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Original Research Article

IRON ORE DEPOSIT AND IT'S TAILING IMPACT ON THE TOXIC METAL LEVEL OF NEIGHBORING AGRICULTURAL SOILS.

Abstract

AIM: This is one of our mineralogical study series aimed at the preliminary characterization of iron ore and its neighboring farmland soils, with focus on ore impact on soil quality, toxic metals concentration and its geo-accumulation status.

Methodology: Mineral (Iron ore) samples and ore rich soils from neighboring farmlands (I-Soil, I-soil-FLA, I-soil-FLB and I-soil-FLC) were collected from Itakpe, Kogi State in North Central Nigeria. Samples were qualitatively characterized using FTIR, SEM, UV-Visible for functional group/ molecular interactions, micro-structural morphology, and spectral profile respectively. Physico-chemical parameters were investigated following routine classical (wet) chemistry procedures. Levels of toxic metals (Fe, Mn, Cu, Zn, Pb, Cd, Ni, Cr) in both ores and soils was estimated using AAS.

Results: The iron ore SEM images appear compact with irregular shape. UV –Visible Spectral shows that the mineral has possibly leached from the parent ore to the nearby soils at similar range. Highlights of this studies shows that the level of metals in farmland soils are statistically significant ($p < 0.05$) with those of the mineral ores, and insignificant ($p > 0.05$) when compared to acceptable or threshold limits prescribed by the USFEPA and WHO. Relying on geo-accumulation index values, this study classified the farmland soil in relative to the iron load as "extremely contaminated". Investigated soil samples are "strongly contaminated" with Pb; "moderately contaminated" with Mn and Zn and "uncontaminated" with Cd and Cu.

Conclusion: Highlights from this work revealed that parametric factors of the soil samples, soil quality and metal distribution among ore-rich soils are linked to both geogenic and anthropogenic activities. It is also implied that the farmland soil's toxic metal levels in the study area might be enriched by either mine tailing from the mineral ore depot or anthropogenic. Our recommendation is strictly on continuous environmental impact assessment, environmental monitoring, environmental auditing and populace awareness campaign.

Keywords: *Geo-accumulation, Iron ore, soil, contamination, Heavy metals, Characterization.*

1. Introduction

Environmental contamination as a result of man's increasing activities has increased considerably in the past century due mainly to significant increases in industrialization and economic activities. It has been discovered that heavy metals are mainly from the activities of man which can build up in the soil [1]. Sector of mining is one of the ways in which heavy metals are introduced into the surrounding of industries. Other air contaminants are introduced with nitrogen oxides and sulfur dioxide including dropping behind much slag, waste tailings and acid drainage. Contact with toxic metals such as, asbestos and silica can happen when milling and mining activities. Ore fragments,

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mining leachates and mine tailings are discharged right into depressions that are natural, with wetlands sites causing composition concentration that is high [2].

Toxic metals are continuous pollutants in our surrounding that are dangerous to both man and the environment. The sources can be anthropogenic and natural [3,4]. Some toxic metals such as Fe, Cu and Zn are important to the body of organisms; while others like As, Pb , Cd, Hg are not important and have no use biologically [5,6] When the concentrations are on the increase, important minerals are harmful [7,8].

Soil, polluted by heavy metals can be dangerous to ecosystem and humans by direct intake and contact with pollutant in the food chain, intake of polluted ground water, low quality of food through phytotoxicity, food insecurity due to decrease land use for agriculture and the problem of land tenure system [9,10]. Changes in their chemical forms (speciation) and bioavailability are, however, possible. The buildup of toxic minerals and metalloids can contaminate the Soil by the release of pollutants from the growing industries, disposal of wastewater irrigation metal wastes, animal manures, mine tailings, coal combustion residues paints and leaded gasoline, land application of fertilizers, sewage sludge, pesticides, atmospheric deposition and spillage of petrochemicals [11,12]. The soils are usually the highest carrier of toxic metals when introduced to the surrounding by anthropogenic activities that are mentioned above.

Nigeria is rich in different kinds of mineral ores ranging from metallic, fossil fuels, non-metallic and radio-active minerals [13] with different types starting from different kinds of stones. The ways these metals are exploited is very minimal compare to the nation's deposits present. Among these minerals, Nigeria is endowed with many iron ore deposit of which some of them have been investigated and some are still under investigation. The main raw material in iron and steel industries is iron ore. More than three billion tons of these minerals are found in Kogi, Niger, Enugu , Kaduna and Zamfara states, Nigeria. Itakpe in Kogi state is currently known for iron mine [14].

The danger that toxic metals cause to the health of man – involving cadmium, lead and mercury has been studied and well documented [15,16,17]. Relatively efficient mining activities cause plenty waste, release to water and atmosphere, and a report of surrounding pollution in closely communities and environment was reported [18]. We hope that the present study will provide a novel platform to survey and characterize certain minerals for their micro structural morphology, functional group and spectra profile as well as estimate heavy metal content and transport of the mineral deposit region, and the possible effects it has on the soil around the farm lands near the ore vicinity. Also it will capture and present reliable and practical baseline information on concentration level of eight heavy

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metals (Pb, Ni, As, Cr, Cd, Iron, Zinc and Cu) in the ore location as well as the characteristics of the minerals and possible explanation on its leaching or release.

In designing the protocol of this study, it is believed that there will be a high metal loading in the mineral deposit region or agricultural farmland, soil, dust, vegetation and water at a level above natural concentrations. In view of this, we investigated mineral (iron ore) characteristics, estimated the levels of heavy metals (Iron, Lead, Manganese, Cadmium, Chromium, Zinc, Nickel, Copper and) in farmland soils and ore samples from mineral deposit region in Itakpe, Nigeria and interpreted soil contamination level based on geochemical index to unveil the role played by possible mine tailing and anthropogenic.

2. Materials and Methods

In this study, Physico-chemical parameters (pH, bulk density, conductivity, moisture content and particle size) were investigated using routine classical analytical methods. Adopted for functional group analysis is FTIR spectrum recorded on an Agilent technologies Cary 630 Fourier Transform Infrared Spectrometer. To characterize the ores samples for their micro structural morphology a Phenomenon Prix MVE016477830 Scanning Electron Microscope (SEM) was used. Spectrophotometer was used to study the spectral profile of the ores while Atomic Adsorption Spectrophotometer (Varian AA240FS) was used to estimate the concentration of heavy metals. Metal distribution and soil contamination factor by heavy metal were predicted by computation. Analytical grade reagents were used throughout the study.

2.1. Site Description

The study area (Figure 1) is iron ore depot of the Nigeria iron ore mining company, Itakpe in Okehi LGA of Kogi State and Farmlands coded I-Soil, FLA, FLB and FLC located within the Lokoja–Okene geological area in North Central Nigeria. Itakpe coordinate include: longitude 6^0 16'E and latitude 7^0 36'N. Mining activities began in late 70s and beneficiation in early 1990s. The mine suspended production in 2008 without any treatment on the mine waste. Mining sites are characterized by dust laden metals spread on every surface in the area and linked to blasting of the ore during mining with deposited concentration on near agricultural soils, water and plants depending on distance from the mine and the mode of transport. Thus, tailings and wastes are distributed by wind and erosion on soils, plants and water in the near vicinity of the mine site. It was documented that Itakpe environs is seen as crystalline basement complex with compositional variability and structural complexity covering over 7,770 square kilometers [19] and with

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sedimentary features of sand stones and mud rocks of cretaceous to tertiary age covering about one third of the area [20]. Tropical climate with 6 months (May to October) of rainy season and 6 months (November-April) dry season is the most probable description of the study area. Majority of the inhabitants of Itakpe are engaged in subsistence agriculture.

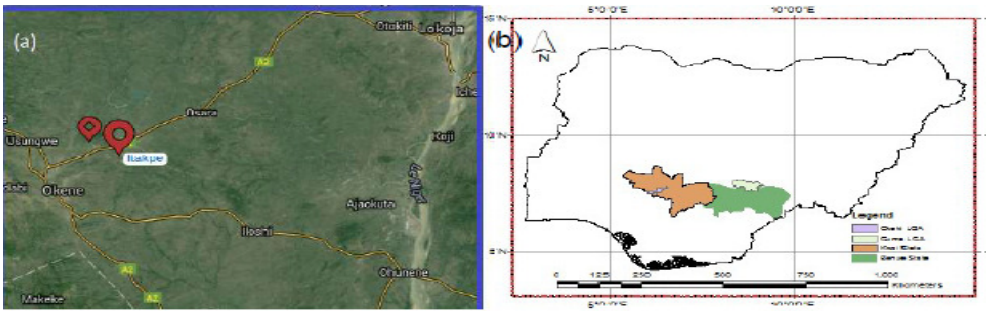

Figure 1: Google earth image of (a) Itakpe and (b) Nigeria Map showing sampling site (Brown portion). Source: Google earth image, 2016

2.2. Sampling

Table 1showstthe the mineral ore, soils and control samples with their respective codes.

Sampling of the ores: The mineral samples were handpicked randomly from the ore depots and stored in a nitric acid pre-treated dry polypropylene bag, labeled and taken to the laboratory and stored under ambient condition [21].

Sampling of the soil: Soil sampling technique reported by Onianwa [21] and Smejkalova *et al* [22] were adopted. Four top soil samples from 0–15 cm were randomly collected by scooping surface soil of the sampling areas (east, west, north and south) using a stainless steel hand trowel, also four soil samples were randomly collected each from three different farm land within the vicinity of both site A and B, the soil samples were stored in a nitric acid pre-treated and dry polypropylene bags and were well labeled (I-soil-FLA, I-soil-FLB and I-soil-FLC) and taken to the laboratory and stored under ambient condition prior to analysis.

Sampling of control: Soil outside mineral depots region (1000 m) away from the mining areas (I-Ref-Soil) or non iron soil (NI-Soil) was taken as control, all the samples collected were stored under ambient condition [21,22].

Table 1: Sample Codes of Iron Ores and Soils from Neighboring Farmland

S/No	Sample Codes	Description
1	Iron Ore	Iron ore from Itakpe, Kogi State
2	I-Soil	Soil samples around Iron ore depot
3	I-Soil-FLA	Iron ore contaminated soil from Farmland A
4	I-Soil-FLB	Iron ore contaminated soil from Farmland B
5	I-Soil-FLC	Iron ore contaminated soil from Farmland C
6	I-Ref-Soil	Control Soil samples for Iron ore richarea

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2.3. Preparation of Stock and Standard Solutions

Stock and standard solution including metal stocks (1000 ppm Iron, lead, manganese , Zink, Chromium , cadmium , Nickel and copper stock solution and other routine bench reagents were prepared following standard laboratory procedures.

2.4. **Preparation of soil sample**

Method by Onianwa [21] and Smejkalova *et al.* [22] were adopted. Soil samples were manually sorted to remove pebbles and coarse materials, and were air-dried under ambient conditions in the laboratory for seventy-two hours. The dried soil samples were passed through a 2 mm sieve to eliminate coarse particles; the soil samples were ground to fine powder in a disc mill crusher in preparation for analysis.

2.5. Physicochemical Parameters

pH measurement: pH was analyzed using the method of McLean [23]. 1:1 g/vol. Mixture of soil and distilled water was prepared by weighing 20 g of fine grained soil into a glass beaker and 20 mL of de-ionized distilled water was added to each beaker and stirred gently to enhance H^+ (Hydrogen ions) release from soil. The pH was determined after the mixtures were allowed to stand for 30 minutes using a pH meter.

Particle size analysis: Bouyoucous hydrometer method [24] was used to determine the particle size of the samples. 50 g of air dried samples which has been passed through a 2-mm sieve was transferred to a "milkshake" mix cup. 50 ml of Calgon (7 g Sodium carbonate and 50 g sodium hexametaphosphate) were mixed to make a litre with distilled water) was then added. The mixture was stirred with a stirring rod and allowed to settle for 30 mins. At the end of 30th minute, the suspension was again stirred for 15 mins with the multimix machine. The suspension was then transferred from the cup to the graduated glass cylinder (1500 cm^3).With hydrometer in suspension; distilled water was then added to give a total volume of 1130 cm^3.The hydrometer was then removed. The top of the cylinder was covered and steadied with the hand and inverted several times until all sample soil and ore was in suspension. The cylinder was place on a flat surface and the noted. The hydrometer was immediately placed into suspension sliding it slowly until floating. The first hydrometer reading, H_1, was taken at 40 seconds after the cylinder was set down. The hydrometer was then removed and the temperature, T_1, of the suspension was recorded with the thermometer. The suspension stood for further 3 hours and the second hydrometer H_2, reading was taken, as well as the temperature T_2. The first reading measured the percentage of the silk and clay in suspension, whereas the second reading indicates the percentage of total clay in the suspension.

The result were corrected to a temperature of 20^0,0.2 reading was added to hydrometer reading before the computation and every degree below 20^0,0.2 reading was subtracted from hydrometer

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reading. Also, 2.0 reading was subtracted from every hydrometer reading to compensate for the added dispersing agent. Soil particle sizes were computed as shown in equations 1-3 [24].

$$\% \text{ Sand} = 100.0-[H_1 + 0.2(T_1 -20)-2.0]2 \quad (1)$$

$$\% \text{ Clay}= [H_2 + 0.2(T_2 – 20) – 2.0] \quad (2)$$

$$\% \text{ Silk} = 100.0 – (\% \text{ sand} +\% \text{ clay}) \quad (3)$$

Where H_1 is Hydrometer reading at 40 seconds, T_1 is Temperature at 40 seconds, H_2 is Hydrometer reading at 3 hours, T_2 is Temperature reading at 3 hours, Temperature correction to be added to hydrometer; Reading = 0.2 (T-20), where T is in degrees Fahrenheit.

Bulk density: The soil sample was filled into 100 mL measuring cylinder to a given volume. The cylinder was tapped for at least 2 minutes to compact the Soil and then weighed. The bulk density was calculated [25].

$$\text{Bulk density} = \frac{Sample\ mass\ (g)}{Vol.\ of\ packed\ sample\ (cm^3)} \quad (4)$$

Conductivity measurement: About 10 g of each soil sample was weighed into 100 mL beakers; 20 mL of distilled water was added to the soil and allowed to settle for 30 mins, the mixture was filtered using Waltman filter paper. The electrode was immersed into the soil solution and conductivity reading of each sample was recorded [26].

Moisture content: The fine soil particle samples (5 g) were transferred into a tarred moisture tin and weighed dried over night at 105°C (lid removed).The tin was removed from oven, and close with lid, it was then cool in desiccators and weighed [27].

The moisture content in wt% (m/m) is obtained by

$$\text{Moist wt } \% = \frac{A-B}{B-tared\ tin} \times 100 \quad (5)$$

Where A and B represents wet and oven dried soil respectively.

2.6. Digestion of Soil and Mineral Ore Samples

Digestion of soil samples: According to the methods adopted from Smejkalova *et al.* [22] and Anderson [27], 10 g each of the fine grained soil sample was weighed into 250 mL teflons beakers earlier treated by soaking in dilute nitric acid (0.001 M) overnight and dried in oven at 50^{0}C. 10 mL nitric acid and 30 mL HCl analar grade reagent was added to each beaker and heated in boiling water in a water bath for two hours. The resulting digests was filtered into 50 mL volumetric flasks and made up to 50 mL mark with distilled water. Procedural blank was prepared by heating 15 mL 2 M nitric acid in 50 cm^3 distilled water for two hours, filtered and made up to 100 mL mark with distilled water.

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2.7. Instrumental Analysis

2.7.1. Metal Characterization Using AAS

The digested sample solutions of soil and mineral Ore in 50 mL volumetric flasks was quantified for heavy metals; Cadmium (Cd), Chromium (Cr), Manganese (Mn), Nickel (Ni), Iron (Fe), Zinc (Zn), Lead (Pb) and Copper (Cu) by use of flame Atomic Absorption Spectrometry (FAAS Varian AA240FS). The instrument was set according to the manufacturer's instruction which determines the present of metals in both mineral and soil digest samples. Such metals include Cd, Cr, Pb, Fe, Zn, Cu, Mn and Ni respectively. The sample solution was aspirated into the flame and absorbance's was recorded for each element [28].

2.7.2 Characterization of Minerals using FTIR

FT-IR measurements were recorded on FTIR model Agilent technologies Cary 630 FTIR machine). Spectrometer in the region of 400-4000cm^{-3} supplied with OMNIC software. The samples were prepared and analysed following the method proposed by Nedjar and Barkat [29].

2.7.3. Characterization of Mineral using SEM

The mineral samples were microscopically characterized by the use of Scanning electron microscopy (SEM).

2.7.4. Spectral Profile Determination using UV-Visible

Minimum of 1 g of the fine ground samples (Iron Ore and Soil samples) was weighed into100 mL beakers, and 2 mL of 11.81 conc of HCl was added and further diluted with 25 mL of deionised water and filtered using Waltman no.1 filter paper. The blank was prepared by diluting 1 mL of 11.81 M of HCl with 25 mL of deionised water [30]. Sample solution collected into the sample cell was scanned at the UV-Visible range for the absorbance maximum.

2.8. Pollution Load Index (PLI)

The level of metal contamination and distribution was assessed using the geo-accumulation Index (Igeo) method reported by Hasrizal *et al.* [31] . In this model, the status of heavy metal concentration is compared with the background values. This index describes the relationship between the measured metal in the ore fraction and the geochemical value in farmland soil. As proposed by Muller [32]

$$I\ geo = log\ [\frac{Cn}{1.5Bn}] \qquad (6)$$

Cn is the measured concentration of the soil and Bn is the geochemical background value. The constant, 1.5, stands for background matrix correction factor linked to lithological variations. Muller [32] as documented in : Hasrizal *et al.,* [31]

2.9. Comparative study (Statistical Treatment of Data)

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The data thus attained was computed and subjected to statistical analysis of variance (ANOVA) via the student t-test. Test of significance was set at 95% confidence level. Description statistics for each parameter was based on mean and standard deviations of triplicate analysis. The mean values were compared with results of similar studies in Nigeria and other countries including their allowable permissible limits set by WHO [33] and USEPA [34].

3. Results and Discussion

3.1. Physical Examination of Sample

Figure 2 is a photograph showing mineral ores and soils from farmlands around their vicinities. Iron Ore appeared rocky, I-Soil, I-Soil-FLA, I-Soil-FLB and I-Soil-FLC appears lumpy while I-Ref-Soil looks more of the sandy sand.

Figure 2: (a) Iron Ore, (b-e) Soils from Itakpe and (f) control soil sample.

3.2. Physicochemical Parameters

Physicochemical parameters of mineral Ores and there corresponding soil samples namely: pH, Conductivity, Bulk density, Moisture content and Particle size are represented in Tables 2.

3.2.1. pH of iron ore and soil sample

The pH of Iron ore and all the soil samples analyzed range from 6.67 to 6.98, with highest value in iron ore. This is in good agreement with the value (7.01 to 7.99) reported by Akpoveta *et al.* [35]. pH is an important soil property, having great effects on solute concentration and absorption in soil. The pH levels that are acidic tend to have an increased micronutrient solubility and mobility as well as increased heavy metal concentration in the soil. These are however, in neutral boundary.

3.2.2. Conductivity measurement of iron ore and soil samples

Result of conductivity measurements ranges from 260 µs/cm to 453 µs/cm the highest value was found in farmland A (453 µs/cm) while the least value was in Iron. The conductivity measurement 165 µs/cm - 210 µs/cm reported by Akpoveta *et al.*, [35] was lower than result reported in the

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present study. The increase in conductivity may be due to increase in the concentration of some soluble salt in the soil [35].

3.2.3. Bulk density of iron ore and soil samples

The bulk density of Iron ore and soil samples range between 1.22 gcm^3 in I-Soil-FLC to 3.08 in Iron ore in. David *et al.* [36] reported the bulk density ranging from 2.0 to 3.12 gcm^3. The bulk density reported in the present study fall within the range reported in literature [36]. High bulk density (> 1.5 gcm^3) reduces water infiltration and plant root penetration resulting in increase in surface water pollution [37]. It is also widely believed that soil BD declines with an increase in soil organic matter because of the increase in porosity volume [38].

3.2.4. Moisture content

The moisture content of Iron ore and soil samples range between 8.5% of Iron ore to 29.2 in I-Soil-FLC. The highest mean was shown in I-Soil-FLC, followed by 27.7% (I-Soil-FLA), 25.4% (I-Soil-FLB), 17.7% (control), 15.5 (I-soil) and the list moisture content was found in Iron to be 8.5%. The average moisture content of 5% was found to be sufficient for plant growth [39].

3.2.5. Particle size of soil samples from iron rich soil region

The result of particle size (Table 3) revealed a higher value of sand ranging from 58.64 to 76.63 %, followed by clay which ranges from 14.07 to 24.73 % and silt ranged from 9.28 to 15.27 % [40] reported on soil particle size of sand 8.40 to 91.42 %, clay from 5.46 to 6.48 % and silt from 9.28 % to 15.27 %. According to Nyles and Ray [41] , soil that has separate increase sand and small clay content has increase pollutant leaching ability. Though Itakpe soil predominantly has high sand fraction (>77.0 %) that permits the increase permeability of water and leachetes, the textural class (loamy sand) can be good for sanitary landfills [42]. The control sites soil consisted of average high clay fractions thus can exhibit plasticity and allows surface water flooding and contamination. The control clayed texture also encourages low permeability of water and leacheates.

Table 2: Physicochemical Characteristics of Iron Ore and Soil Samples from Itakpe

Samples	Parameters			
	pH	Conductivity(µs/cm))	Bulk density (g/cm^3)	Moisture content (%)
Iron Ore	6.98 ± 0.0003	260 ± 0.3300	3.08 ± 0.0003	8.50 ± 0.0130
I-Soil	6.67 ± 0.0001	352 ± 3.0000	2.10 ± 0.0003	15.6 ± 0.0300
I-Soil-FLA	6.84 ± 0.0003	453 ± 1.3300	1.26 ± 0.0003	27.7 ± 0.1300
I-Soil-FLB	6.76 ± 0.0003	394 ± 3.0000	1.35 ± 0.0001	25.4 ± 0.0130

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I-Soil-FLC	6.67 ± 0.0050	447 ± 3.0000	1.22 ± 0.0004	29.0 ± 0.0130
I-Ref-Soil	6.92 ± 0.0010	309 ± 1.3300	1.74 ± 0.0001	17.7 ± 0.0130

Table 3: Particle Size of Soil Samples from Itakpe Iron Ore rich Region

	Parameters		
Samples	**Silt (%)**	**Clay (%)**	**Sand (%)**
I-Soil	14.01 ± 0.0003	20.07 ± 0.0001	65.92 ± 0.0003
I-Soil-FLA	10.01 ± 0.0001	18.64 ± 0.0001	71.35 ± 0.0005
I-Soil-FLB	12.55 ± 0.0003	22.07 ± 0.0003	65.35 ± 0.0001
I-Soil-FLC	15.27 ± 0.0001	24.73 ± 0.9400	58.64 ± 0.0003
I-Ref-Soil	9.280 ± 0.0001	14.07 ± 0.0001	76.63 ± 0.0001

3.3. Scanning Electron Microscopy (SEM)

Characterization of the mineral Ores was also carried out using Scanning Electron Microscopy to determine the surface morphology of the particles. Iron Ore the images appear compact with irregular shape (Figure 3), unlike that observed by Sahoo *et al*. [43] which has irregular, bulkier and agglomerated. Leaching metals may result after weathering or blasting of ore.

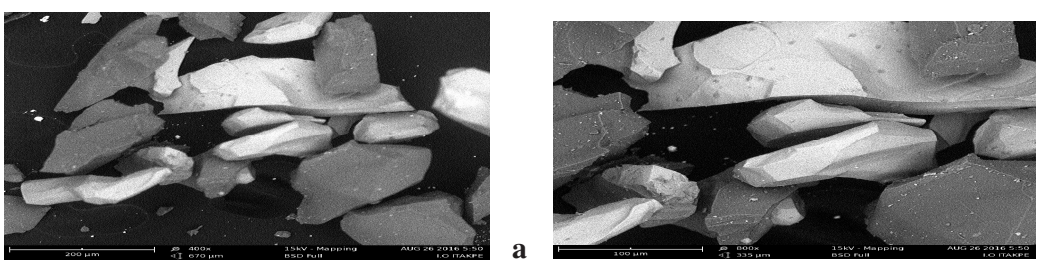

Figure 3: SEM Micrographs of Iron Ore samples recorded at (a) 400x (b) 800x magnifications.

3.4. Fourier Transform Infra-red (FT-IR) Spectroscopic Study

FTIR analytical data (Table 4) is typical of interpretations of spectra shown as Figure 4. FTIR Characterization was carried out to determine the molecular interaction(s) and functional groups of the mineral ores. Different intensity peak values were recorded to enable easy identification of the functional groups involved. Peaks were observed at 2322-2005 cm^{-1},2087-1880 cm^{-1},1982-1029 cm^{-1},913-910 cm^{-1}, 893-882 cm^{-1} and 798-753 cm^{-1},which confirms that HPO_4 ion, CN ion, Si-O ion, Si-O ion,CO_3 ion and Si-O quartz were active and this may be as a result of $NaHPOH_2O$, $K_3Fe(CN)$, SiO_2, $BaSO_3$, K_2CO_3 and SiO_2 assignment.

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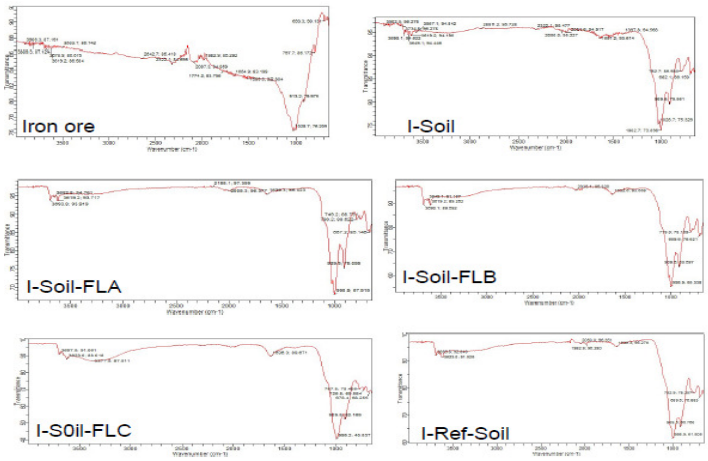

Figure 4: FTIR Spectrum of Iron ore and soil samples around neighboring farmlands (Inserted: photographs of samples)

Table 4: FT-IR Analysis of Iron Ore and Soil samples within the ore rich region.

Vib. Freq. (cm^{-1})	Functional groups	Observed vibrational frequencies (cm^{-1}) for samples				Assignment
		Iron Ore	I-Soil	I-Soil-FLA	I-Ref-Soil	
2322-2005	HPO_4^-	2332	2001	2005	-	$NaHPOH_2O$
2087-1880	CN^-	2087	2001	1830	1880	$K_3Fe(CN)_6$
1982-1029	Si-O stretching	1029	1029	-	1982	SiO_2
913-910	Silicate ions	913	910	910	910	SiO_2
893-882	CO_3^-	893	882	887	889	K_2CO_3
798-753	Si-O quartz	798	789	790	753	SiO_2

3.5. UV-Visible of iron ore and soil samples

Table 5 is the results of wavelengths at maximum absorbance for samples. From the analysis, iron ore and their corresponding soil samples gave the λmax of 334 nm, 331 nm and 324 with the following absorbance 4.770, 2.292 and 1.154 for iron ore, I-Soil and I-Soil-FLA respectively. This close values could be an indication that there is leaching from the parent ore to the environment.

Table 5: UV-Visible for Iron Ore and its corresponding soil

Samples	λ Max. (nm)	Abs.
Iron ore	334	4.770
I- Soil	331	2.292
I-Soil-FLA	324	1.154

3.6. Heavy metal Analysis

Table 6 shows the mean Concentration (mg/kg) of heavy metals in iron ore and neighboring soil samples.

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Iron (Fe) concentration: The highest mean concentration of iron was 6898.743 mg/kg for the ore and the lowest was 1793.331 mg/kg. This was more than the permissible limits set by the United States environmental protection agency [34] and were higher than that reported by Kakulu *et al.* [44]. The relatively high Iron could be as a result of the presence of Iron sulphide (marcasite or pyrite) [45].

Lead (Pb) concentration: The highest mean concentration of lead was 179.59 mg/kg as the lowest was 100.070 mg/kg. This was higher than 0.07 mg/kg reported by Kakulu *et al.* [44], but lower than the maximum permissible limit of 420 mg/kg, set by USEPA. The allowable limits also vary widely with countries 300 mg/kg in United Kingdom and luxem boury 100 mg/kg in France and Austria. Pb values therefore reflect the presence of mine wastes and tailings resulting from mining activities [45].

Copper (Cu) concentration: Copper mean concentration was 2.822 mg/kg and the lowest was 0.214 mg/kg. This was higher than 0.13 mg/kg reported by Kakulu *et al.* [44], but was below the 45 mg/kg set by USEPA. This level poses no threat to the local environment [46]. Although copper Toxicity in human is rare, aquatic organism are more prone at risk from Cu.

Zinc (Zn) concentration: Zn ranges from 18.308 mg/kg to 7.039 mg/kg in this work. This value was higher than 0.04 mg/kg reported by Kakulu *et al.*[44], but lower than 95 mg/kg set by WHO. Zinc is an essential macronutrient for plants but it's phytotoxic in excess photoxicity may cause decrease crop yield and quality and likehood and Zn transfer into the food chain.

Nickel (Ni) concentration: Ni has the average value of 1.348 mg/kg and 0.890 mg/kg. The value was higher than 0.15 mg/kg reported by Kakulu *et al.* [44], but lower than 75 mg/kg maximum permissible limits for Nikel by USEPA [34]. Ni is also relatively immobile, limited by co-precipitation with limonite and by hydrolysis.

Cadmium (Cd) concentration: Cd in the study area has a mean value of 0.060 mg/kg and 0.001 mg/kg. This was lower than 0.18 mg/kg reported by Kakulu and Matthew [47] and lower than the permissible limits by USEPA. Cd is more volatile than most heavy metals and significant amount is released to the atmosphere during the processing also through weathering of the sulphides (abandoned mine wastes). The source of Cd is anthropogenic [45].

Manganese (Mn) concentration: The highest mean concentration of manganese was 70.560 mg/kg and the lowest was 34.549 mg/kg. This was lower than 770 and 850 mg/kg set by WHO and USEPA respectively. The value falls within the acceptable limits. The presence of Mn could be as a result of manganiferous siderite gangue in the area [45].

Chromium (Cr) concentration: The average concentration of Chromium ranges from 3.771 mg/kg to 0.883 mg/kg. Chromium range in this study is lower than 40-90 mg/kg maximum permissible unit

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reported by Onyeobi and Imeoparia [45]. It was also observed that the level of chromium in this study was far lower than maximum permissible limits of most countries, except for Nether lands and Ontario whose maximum permissible levels are 30 mg/kg and 26 mg/kg respectively.The low values of Cr recorded in the soils around the mines could also suggest very low mobility for these elements during weathering and soil formation.

Table 6: Mean Concentration (mg/kg) of Heavy Metals in Soil around Iron Ore contaminated Farmlands.

Toxic Metals	I-Soil-FLA	I-Soil-FLB	I-Soil-FLC	I-Soil	I- Ref-Soil	Iron Ore
Cd	0.045 ± 0.0003	0.022 ± 0.0005	0.019 ± 0.0004	0.002 ± 0.0002	0.060 ± 0.0004	0.001 ± 0..0003
Cr	2.930 ± 0.0007	2.184 ± 0.0003	2.217 ± 0.0005	1.928 ± 0.0007	3.771 ± 0.0003	0.883 ± 0.0057
Ni	1.319 ± 0.0018	0.888 ± 0.0034	1.065 ± 0.0037	1.348 ± 0.0038	0.890 ± 0.0034	0.833 ± 0.0020
Mn	51.28 ± 0.0008	34.55 ± 0.0009	41.61 ± 0.0005	70.56 ± 0.0009	48.56 ± 0.0013	41.81 ± 0.0007
Zn	15.47 ± 0.0007	8.710 ± 0.0012	11.68 ± 0.0015	18.02 ± 0.0012	7.039 ± 0.0045	18.31 ± 0.0009
Cu	2.822 ± 0.0013	1.287 ± 0.0007	2.193 ± 0.0012	0.968 ± 0.0004	2.361 ± 0.0006	0.214 ± 0.0003
Pb	109.9 ± 0.0001	100.9 ± 0.0005	100.1 ± 0.0002	176.6 ± 0.0026	150.1 ± 0.0003	103.1 ± 0.0003
Fe	2476.133±0.002	3082.884±0.001	1793.331±0.001	6898.743±0.001	2220.918±0.001	6291.989±0.003

3.7. Heavy Metal Pollution Assessment for Iron ore and Neighbouring soils

Table 7 is a data that summarises the contamination factor in Iron rich soil region based on geo-accumulation index. Results shows that Cd was low in iron ore, I-Soil and I-Soil-FLA, Cr was low in iron ore and I-Soil but moderate in I-Soil-FLA, Ni was discovered to be low in iron ore, I-Soil-FLA but moderate in I-Soil. Mn was low in iron ore, I-Soil-FLA but moderate in I-Soil, Zn was moderate in I-Soil and iron ore but low in I-Soil-FLA, Cu was found to be low in iron ore and I-Soil but moderate in I-Soil-FLA. Pb was found to be low in iron ore, I-Soil-FLA but moderate in I-Soil while Fe was found to be moderate in iron ore, I-Soil-FLA but considerable in I-Soil.

Computation based on geo-accumulation index classified the soil in relative to the Fe level as “extremely contaminated. Sequel to the loading of soil by other metals, the farmland soils are grouped into strongly contaminated with Pb; moderately contaminated with with Mn and Zn and uncontaminated with Cd and Cu [31].

3.8. Comparative Study

Figure five shows some of the trends observed by selected metals. Presents of these metals are responsible for the observed conductivity profile, also shown i Figure 5. One way analysis of variance ANOVA was carried out to determine if there is any significant difference in the heavy metals and physicochemical parameters for the mineral rich soils with reference to the control sample. Results shows that there is no significant difference in Cr, Ni and Pb when compared statistically, hence, an indication that the metals are evenly distributed, while that of Cd, Cu, Mn and

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Zn are significantly different. The physicochemical parameters analysis of variance shows there is significant difference in the pH, conductivity, bulk density, moisture content and particle size.

Table 7: Geo-accumulation Index of heavy metals in Soils from Farmlands near Iron ore deposits (Based on legislative reference as Bn values).

Toxic Metal	Geo-accumulation index (Igeo) values				Igeo grouping	Soil Quality w.r.t. metal level.
	I-Soil-FLA	I-Soil-FLB	I-Soil-FLC	I-Soil		
Cd	-1.875	-0.533	-0.596	-1.574	< 0	Uncontaminated
Cr	1.469	1.862	1.869	1.808	1-2	Moderately contaminated
Ni	0.046	0.073	0.152	0.254	0-1	Uncontaminated to moderately contaminated
Mn	2.746	2.663	2.744	2.973	2-3	Moderately to strongly contaminated
Zn	0.609	0.287	0.414	0.603	0-1	Uncontaminated to moderately contaminated
Cu	-0.846	-0.066	0.165*	-0.19	< 0	Uncontaminated
Pb	3.138	3.129	3.125	3.372	3-4	Strongly contaminated
Fe	4.146**	3.836	3.6	4.186**	**4-5**	** extremely strongly contaminated

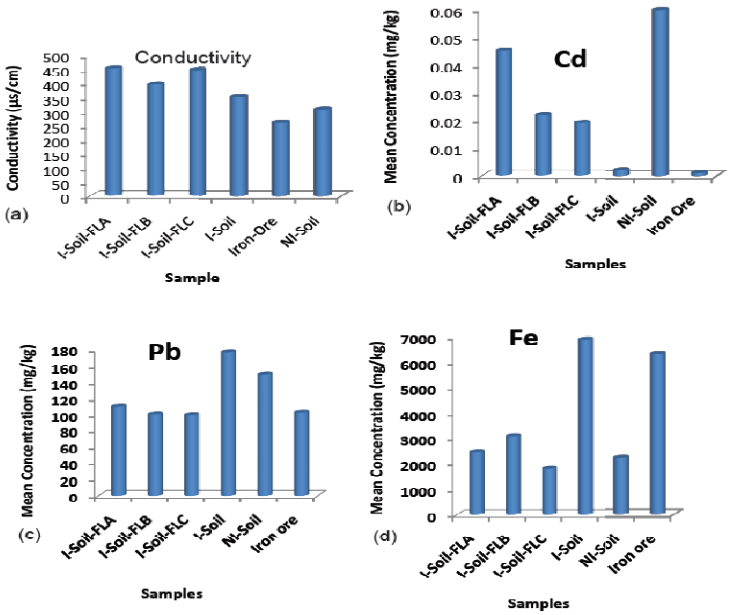

Figure 5: Charts, showing (a) conductivity values and (b-d) level of cadmium, lead and iron in farmland soils near iron ore depot

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4. Conclusion

Deductions from this work using FTIR, SEM and UV-Vis, indicated that mineral ore and soil physicochemical parameters as well as characteristics are in good agreement in terms of quality and compositions. Analysis of Iron rich soil indicates that the pH of Iron Ore falls within the neutral boundary. The conductivity measurement was found to be high as a result of soluble salt in the soil. Analysis for bulk density was found to be low and may be as a result of increase soil organic matter. Moisture content analysis was also on the high side. The analyzed particle size indicates high level for sand followed by clay and then silt. The pattern below indicates the trend of heavy metal concentration in Iron rich soil. Iron Ore, Fe > Pd > Mn > Zn > Cr > Ni > Cu > Cd . I-Soil and the farmland soils I-Soil-FLA,B and C gave similar metal load trend as the mineral ore. This is an indication of mine tailing and metal distribution from ore to farmland soils. The computed contamination factor of the soil pollution by heavy metals shows that, in Iron rich soil, Cd, Cr, Ni, Mn, Cu and Pb were low; Fe and Zn were moderate while I-Soil Fe was considerably high. Computation based on geo-accumulation index classified the soil in relative to the Fe level as "extremely contaminated. Based on the highlights from this study, valuable information about the current status of heavy metal level is presented as baseline data for awareness on possible metal leaching, mobility and distribution along the mine region. It is strongly recommended that there is a need to develop an environmental monitoring and management programme for heavy metals.

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