subsurface soil

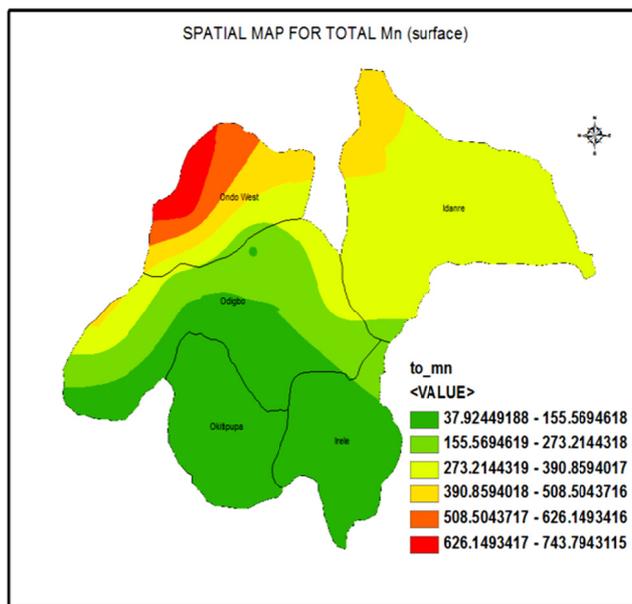


Figure 7. Spatial distribution map of total manganese for surface soil

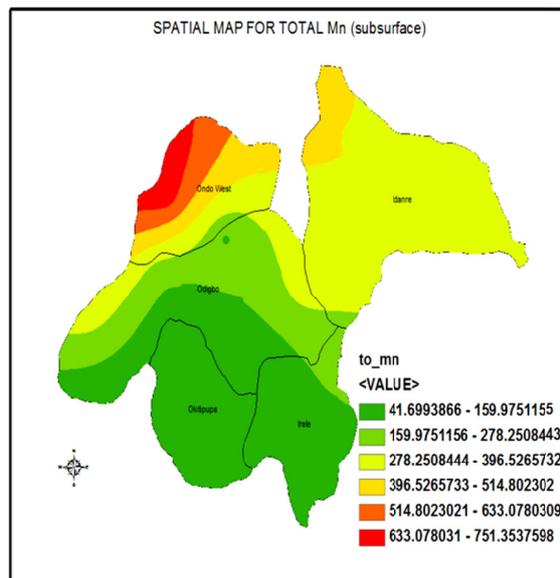


Figure 8. Spatial distribution map of total manganese for subsurface soil

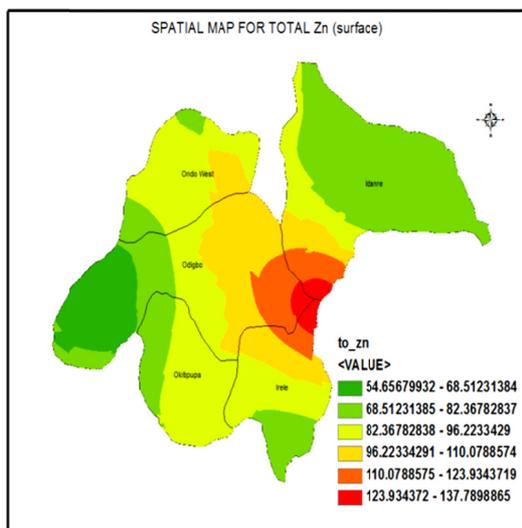


Figure 9. Spatial distribution map of total zinc for surface soil

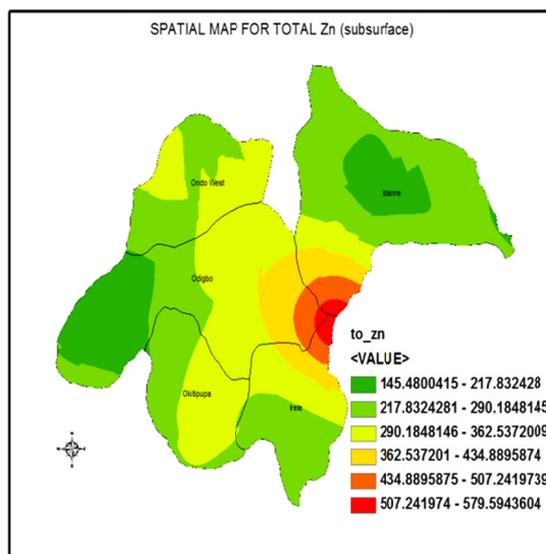


Figure 10. Spatial distribution map of total zinc for subsurface soil

3.2 Bioavailability of Cu, Fe, Mn and Zn from the Soil Matrix

The results for the selective extraction of the trace elements are shown in Table 3 below:

According to Ma & Rao (1997) assuming that bioavailability is related to solubility, metal bioavailability should decrease in the order:

Exchangeable>Carbonate>Fe-Mn oxide>Organic>Sulphide>Residual

Thus metals in the non-residual fractions are more bioavailable than in residual fraction. It can be said that nonresidual fractions in the present study for the metals (Cu, Mn, Zn) were greater than the residual fractions except Fe in the surface soil environment while residual fractions for metals (Fe, Mn, Zn) were greater than non residual fractions in the subsurface environment except Cu. Hence, Cu, Mn and Zn seem to be more mobile in

surface environment while only Cu is therefore potentially mobile in subsurface soil environment. This could be tantamount to their bioavailability considering the conclusion of Ma & Rao (1997). Rastmanesh *et al.*, (2010) has expressed that residual fraction constitutes a significant proportion for all elements.

Table 3. Percent phase fractionation of trace elements in surface and subsurface soil environment

	Co %	Fe %	Mn %	Zn %	Cu %	Fe %	Mn %	Zn %
	Surface Soil				Subsurface Soil			
F1	1.63	0.31	3.03	2.63	3.33	0.34	1.04	2.88
F2	10.33	0.32	13.56	6.25	15.70	0.31	6.30	6.42
F3	7.61	3.55	6.49	13.51	13.65	1.68	7.27	6.35
F4	25.27	6.91	14.00	12.91	13.37	4.31	10.94	8.70
F5	13.24	19.27	16.82	18.92	8.23	18.38	12.28	15.18
F6	41.91	69.63	46.10	45.79	45.72	75.00	62.16	60.47

F1-Soluble+Exchangeables; F2-Organically Bound; F3-Carbonate Bound; F4-Fe/Mn Oxides Bound; F5-Sulphide Bound; F6-Residue

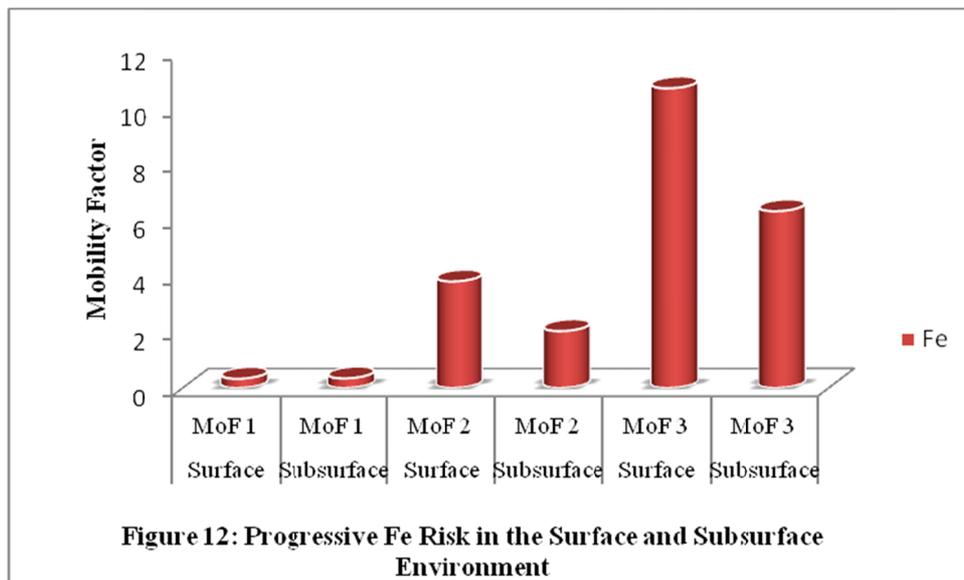
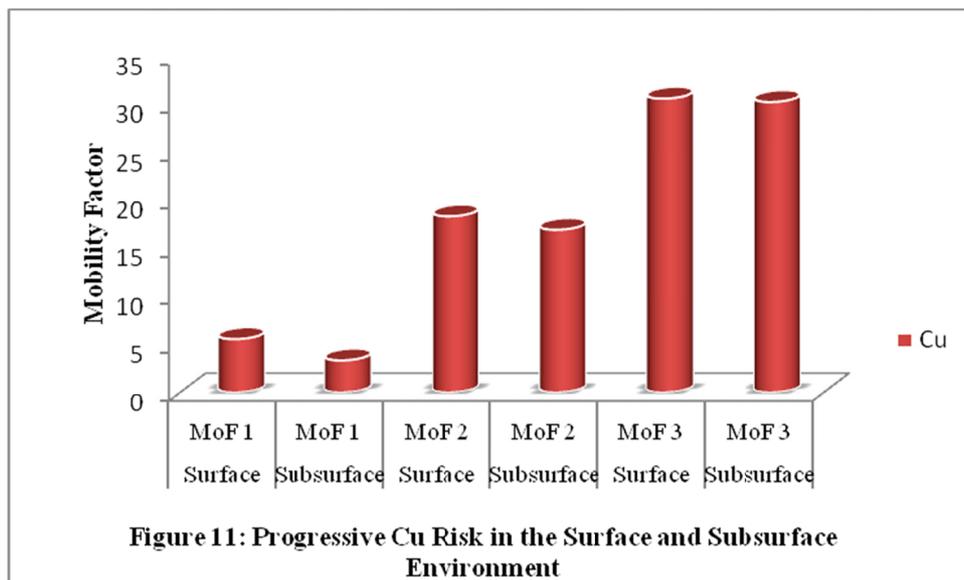
According to Kaasalainen & Yli-Halla (2003), the proportion of the residual fraction reflects native metal concentration in soil. Consequently, the metal Fe in the surface and Fe, Mn, Zn in the subsurface environment of the southern part of Ondo State, Nigeria were not potentially bioavailable and they constitute probably the native concentrations in soil of the area under study. There was similar observation in the work of Agbaire & Akporhonor (2014) but the view of Aikpokpodion *et al.* (2012, 2013) differs. Generally, the metals in the surface environment were more bioavailable than subsurface environment considering the relative larger value of residual fractions of the latter. Water soluble + Exchangeables were very low in all metals and within the surface and subsurface environment. Percentage of metals that are acid leachable or oxidisable were very high and a change in these conditions would increase the bioavailable metals in the two environment. The order is as follows for metals in surface and subsurface environment:

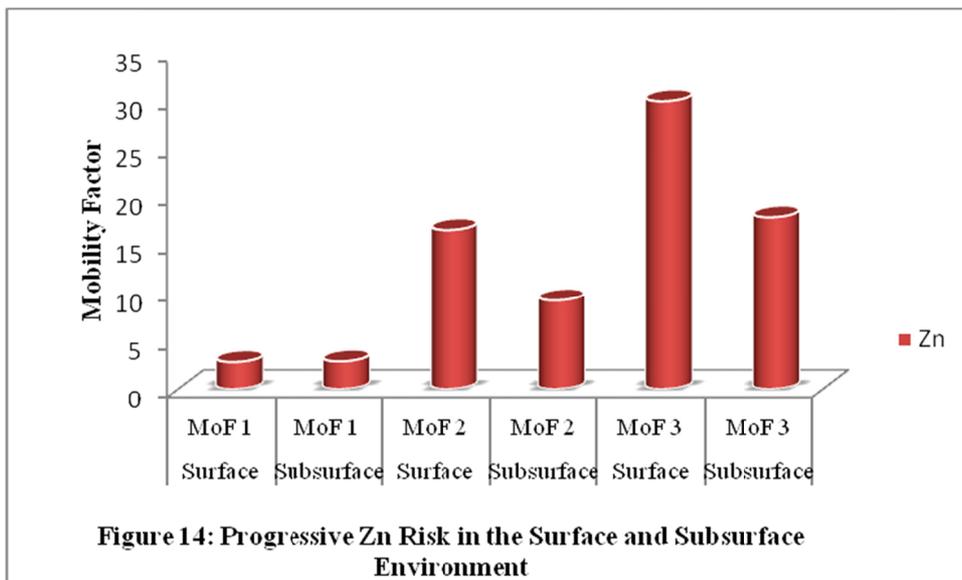
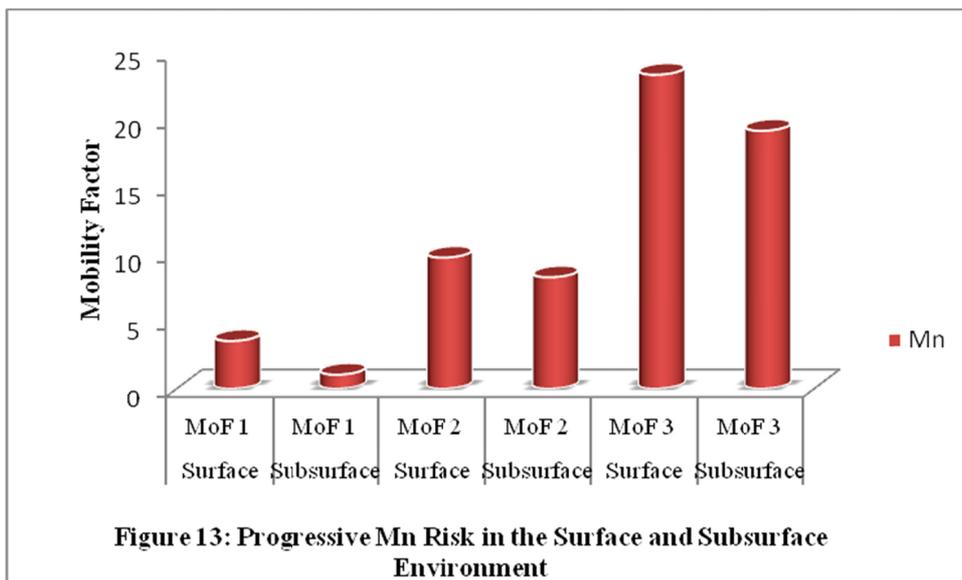
Surface: Cu, F6>F2>F3>F4>F5>F1; Fe, F6>F5>F4>F3>F2>F1; Mn, F6>F5>F4>F2>F3>F1; Zn, F6>F5>F3>F4>F2>F1

Subsurface: Cu, F6>F2>F3>F4>F5>F1; Fe, F6>F5>F4>F3>F1>F2; Mn, F6>F5>F2>F2>F3>F1; Zn, F6>F5>F4>F2>F3>F1

3.3 Mobility of Cu, Fe, Mn and Zn from the Soil Matrix

Three mobility factors were defined thus: (i) soluble+exchangeable, (ii) soluble+exchangeable + carbonates and (iii) soluble+exchangeable + carbonates + bound to Fe/Mn oxides to total concentrations of the element in the soil. According to Rodriguez *et al* (2009), there may be no risk when these fractions represent lower than 1% of the total concentrations, low risk for 1-10%, medium risk for 11-30%, a high risk for 30-50% and a very high risk for higher percentages. All the metals in this study were more mobile in the surface than the subsurface environment (Figures 11-14). Considering the mobility factor in terms of relative percent of soluble + exchangeables for the elements shows that Fe was with no risk at both surface and subsurface environment while Cu, Mn and Zn were with low risk. However, Fe was with low risk at both surface and subsurface environment; Cu was associated with medium risk in both environments, Mn was with low risk in the surface and medium risk in the subsurface; Zn was associated with medium risk in the surface and low risk in the subsurface when the relative percent of soluble + exchangeables + carbonate were considered. Moreover, the relative percent of soluble + exchangeables + carbonate + Fe/Mn oxides indicated that Cu was with high risk in both surface and subsurface environment; Fe was with low risk in both; Mn was with medium risk in both while Zn was with high risk in the surface and medium risk in the subsurface. The mobility of Cu, Fe, Mn and Zn increases progressively with severity of prevailing conditions. However, the progressive increase in the risk of Cu from low risk through medium risk to high risk in both surface and subsurface environment and similarly that of Zn in surface environment is noteworthy.





3.4 Assessment of Possible Sources of Cu, Fe, Mn and Zn in the Surface Environment

Surface soil metal concentrations are a product of a variety of natural and anthropogenic sources. It has been said, however, that rural, non-highly agricultural areas should not be assumed to have low soil metal concentrations (Davis *et al.*, 2009) indicative of non anthropogenic sources. The results indicated that Cu and Mn might be associated with anthropogenic sources with their values higher than 1 while Fe and Zn might have been lost during pedogenic processes since their value was less than 1 (Table 4). Davis *et al.*, (2009) have earlier expressed that some metals like Mn were consistently associated with natural sources in both the rural and the urban areas while metal like Cu was associated with both natural and anthropogenic sources. Their observation about Cu was found to be the same with this study but that of Mn was not. Kabala & Singh (2001) also found Cu to be associated with contamination and anthropogenic sources. For some metals associated with anthropogenic inputs, land use and the density of industrial facilities appeared to play a role in the higher concentrations measured and their mobility, e.g. application of copper based fungicides and other similar chemicals could be attributed to Cu behavior in this study.

Table 4. Assessment of sources of Cu, Fe, Mn and Zn in surface environment with Ti as normalizer

	Elements Average	Min	Max
Cu	1.22	0.92	1.57
Fe	0.66	0.46	1
Mn	1.11	0.81	1.53
Zn	0.35	0.27	0.45

4. Conclusion

Total trace metal composition of soils are of little importance in determining the total trace metal uptake by plants and consequent level of risk these elements may pose to plants and the food chain. This is because different binding forms have different mobilities, bioavailabilities and potential environmental threat. Forest areas can be prone to trace element changes when industrial and mining activities are introduced and the consequences of bioaccumulation of these elements are obvious. Southern Ondo State is prone to future industrial and bitumen exploitations and there is need to document the industrial and mining pre activities. This studies has therefore indicated that Cu and probably Zn could be very mobile in this environment and may pose some level of risk to ecosystem and underground water aquifers. This risk may be greater than predicted as future industrial and mining activities may increase the total concentration load of the metals and also may have negative impact on the soil physicochemical properties most especially soil acidity. This will increase the portion that may be soluble, exchangeable and bound to carbonate including oxidisable or reducible.

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