Evaluation of background geochemical speciation of heavy metals in overburden topsoil of bituminous sand deposit area, Ondo state, Nigeria

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Abstract
Metals are ubiquitous within the earth crust. However, the exceptional high-level concentration of heavy metals in the soil due to natural or anthropogenic activities and the chemical forms in which they exist determine the level of risk they portend to the environment. This work was aimed at determining the background level of the presence of seven priority toxic metals (Cr, Ni, Pb, As, Cd, Cu, Zn) in the chemical phases of the overburden topsoil of a bituminous deposit prior to mining activities through the speciation analysis. The grab samples of overburden topsoil were initially obtained and homogenized to composites based on locations for the subsequent sequential extraction procedure (SEP). The specific physico-chemical properties of the sampled soils were simultaneously determined to complement the SEP inferential analysis. The results obtained showed that most metals were spatially bounded to the Fe-Mn oxides (reducible phase) followed by the organic (oxidizable) and the carbonates phases, respectively. Fractionally, the dominant soil texture in the studied area was sand (55.45%); however, the colloidal organic matter and Fe-Mn oxide phases played the dominant roles in the sorption activities of the selected metals. The soil chemical phase with the least metal pool was the exchangeable (water/salt) soluble fraction. The overall assessment revealed that the geogenic heavy metals in the topsoil posed no threats since a marginal fraction of the metals existed in the bio-available form in non-toxic concentrations in the order of Pb > Zn > Cu, while the potential mobility of metals showed that Zn was preferentially higher than Pb and Cu, respectively.

1. Introduction
Open-pit mining of sub-surface mineral deposits often entails removal of overburden materials in order to gain access to the target minerals. As a result, serious disruption of landforms of which soil, a major component of the ecosystem, is removed and its natural physico-chemical structure is altered partially or totally [1-4]. This often impacts the soil ecosystem functions, particularly in circumstances where the overburden materials are completely removed or displaced from the mine area. One of the several ways by which mining activities may impact the surrounding soil environment is through the anthropogenic introduction of contaminants in the form of chemicals or high-level loads of heavy metals [2, 5, 6]. Metal contamination of soil is a phenomenon common to mining operations including the extraction of bituminous sands. The extent and effects of these contaminations vary by the type of metal concerned, its chemical state and form, concentration of the contaminant, and the chemical state of the transmitting medium.

1.2. Soil and naturally occurring metals
Soil naturally contains some macro and trace metals by nature. It also exhibits repository capacity for heavy metals and other contaminants due to its ability to adsorb these elements onto the

surface of its inorganic (clay) minerals and also bind various chemicals [7]. Metals in soil are ubiquitous, and a number of these metals are essential for plant growth within the range of certain concentrations. Within this concentration range, soils tend to be at their optimum productivity supporting vegetation and other forms of life within the ecosystem. However, the excessive or high-level concentrations of some of these metals in the soil pose serious environmental challenges including health risks to the plant, animal, aquatic, and human lives. This risk is due to the fact that the metals in soil solution can be transported by water or plants; this, in turn, controls their reactivity, and hence, their mobility and bio-availability [8, 9]. Heavy metals are generally referred to as metals and metalloids that have densities greater than 5 g/cm^3 such as lead (Pb), zinc (Zn), cadmium (Cd), chromium (Cr), arsenic (As), and copper (Cu) at the least. It has been noted that heavy metals do not biodegrade naturally within the soil environment. Hence, they remain substantially for a long time within the soil environment [6, 10, 11]. Enrichment of heavy metals in soil could pose severe threats to the human and animals' health exposed to the soil due to the carcinogenic and mutagenic effects of these metals. The effects associated with heavy metals are significantly dependent on their chemical species [12]. The propensity for the increased exposure of organisms to heavy metals through the existing or potential industrial process underscores the requirement to identify and quantify those species in soils that pose the greatest potential threat to organisms [13].

The mechanism of metal transport in the soil could either be physical, chemical or biological. Metals exist in different chemical forms, which dictate their reactivity and mobility in the soil medium [14, 15]. This is known as chemical speciation, and it refers to the distribution of an element amongst the chemical species present in a system. The understanding of the speciation of these elements is crucial in determining the chemical toxicity, bio-availability (risk to humans and ecosystems), and environmental fate and transport [16]. In the soil, metals are found in one or more of several "pools", as illustrated by Shuman [17]. They are (i) dissolved in the soil solution; (ii) occupying exchange sites on inorganic soil constituents; iii) specifically adsorbed on inorganic soil constituents; (iv) associated with insoluble soil organic matter; (v) precipitated as pure or mixed solids; (vi) present

in the structure of secondary minerals; and/or vii) present in the structure of primary minerals. The metals that are introduced into the environment through anthropogenic activities (human activities) are associated with the first five pools [18], while the naturally occurring metals may be associated with any of the pools depending on the geological history of the area.

In environmental studies, metals in aqueous solution, and those fractions in equilibrium with this fraction, i.e. the exchange fraction, are of primary concern [18]. More accurate information has been derived by determination of the metal speciation on the potential for release of contaminants as well as further derived processes of migration and toxicity [19]. Although many studies have focused on examination of the total metal concentration in soil as a means of assessing the degree of soil metal contamination, other studies [13, 20] have shown that the speciation of these metals among different chemical forms in the soil is of greater significance. This shows the intensity factor (concentration of a particular ion in the soil solution) and the capacity factor (ability of solid components in soils to re-supply an ion that is depleted in the soil solution) [21] by identification and quantification of different species, forms, and phases in which these elements occur. Metal speciation in soil tells the manner of interaction of the metal species with soil environment suggesting their mobility potential (bio-availability), and hence, their toxicity, pathways, and fate. It is the free metal (mobile) ions that are toxic, and not the total metal concentration, since some metals may be complexed with stable organic and lattice bonds of the inorganic mineral, and thus making them non-bio-available (non-toxic).

The bituminous deposits in the studied area have been reported to contain some natural heavy metals. Through the mining activities, some of these metals in the deposit may be released into the environment through certain mechanisms such as extraction of oil from the sand matrix and the subsequent disposal of the tailings waste. The objectives of this work were to analyse the background heavy metal speciation in the yet to be disturbed overburden soils of bituminous sand region of Ondo State, Nigeria; establish a baseline heavy metal chemical partitioning of the pristine (pre-mine) status of topsoil in the studied area; and determine the mobility potential of the specific potentially toxic heavy metals in correlation with certain soil geophysico-chemical properties.

2. Materials and methods
2.1. Studied area
The studied area is located between the coordinates $6°39'46.13''$ N-$6°39'41.09''$ N and $4°49'15.22''$ E-$4°53'31.65''$ E, respectively, in the Ondo State, Southwestern belt of Nigeria. It falls within the rain forest belt of the country in the eastern part of the Benin (Dahomey) basin. Geologically, the Dahomey (Benin) basin is part of a system of West African peri-cratonic basin covering much of the continental margin of the Gulf of Guinea, extending from Volta-delta in Ghana on the West to the Okitipupa Ridge in Nigeria on the East [22]. In studying the background speciation of metals in the soil, information on the origin of the soil in the area is crucial. This helps to understand the pedogenic source of the constituent elements in the soil system. Stratigraphically, the depositional sequence of the geologic materials in the Dahomey basin spans from the Cretaceous-Tertiary-Recent (Quaternary).

The cretaceous sediments, also known as the Abeokuta Group, uncomformably overlie the basement complex. It comprises the Ise, Afowo, and Araromi formations overlying each other in order of succession. The petrology of the formations reveal that the Ise formation unconformably overlie the Precambrian basement complex and consists of imbricated basal conglomerates overlain by coarse- to medium-grained loose sands, sandstones, and grits containing kaolinitic clays [22, 23]. The Afowo formation overlying the Ise formation is composed of coarse- to medium-grained sandstones with thick intercalations of shales, siltstones, and pyrite bearing claystones. It is within the Afowo formation that the petroleum hydrocarbon, bitumen is hosted. The Araromi formation is constituted by fine- to medium-grained sandstone overlain by shales, siltstones (with limestone inclusions), marls, and lignite [22]. Succeeding the Cretaceous is the Tertiary sediments, which consists of the Ewekoro, Akinbo, Oshosun, Ilaro, and Benin (Coastal Plain Sands) formations [24]. The Tertiary sediments comprise the Ewekoro, Akinbo, Oshosun, Ilaro, and Benin (Coastal Plain Sands) formations. The Ewekoro formation is an extensive fossiliferous well-bedded limestone body. Lying above the Ewekoro formation is the Akinbo formation, which is made up of shale and clayey sequence [25]. The claystones are concretionary, and are predominantly kaolinite. Overlying the Akinbo formation is the Oshosun formations. It consists of greenish–grey clay with sandstones. The geologic boundary between the Ewekoro and Akinbo formations is characterized by glauconitic rock bands and phosphatic beds. The Ilaro formation, which consists of massive, yellowish, poorly consolidated, cross-bedded sandstones, conformably overlies the Oshosun formation. The Benin formation (coastal plain sands) caps the sedimentary profile with predominantly coarse sandy estuarine, deltaic, and continental beds with lenses of clays [24, 25].

Characteristically, the sediments constituting the surface to sub-surface materials of the studied area are made up of a number of primary inorganic minerals including the carbonate and silicate minerals. According to the Food and Agricultural Organization (FAO) [26], the soil of the studied area falls within the "Acrisol" Reference Soil Group.

2.2. Field sampling
Forty grab surface (topsoil) samples were collected from within (0-20) cm soil depth of the overburden material from eight locations in the studied area. At each location, five samples were obtained with four of the samples collected at 10 m radius and perpendicular to the fifth sample in central location similar to the procedure described by [19, 27]. The five primary (grab) samples obtained from each location were then composited to obtain eight different secondary samples according to location. The samples were preliminarily cleaned of plant roots, leaves, and other debris at the field before being transferred in labelled polythene bags to the laboratory for analysis.

2.3. Experimental analysis
2.3.1. Sequential extraction procedure of heavy metals from soil samples
The eight composite samples were analyzed for metal speciation (chemical partitioning) of seven heavy metals including Cr, Ni, Pb, As, Cd, Cu, and Zn into five distinct fractions; (i) exchangeable (ii) bound to carbonates (iii) bound to Fe-Mn oxides (iv) bound to organic matters, and (v) the residuals using the sequential extraction procedure (SEP) proposed by Tessier *et al*. [28].

Prior to the extraction processes, the soil sample composites were air-dried, sieved with < 2 mm sieve aperture, and thereafter, ground with agate mortar and pestle.

(i) Exchangeable: 1 g of each air-dried soil sample was placed inside 50 mL polypropylene centrifuge

tubes and extracted at room temperature for 1 h with 8 mL calcium chloride solution (1 M $CaCl_2$, pH 7.0). The soil sample and the extractant were thoroughly agitated to equilibrium throughout the extraction using an optical shaker.

(ii) Bound to carbonates: The solid (residue) obtained from (i) was leached at room temperature for 5 h with 8 mL of 1 M NaOAc adjusted to pH 5.0 with acetic acid (HOAc). During the process, the solution was continuously agitated.

(iii) Bound to Fe-Mn oxides: The extraction of metals bound to Fe-Mn oxides was carried out on residue from (ii). It was extracted with 20 mL 0.04 M NH_2OH-HCl in 25% (v/v) acetic acid at 96 °C for 6 h with occasional agitation to ensure complete dissolution of the free iron oxides.

(iv) Bound to organic matter: The residue from (iii) was leached by addition of 3 mL of 0.02 M nitric acid (HNO_3) and 5 mL of 30% hydrogen peroxide (H_2O_2) adjusted to pH 2.0 with HNO_3. The mixture was heated to 85 ± 2 °C for 2 h with occasional agitation. A second 3-mL aliquot of 30% H_2O_2 (pH 2, with HNO_3) was then added, and the sample was subsequently heated again at 85 ± 2 °C for 3 h with intermittent agitation. After cooling, 5 mL of 3.2 M ammonium acetate (NH_4OAc) in 20% (v/v) HNO_3 was added, and the sample was diluted to 20 mL and agitated continuously for 20 min. The addition of NH_4OAc was to prevent adsorption of metals extracted onto the oxidized sediment.

(v) Residuals: The residue from (iv) was digested with a combination of HNO_3 and hydrochloric acid (HCl) (aqua-regia). Between the successive extractions, separation was effected by centrifugation at 5000 rpm (6000 g) for 30 min. The supernatant solution was removed using a pipette and analyzed for the heavy metals, while the residue was washed with 8 mL of deionized water; after centrifugation for 30 min, the second supernatant solution was discarded. The volume of water used to rinse was kept to a minimum to avoid excessive solubility of solid material, particularly organic matter. The trace metal concentrations were determined by flame atomic absorption spectrophotometry (FAAS) using bulk scientific VGP 210 model by direct aspiration of the aqueous solution into its air-acetylene flame.

2.3.2. Determination of physico-chemical properties of soil samples

The particle size distribution of the soil samples was carried out by the sieve analysis and sedimentation (hydrometer 152 H) in accordance with America Society for testing and Materials ASTM D 422 [29]; the pH values of the samples were determined in accordance with ASTM D 4972 [30] using pH electronic meter Jenway (3510) soil:water (w:v) of 1:2.5, while the soil organic carbon and organic matter were determined by the Walkley-Black dichromate method, as described by [31].

3. Results and discussion

The speciation analysis of the sampled soils showed that the heavy metals were distributed in varying concentrations among the five operationally defined chemical forms. The results obtained accentuate the fact that the concentration of each metal in a particular chemical phase at a particular time is a dynamic phenomenon influenced by a number of factors state them and link up with the results. The total concentration of the understudied metals, their association with all the five chemical forms exchangeables, carbonates, oxides of iron and manganese, organic matter and the residuals (absorbed and occluded in the crystal lattices of the soil inorganic mineral matter) were tabulated in Table 1. The results of some of the underlying factors capable of influencing the speciation and sorption of these metals in the studied soils were tabulated in Table 2. From the total metal concentration table, the results show that zinc (3.136 mg/kg) has the highest concentration closely, followed by copper (1.68 mg/kg). The result further shows that lead, which has the fourth highest concentration of 1.622 mg/kg, has the second highest mean concentration value of 1.128 mg/kg second to zinc with a mean concentration of 1.498 mg/kg. This implies that lead concentration is comparatively more than the rest of the metals, with the exception of Zn. As earlier remarked, the assessment of total metal concentration exclusively in soil is less informative with regard to the toxicological effects on ecosystem components both terrestrial and aquatic organisms (plants, animals, and humans), compared to the mobile and bio-available metal fraction. In order to show the clear picture of the chemical state and mobility potential of the metals in soil, the detailed graphical partitioning of the metals into the operationally defined soil chemical phases is shown in Figures (1-9).

Table 1. Descriptive statistics of total heavy metal concentrations in soil composite samples.

Heavy metal Sample	Cr (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	As (mg/kg)	Cd (mg/kg)	Cu (mg/kg)	Zn (mg/kg)
Total A	0.078	0.018	0.215	0.191	0.09	0.351	1.156
Total B	0.752	0.766	1.622	0.54	0.391	0.93	1.708
Total C	0.617	0.54	1.433	0.562	0.352	0.418	1.025
Total D	0.792	0.73	1.525	0.624	0.43	1.348	2.206
Total E	0.552	0.481	1.32	0.636	0.344	0.477	0.957
Total F	0.176	0.72	0.845	0.435	0.228	0.425	0.927
Total G	1.663	1.328	1.48	0.566	0.891	1.68	3.136
Total H	0.124	0.115	0.586	0.332	0.315	0.294	0.874
Min.	0.078	0.018	0.215	0.191	0.09	0.294	0.874
Max.	1.663	1.328	1.622	0.636	0.891	1.68	3.136
Mean	0.59425	0.58725	1.1283	0.4858	0.3801	0.74037	1.4986
Std. dev.	0.51701	0.41044	0.51587	0.1558	0.2321	0.52259	0.80863

Table 2. Physico-chemical properties of soil composites at various sample locations.

ParametersSample	Sand (%)	Silt (%)	Clay (%)	pH	OC (%)	OM (%)
A	76.8	11.7	11.5	5.84	3.59	6.19
B	11.9	17.6	70.5	5.51	4.07	7.02
C	84.9	6.9	8.20	5.89	4.03	6.95
D	91.8	4.3	3.90	6.32	1.56	2.68
E	5.50	19.3	75.1	6.40	2.07	3.58
F	44.0	34.3	21.7	6.72	6.82	11.76
G	64.0	16.0	20.0	6.21	3.39	5.85
H	63.9	19.9	16.2	6.15	3.51	6.05

Note: OC = organic carbon; OM = organic matter.

The statistical analysis of the results presented in Figures (1-8) revealed that the heavy metals tested for were partitioned among the soil chemical phases in varying degrees of concentrations. Figure 1 shows that more than 40% of each metal (Cr, Ni, Pb, As, Cd) was sorbed to the carbonate fraction of the soil chemical phase. The carbonate phase is an important sink for metals, and it is affected by pH and ion exchange [19, 32]. Cd (92.22%) was the most adsorbed to the carbonate phase followed by the duo of Pb (83.72%) and Cr (83.33%), respectively. Considering the percentage sand fractions (76.8%) of the composite soil A in Table 2 in addition to its slightly acidic nature, there is a high probability that the metals can preferentially be dislodged in the soil aqueous solution since they are weakly adsorbed to the carbonate phase with a high proportion of sands that usually has low surface negative charges. Since this phase is easily affected by pH, the tendency to promote metal accumulation in soil due to induced exposure and liberation of soil minerals.

In Figure 2, the heavy metal partitioning in soil Sample B differs from that of sample A in Figure 1 with the bulk of the metals being adsorbed onto the more stable fraction of the organic matter phase. The percentage contribution of organically bounded metals to the pool of total metal in soil B

is 44.34%. This organic phase usually consists of humic, fulvic, and other acids with ligands forming complexes with these metals, thus bonding them into more stable forms. This phenomenon is strengthened by the sample's comparatively high organic matter (7%), relative to the other samples.

The percentage adsorbed Ni (58.74%) out of the total Ni present in the sample was comparatively higher than the percentage adsorbed in other metals on an individual basis. The closest metal contributing to the organically adsorbed (oxidizable) metal was Pb with 46.23% out of the total Pb present in the soil sample. However, considering the concentration of the individual adsorbed metal, Pb had a higher fractional concentration (25.21%) compared to Ni (15.2%). In the soil sample C, the larger fraction of soil heavy metals was observed to be bound to the latter two more stable fractions of organic matter and residuals, as shown in Figure 3. This implies that the naturally occurring metals of sample C soil are likely to be more chemically stable with 29.97% and 34.20% of the total metals in the soil bound to the oxidizable (organic matter) and silicate minerals (residuals), respectively.

This occurrence correlates with the relatively high percentage of the organic matter content of 6.95% in the soil sample (Table 2). Metals in sample D

(Figure 4) were found to be associated majorly with the carbonates with a total of 27.36% and the reducible (Fe-Mn oxides) with 32.18%. The Fe-Mn oxides play a very crucial role in soil chemistry. They contribute significant effects to soil chemical processes such as sorption and redox due to their high specific surface area and reactivity [10].
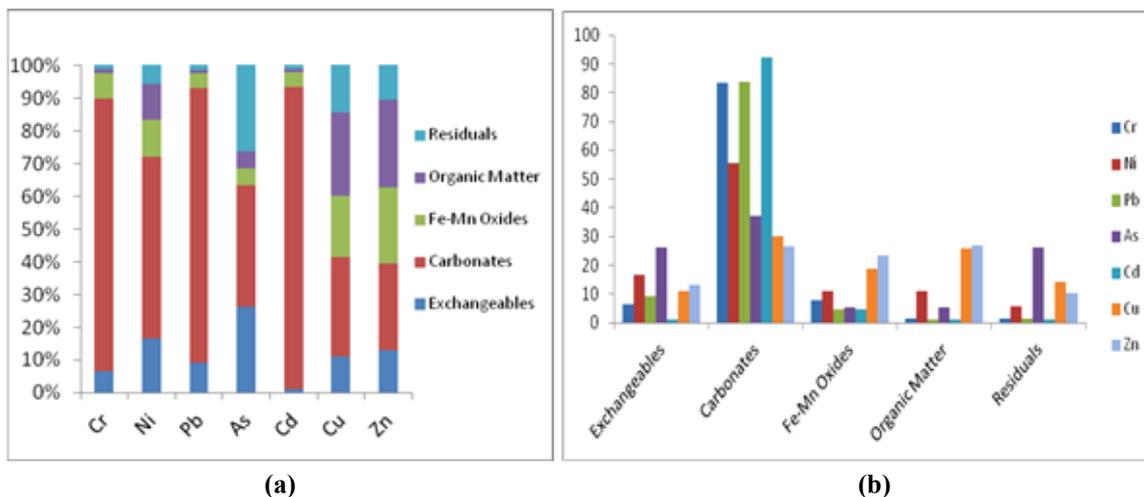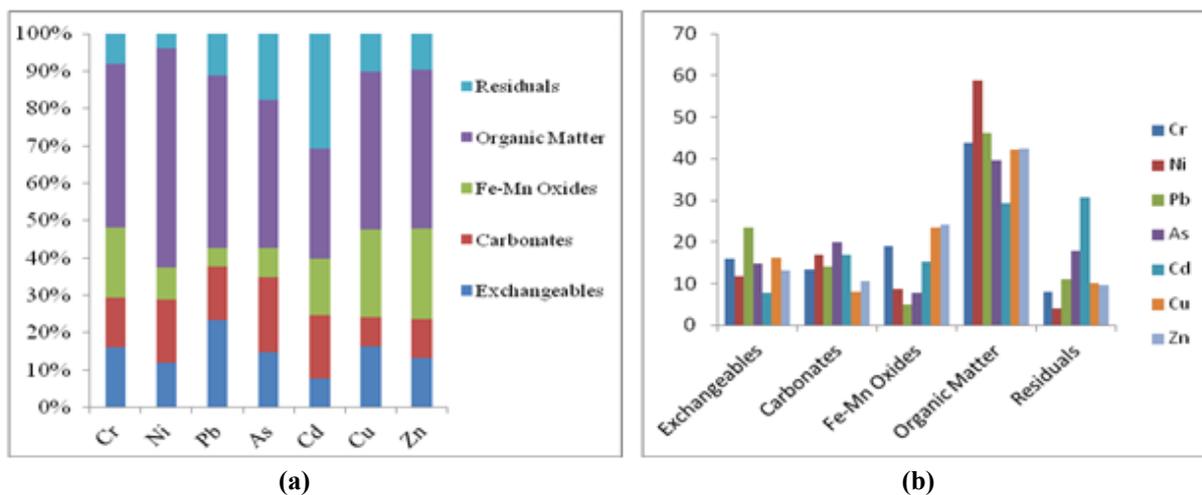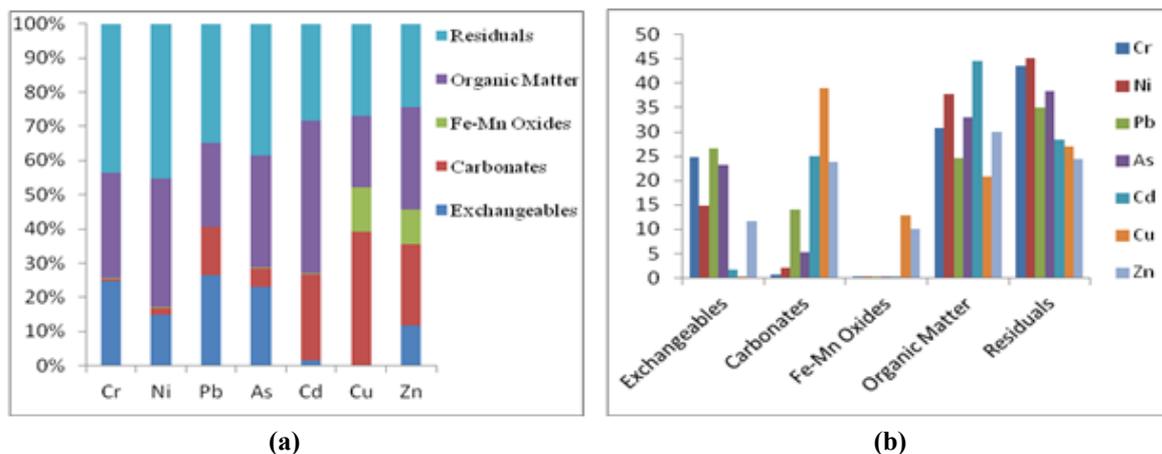

(a)

(b)

Figure 1. Metal fractionation in soil composite sample A (a) percentage contribution of each metal to the extraction phase; (b) combined metal pool in each phase.

(a)

(b)

Figure 2. Metal fractionation in soil composite sample B (a) percentage contribution of each metal to the extraction phase; (b) combined metal pool in each chemical phase.

(a)

(b)

Figure 3. Metal fractionation in soil composite sample C (a) percentage contribution of each metal to the extraction phase; (b) combined metal pool in each chemical phase.
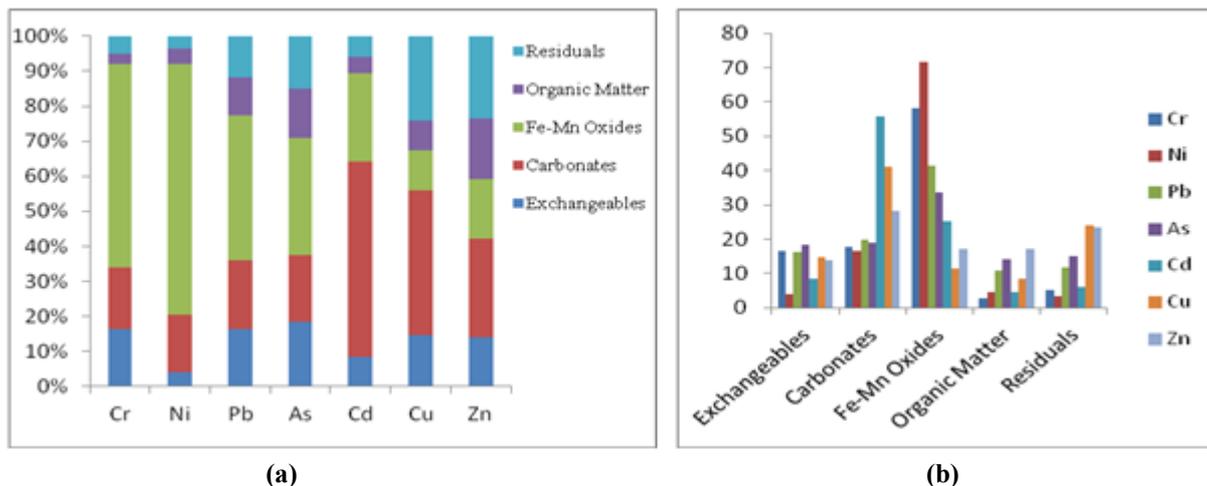
Figure 4. Metal fractionation in soil composite sample D (a) percentage contribution of each metal to the extraction phase; (b) combined metal pool in each chemical phase.

Sample D had significantly low organic matter content (2.68%) (Table 2), most probably indicating a low level of crystalline silicate minerals in the soil, thus the adsorption of most metals to the oxides and the extractable carbonate phases. The order of sorption of metals to this phase is Ni > Cr > Pb > As > Cd > Zn > Cu with the corresponding percentages of individual metal sorption of 71.31%, 58.08%, 41.31%, 33.49%, 25.12%, 17.23%, and 11.50%, respectively. Only 13.91% of the total metal concentration in this soil was in the mobile fraction. The mobilizable fraction of these heavy metals in soil is an indicator of a hazard that portends a serious environmental challenge to the surroundings when in excess of the tolerance threshold. Although the total concentration of each metal was lower than the toxic threshold level for each metal in the soil, the pool of metal associated with the water/salts soluble (the exchangeable fraction and those bound to the carbonates fraction) was a pointer to a potential risk of toxic heavy metal accumulation in the soil during active mining activities, the fact that could be a risk of potential toxic heavy metal accumulation. Quantitatively, 31.31%, 31.99%, and 24.98% of the total metals in the sample are associated with the exchangeable, the carbonates, and the reducible (Fe-Mn oxides), respectively. In the mobile fraction, the metal with the highest mobility potential is arsenic (41.82%) in the labile fraction closely followed by Ni (38.87%) and Pb (36.36%), respectively. The partitioning is, however, different in the carbonates and the Fe-Mn oxide fractions. In these cases, the order of adsorption to the carbonate fraction for the first three metals is Cd, As, and Pb; while for the oxides, the preferential order of metal adsorption for the first three metals is Cu, Cr, and Zn (Figure 5).
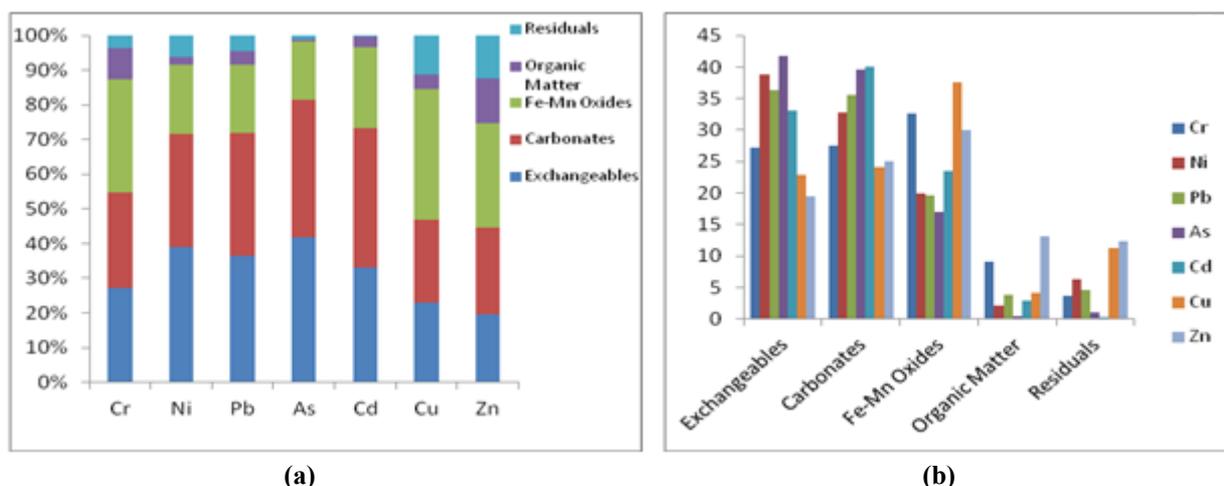

Figure 5. Metal fractionation in soil composite sample E (a) percentage contribution of each metal to the extraction phase (b) Combined metal pool in each chemical phase.

Analyses of the samples F and H showed that the metals were bound more to the organic matter and residual fractions, as shown in Figures 6 and 8. Sample G, however, presented a different bounding structure as most metals were adsorbed to the carbonates and the Fe-Mn oxides (Figure 7). The analysis indicated that 36.95% of the total metals extracted in soil F was adsorbed to the organic matter phase, while 25.74% was adsorbed to the residuals and only 8.17% was associated with the water/salt soluble mobile fraction. The adsorption order of the first three metals in organic matter and residual phases of sample F were Cr > Ni > Pb and As > Cd > Cu, respectively. Similarly, in sample H, metals adsorbed to the organic colloidal phase were 51.78% of the total metals in the sample, while 30.30% was in the crystalline residuals. The distribution of the heavy metals also shows that 8.17% of the total metals was in the exchangeable fraction. Cr had the highest percentage adsorption to the organic matter phase, followed by Cd and Pb, respectively, with copper as the least adsorbed metal. In the residual phase, As ranked the highest in the adsorption profile followed by Pb and Cd in the decreasing order. Observation of the textural pattern of the soils shows that the samples F and G belong to the loam and sandy loam classes, respectively. The preferential sorption of metals to the organic matter phase, compared to other chemical phases, in the samples F and H is, to a large extent, connected with the 11.76% and 6.05% percentage composition of organic matter in the respective soil samples.
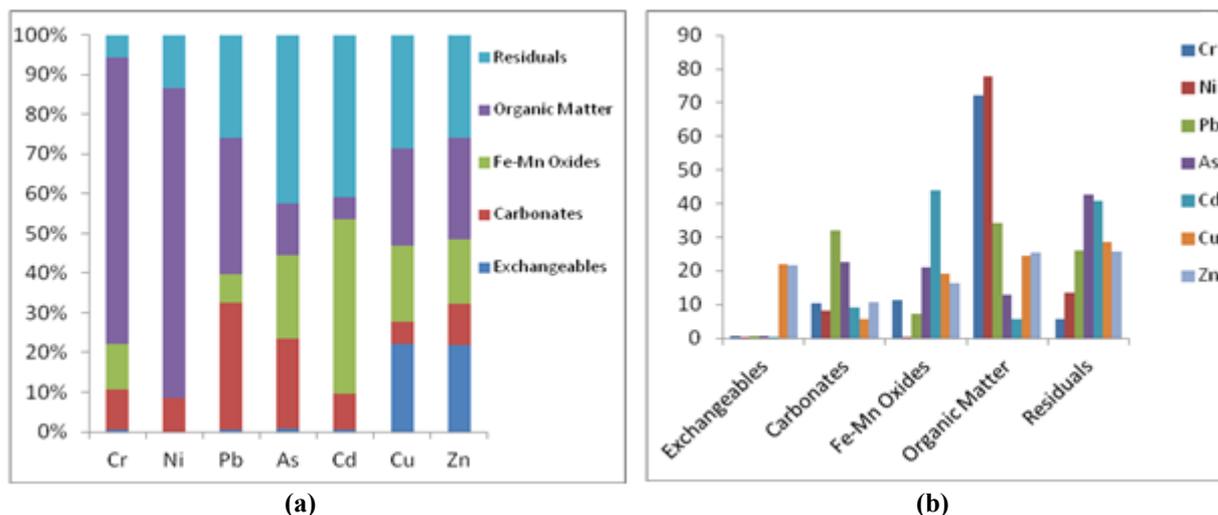

Figure 6. Metal fractionation in soil composite sample F (a) percentage contribution of each metal to the extraction phase; (b) combined metal pool in each chemical phase.
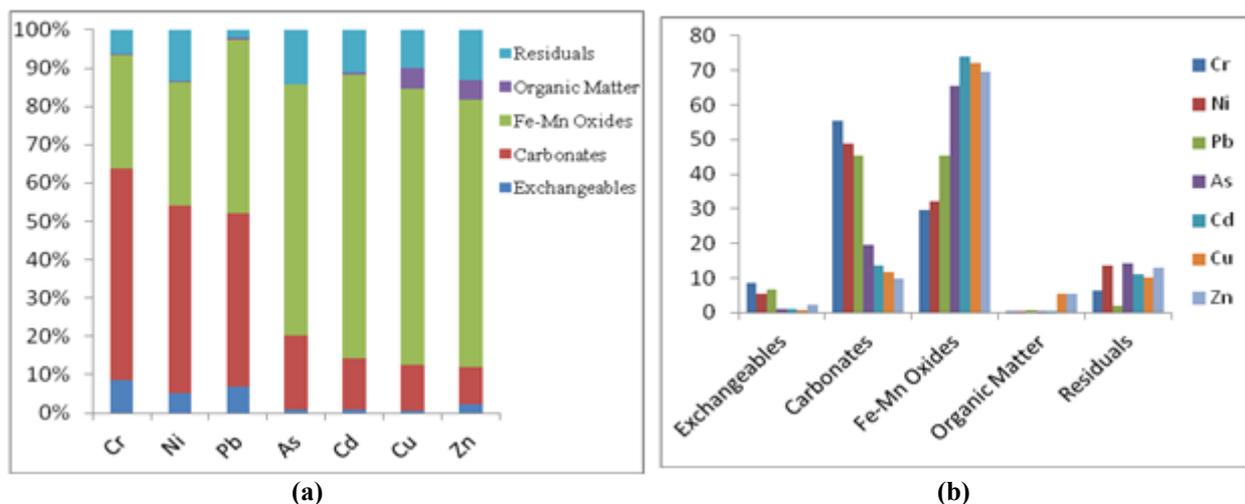

Figure 7. Metal fractionation in soil composite sample G (a) percentage contribution of each metal to the extraction phase; (b) combined metal pool in each phase.
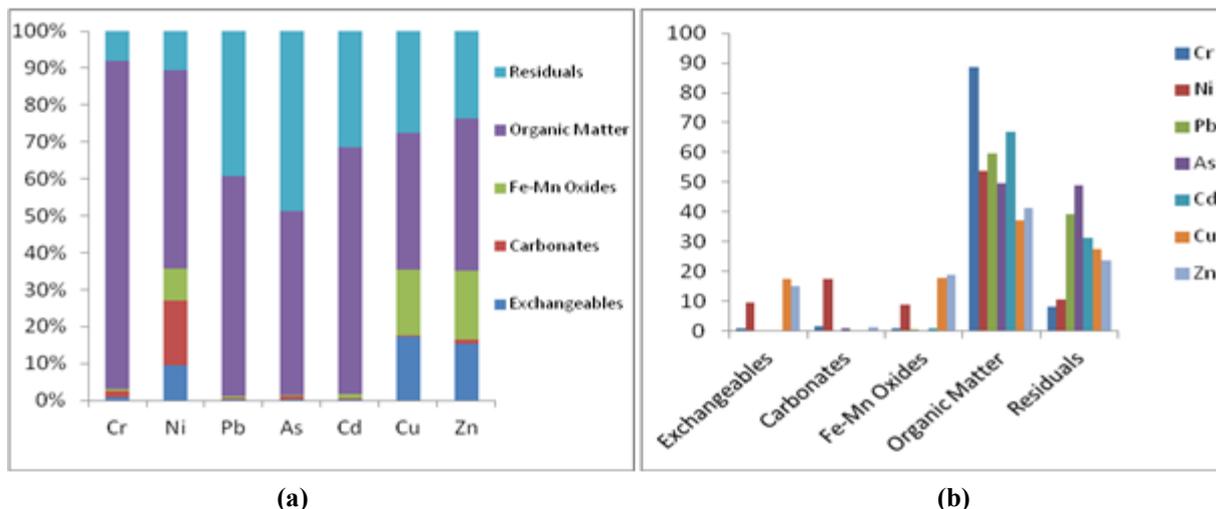
Figure 8. Metal fractionation in soil composite sample H; (a) percentage contribution of each metal to the extraction phase; (b) combined metal pool in each chemical phase.

The metals in sample G bounded more to the surface of the carbonates and the Fe-Mn oxides in the increasing order of 27.7% and 55.99%, respectively. Only 3.75% of the metals was found in the exchangeable fraction of the soil. The preferential adsorption to these chemical phases was also obvious in sample G as the adsorption of the metals to Fe-Mn oxides in the decreasing order was Cd > Cu > Zn > As > Pb > Ni > Cr, which differed substantially from Cr > Ni > Pb > As > Cd > Cu > Zn decreasing order of adsorption to the carbonate phase of the sample. Comparatively, few metals were found attached to the organic matter and the residuals in the sample, as shown in Figure 7.

The analysis of combined metal speciation across the studied samples shows that samples A and E,

and partly G, have metal mobility index (this is the ratio of metals in the first two fractions to the total fractions) higher than 40% (Figure 9a). Figure 9b shows that the metals with the highest potential mobility are Zn and Pb. These metals occupy the largest concentration pools within the first four chemical fractions. However, the most bio-available of the metals substantially occupying the exchangeable and carbonate phases are Pb and Zn in the decreasing order.

Figure 10 shows the combined fractions of each metal associated with the mobilizable (salt soluble exchangeable, carbonate sorbed, reducible oxides, and oxidizable organic) fractions of the soil chemical phase. In Figure 10b, however, only the free metals (ionic metal species) that are readily exchangeable with the soil solution are depicted.
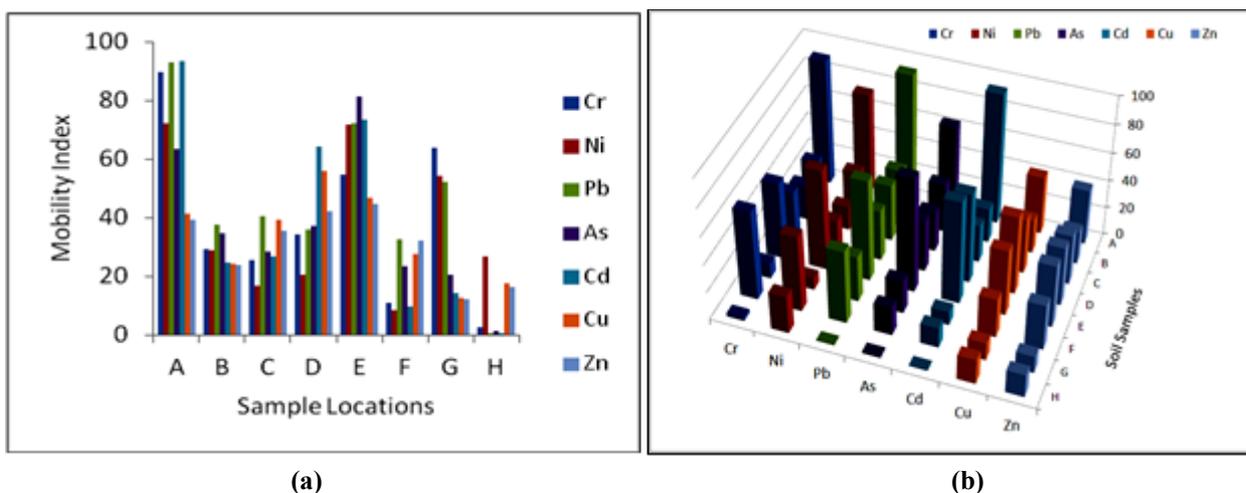

Figure 9. Mobility index and potential mobility of metals in all soil samples (a) metal mobility index; (b) mobility potential of metals in soil of each composite location in the studied area.
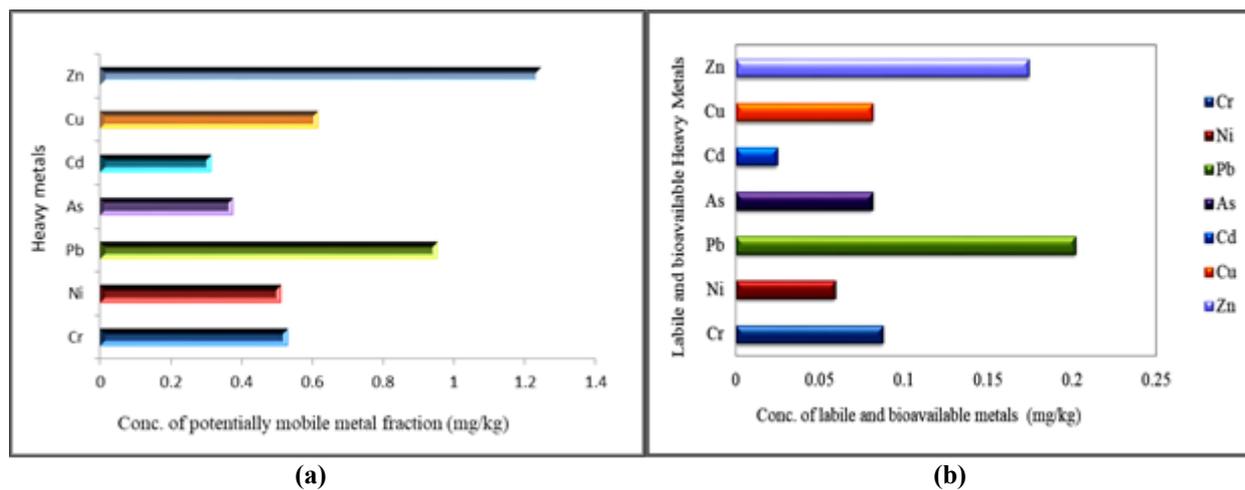
(a)   **(b)**

Figure 10. Metal mobility (a) potential mobility of heavy metals in the studied area; (b) bio-available metal concentrations in the studied area.

The preferential sorption of metals to the five soil solid phases in this work revealed that the Fe-Mn oxides had the highest sorption compared to the other chemical phases. The mean order of sorption profile is Fe–Mn oxides > carbonates > organics >> residuals > exchangeables, as shown in Figure 11a. On an individual basis, the contribution to each phase metal pool is shown in Figure 11b. Figure 12 shows the comparative composition of the organic and inorganic constituents of the sampled soils, where the 1st, 2nd, and 3rd percentiles of the grain size distribution of all the samples and chemical parameters are depicted.

The background speciation of the analyzed soil heavy metals revealed differential sorption of the metals into mobile, potentially mobile, and immobile (residual) fractions of the soil solid phases. The preferential adsorption of metals to the solid phases typifies the dynamics (kinetics) of metals within the soil system under the influence of certain factors. A closer observation of the overall analysis showed that samples A and E had the highest proportions of metal mobility indices, as shown in Figure 9a. These results imply that at locations A and E, most of the metals are either not sufficiently absorbed or crystallized into the lattices of the primary inorganic minerals that constitute the sedimentary rocks during the lithogenic process or they are dislodged and re-distributed into the potentially mobile phases in the course of secondary pedogenic activities or weathering. Judging from Figure 11, the highest mean adsorption falls within the Fe-Mn oxides, followed by carbonates and organics. The other two chemical phases, exchangeables, and residuals had the least metal adsorption.

Basically, soil metals are attracted by ionic bond onto the negatively charged surfaces of soil particles. From the results obtained, the pattern of metal sorption represents two sets of bonding to the soil solids: adsorbed fraction (sorbed to the soil surface) including carbonate, Fe-Mn oxides, and organic fractions; and secondly, the absorbed fraction (absorbed, incorporated or occluded into the inorganic mineral crystalline structure), which is the residual fraction. Both sets of fractions are classified into organic and inorganic fractions of the soil. Basically, metals are attached to the soil colloidal particles, the organic matter portion, and the inorganic (mainly the clay portion). From the various tests carried out, the primary inorganic sand fraction constitutes approximately 55.39% and dominates the soil in the studied area (Figure 12). Though larger in proportion, it rarely partakes in the sorption processes due to its inert nature. It is made up of unaltered mineral structure such as quartz in sedimentary formations, feldspar, and minute traces of olivine [4]. Conversely, the clay fraction makes up approximately 28.40% of the total soil in the studied area and as inorganic secondary mineral; it is responsible for crucial chemical reactivity in the soil. Clay fraction of the soil results from the weathering (dissolution) of the primary inorganic minerals. They are majorly phyllosilicates comprising either of kaolinite, montmorillonites (smectites), oxides, and carbonate minerals [10, 33]. According to the speciation analysis, metals were majorly partitioned (adsorbed) into the carbonates, Fe-Mn oxides, and the organic phases (Figure 11). These phases largely originate from the colloidal components of the soil, with the carbonates and oxides having their roots from the inorganic (clay) component, particularly montmorillonite clays and the organic phase from soil organic matter. The findings by McLean and Bledsoe [18] and

Banjaree [34] revealed that Zn and Cu were mostly adsorbed to the Fe-Mn oxides, while Giacalone *et al*. [35] noted that Pb and Cd were more preferentially bound to the Fe-Mn oxides. This is consistent with the findings in this work (Figure 11b). Metals attached to the oxide group are affected by pH and the reducing conditions. This condition is sometimes initiated by the deficiency of oxygen (anaerobic) conditions resulting from consumption of oxygen at a greater rate than it can be replenished into the soil system [18]. Closely followed in the adsorption profile was organic phase of the soil, which likes the Fe-Mn oxides, had metal largely adsorbed onto its charged surface.

The soil organic matter has a strong affinity for cationic elements, and this explains its high adsorption profile among the five operationally defined soil chemical forms. Due to its large surface area as a colloidal material, the soil organic phase exhibits a great potential for metal adsorption. The study analysis clearly shows the preferential adsorption of metals onto the surfaces

of this fraction of the soil solid phase (Figure 11). Closely following the organics phase is the carbonate phase. The carbonates phase is influenced by the reaction of metals in soil [36-38]. The carbonate phase that has the third largest concentration of adsorbed metals is considered to have weak metal bonding that is susceptible to pH and ion exchange [38]. Figure 11b shows the sorption preference to the carbonate phase in the order of Pb > Zn > Cr, indicating that lead is the most adsorbed geogenic metal in the carbonate phase. Sposito *et al*. [39] reported a similar trend as the outcome of a research carried out on soils in the arid region. In the mobile phase, which signifies the risk potential of the metals to the environment (bio-availability), the order of mobility is Pb > Zn > Cu, while the overall mobilizable metals (potential mobility) indicate that Zn is the highest followed by Pb and Cu, respectively (Figure 10 a,b). Takáč *et al*. [40] also noted that Pb was more preferentially labile compared to Zn and Cu in an experiment conducted on soils.
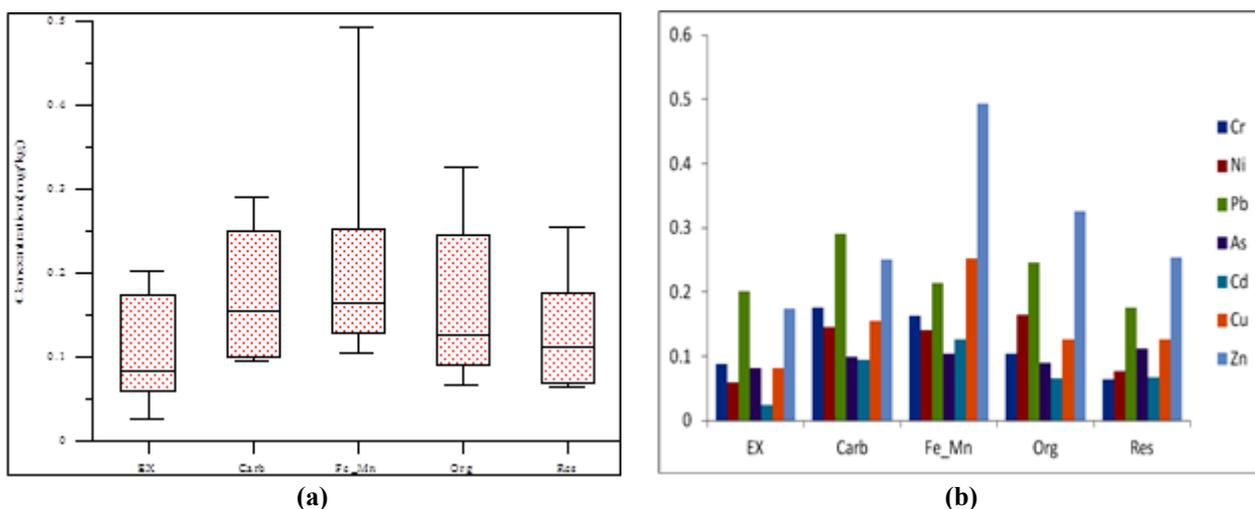

| (a) | (b) |

Figure 11. Preferential sorption of metals to operationally-defined chemical phases (a) box plot of the mean metal sorption to the different soil chemical phases; (b) individual metal sorption to each soil chemical phase. EX: exchangeables; Carb: carbonates; Fe-Mn: Fe-Mn oxides; Org: organics; Res: residuals.

4. Conclusions

This work is a pioneer work to evaluate the metal background spatial distribution in the virgin soil (topsoil) of the overburden material overlying the subsurface bituminous sand deposit in the studied area in the Ondo State. The evaluation serves as a part of pre-conditions to the environmental impact assessment required to establish an environmental management plan in the event of commencement of mining operation. In this work, it was revealed that the seven selected heavy metals were spatially adsorbed to the mobilizable fractions of

the soil solid phases, which included the reducible Fe-Mn oxides, oxidizable organics, and carbonates in the decreasing order. This assessment further showed that the metals were of geogenic source, considering the generally low total metal concentration of each metal. Furthermore, the results of this work revealed that small fractions of the heavy metals were generally bio-available in the mobile phase of the sample soils. Greater fractions of the metals were in the forms that required conditions to mobilize them into the toxic mobile phase. Among these

conditions are factors that trigger redox reactions, which can greatly affect the chemical states of the phases where most of the metals are adsorbed such as the Fe-Mn oxides and organic matter phases. The potential mobility of the background metals shows Zn topping the list of potentially mobilizable metals, while Pb tops the list of the heavy metals that are in the labile and bio-available form. Therefore, since mining activity exposes these soils to different and sometimes unpredictable conditions, there is the need for objective and consistent assessment and monitoring of the soil to ensure that the current background measured metal concentration levels are not raised to unacceptable limits in the course of actual mining.
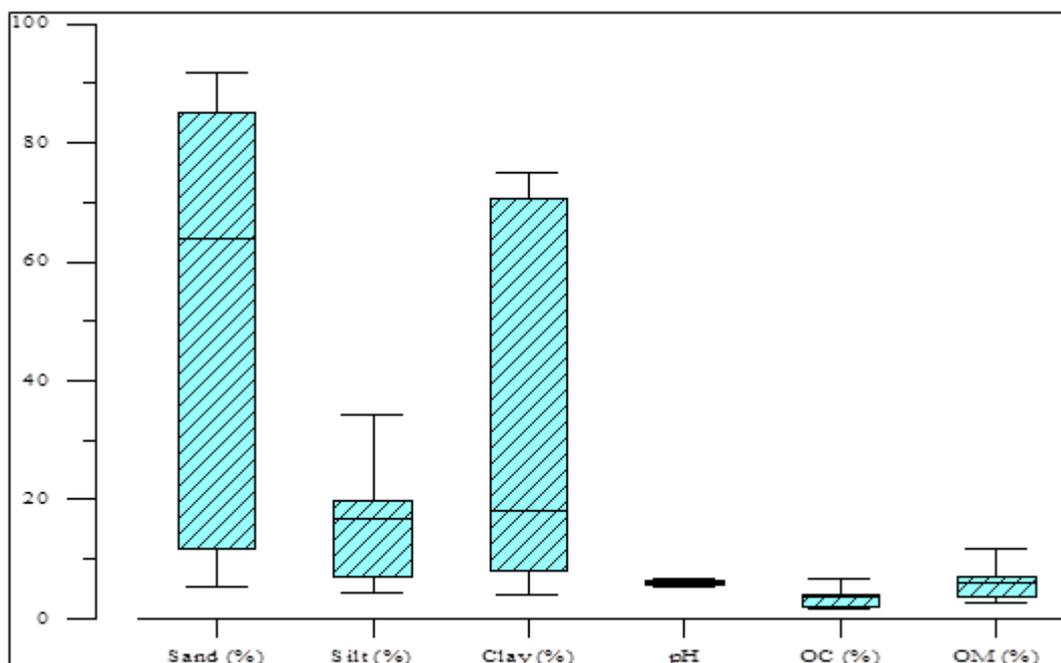

Figure 12. Percentile distribution of soil sample physico-chemical parameters. The dominant sand fraction is chemically inert, while clay compared to organic matter appears to dominate the sorption activities in the soil.

Acknowledgments

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Evaluation of background geochemical speciation of heavy metals in overburden topsoil of bituminous sand deposit area, Ondo state, Nigeria

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Abstract:

Metals are ubiquitous within the earth crust. However, the exceptional high-level concentration of heavy metals in the soil due to natural or anthropogenic activities and the chemical forms in which they exist determine the level of risk they portend to the environment. This work was aimed at determining the background level of the presence of seven priority toxic metals (Cr, Ni, Pb, As, Cd, Cu, Zn) in the chemical phases of the overburden topsoil of a bituminous deposit prior to mining activities through the speciation analysis. The grab samples of overburden topsoil were initially obtained and homogenized to composites based on locations for the subsequent sequential extraction procedure (SEP). The specific physico-chemical properties of the sampled soils were simultaneously determined to complement the SEP inferential analysis. The results obtained showed that most metals were spatially bounded to the Fe-Mn oxides (reducible phase) followed by the organic (oxidizable) and the carbonates phases, respectively. Fractionally, the dominant soil texture in the studied area was sand (55.45%); however, the colloidal organic matter and Fe-Mn oxide phases played the dominant roles in the sorption activities of the selected metals. The soil chemical phase with the least metal pool was the exchangeable (water/salt) soluble fraction. The overall assessment revealed that the geogenic heavy metals in the topsoil posed no threats since a marginal fraction of the metals existed in the bio-available form in non-toxic concentrations in the order of Pb > Zn > Cu, while the potential mobility of metals showed that Zn was preferentially higher than Pb and Cu, respectively.

Keywords: Heavy Metal, Speciation, Overburden Topsoil, Bio-Availability, Environment, Sorption.