## Bioavailable Trace Elements in Soils around Nnpc Oil Depot Jos, Nigeria.

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**Abstract:** The concentrations of trace elements (Cu, Zn, Cr, Pb and Cd) in soil samples around NNPC Oil Depot Jos and those of a control area (about a kilometer away from the depot) were investigated by sequential extraction method using Atomic Absorption Spectrometer (AAS). Results obtained showed the concentrations (mg/kg) of Cu, Zn, Cr, Pb and Cd in soil of study area as 22.14, 25.06, 12.41, 14.13 and 9.11 respectively while in control area soil Cu, Zn, Cr, Pb and Cd had concentrations (mg/kg) of 19.69, 22.79, 7.09, 13.53 and 1.24 respectively. The bioavailable components (obtained from exchangeable, water and acid-soluble, and reducible phases) of Cu, Zn, Cr, Pb and Cd were 48.19%, 47.61%, 37.87%, 43.52% and 50.71% of their total concentrations respectively in study area soil while in control area 40.49%, 45.37%, 64.03%, 36.07% and 45.02% were obtained for Cu, Zn, Cr, Pb and Cd respectively. Levels of the trace elements in soils of both study area and control area were observed to be within European Union safe limits except for Cd in the study area. **Keywords:** Bioavailable fraction, Oil depot, Pollution, Sequential extraction, Trace elements.

### I. Introduction

Pollution is the introduction of contaminants into an environment that causes instability, disorder, harm or discomfort to the ecosystem i.e. physical systems or living organisms. The elements of pollution, otherwise known as pollutants can be foreign substances or energies such as noise, heat or light. They are considered pollutants when they exceed natural levels [1]. Contamination of heavy metals in the environment has been shown to be of major concern because of their toxicity and threat to human life and the environment. Several studies have been carried out on trace elements contamination in soils from various anthropogenic sources such as industrial wastes [2, 3, 4, 5, 6, 7, and 8].

Contaminants are mostly introduced into the environment by the activities of man. Most of these contaminants result from wastes generated by industries and residences and are disposed of on land and in water bodies without proper treatment [9].

Depending on their origin, trace elements exist in different mineral forms and chemical compounds and in different combinations with mineral and organic components of soil and sediments which may vary according to various conditions. For instance, pH has an influence on trace element forms, other parameters affecting their concentration levels, mobility, transformation and accumulation processes in the ecosystem are redox conditions, oxidation states, temperature, the presence of organic matter and microbiological activity. All these factors influence the biogeochemical cycles of elements in our environment [10]. All trace metal hydroxide, oxide, carbonate and phosphate precipitates form only under alkaline conditions [11]. The dissolution of these metal precipitates is strongly dependent on the pH of the system. In acidic soils, simple cations and complexes of chlorides and sulphates usually exist, while in neutral and slightly alkaline conditions carbonate complexes dominate [12].

Total metal concentrations do not necessarily correspond with metal bioavailability [13 and 14]. For example, sulfide minerals may be encapsulated in quartz or other chemically inert minerals, and despite high total concentrations of metals in sediment and soil containing these minerals, metals are not readily available for incorporation in the biota; associated environmental effects may be low [15]. Metals of major interest in bioavailability studies, as listed by the U.S. Environmental Protection Agency (EPA) are Al, As, Be, Cd, Cr, Cu, Hg, Ni, Zn, Pb, Se, and Sb [16].

An oil depot (sometimes called a tank farm, installation or oil terminal) is an industrial facility for the storage of oil and/or petrochemical products and from which these products are usually transported to end users or further storage facility. Oil depots are usually situated close to oil refineries or in locations where marine tankers containing products can discharge their cargo. Some depots are attached to pipelines from which they draw their supplies [1]. Pipelines traversing the nooks and crannies of Nigeria have been reported by NUPENG to be vandalized and some ruptured due to old age, and that some of the NNPC depots nationwide are not operational but are crying for attention from the Federal Government [17].

This research was to determine the presence of bioavailable trace elements (i.e. Cu, Pb, Cr, Cd, and Zn) in soils around NNPC oil depot Jos and to compare result obtained with those of a control area (about 1 Km

away from the depot). Also, results obtained were to be compared to prescribed levels by the European Union standard [18] for the elements in soils.

#### II. Materials And Methods

Analytical (AnalaR) grade reagents and distilled water were used for the experiment. All glassware and plastic containers used were washed with liquid soap, rinsed with water, soaked in 10% (v/v) nitric acid for 24 hrs, cleaned thoroughly with distilled water and dried.

#### SAMPLING SITE

The samples were collected around the Jos NNPC Oil Depot, situated along Zaria road, Jos (longitude 8° 54' and latitude 9 ° 55'). The sampling sites are indicated in Fig. 1.



Sampling sites

Fig: 3.1 Map of Jos environs showing NNPC Depot

#### SAMPLE COLLECTION

Soil samples (3 samples each per site) were collected at a depth of 0-30 cm using stainless steel spoon from ten (10) different points 50 metres away from the oil depot. The distance from one sampling point to the other was about 10 metres.

Control soil samples (3 samples each per site) were collected from six (6) different points of control area at a distance of about 1Km away from the oil depot. A polythene bag was used for the storage of the samples.

Composite samples were prepared for soil samples by combining together the triplicate (3) samples collected from each site.

#### SAMPLE TREATMENT AND PRESERVATION

Soil samples were sieved using 2mm sieve to remove stones and plant fragments, dried at 105 °C in an oven and crushed into fine powder using an agate mortar.

#### SAMPLE PREPARATION (DIGESTION)

Sequential extraction procedure proposed by the Standard Measurements and Testing Programme (SM&T- formerly Community Bureau of Reference) of the European Union, as reported in similar study [12] was employed to analyze for the trace elements in soil.

- i. Exchangeable metals (Fraction I): 40 cm<sup>3</sup> of 0.11 mol dm<sup>-3</sup> acetic acid was added to 1.00g of dry soil sample in a 50 cm<sup>3</sup> polypropylene tube. The mixture was shaken (400 rpm) using a Clifton shaker for 16 h at room temperature. The extract was separated from the solid phase by centrifugation at 3800 rpm for 20 min. The supernatant liquid was decanted into a 100 cm<sup>3</sup> beaker and then covered with a watch-glass. The residue was washed by adding 20 cm<sup>3</sup> of deionized water, shaking for 15 min, and then centrifuging. The second supernatant liquid was discarded without any loss of residue.
- ii. Metals bound to Iron and Manganese oxides (Fraction II): Metals bound to iron and manganese oxides were extracted by adding 40 cm<sup>3</sup> of 0.1 mol dm<sup>-3</sup> hydroxylammonium chloride (adjusted to pH 2.0 with 2 mol dm<sup>-3</sup>)

 $^{3}$  nitric acid) onto the residue from the first step. After shaking the mixture for 16 h at room temperature, it was centrifuged for 15 min, and then decanted into a beaker. Using 20 cm<sup>3</sup> of deionized water, the residue was washed, centrifuged, and the supernatant discarded.

- iii. Metals bound to organic matter and sulphides (Fraction III): 10 cm<sup>3</sup> of 8.8 mol dm<sup>-3</sup> of hydrogen peroxide was carefully added in small aliquots to the residue in the centrifuge tube. The tube ingredients were digested at room temperature for 1 h with occasional manual shaking. The procedure was continued for 1 h at 85 °C and the volume reduced to a few millilitres by further heating in a water bath. A second aliquot of 10 cm<sup>3</sup> of hydrogen peroxide was added to the residue and the digestion procedure was repeated. The solution was heated to near dryness, and 50 cm<sup>3</sup> of 1.0 mol dm<sup>-3</sup> ammonium acetate solution adjusted to pH 2.0 with nitric acid) was added to the moist residue. The sample solution was shaken and centrifuged, and the extract was separated as described above.
- iv. Residual (Fraction IV): The analysis of the residue was performed using aqua regia (65% v/v HCl + 35% v/v HNO<sub>3</sub>) for metals insoluble in the previous steps. For this purpose, first, 6 cm<sup>3</sup> of double-distilled water and then aqua regia solution in a sequence of 15 and 10 cm<sup>3</sup> were added to the remaining residue. After adding each aqua regia solution, the residue was evaporated to near dryness on a water bath. The extract was filtered through filter paper by adding 1.0 mol dm<sup>-3</sup> HNO<sub>3</sub> solution in small amounts on the last residue in the centrifuge tube. The tube walls were carefully washed with the same acid solution and then the dregs were collected in a beaker.

#### ELEMENTAL ANALYSIS

Digests of soil samples were analyzed by Flame Atomic Absorption Spectrometer (BUCK SCIENTIFIC MODEL 210) for the concentrations of Cu, Pb, Cr, Cd and Zn. Also, elemental analysis was conducted for standard solutions prepared. The wavelengths of the machine used for Cu, Zn, Cr, Pb and Cd were 324.7, 213.9, 357.9, 283.3 and 228.8 nm respectively.

#### STATISTICAL ANALYSIS

Descriptive statistical analysis and Pearson's correlation coefficients were employed to analyze data obtained for soil in study and control areas.

#### **QUALITY ASSURANCE/ RECOVERY STUDIES**

Quality control test was conducted on soil samples in order to evaluate the efficiency of Atomic Absorption Spectrometer. The spectrometer was calibrated according to manufacturer's recommendations. An acid blank and 10mg/cm<sup>3</sup> multi-element metal standard solution was used. Standards were analyzed for soil samples. The digests of soil samples were spiked with the multi-element metal standard solution and the recovery measurement determined by subtracting the metal concentration in the unspiked portion of the sample from the spiked portion [19].

### III. Results

The results obtained from the recovery studies show that all the elements have more than 80% recovery as presented in Table 1. This indicated that all the procedures employed with respect to sample preparation and instrumentation gave reproducible results for the research work. The percentage recoveries were acceptable recoveries which validate the efficiency of the Atomic Absorption Spectrometer.

Table 1. Mean	Percentage	(%) re	coveries	of soi	l samples.

	Cu	Zn	Cr	Pb	Cd
Soil	84.10	92.00	88.00	93.20	88.10

All the trace elements studied (i.e. Cu, Zn, Cr, Pb and Cd) were observed to be present in the soils of study area and control area. Table 2 shows the concentrations of the trace elements in sequential extraction fractions (I, II, III and IV) in soils of study area. The mobile components are fractions I and II. Table 3 shows the total concentrations (per sample) of the trace elements in soils of study area. Table 4 shows the concentrations of the trace elements in soils of control area and Table 5 shows the total concentrations (per sample) of the trace elements in soils of control area. Table 6 shows the descriptive statistics of the total concentrations of the trace elements in soils of both study area.

Fraction I (mobile)	i				
Sample	Cu	Zn	Cr	Pb	Cd
1	5.28	7.38	5.81	3.70	2.04
3	4.09	4.81	1.67	2.50	2.30
4	1.27	4.42	1.89	2.34	2.09
5	3.39	2.88	1.89	0.69	2.83
6	4.34	2.62	3.68	0.23	2.63
7	1.98	3.14	6.59	2.34	2.88
8	2.57	2.24	1.11	0.99	2.52
9	6.70	6.22	0.77	2.34	1.97
10	1.62	4.17	0.55	1.94	1.94
Mean	3.29	4.28	2.45	1.85	2.35
Fraction II (Mobile)					
1	4.10	9.30	5.58	3.70	2.27
2	9.29	7.63	2.23	4.00	2.65
3	9.65	8.28	4.58	4.46	2.45
4	6.93	6.86	2.00	1.44	2.15
5	4.93	12.64	0.43	3.55	2.07
6	12.83	8.28	0.32	8.04	2.04
7	3.28	4.55	1.33	2.80	2.04
8	7.76	5.45	0.66	5.36	2.08
9	9.65	6.09	5.03	6.42	1.87
10	5.40	7.38	0.32	3.16	3.16
Mean	7.38	7.65	2.25	4.30	2.28
Mobile component	10.67	11.93	4.70	6.15	4.62
(I+II)	10101	1100		0.120	
Fraction III					
1	4.22	6.86	3.57	4.91	2.14
2	8.58	6.73	2.78	7.77	2.01
3	5.99	5.58	2.78	4.30	2.30
4	5.28	7.12	3.57	6.87	2.42
5					
5	4.22	4.81	1.22	3.85	2.65
6	4.22 2.69	4.81 5.96	1.22 11.41	3.85 4.15	2.65 2.25
6 7	4.22 2.69 3.75	4.81 5.96 5.06	1.22 11.41 2.67	3.85 4.15 8.68	2.65 2.25 2.02
6 7 8	4.22         2.69         3.75         6.22	4.81 5.96 5.06 8.15	1.22         11.41         2.67         2.45	3.85 4.15 8.68 6.87	2.65 2.25 2.02 2.90
6 7 8 9	4.22         2.69         3.75         6.22         2.33	4.81 5.96 5.06 8.15 3.91	1.22         11.41         2.67         2.45         0.55	3.85 4.15 8.68 6.87 3.70	2.65 2.25 2.02 2.90 2.37
6 7 8 9 10	4.22         2.69         3.75         6.22         2.33         0.45	4.81 5.96 5.06 8.15 3.91 5.19	1.22         11.41         2.67         2.45         0.55         5.92	3.85 4.15 8.68 6.87 3.70 1.94	2.65 2.25 2.02 2.90 2.37 1.94
6 7 8 9 10 Mean	4.22         2.69         3.75         6.22         2.33         0.45 <b>4.37</b>	4.81 5.96 5.06 8.15 3.91 5.19 <b>5.94</b>	1.22         11.41         2.67         2.45         0.55         5.92 <b>3.69</b>	3.85 4.15 8.68 6.87 3.70 1.94 <b>5.30</b>	2.65 2.25 2.02 2.90 2.37 1.94 <b>2.30</b>
6 7 8 9 10 Mean Fraction IV	4.22         2.69         3.75         6.22         2.33         0.45 <b>4.37</b>	4.81 5.96 5.06 8.15 3.91 5.19 <b>5.94</b>	1.22         11.41         2.67         2.45         0.55         5.92 <b>3.69</b>	3.85 4.15 8.68 6.87 3.70 1.94 <b>5.30</b>	2.65 2.25 2.02 2.90 2.37 1.94 <b>2.30</b>
6 7 8 9 10 Mean Fraction IV 1	4.22 2.69 3.75 6.22 2.33 0.45 <b>4.37</b> 4.34	4.81 5.96 5.06 8.15 3.91 5.19 5.94 5.84	1.22         11.41         2.67         2.45         0.55         5.92 <b>3.69</b> 3.68	3.85 4.15 8.68 6.87 3.70 1.94 <b>5.30</b> 0.38	2.65 2.25 2.02 2.90 2.37 1.94 <b>2.30</b> 3.13
6 7 8 9 10 Mean Fraction IV 1 2	4.22 2.69 3.75 6.22 2.33 0.45 <b>4.37</b> 4.34 3.39	4.81 5.96 5.06 8.15 3.91 5.19 5.94 5.84 5.96	1.22 11.41 2.67 2.45 0.55 5.92 <b>3.69</b> 3.68 3.79	3.85 4.15 8.68 6.87 3.70 1.94 <b>5.30</b> 0.38 0.84	2.65 2.25 2.02 2.90 2.37 1.94 <b>2.30</b> 3.13 1.97
6 7 8 9 10 Mean Fraction IV 1 2 3	4.22 2.69 3.75 6.22 2.33 0.45 <b>4.37</b> 4.34 3.39 10.00	4.81 5.96 5.06 8.15 3.91 5.19 5.94 5.84 5.96 7.12	1.22 11.41 2.67 2.45 0.55 5.92 <b>3.69</b> 3.68 3.79 3.79	3.85 4.15 8.68 6.87 3.70 1.94 5.30 0.38 0.84 2.04	2.65 2.25 2.02 2.90 2.37 1.94 <b>2.30</b> 3.13 1.97 2.02
6 7 8 9 10 Mean Fraction IV 1 2 3 4	4.22 2.69 3.75 6.22 2.33 0.45 <b>4.37</b> 4.34 3.39 10.00 14.13	4.81 5.96 5.06 8.15 3.91 5.19 5.94 5.84 5.96 7.12 7.12	1.22 11.41 2.67 2.45 0.55 5.92 <b>3.69</b> 3.68 3.79 3.79 8.61	3.85 4.15 8.68 6.87 3.70 1.94 <b>5.30</b> 0.38 0.84 2.04 4.15	2.65 2.25 2.02 2.90 2.37 1.94 <b>2.30</b> 3.13 1.97 2.02 1.89
6 7 8 9 10 Mean Fraction IV 1 2 3 4 5	4.22 2.69 3.75 6.22 2.33 0.45 <b>4.37</b> 4.34 3.39 10.00 14.13 3.87	4.81 5.96 5.06 8.15 3.91 5.19 5.94 5.84 5.96 7.12 7.12 5.06	1.22 11.41 2.67 2.45 0.55 5.92 <b>3.69</b> <b>3.68</b> 3.79 3.79 8.61 0.43	3.85 4.15 8.68 6.87 3.70 1.94 <b>5.30</b> 0.38 0.84 2.04 4.15 2.95	2.65 2.25 2.02 2.90 2.37 1.94 <b>2.30</b> 3.13 1.97 2.02 1.89 1.92
6 7 8 9 10 Mean Fraction IV 1 2 3 4 5 6	4.22 2.69 3.75 6.22 2.33 0.45 <b>4.37</b> 4.34 3.39 10.00 14.13 3.87 2.10	4.81 5.96 5.06 8.15 3.91 5.19 5.94 5.84 5.96 7.12 7.12 5.06 6.61	1.22 11.41 2.67 2.45 0.55 5.92 <b>3.69</b> <b>3.68</b> 3.79 <b>3.79</b> <b>3.79</b> <b>8.61</b> 0.43 <b>3.90</b>	3.85 4.15 8.68 6.87 3.70 1.94 <b>5.30</b> 0.38 0.84 2.04 4.15 2.95 2.34	2.65 2.25 2.02 2.90 2.37 1.94 <b>2.30</b> 3.13 1.97 2.02 1.89 1.92 2.25
6 7 8 9 10 Mean Fraction IV 1 2 3 4 5 6 7	4.22 2.69 3.75 6.22 2.33 0.45 <b>4.37</b> 4.34 3.39 10.00 14.13 3.87 2.10 6.81	4.81 5.96 5.06 8.15 3.91 5.19 5.94 5.84 5.96 7.12 7.12 5.06 6.61 8.53	1.22 11.41 2.67 2.45 0.55 5.92 <b>3.69</b> 3.68 3.79 3.79 8.61 0.43 3.90 0.77	3.85 4.15 8.68 6.87 3.70 1.94 <b>5.30</b> 0.38 0.84 2.04 4.15 2.95 2.34 0.84	2.65 2.25 2.02 2.90 2.37 1.94 <b>2.30</b> 3.13 1.97 2.02 1.89 1.92 2.25 2.20
6 7 8 9 10 Mean Fraction IV 1 2 3 4 5 6 7 8	4.22 2.69 3.75 6.22 2.33 0.45 <b>4.37</b> <b>4.34</b> 3.39 10.00 14.13 3.87 2.10 6.81 5.52	4.81 5.96 5.06 8.15 3.91 5.19 5.94 5.84 5.96 7.12 7.12 7.12 5.06 6.61 8.53 9.05	1.22 11.41 2.67 2.45 0.55 5.92 <b>3.69</b> <b>3.68</b> <b>3.79</b> <b>3.68</b> <b>3.79</b> <b>3.79</b> <b>8.61</b> 0.43 <b>3.90</b> 0.77 7.15	3.85 4.15 8.68 6.87 3.70 1.94 <b>5.30</b> 0.38 0.84 2.04 4.15 2.95 2.34 0.84 9.58	2.65 2.25 2.02 2.90 2.37 1.94 <b>2.30</b> 3.13 1.97 2.02 1.89 1.92 2.25 2.20 2.65
6 7 8 9 10 Mean Fraction IV 1 2 3 4 5 6 7 8 9 9	4.22 2.69 3.75 6.22 2.33 0.45 <b>4.37</b> 4.34 3.39 10.00 14.13 3.87 2.10 6.81 5.52 3.98	4.81 5.96 5.06 8.15 3.91 5.19 5.94 5.94 5.84 5.96 7.12 7.12 5.06 6.61 8.53 9.05 10.33	1.22 11.41 2.67 2.45 0.55 5.92 <b>3.69</b> <b>3.68</b> <b>3.79</b> <b>3.68</b> <b>3.79</b> <b>3.79</b> <b>8.61</b> 0.43 <b>3.90</b> 0.77 7.15 <b>6.59</b>	3.85 4.15 8.68 6.87 3.70 1.94 <b>5.30</b> 0.38 0.84 2.04 4.15 2.95 2.34 0.84 9.58 1.74	2.65 2.25 2.02 2.90 2.37 1.94 <b>2.30</b> 3.13 1.97 2.02 1.89 1.92 2.25 2.20 2.65 1.94
6 7 8 9 10 Mean Fraction IV 1 2 3 4 5 6 7 8 9 10	4.22 2.69 3.75 6.22 2.33 0.45 <b>4.37</b> 4.34 3.39 10.00 14.13 3.87 2.10 6.81 5.52 3.98 16.84	4.81 5.96 5.06 8.15 3.91 5.19 5.94 5.94 5.94 5.94 5.94 7.12 7.12 7.12 5.06 6.61 8.53 9.05 10.33 6.35	1.22 11.41 2.67 2.45 0.55 5.92 <b>3.69</b> <b>3.68</b> 3.79 <b>3.79</b> <b>8.61</b> 0.43 <b>3.90</b> 0.77 7.15 <b>6.59</b> 1.55	3.85 4.15 8.68 6.87 3.70 1.94 <b>5.30</b> 0.38 0.84 2.04 4.15 2.95 2.34 0.84 9.58 1.74 1.92	2.65 2.25 2.02 2.90 2.37 1.94 <b>2.30</b> 3.13 1.97 2.02 1.89 1.92 2.25 2.20 2.65 1.94 1.92
6 7 8 9 10 Mean Fraction IV 1 2 3 4 5 6 7 8 9 10 Mean 1 2 3 4 5 6 7 8 9 10 Mean 10 10 10 10 10 10 10 10 10 10	4.22 2.69 3.75 6.22 2.33 0.45 4.37 4.34 3.39 10.00 14.13 3.87 2.10 6.81 5.52 3.98 16.84 7.10	4.81 5.96 5.06 8.15 3.91 5.19 5.94 5.84 5.96 7.12 7.12 5.06 6.61 8.53 9.05 10.33 6.35 <b>7.20</b>	1.22 11.41 2.67 2.45 0.55 5.92 <b>3.69</b> <b>3.68</b> 3.79 <b>3.79</b> <b>3.79</b> <b>3.79</b> <b>3.68</b> <b>3.79</b> <b>3.79</b> <b>3.79</b> <b>3.79</b> <b>3.61</b> 0.43 <b>3.90</b> 0.77 <b>7.15</b> <b>6.59</b> <b>1.55</b> <b>4.03</b>	3.85 4.15 8.68 6.87 3.70 1.94 <b>5.30</b> 0.38 0.84 2.04 4.15 2.95 2.34 0.84 9.58 1.74 1.92 <b>2.68</b>	2.65 2.25 2.02 2.90 2.37 1.94 <b>2.30</b> 3.13 1.97 2.02 1.89 1.92 2.25 2.20 2.65 1.94 1.92 <b>2.19</b>

# Table 2: Concentrations of trace elements in sequential extraction fractions (I, II, III and IV) in soils of study area.

Concentrations of Elements in Samples 1-10											
Samples	Cu	Zn	Cr	Pb	Cd						
1	17.94	29.38	18.64	12.69	9.59						
2	25.96	25.14	9.35	14.05	8.93						
3	26.67	25.91	12.82	13.30	9.03						
4	27.61	25.53	16.06	14.80	8.55						
5	16.41	25.40	3.97	11.04	9.46						
6	21.95	23.47	19.31	14.80	9.16						
7	15.82	21.29	11.36	14.65	9.13						
8	22.07	24.88	11.36	22.80	10.16						
9	22.66	26.55	12.93	14.20	8.15						
10	24.32	23.08	8.34	8.96	8.96						

Table 3: Total concer	ntrations	(per	sample)	of	the	trace	e elements	s in soils of study area
	<i>~</i>		0.771		a		1 10	

<b>Table 4: Concentrations</b>	of trace elements	in sequential	extraction	fractions	(I, II	, III a	nd IV)	in soil	s of
control area									

Fraction I (Mobile)					
	Cu	Zn	Cr	Pb	Cd
1	0.56	3.39	1.89	1.14	0.20
2	4.10	5.58	2.42	0.38	0.23
3	8.58	6.22	7.03	0.23	0.68
4	3.11	4.00	3.07	0.30	0.21
5	2.03	5.44	2.33	0.31	0.13
6	4.99	5.43	4.00	0.51	0.23
Mean	3.90	5.01	3.46	0.48	0.28
Fraction II (Mobile)					
1	7.29	1.06	3.21	4.61	0.23
2	3.75	8.15	0.44	3.10	0.23
3	3.39	8.66	0.44	6.11	0.29
4	2.91	4.23	1.31	2.79	0.30
5	4.01	4.01	0.43	3.79	0.43
6	3.11	5.89	0.67	6.00	0.21
Mean	4.08	5.33	1.08	4.40	0.28
Fraction III					
1	4.85	6.86	0.71	1.59	0.26
2	1.18	8.28	2.02	2.02	0.25
3	3.39	8.79	2.29	5.66	0.21
4	7.89	8.80	1.87	3.40	0.24
5	6.54	4.33	1.00	5.99	0.19
6	8.90	5.11	2.31	4.89	0.88
Mean	5.46	7.03	1.70	3.92	0.34
Fraction IV					
1	5.75	1.01	1.63	3.85	0.25
2	8.47	8.15	0.71	5.66	0.28
3	1.34	1.17	0.71	6.72	0.21
4	4.21	7.72	0.71	5.73	0.81
5	9.00	8.44	0.44	2.28	0.21
6	8.77	6.02	0.92	4.11	0.32
Mean	6.26	5.42	0.85	4.73	0.35
		•			
Mobile component (I+II)	7.97	10.34	4.54	4.88	0.56
pH	5.62				

Concentration of Elements in samples									
Sample	Cu	Zn Cr		Pb	Cd				
1	18.45	12.32	7.44	11.19	0.93				
2	17.49	30.15	5.59	11.16	0.99				
3	16.71	24.85	10.47	18.72	1.39				
4	18.13	24.75	6.97	12.22	1.56				
5	21.58	22.23	4.21	12.37	0.96				
6	25.77	22.46	7.89	15.51	1.64				

 Table 5: Total concentrations (per sample) of the trace elements in soils of control area

#### Table 6: Descriptive statistics of soil of study area and control area

	Cu	Cu	Zn	Zn	Cr (study	Cr	Pb (study	Pb	Cd (study	Cd
	(study)	(Control)	(study)	(Control	)	(Control	)	(Control	)	(Control
				)		)		)		)
Mean	22.14	19.69	25.06	22.79	12.41	7.09	14.13	13.53	9.11	1.24
Median	22.36	18.29	25.27	23.60	12.09	7.20	14.13	12.29	9.08	1.19
Standard	4.22	3.41	2.18	5.87	4.71	2.13	3.58	3.00	0.55	0.33
Deviation										
Minimum	15.82	16.71	21.29	12.32	3.97	4.21	8.96	11.16	8.15	0.93
Maximum	27.61	25.77	29.38	30.15	19.31	10.47	22.80	18.72	10.16	1.64
Sum	221.37	118.12	250.62	136.75	124.14	42.56	141.29	81.17	91.12	7.47
Count	10	6	10	6	10	6	10	6	10	6
Confidence	3.02	3.58	1.56	6.16	3.37	2.24	2.56	3.15	0.40	0.34
Level(95.0%)										

#### IV. Discussion

It was observed that the total concentrations of the trace elements as obtained from sequential extraction and residual fractions (i.e. I+II+III+IV) in study area were higher than those of control area.

Copper (Cu) was observed to have total concentrations of 22.14 mg/kg in study area and 19.69 mg/kg in control area. The bioavailable component of Cu observed in study area and control area were 48.19% and 40.49% of the total concentration of Cu respectively. The high value of Cu and its high mobile component in study area could be attributed to anthropogenic activities such as discharge of effluents into surrounding environment by the oil facility during turn-around maintenance, traffic of heavy-duty vehicles that lift oil at the depot, corrosion of feed pipelines and other alloys, oil leakages and spillage [20, 21].

The concentration of Cu (22.14 mg/kg) reported in this study is lower than 47.0 mg/kg reported by Fisseha et al. (2008)[22]; 61 mg/kg by Ndiokwere (1984)[23]; 27 mg/kg by Ward et al. (1977[24]); 29.7 mg/kg by Jaradat and Momani (1999)[25]; it is however higher than 2.78 mg/kg reported by Bai et al. (2008)[26]. The bioavailable component of Cu in study area (48.19%) is lower than 6-72% and 0.4-74.4% reported by Nastja, R. S. (2011)[3]; Lena and Gade (1997)[4] respectively, while the value is higher than 16% and 3-30% reported by Yobouet et al. (2010)[5] and Erika-Andrea et al. (2005)27] respectively.

Zn in this study was observed to have total concentrations (mg/kg dry weight) of 25.06 and 22.79 in study area and control area respectively. The bioavailable component of Zn observed in study area and control area were 47.61% and 45.37% of the total concentration of Zn respectively. The high value of Zn observed in the study area could be attributed to corrosion and leakage of feed pipelines and storage tanks, emissions from traffic of heavy duty vehicles that lift oil at the depot and discharge of effluents during turn-around maintenance. The level of Zn reported in study area is lower than 237.96 mg/kg reported by Okunola et al. (2007)[28]; 761 mg/kg reported by Sitkol et al. (2004)[29] and higher than values reported by Mitsios et al. (2005)[30] which ranged between 0.03-5.5 mg/kg. Srinivas et al. (2009)[31] also reported Zn concentration in industrial area as 49.7 mg/kg and 32.2 mg/kg in rural area (control), these values are higher than the concentration of Zn (25.06 mg/kg) in study area and 22.79 mg/kg in control area reported by Nastja, R. S. (2011)[3] and Yobouet et al. (2010) [5]respectively. The value is however higher than 2.4-44.2%, 5-20% and 33.35% reported by Lena and Gade (1997)[4]; Erika-Andrea et al. (2005)[27] and Olayinka et al. (2011)[32] respectively.

Chromium concentrations were observed as 12.41 mg/kg and 7.09 mg/kg in study area and control area respectively. The bioavailable component of Cr observed in study area and control area were 37.87% and 64.03% of the total concentration of Cr respectively. The observed concentration of Cr in study area could be due to leakage of feed pipelines or storage tanks and spillage of oil which has been reported by Nwachukwu et al. (1995)[33] to still contain minute concentrations of transition metals including Cr after refining. Other reasons for the concentration in the study area could be due to corrosion of pipelines and storage reservoirs,

emissions from exhaust of heavy-duty vehicles and discharge of effluents during turn-around maintenance. The concentration of Cr in present study is less than 29.75 mg/kg reported by Adelekan and Abegunde (2011)[34]; and 10-50 mg/kg by Adriano (2001)[35]. The bioavailable component of Cr in study area (37.87%) is higher than 22.36% reported by Olayinka et al. (2011)[32].

Lead (Pb) was observed to have concentration of 14.13 mg/kg in study area and 13.53 mg/kg in control area. The bioavailable component of Pb observed in study area and control area were 43.52% and 36.07% of the total concentration of Pb respectively. The observed level of Pb in study area and its higher mobile component could be attributed to automobile exhaust emissions around the oil depot as reported by Aribike (1996)[36]; Lagerwerff and Specht (1970)[37]; Grigalaviciene et al. (2005)[38] and Awode et al. (2008)[39]. It could also be due to leakage of leaded-gasoline into the surrounding as reported by Ademorati (1986)[40] and Nwachukwu et al. (1995)[33]. The concentration of Pb in both study and control areas are lower than 76.92 mg/kg, 15,100 mg/kg and 203 mg/kg reported by Okunola et al. (2007)[28]; Adelekan and Abegunde (2011)[34] and Sitkol et al. (2004)[29] respectively. Srinivas et al., (2009)[31] reported 47.8 mg/kg in industrial area which is higher than level of Pb reported in soil around NNPC depot in present study while 8.1 mg/kg reported in rural area (control) was observed to be higher than the level of Pb reported in control area of present study. The bioavailable component of Pb in study area (43.52%) is lower than 18-56% and 70.44% reported by Nastja, R. S. (2011)[3] and Olayinka et al. (2011)[32] respectively, and higher than 20% and 30% reported by Erika-Andrea et al. (2005)[27] and Yobouet et al. (2010)[5] respectively.

Cadmium (Cd) was observed to have a higher concentration (9.11 mg/kg) in study area than in control area (1.24 mg/kg). The bioavailable component of Cd observed in study area and control area were 50.71% and 45.02% of the total concentration of Cd respectively. The observed high concentration in study area could be due to discharge of effluents into the surrounding environment during turn-around maintenance, spillage of lubricating oils, wear and tear of tyres of vehicles, emissions by heavy-duty vehicles that lift oil at the depot and particles from gasoline combustion. This agrees with other literature on higher Cd concentration in industrial areas than in control areas [41, 37, and 42]. Adelekan and Abegunde, (2011)[34] reported Cd concentration of 17.23 mg/kg which was higher than the concentrations of Cd in study area and control area reported in present study, however Cd concentrations in both study and control area in present study were observed to be higher than 0.75 mg/kg reported by Jaradat and Momani (1999)[25] and 0.88 mg/kg by Bai et al. (2008)[26]. Cadmium concentration of 2.11 mg/kg reported by Amusan et al. (2003)[43] was also observed to be lower than the concentration in control area of present study. The bioavailable component of Cd in study area (50.71%) is lower than 50-66% and 2.0-70% reported by Nastja, R. S. (2011)[3]; Lena and Gade (1997)[4] respectively, and higher than 30% and 48% reported by Erika-Andrea et al. (2005)[27] and Yobouet et al. (2010)[5] respectively.

Trace elements exhibit mobility in exchangeable phase (Fraction I) and reducible phase (Fraction II). Fig. 2 shows the mobile components of the trace elements in both study area and control area.



Fig. 2. Mobile Fractions (I+II) of soil in Study Area and Control Area.

It was observed that in exchangeable phase (Fraction I) and reducible phase (Fraction II), Cu and Zn exhibited highest mobility (10.67 mg/kg and 11.93 mg/kg respectively) than Cr, Pb and Cd (4.70 mg/kg, 6.15 mg/kg and 4.62 mg/kg respectively) in study area. In control area soils, Cu and Zn exhibited highest mobility (7.97 mg/kg and 10.34 mg/kg respectively) than Cr, Pb and Cd (4.54 mg/kg, 4.88 mg/kg and 0.56 mg/kg respectively). Hence, this suggests that Cu and Zn are more readily bioavailable in both study area and control soils. This agrees with the soil pH values (5.46 and 5.62) for study area and control area respectively as has been reported by McBride et al. (2004)[7] that Cu and Zn exhibit high extractability at low soil pH values than at high pH values (alkaline medium).

The results in Tables 2 and 4 were subjected to linear regression analysis in order to find associations between all possible trace element pairs with a view to ascertaining whether they are from a common source. The Pearson's correlation coefficients obtained from the statistical computation are given in Table 7 (study area) and Table 8 (control area).

	Cu	Zn	Cr	Pb	Cd
Cu	1				
Zn	0.088182	1			
Cr	0.163008	0.301888	1		
Pb	0.059827	-0.02715	0.234974	1	
Cd	-0.43646	0.033218	-0.09288	0.436641	1

Table 7: <u>Pearson's Correlation of Trace Element Pairs in</u> soil of study area

Table 8: I	Pears	on's Corr	elation of	Trace Ele	ment Pair	s in s	soil of control area	a

	Cu	Zn	Cr	Pb	Cd
Cu	1				
Zn	-0.15437	1			
Cr	-0.20737	-0.10542	1		
Pb	0.088836	0.172654	0.79305	1	
Cd	0.341932	0.247415	0.539447	0.573294	1

The Pearson's correlation coefficient values show that no significant correlation occurred between the trace element pairs in the soil of study area (Table 7). This suggests that all the trace elements are probably from different sources acting on the surroundings of the oil depot. These sources could be leakages from feed pipelines and storage facilities, exhaust emissions of fuel combustion by heavy duty vehicles that frequently lift oil at the depot, discharge of effluents into surrounding environment during turn-around maintenance and corrosion of storage facilities etc.

The correlation coefficient values for trace elements in control area (Table 8) were observed to be significant for Cd-Cr and Cd-Pb while for Pb-Cr pair it was highly significant. This suggests that Pb and Cr are probably from the same source and this could be attributed to their primary natural mineral sources which when exposed to weathering releases the elements into the environment.

Generally, the concentrations of the trace elements in both study area and control area were observed to be within European Union (2002)[18] standards for permissible limits (mg/kg) of the trace elements in soils (135.00 for Cu, 300.00 for Zn, 400.00 for Cr, 300.00 for Pb and 3.00 for Cd) except for Cd concentration in study area which was observed to be higher than the permissible limit.

### V. Conclusion

Speciation analyses give relevant information on the toxicity and biological activity of elements because the effects of these elements in soils do not depend on their concentrations alone, but also on their oxidation states and/or chemical forms. The results obtained from the sequential extraction analysis of soils collected around NNPC Oil depot Jos indicated that the concentrations of Zn, Cu, Cr and Pb were within permissible levels except for Cd which required attention.

Generally, the levels of trace elements in soils and their bioavailable components in the study area were observed to be lower than those of previous studies in industrial and residential areas and also lower than allowable limits by relevant standard organizations, this may be due partly to the controlled and cautious activity of the NNPC oil depot. However, it is important that the activities of the oil facility should be highly regulated to reduce the potential risks associated with the release of harmful trace elements into the surroundings. Also, periodic assessment of trace elements contents of soils and plants around the oil facility should be carried out.

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