

Evaluation of the Speciation Patterns of Some Heavy Metals along the Major Roads of Owerri Industrial Layout

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Abstract: Topsoil samples were collected along the major roads within Owerri industrial layout for the period of April to July. The pH and the moisture content were determined by pH meter and difference in wet and dry weight method respectively. The pH of the soil had a range of 6.1 to 6.7 while moisture content had a range of 5.177 to 13.572%. The highest metal concentration (832.830mg/kg) was Fe found in the Gmicord Road (RX2), while the metal with the least concentration (0.067mg/kg) was Cd. The observed trend in the concentration of the metals was Fe > Ca > Mn > Zn > Cr > Pb > Ni > Co > Cu > Cd. There were no significant differences between the pH and the concentration of the soil samples. Most of the metals in the soil samples were distributed within the residual fraction which is an indication of geochemical sources.

Key Words: Bioavailability, Concentration, Metal, Speciation, Soil.

I. Introduction

Human evolution has led to immense scientific and technological progress. Global development (industrialization), however, raises new challenges, especially in the field of environmental protection and conservation [1]. Nearly every government around the world advocates for an environment free from harmful contamination for their citizens. However, the demand for a country's economic, agriculture and industrial development outweigh the demand for a safe, pure and natural environment. Ironically, it is the economic, agricultural and industrial developments that are often linked to polluting the environment [2]. Since the beginning of the industrial revolution, soil pollution by toxic metals has increased dramatically. According to report, about 90% of the anthropogenic emissions of heavy metals have occurred since 1900AD [3]; it is now well recognized that human activities lead to a substantial accumulation of metals in soils on a global scale. A number of chemicals, heavy metals and other industrial wastes have resulted in significant discharge of industrial effluents into the nearby water bodies and soils and environment at large. These effluents which contain toxic metals or substances are released into the environment which contributes to a variety of toxic effects on living organisms in the food chain by bioaccumulation and bio-magnification. Heavy metals, such as cadmium, copper, lead, chromium, zinc, and nickel are important environmental pollutants, particularly in areas with high anthropogenic pressure [4] such as Owerri industrial layout. The soil has been traditionally the site for disposal for most of the metal wastes which need to be treated. Sources of anthropogenic metal contamination include industrial effluents, fuel production, mining, smelting processes, military operations utilization of agricultural chemicals, small-scale industrial (including battery production, metal products, metal smelting and cable coating industries) brick kilns and coal combustion [5]. One of the prominent sources contributing to increased load of soil contamination is disposal of municipal waste. These wastes are either dumped on roadsides or used as landfills, while sewage is used for irrigation. These wastes, although useful as a source of nutrients, are also sources of carcinogens and toxic metals.

Around the world several studies have evaluated the metal concentration in the soils [6, 7, 8, 9, 10]. In Owerri industrial layout, such studies are non-existent to date and therefore, very little are known about the distribution of such elements. At present, it is widely recognized that the distribution, mobility and bioavailability of heavy metals and radionuclide in the environment depends not only on their total concentration but also on the association form in the solid phase to which they are bound. Some variations of the chemical or physical conditions in the environment can accelerate to some extent the release of toxic metals into it, thus causing contamination.

Bioavailability of metals depends greatly on the characteristics of the particle surface, on the kind of strength of the bond and on the properties of the solution in contact with the solid samples. Metal ions in soils and sediments are partitioned between the different phase's present i.e. organic matter, oxyhydroxides of iron, aluminum and manganese, phyllosilicate minerals, carbonates and sulfides. In addition, metal ions are retained on these solid phases by different mechanisms (ion exchange, outer and inner-sphere surface complexation (adsorption), precipitation or co-precipitation). Sediment samples have been found as a carrier of most metals and some elements may be recycled through biological and chemical reactions within the water column. In soil,

there is a concern to know the metal bioavailability and toxicity to plants, animals and man, the efficiency of the soil as a sink for metals and the potential capacity of a metal to be mobilized from the soil [11].

Natural and anthropogenic environmental changes greatly influence the behaviour of metallic pollutants as the association form in which they occur can be changed. Such external influences can include pH, temperature, redox potential, organic matter decomposition, leaching and ion exchange processes and microbial activities. Thus, the exchangeable fractions corresponds to the form of metals that is most available for plant uptake and can be released by merely changing the ionic strength of the medium, the metal content bound to carbonates is sensitive to pH changes and can become mobilisable when pH is lowered. The metal fraction bound to Fe-Mn oxides and organic matter can be mobilized with increasing, reducing or oxidizing conditions in the environment. Finally the metal fractions associated with the residual fraction e.g. silicate can only be mobilized as a result of weathering which can only cause long term effects [12].

II. Materials And Methods

Soil samples were collected in the vicinity of Owerri Industrial layout between April and July. The sampling site comprised of five major roads, Raycon road (road 1), Gmicord road (road 2), Coca-cola road (road 3), Modern Home Aluminum road (road 4) and Assumpta Press road (road 5) covering the whole length of the area. A total of 5 samples were collected from each road and merged to form a composite sample, a representative of each road using a plastic scoop into a polythene bag well labelled. The sampling site is surrounded by industries. A residential estate (Graceland/Egbeada Estate) is located north – east of the estate. Also to the south – east of the industrial layout is located another estate (Umuguma Housing Estate) and on the north – east is a highway (Onitsha – Owerri Road).

In the laboratory, samples were dried at room temperature and sieved through a 200mesh before analysis. Drying sediments at higher temperature was avoided to ensure that organic matter content and the metal binding properties of the sediments remained intact. Care was also taken while sieving the sediments to prevent excess loss of the fine particles. All chemicals and acids used were of Analytical Reagent Grade (ARG), and were used without further purification.

2.1 Procedure for Moisture Content Determination

The moisture content of the samples was determined using the dry-weight-difference method.

2.2 Procedure for pH Determination

5g of the soil sample was weighed into 250ml Beaker and 20ml of deionized water added. It was agitated for about 20minutes and allowed to equilibrate. Finally, a standardized pH meter was used to read the pH by dipping the electrode into the 250ml Beaker containing the solution.

2.3 Procedure for Determination of Total Metal Content

About 5g of the soil sample was weighed into sample rubber and 5ml of Hydrofluoric acid (HF) added. Also 10ml Aqua Regia was added and the mixture heated over water bath for 1hour, 30minutes. Then, it was allowed to cool. The process was repeated again and 20ml boric acid was added. Thereafter, the solution was filtered and made-up to 50ml with deionized water. Finally, analysis of the extracts was carried out by Flame Atomic Absorption Spectrometry (Analyst 200).

2.4 Sequential Extraction

Sequential extraction protocol for analysis of heavy metal speciation in soil and sediments (modified from Tessier et al., 1979) were used to establish the association of the total concentration of the metals in the soil samples with their contents in the water soluble, exchangeable, carbonate, reducible (Fe/Mn oxide), oxidisable (organic and sulfide bound) and residual fraction [13].

III. Results And Discussion

The moisture contents and the pH of the various soil samples collected from the five major roads are as shown below (Table 1). The pH of the soil is an important parameter that directly influences mineral mobility. The soil pH of the sampling sites varied on the average from 6.1 to 6.7 in water indicating of slight acidity to neutrality. The moisture contents fell within the range of 5.177% to 13.572%. Looking at table 1, it showed that sample RX1 – RX5 had relatively low values of moisture contents.

TABLE 1: Percentage Moisture Content and the pH of the Soil Samples.

Sample code	% Moisture Content	pH
R1X	5.177	6.6
R2X	5.398	6.1
R3X	6.099	6.4
R4X	6.084	6.3
R5X	13.572	6.7

NOTE: R is referring to as road where the sample was collected, Numbers 1 – 5 represent the road numbers, X means the topsoil sample

TABLE 2: Total Metal Concentration (mg/kg).

Sample code	Cu	Ca	Mn	Pb	Ni	Fe	Co	Zn	Cr	Cd	Total	Mean
RX1	0.422 ±0.11	4.880 ±0.12	3.135 ±0.16	1.004 ±0.01	1.582 ±0.006	4.100 ±0.002	1.053 ±0.004	1.813 ±0.006	2.911 ±0.11	0.123 ±0.14	21.023	2.1023
RX2	0.292 ±0.03	6.226 ±0.18	3.640 ±0.09	1.041 ±0.07	1.274 ±0.020	832.830 ±0.038	1.158 ±0.065	2.709 ±0.012	1.392 ±0.11	0.139 ±0.05	850.661	85.066
RX3	0.357 ±0.02	2.672 ±0.07	2.791 ±0.045	0.482 ±0.08	0.734 ±0.009	350.070 ±0.196	0.583 ±0.004	1.602 ±0.006	0.858 ±0.032	0.067 ±0.03	360.661	36.022
RX4	0.663 ±0.06	59.38 ±0.02	3.589 ±0.066	4.162 ±0.06	0.980 ±0.021	750.210 ±0.152	0.931 ±0.013	2.730 ±0.005	1.447 ±0.18	0.627 ±0.19	824.727	82.473
RX5	0.332 ±0.01	3.220 ±0.01	2.196 ±0.04	0.591 ±0.041	1.349 ±0.011	4.500 ±0.015	0.792 ±0.002	2.510 ±0.013	4.210 ±0.13	0.090 ±0.00	19.790	1.979
Total	2.066	76.386	15.351	7.280	5.919	1941.710	4.517	11.634	10.778	1.046	2076.426	
Mean	0.4137	15.277	3.070	1.456	1.184	388.342	0.903	2.273	2.156	0.209	415.283	

Table 2 and figure 1, indicate the total metal concentration. The result indicated that the occurrence of Fe was at relatively higher concentration (832.830mg/kg) in the soil sample (RX2). This may be as a result of auto rust, motor spare parts and other human activities found around the industrial layout.

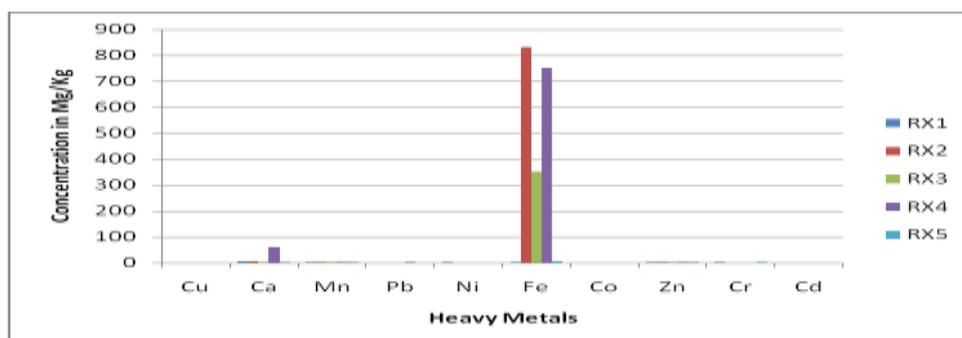


Figure 1: Total Metal Concentration

It also showed that Cd had the least concentration (0.067mg/kg) as found in sample RX3. The observed trends with various soil samples for the heavy metal concentration are as follows: for RX1 it was Ca > Fe > Mn > Cr > Zn > Ni > Co > Pb > Cu > Cd, while for RX2 it was Fe > Ca > Mn > Zn > Cr > Ni > Co > Pb > Cu > Cd.

TABLE 3: Percentage Total Metal Concentration

Sample code	Cu	Ca	Mn	Pb	Ni	Fe	Co	Zn	Cr	Cd
RX1	2.007	23.217	14.912	4.776	7.525	19.502	5.009	8.624	13.847	0.585
RX2	0.034	0.732	0.428	0.122	0.150	97.904	0.136	0.218	0.159	0.016
RX3	0.099	0.742	0.772	0.134	0.204	97.183	0.162	0.445	0.238	0.019
RX4	0.080	7.201	0.435	0.505	0.119	90.965	0.113	0.331	0.175	0.076
RX5	1.678	4.036	11.097	2.986	6.817	22.739	4.002	12.683	21.273	0.455

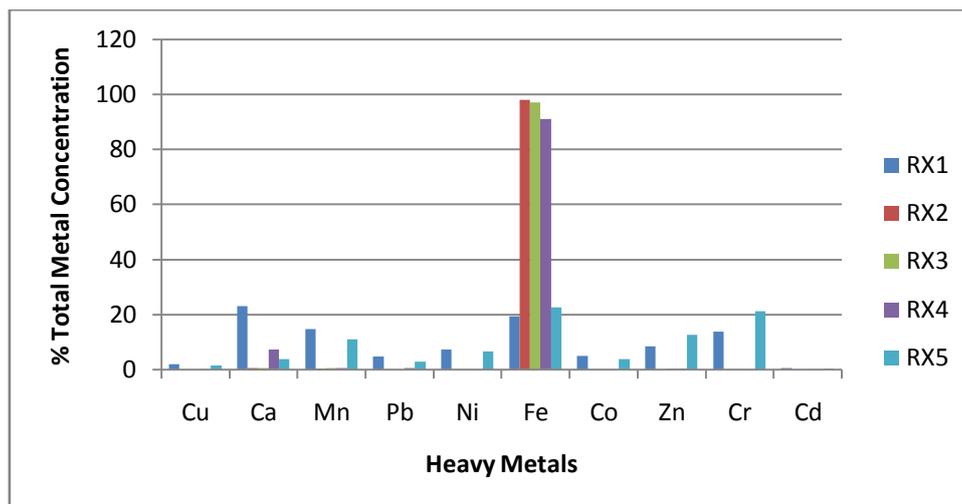


Figure 2: Percentage Total Metal Concentration

The trend $Fe > Mn > Ca > Zn > Cr > Ni > Co > Pb > Cu > Cd$, $Fe > Ca > Pb > Mn > Zn > Cr > Ni > Co > Cu > Cd$ and $Fe > Cr > Zn > Mn > Ni > Ca > Co > Pb > Cu > Cd$ are for RX3, RX4 and RX5 samples respectively. Cd had the least total concentration and Fe had the highest total concentration except for RX1 where Ca had the maximum value in the soil samples.

TABLE 4: Fractional Concentration of Cu in the Various Soils Samples (mg/kg).

Sample code	F1	F2	F3	F4	F5	F6	Total	Mean	BAF	% BAF
RX1	0.092 ±0.000	0.070 ±0.001	0.166 ±0.001	0.088 ±0.001	0.112 ±0.002	0.315 ±0.009	0.843	0.141	0.328	38.909
RX2	0.651 ±0.152	ND	0.107 ±0.003	0.059 ±0.001	0.150 ±0.014	0.311 ±0.003	1.278	0.213	0.758	59.311
RX3	ND	0.076 ±0.004	0.132 ±0.000	0.079 ±0.003	0.104 ±0.001	0.211 ±0.003	0.602	0.100	0.208	34.551
RX4	ND	0.076 ±0.002	0.193 ±0.004	0.143 ±0.003	0.244 ±0.004	0.086 ±0.001	0.742	0.124	0.269	36.253
RX5	0.099 ±0.0012	0.023 ±0.001	0.112 ±0.000	0.091 ±0.002	0.149 ±0.000	0.289 ±0.003	0.763	0.127	0.234	30.668
Total	0.842	0.245	0.708	0.460	0.759	1.212	4.366	0.728	1.795	199.692
Mean	0.164	0.049	0.142	0.092	0.152	0.242	0.841	0.140	0.355	39.938

F1 = Water soluble Fraction, F2 = exchangeable metal fraction, F3 = carbonate fractions, F4 = reducible Fractions, F5 = oxidizable and F6 = residual fractions. ND = not detected.

In the soil samples, much of the copper was associated with residual fractions with a mean value of 0.242mg/kg (Table 4). The observed trend in the range of copper concentration in the various fractions was $F6 > F1 > F5 > F3 > F4 > F2$. Also the trend in the percentage bioavailability of the samples was $RX2 > RX1 > RX4 > RX3 > RX5$. The water soluble fractions of samples RX3 and RX4 was at non-detectable level of the FAAS. So also it was for the exchangeable fraction of the RX2 sample. The highest fraction of Cu was found in sample RX2 (0.651mg/kg) in the water soluble fraction (F1), and this contributed to the high value of the %BAF of Cu (59.311%) more than every other sample in the study area.

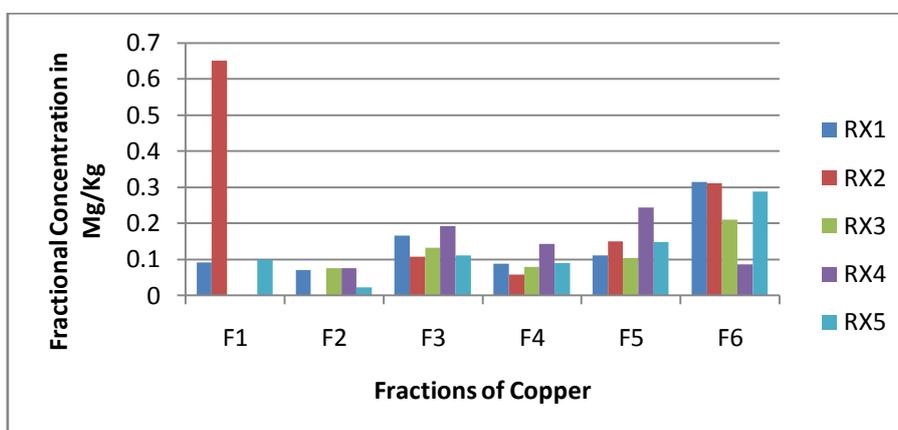


Figure 3: Fractional Concentration of Cu in the Various Topsoil Samples (mg/kg).

TABLE 5: Fractional Concentration of Ca in the Various Soil Samples (mg/kg).

Sample code	F1	F2	F3	F4	F5	F6	Total	Mean	BAF	% BAF
RX1	3.210 ±0.015	4.966 ±0.008	2.166 ±0.019	5.446 ±0.052	1.332 ±0.019	0.689 ±0.049	17.809	2.968	10.342	58.072
RX2	2.415 ±0.016	5.259 ±0.012	2.949 ±0.041	3.948 ±0.016	1.477 ±0.001	6.992 ±0.055	23.040	3.840	10.623	46.107
RX3	1.575 ±0.041	2.793 ±0.047	1.693 ±0.017	1.866 ±0.084	0.954 ±0.018	0.417 ±0.001	9.298	1.550	6.061	65.186
RX4	1.220 ±0.011	3.809 ±0.171	2.746 ±0.015	8.213 ±0.219	18.963 ±0.053	8.225 ±0.200	43.176	7.196	7.775	18.008
RX5	2.330 ±0.033	3.298 ±0.062	1.220 ±0.012	2.386 ±0.016	1.168 ±0.005	0.455 ±0.001	10.857	1.810	6.848	63.075
Total	10.750	20.125	10.774	21.859	23.894	16.778	104.180	17.363	41.649	250.448
Mean	2.150	4.025	2.155	4.372	4.779	3.356	20.837	3.473	8.330	50.089

In the soil samples, much of the Ca was associated with the oxidisable fractions with a mean value of 4.779mg/kg. The observed trend in the range of Ca concentration in the various fractions was F5 > F4 > F2 > F6 > F3 > F1. Also the trend in the percentage bioavailability of the samples was RX3 > RX5 > RX1 > RX2 > RX4. The least fractional concentration of Ca was found in sample RX3 (0.417mg/kg) also at the residual fraction.

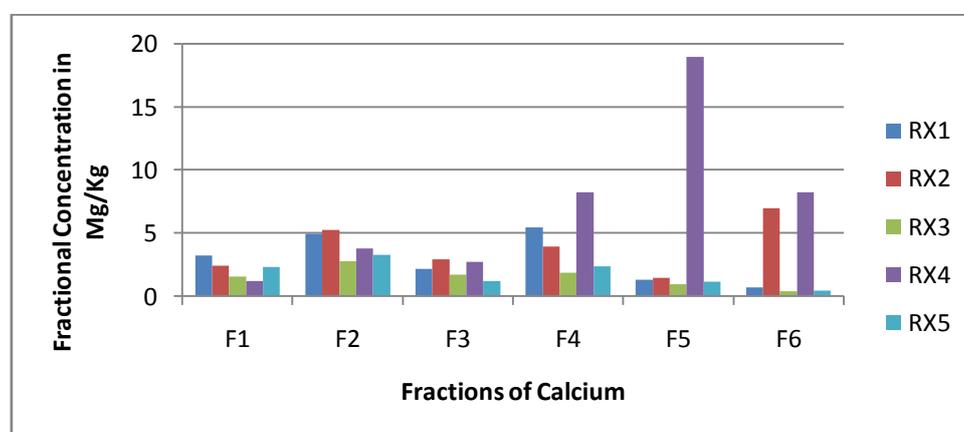


Figure 4: Fractional Concentration of Ca in the Various Soil samples (mg/kg).

From fig. 4, we can see that Road 4 (RX4) recorded the most fractional concentration of Ca (18.963mg/kg) at the oxidizable fractions. The mean % BAF of Ca is 50.089%, which is slightly above average and it shows that Ca is potentially bioavailable for organism's uptake in the studied area.

TABLE 6: Fractional Concentration of Mn in the Various Soil Samples (mg/kg).

Sample code	F1	F2	F3	F4	F5	F6	Total	Mean	BAF	% BAF
RX1	0.221 ±0.013	0.681 ±0.003	1.021 ±0.000	0.886 ±0.012	0.945 ±0.005	2.311 ±0.019	6.065	1.010	1.923	31.707
RX2	0.024 ±0.006	0.992 ±0.002	1.044 ±0.032	0.879 ±0.018	1.232 ±0.005	2.477 ±0.065	6.648	1.108	2.060	30.987
RX3	0.106 ±0.003	0.653 ±0.021	0.673 ±0.013	0.652 ±0.017	0.759 ±0.017	2.070 ±0.084	4.913	0.818	1.432	29.147
RX4	0.139 ±0.005	0.388 ±0.005	0.856 ±0.031	1.047 ±0.023	0.849 ±0.018	0.465 ±0.007	3.744	0.624	1.383	36.939
RX5	0.142 ±0.062	0.728 ±0.011	1.001 ±0.000	0.924 ±0.062	0.681 ±0.036	1.677 ±0.029	5.203	0.867	1.921	36.921
Total	0.682	3.442	4.595	4.388	4.466	9.000	26.573	4.429	8.719	165.701
Mean	0.136	0.688	0.919	0.878	0.893	1.800	5.314	0.886	1.743	33.140

The mean %BAF of Mn is 33.140% which is below average and so Mn has a high non-bioavailable fraction in the studied area (Table 6). This is also supported by the observed trend in the concentration of Mn in the various fractions – F6 > F3 > F5 > F4 > F2 > F1. The trend in the percentage bioavailability of Mn in the soil samples is RX4 > RX5 > RX1 > RX2 > RX3. Much of the Mn fractions were associated with the residual fraction (F6) with mean value of 1.800mg/kg.

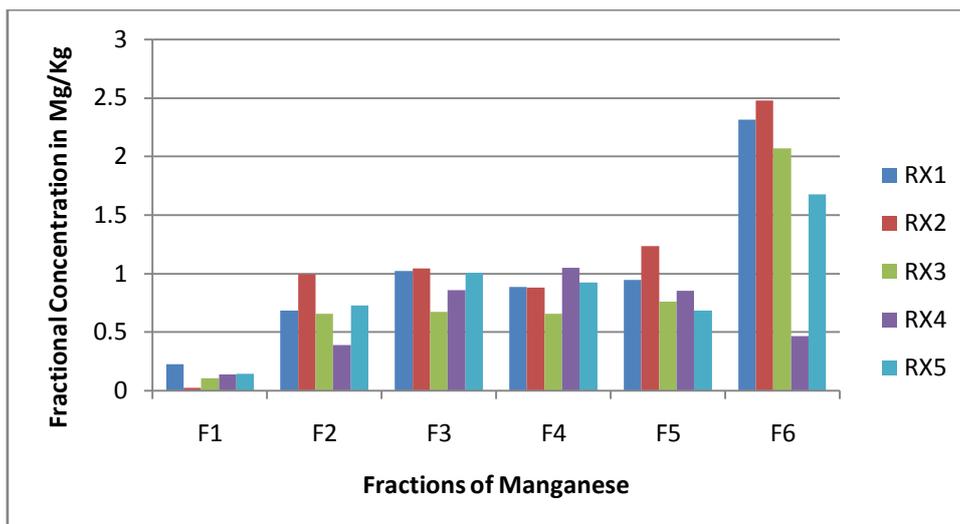


Figure 5: Fractional Concentration of Mn in the Various Soil Samples (mg/kg).

TABLE 7: Fractional Concentration of Pb in the Various Soil Samples (mg/kg).

Sample code	F1	F2	F3	F4	F5	F6	Total	Mean	BAF	% BAF
RX1	ND	ND	0.398 ±0.015	0.049 ±0.003	ND	0.050 ±0.050	0.497	0.083	0.398	80.080
RX2	ND	ND	0.207 ±0.015	0.001 ±0.007	ND	0.561 ±0.004	0.769	0.154	0.207	26.918
RX3	ND	ND	0.222 ±0.006	ND	ND	0.226 ±0.015	0.448	0.075	0.222	49.553
RX4	ND	0.002 ±0.007	0.711 ±0.009	0.334 ±0.007	0.292 ±0.027	ND	1.339	0.223	0.112	8.364
RX5	ND	0.023 ±0.002	0.538 ±0.014	0.039 ±0.000	ND	0.089 ±0.006	0.689	0.115	0.561	81.422
Total	0.000	0.025	2.076	0.423	0.292	0.926	3.742	0.624	2.101	246.337
Mean	0.000	0.005	0.415	0.085	0.058	0.185	0.748	0.125	0.420	49.267

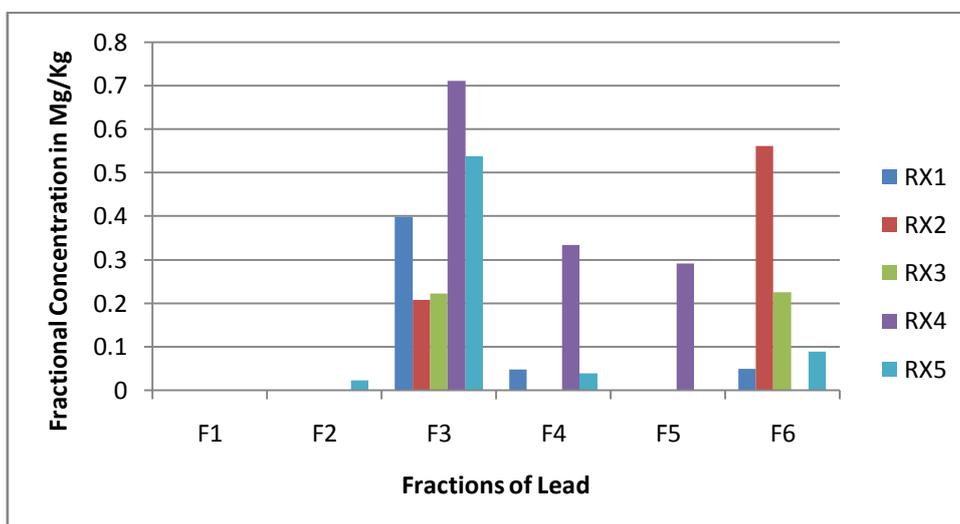


Figure 6: Fractional Concentration of Pb in the Various Soil Samples (mg/kg).

From table 7 much of the Pb was associated with the carbonate fraction were the mean concentration is 0.415mg/kg. This is also shown by the observed trend of the various fractions of Pb – F3 > F6 > F4 > F5 > F2 > F1. Pb was not detectable by the FAAS on the water soluble fraction. It was detectable at the exchangeable fraction only in samples RX4 and RX5. Also it was not found in sample RX3 on the reducible fraction and in the oxidisable fraction, it was not detectable except for sample RX4 only and on the residual fraction, it was seen in all the samples except for sample RX4. The observed trend in the percentage bioavailable fractions of the samples was RX5 > RX1 > RX3 > RX2 > RX4 (Table 7). Much of the Pb was associated with the carbonate

bound fraction and is potentially bioavailable in most of the studied area (fig. 6), except for road 2 (RX2) were the %BAF was below 50% in the carbonate bound fraction, but rather higher in the residual fraction.

TABLE 8: Fractional Concentration of Ni in the Various Soil Samples (mg/kg).

Sample code	F1	F2	F3	F4	F5	F6	Total	Mean	BAF	% BAF
RX1	0.019 ±0.001	0.218 ±0.000	0.309 ±0.002	0.065 ±0.001	0.057 ±0.000	0.728 ±0.000	1.396	0.233	0.546	39.112
RX2	0.027 ±0.006	0.136 ±0.002	0.226 ±0.014	0.050 ±0.003	0.080 ±0.003	0.720 ±0.007	1.239	0.207	0.389	31.396
RX3	0.016 ±0.001	0.125 ±0.001	0.245 ±0.006	0.048 ±0.000	0.044 ±0.000	0.506 ±0.001	0.984	0.164	0.386	39.228
RX4	0.029 ±0.002	0.138 ±0.004	0.332 ±0.068	0.076 ±0.000	0.069 ±0.005	0.114 ±0.005	0.758	0.126	0.499	65.831
RX5	0.032 ±0.002	0.334 ±0.011	0.292 ±0.000	0.054 ±0.000	0.060 ±0.000	0.438 ±0.002	1.210	0.202	0.658	54.380
Total	0.123	0.951	1.404	0.293	0.310	2.506	5.587	0.931	2.478	229.947
Mean	0.025	0.190	0.281	0.059	0.062	0.501	1.118	0.186	0.496	45.989

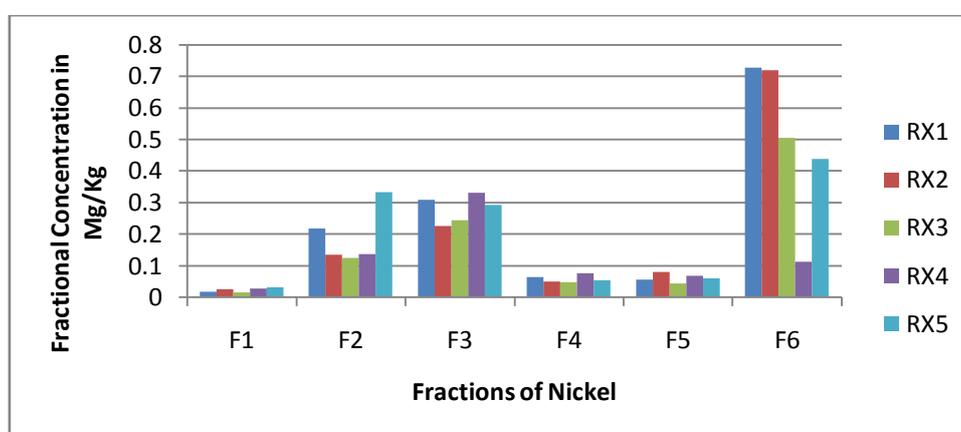


Figure 7: Fractional Concentration of Ni in the Various Soils Samples (mg/kg).

Table 8 represents the various fractions of Ni in the soil samples. The highest concentration of Ni in the various samples was recorded in the residual fraction (F6) with a value 0.728mg/kg (RX1) and the least was found on sample RX3 in the water soluble fraction with a value of 0.016mg/kg. The observed trends in the percentage BAF and the mean concentration of the samples in the fractions are RX4 > RX5 > RX3 > RX1 > RX2 and F6 > F3 > F2 > F5 > F4 > F1 respectively. The bioavailable fraction of Ni is generally low since the %BAF of all the samples were below 50% except for samples of road 4 and 5.

TABLE 9: Fractional Concentration of Fe in the Various Soil Samples (mg/kg).

Sample code	F1	F2	F3	F4	F5	F6	Total	Mean	BAF	% BAF
RX1	0.200 ±0.039	9.100 ±0.066	8.100 ±0.142	10.100 ±0.055	4.600 ±0.039	14.000 ±0.123	46.100	7.683	17.400	37.744
RX2	ND	12.380 ±0.060	25.431 ±0.035	42.924 ±0.028	114.618 ±0.146	27.800 ±0.139	223.153	37.192	37.811	16.944
RX3	ND	4.242 ±0.017	15.090 ±0.013	90.741 ±0.002	61.215 ±0.085	255.360 ±0.014	426.648	71.100	19.332	4.531
RX4	ND	14.150 ±0.094	20.916 ±0.058	109.683 ±0.090	76.398 ±0.062	10.840 ±0.457	231.987	38.665	35.066	15.115
RX5	0.200 ±0.022	5.881 ±0.046	9.100 ±0.022	7.000 ±0.056	8.000 ±0.029	10.400 ±0.049	40.581	6.764	15.181	37.409
Total	0.400	45.753	78.637	260.448	264.831	318.400	968.469	161.412	124.790	111.743
Mean	0.080	9.151	15.727	52.090	52.966	63.680	193.694	32.282	24.958	22.349

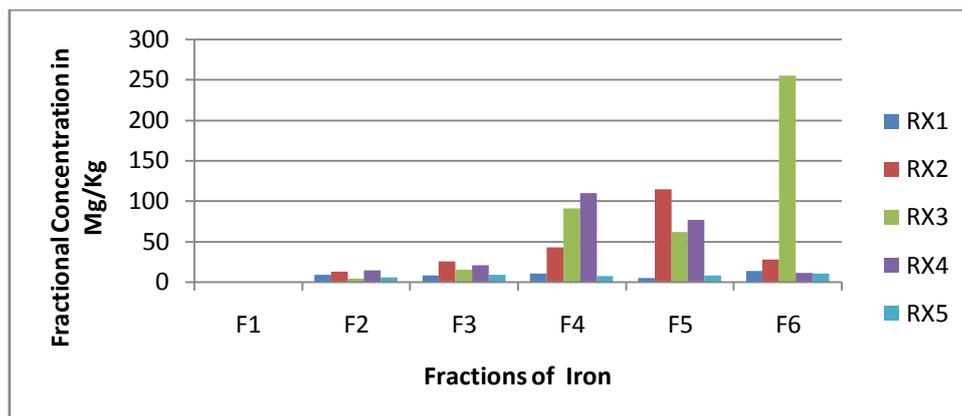


Figure 8: Fractional Concentration of Fe in the Various Soil Samples (mg/kg).

Represented in table 9 is the fractionation pattern of Fe in the soil samples. On the water soluble fraction Fe was not detectable by the FAAS in all the samples except for samples RX1 and RX5, this lead to low mobility of Fe and its low bioavailability.

TABLE 10: Fractional Concentration of Co in the Various Soil Samples (mg/kg).

Sample code	F1	F2	F3	F4	F5	F6	Total	Mean	BAF	% BAF
RX1	0.012 ±0.001	0.215 ±0.005	0.226 ±0.006	0.010 ±0.010	0.030 ±0.003	0.556 ±0.001	1.049	0.181	0.487	44.968
RX2	ND	0.091 ±0.004	0.166 ±0.002	ND	0.024 ±0.004	0.639 ±0.011	0.920	0.153	0.257	27.934
RX3	ND	0.076 ±0.001	6.135 ±0.004	0.016 ±0.001	0.023 ±0.004	0.494 ±0.005	6.744	1.124	6.211	92.097
RX4	0.014 ±0.002	0.126 ±0.002	0.250 ±0.005	0.034 ±0.003	0.039 ±0.004	0.098 ±0.001	0.561	0.094	0.390	69.519
RX5	ND	0.010 ±0.000	0.186 ±0.001	0.002 ±0.002	0.028 ±0.000	0.518 ±0.005	0.744	0.124	0.196	26.344
Total	0.026	0.518	6.963	0.062	0.144	2.305	10.018	1.670	7.507	260.862
Mean	0.005	0.104	1.393	0.012	0.029	0.461	2.004	0.334	1.502	52.172

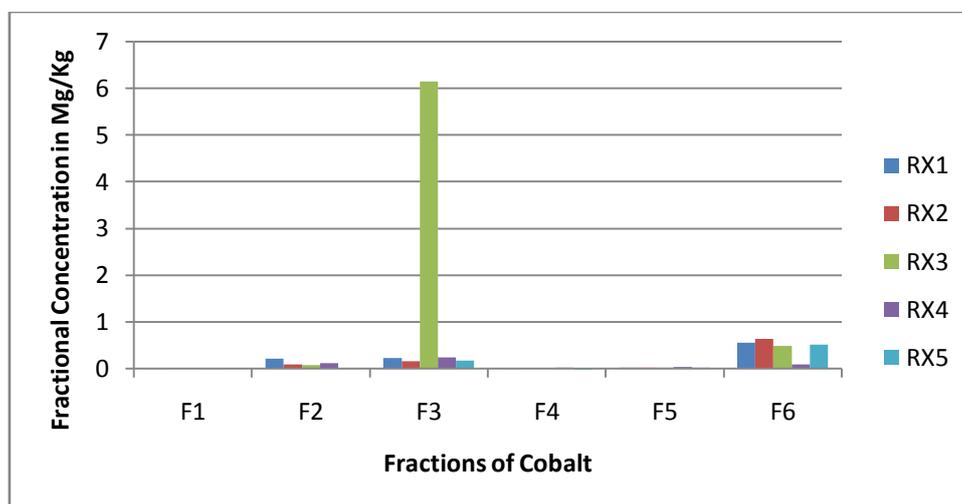


Figure 9: Fractional Concentration of Co in the Various Soil Samples (mg/kg).

It was most in sample RX3 on the residual fraction (255.360mg/kg) while the least value of Fe was found in samples RX1 and RX5 (0.200mg/kg) on their water soluble fractions. The observed trend in the percentage BAF of the samples is RX1 > RX5 > RX2 > RX4 > RX3, while that of the mean concentration of their various fractions is F6 > F5 > F4 > F3 > F2 > F1. Since most of the Fe is associated with the residual fraction, it means that it is mainly from geochemical sources.

The observed trend in the mean concentration of the fractions of Co was F3 > F6 > F2 > F5 > F4 > F1 while the trend in the percentage BAF of the samples is RX3 > RX4 > RX1 > RX2 > RX5 (Table 10). Co had its highest concentration in sample RX3 at the reducible fraction (F3) (6.135mg/kg) and the least value in sample RX5 (0.002mg/kg) also at the reducible fraction, but it was undetectable in samples RX2, RX3 and RX5

in their water soluble fractions (F1) and also in the reducible fraction of sample RX2. The % bioavailable fraction of Co was considerably high since the mean %BAF is 52.172%, though it was low for roads 5 and 2.

TABLE 11: Fractional Concentration of Zn in the Various Soil Samples (mg/kg).

Sample code	F1	F2	F3	F4	F5	F6	Total	Mean	BAF	% BAF
RX1	0.711 ±0.010	0.311 ±0.012	0.623 ±0.006	0.213 ±0.005	0.326 ±0.015	6.321 ±0.002	8.505	1.418	1.645	19.342
RX2	0.082 ±0.011	0.262 ±0.015	0.471 ±0.011	0.370 ±0.015	0.423 ±0.003	15.225 ±0.013	16.833	2.806	0.815	4.842
RX3	0.103 ±0.005	0.249 ±0.002	0.538 ±0.011	0.454 ±0.011	0.437 ±0.008	5.208 ±0.015	6.989	1.164	0.890	12.734
RX4	0.204 ±0.006	0.259 ±0.001	1.375 ±0.014	0.824 ±0.016	0.917 ±0.017	0.330 ±0.005	3.909	0.652	1.838	47.020
RX5	0.166 ±0.012	0.255 ±0.015	0.332 ±0.002	0.232 ±0.005	0.365 ±0.008	8.133 ±0.005	9.483	1.581	0.753	7.941
Total	1.266	1.694	3.339	2.093	2.468	35.217	46.077	7.680	6.299	91.879
Mean	0.253	0.339	0.668	0.419	0.494	7.043	9.216	1536	1.260	18.376

The fractional concentration of Zn in the various soil samples represented by table 11 showed that most of the zinc concentration was found in the residual fractions. The mean concentration is 7.043mg/kg at the residual fraction and the least was in the water soluble fraction with a value of 0.253mg/kg.

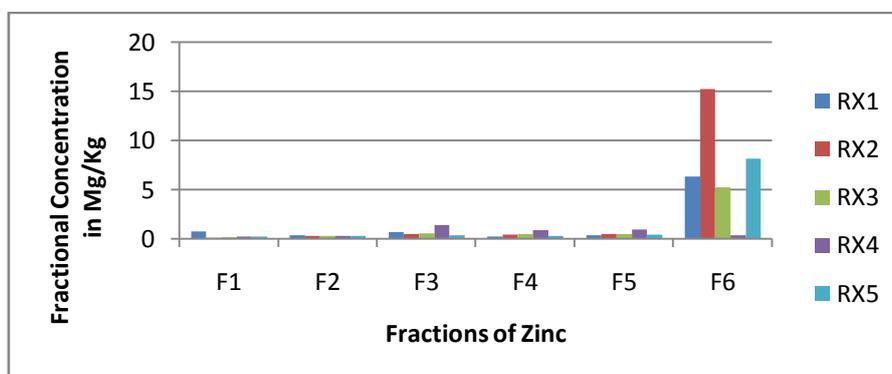


Figure 10: Fractional Concentration of Zn in the Various Soil Samples (mg/kg).

TABLE 12: Fractional Concentration of Cr in the Various Soil Samples (mg/kg).

Sample code	F1	F2	F3	F4	F5	F6	Total	Mean	BAF	% BAF
RX1	0.055 ±0.015	0.050 ±0.001	0.160 ±0.006	0.210 ±0.004	0.271 ±0.011	0.623 ±0.018	1.369	0.228	0.265	19.357
RX2	0.018 ±0.025	0.060 ±0.000	0.154 ±0.008	0.141 ±0.003	0.305 ±0.020	0.874 ±0.014	1.552	0.259	0.232	14.948
RX3	0.027 ±0.016	0.070 ±0.022	0.147 ±0.021	0.240 ±0.011	0.167 ±0.000	0.643 ±0.000	1.294	0.216	0.244	18.856
RX4	0.040 ±0.003	0.103 ±0.004	0.170 ±0.026	0.311 ±0.010	0.245 ±0.003	0.103 ±0.017	0.972	0.162	0.313	32.202
RX5	0.010 ±0.000	0.011 ±0.002	0.110 ±0.009	0.189 ±0.016	0.266 ±0.008	0.682 ±0.003	1.268	0.211	0.131	10.331
Total	0.150	0.294	0.741	1.091	1.254	2.925	6.455	1.076	1.185	95.694
Mean	0.030	0.059	0.148	0.218	0.251	0.585	1.291	0.215	0.237	19.139

The observed trend in the percentage BAF in the various samples is RX4 > RX1 > RX3 > RX5 > RX2 while the trend for the mean fractional concentration is F6 > F3 > F5 > F4 > F2 > F1. Generally the %BAF of Zn in the samples was low and so led to a mean %BAF of 18.376%. Figure 10 shows the speciation pattern of Zn in the various fractions of the soil samples and it showed that the residual fraction had the most occurrences.

In table 12, the highest fractional concentration of Cr (mean 0.585mg/kg) is found in the residual fraction. The least mean concentration was found in the water soluble fraction (0.030mg/kg).

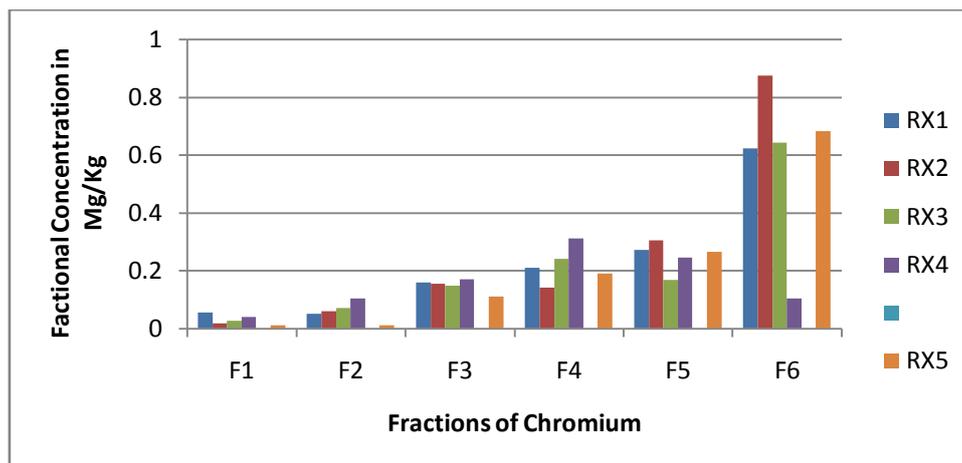


Figure 11: Fractional Concentration of Cr in the Various Soil Samples (mg/kg).

Figure 11, indicated that, the concentration was on the increase from F1 through F6. The observed trend in the mean concentration of Cr in the various fractions is $F6 > F5 > F4 > F3 > F2 > F1$. The speciation followed a particular pattern and the %BAF of Cr in all the soil samples was generally low with a mean 19.139% (Table 12).

TABLE 13: Fractional Concentration of Cd in the Various Soil Samples (mg/kg).

Sample code	F1	F2	F3	F4	F5	F6	Total	Mean	BAF	% BAF
RX1	ND	0.021 ±0.002	0.033 ±0.001	ND	ND	0.042 ±0.001	0.096	0.016	0.054	56.250
RX2	ND	0.023 ±0.003	0.049 ±0.002	ND	ND	0.061 ±0.004	0.133	0.022	0.072	54.135
RX3	ND	0.026 ±0.001	0.050 ±0.001	ND	ND	0.057 ±0.000	0.133	0.022	0.076	57.143
RX4	ND	0.041 ±0.006	0.034 ±0.001	ND	0.007 ±0.000	0.025 ±0.006	0.107	0.018	0.075	70.093
RX5	ND	0.011 ±0.002	0.033 ±0.001	ND	0.001 ±0.000	0.085 ±0.000	0.130	0.022	0.044	33.845
Total	ND	0.122	0.199	ND	0.008	0.270	0.599	0.100	0.321	271.466
Mean	ND	0.024	0.040	ND	0.002	0.054	0.120	0.020	0.064	54.293

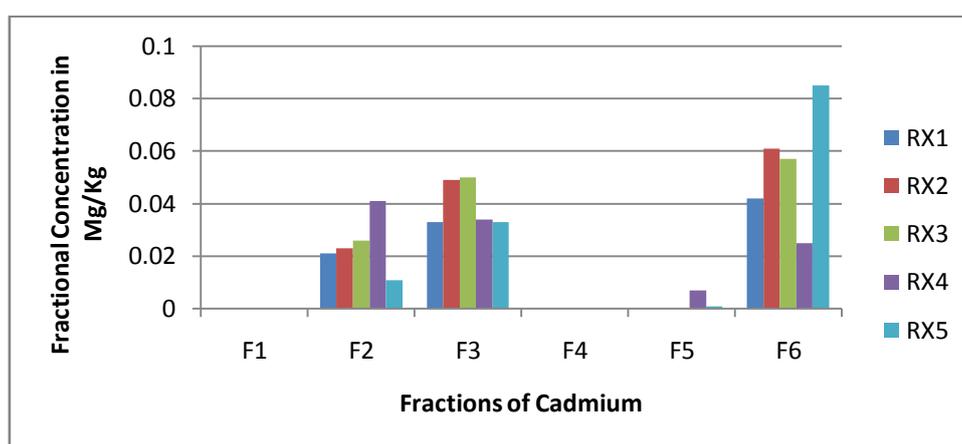


Figure 12: Fractional Concentration of Cd in the Various Soil Samples (mg/kg).

Cd was undetectable at the water soluble fraction and at the reducible fraction in all the samples (Table 13), so also it is in the oxidisable fraction except on samples RX4 and RX5. The trend in the mean concentration of Cd was $F6 > F3 > F2 > F5 > F4 > F1$. Figure 27, indicated that the speciation was more in the residual fraction followed by the carbonate fraction. Even though Cd was undetectable at the water soluble fraction, its %BAF was still high with a mean of 54.293%, suggesting that Cd is potentially bioavailable in the studied area.

TABLE 14: Percentage Bioavailability of Metal Concentration in the Soil Samples.

Sample code	Cu	Ca	Mn	Pb	Ni	Fe	Co	Zn	Cr	Cd
RX1	38.909	58.072	31.707	80.080	39.112	37.744	44.968	19.342	19.357	56.250
RX2	59.311	46.107	30.987	26.918	31.396	16.944	27.934	4.842	14.948	54.135
RX3	34.551	65.186	29.147	49.553	39.228	4.531	92.097	12.734	18.856	57.143
RX4	36.253	18.008	36.939	8.364	65.831	15.115	69.519	47.020	32.202	70.093
RX5	30.668	63.075	36.921	81.422	54.380	37.409	26.344	7.941	10.331	33.845
GT	199.692	250.448	165.701	246.337	229.947	111.743	260.862	91.879	95.694	271.466
GM	39.938	50.090	33.140	49.267	45.989	22.349	52.172	18.376	19.139	54.293

GT = Ground Total and GM = Ground Mean.

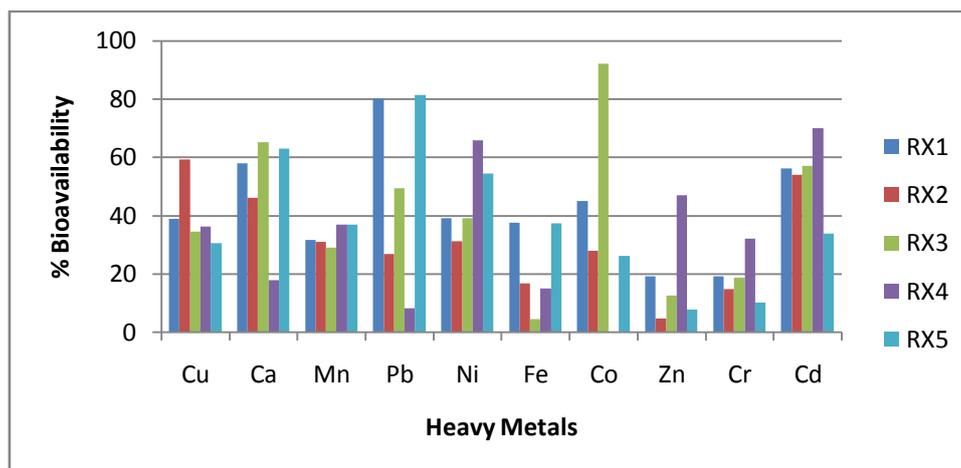


Figure 13: Percentage Bioavailability of Metal Concentration in the soil Samples.

We observed that Cd is the most available metal for organism’s uptake in the studied area since it had the highest %BAF in the soil samples (Erwin, 2006). The trends in the percentage bioavailability of the various heavy metals are as follows: for RX1 it was Pb > Ca > Cd > Co > Ni > Cu > Fe > Mn > Cr > Zn, and for RX2, it was – Cu > Cd > Ca > Ni > Mn > Co > Pb > Fe > Cr > Zn, for RX3, it was Co > Ca > Cd > Pb > Ni > Cu > Mn > Cr > Zn > Fe, while for RX4 and RX5 it was Cd > Co > Ni > Zn > Mn > Cu > Cr > Ca > Fe > Pb, and Pb > Ca > Ni > Fe > Mn > Cd > Cu > Co > Cr > Zn respectively.

It can be inferred from the trends that Zn had the least bioavailable fractions in most of the soil samples. Cd recorded the highest ground mean concentration (54.213%) and the least was found in Zinc (18.376%). The trend of the ground mean percentage bioavailability for the various heavy metals was Cd > Co > Ca > Pb > Ni > Cu > Mn > Fe > Cr > Zn.

Correlation analysis was conducted to determine the extent of the relationship among metal fractions and among metals in the soils over the studied area. A probability of less than 5% ($P > 0.05$) was considered to be statistically significant.

Cu – In the correlation of various fractions of Cu in the soil samples, we observed that there was no significant difference in the result at 95% confidence interval in all the fractions. **Ca** – There was no significant difference in the correlation of the various fractions of Ca in the soil samples. **Mn** – The correlations of the various fractions of manganese in the soil samples indicated that there was no significance difference. **Pb** – There was a positive significance difference in the correlation between the reducible fraction and the oxidizable fraction of the soil samples. **Ni** – In the correlation of various fractions of nickel in the soil samples, there was positive significance difference in the carbonate and the reducible fractions. **Fe** - The correlation of the oxidizable fraction of Fe and the water soluble fraction of Fe was positively significant in the soil samples and between the carbonate and the oxidisable fractions but, negatively significant between the water soluble and the oxidisable fractions. **Co** – The correlation of the various fractions of Co in the soil samples shows a positive significance difference between the exchangeable fraction and the water soluble fraction, **Zn** – The Correlation of zinc fractions in the soil sample shows that it was positively significant between their oxidisable fractions. The correlation also showed a positive significant difference between carbonate and exchangeable, oxidisable and exchangeable, oxidisable and carbonate and between reducible and the residual fractions. The T-test indicates no significance in all. **Cr** – in the correlations of Cr, there was positive significant difference between the residual and the water soluble fraction in the soil samples. **Cd** - The T-test showed a positive relationship between all the fractions of the soil samples.

IV. Conclusion

The ANOVA indicates that Ca had a significant mean difference in the water soluble fractions of the soil samples and so also it is in the exchangeable fractions of the soil samples. Fe was also significant in the exchangeable fraction. But in the carbonate bound, reducible, oxidisable and residual fractions, it was only Fe that had a significant mean difference at 95% confidence interval in the soil samples. This suggests that there are several location (sites) having greater Ca and Fe concentration and the soil have been contaminated more severely by these metals, Though Ca and Fe are among the micronutrient elements. This means that the human activities in and around the area have significant effects on the level of almost all metals in the soils over this studied area. The speciation of Ca was different as the concentration was evenly distributed in all the fractions of the soil samples and speciation of Cu showed higher concentration in the water soluble fraction in the soil samples.

Further work is recommended in the area with reference to the heavy metal speciation some centimetres (about 30cm) below the soil surface so as to determine the solubility as well as the bioavailability of these metals.

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