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Assessment of the Fractionation Patterns and Effects of Leaching Of Some Selected Heavy Metals in Owerri Industrial Layout, Nigeria

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***Abstract**: Fractionation of Cu, Ca, Mn, Pb, Ni, Fe, Co, Zn, Cr, and Cd was carried out on 30cm depth soil samples collected along the major roads of Owerri Industrial layout, Nigeria, with a sequential extraction procedure in the rainy (April to July) season, using atomic absorption spectroscopy. The pH of the soil had a range of 6.2 to 6.8 while moisture content had a range of 10.023to 13.782. Fe was discovered to occur at elevated concentrations in all the soil samples with the highest concentration (1462.480mg/kg). The metal with least concentration (0.067mg/kg) was Cd. Ca (52.070) was mostly abundant in the Exchangeable fraction while Cu (1.984mg/kg), Mn (12.169mg/kg), Pb (3.013mg/kg), Ni (3.845mg/kg), Fe (1360.790mg/kg), Co (3.871mg/kg), Zn (46.259mg/kg), Cr (3.817mg/kg) and Cd (0.257mg/kg) were mostly abundant in Residual fraction. From the fractionation results, most of the metals had high abundance in Residual fraction indicating lithogenic origin and low bioavailability of the metals considered. The average potential mobility was calculated for the metals in the soil 30cm depth and it was in the order: Ca>Cd>Cu>Pb>Mn>Co>Fe>Ni>Cr>Zn*

***Keywords:** bioavailability, concentration, extraction, residual, sequential.*

I. Introduction

In soils, elements of interest exist in several different forms and are associated with a range of components [1]. Heavy metals concentration in soil are associated with biological and geochemical cycles and are influenced by anthropogenic activities such as agricultural practices, industrial activities and waste disposal methods [2]. Speciation can be defined as identification and quantification of the different species or forms of phases in which the elements occur. It is generally recognized that information about the physico-chemical forms of the elements is required for understanding their mobility, pathways and bioavailability. Studies on the distribution and speciation of heavy metals in soil can provide not only information on the degree of pollution, but specially the actual environmental impact, metal bioavailability as well as their origin [3]. Speciation techniques were useful in studies of metal partitioning, distribution, accumulation, and mobility in soil to support hypothesis and to gain a better understanding on the different processes and mechanism hypothesized. Today it is generally recognized that the particular behaviour of trace metals in the environment is determined by their specific physicochemical forms rather than by their total concentration. Speciation of metals largely determines their bioavailability and toxicity [1].

Heavy metals usually occur in soil at low concentration as a result of weathering and other pedigenic processes acting as the parent materials on which the soil develops. The natural occurrence of heavy metals varies between rock types and certain bed-rocks which provide exceptionally high metal concentration to overlying soils. Soils are clearly of enormous environmental importance, being the media that support virtually all plants life; hence their potential for environmental pollution requires attention [4, 5]. While soils are important sinks for heavy metals, they can also release them into the ecosystem. It is therefore important to understand the content, chemistry and geology of heavy metals in soil as well as the chemical forms. However, the determination of specific chemical species or binding forms is difficult and often virtually impossible. For this reason, sequential extraction procedures are commonly applied because they provide information about the fractionation of metals in the different lattices of the solid sample, which is a good compromise method that gives information on the environmental contamination [6, 7]. Polluted soils constitute major environmental problems and therefore are subjected to detailed risk assessment and management studies.

In this paper, soil samples collected from five major roads of Owerri industrial layout were examined to systematically study the speciation of some heavy metals in the soil which allows a distinction to be made between residual metals (insoluble forms) and metal bound to organic matter, iron and manganese oxide, carbonate and exchangeable, water soluble (soluble forms). This evaluation gives a relative distribution of Cu, Ca, Mn, Pb, Ni, Fe, Co, Zn, Cr, and Cd fraction in the soluble (bioavailable) and insoluble (non-bioavailable form) using FAAS to assess their potential environmental impacts. This is in continuation of the recommendation made by Abugu, et al (2012) in the ''evaluation of the speciation patterns of some heavy metals along the major roads of Owerri industrial layout''

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(3:1) 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 [8].

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 6.2 to 6.8 in water indicating of slight acidity to neutrality. The moisture contents fell within the range of 10.023% to 13.782%. Looking at table 1, it showed that sample RY1 – RY5 had relatively high values of moisture contents indicating that the samples were collected during the rainy season and as well 30cm depth from soil surface.

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

Sample code	% Moisture Content	pH
R1Y	13.782	6.2
R2Y	12.280	6.3
R3Y	11.289	6.8
R4Y	11.785	6.5
R5Y	10.023	6.7

NOTE: R is refer to as road were the sample was collected, Numbers 1 – 5 represent the road numbers, and Y represent the soil sample 30cm depth.

Table 2: Total Metal Concentration for Soil 30cm Depth (mg/kg).

Sample code	Cu	Ca	Mn	Pb	Ni	Fe	Co	Zn	Cr	Cd	Total	Mean
RY1	0.566 ±0.002	1.250 ±0.004	5.220 ±0.000	1.432 ±0.011	1.528 ±0.005	6.300 ±0.012	1.192 ±0.051	2.911 ±0.013	1.890 ±0.009	0.092 ±0.000	22.381	2.238
RY2	0.374 ±0.004	0.634 ±0.019	4.037 ±0.059	2.111 ±1.128	1.396 ±0.022	830.280 ±0.069	1.172 ±0.029	1.487 ±0.054	1.348 ±0.033	0.148 ±0.003	842.847	84.299
RY3	0.811 ±0.004	0.306 ±0.007	16.291 ±0.031	2.709 ±0.749	1.685 ±0.002	1450.360 ±0.003	1.399 ±0.005	3.423 ±0.008	4.326 ±0.004	0.164 ±0.011	1481.474	148.147
RY4	0.846 ±0.002	0.285 ±0.015	4.578 ±0.054	1.558 ±0.031	1.526 ±0.027	1462.480 ±0.162	1.254 ±0.018	3.069 ±0.001	3.759 ±0.004	0.158 ±0.004	1479.516	147.952
RY5	0.744 ±0.001	0.910 ±0.011	5.330 ±0.005	1.308 ±0.001	0.492 ±0.051	6.321 ±0.031	1.247 ±0.018	2.621 ±0.002	3.111 ±0.001	0.160 ±0.004	22.244	2.224
Total	3.344	3.389	35.456	9.118	6.627	3755.741	6.264	13.511	14.434	0.722	**3848.602**	
Mean	0.669	0.677	7.091	1.824	1.325	751.148	1.253	2.702	2.887	0.144	**769.72**	

The FAAS (Analyst 200) analysis result of the soil samples 30cm depth are as tabulated (Table 2) and shown statistically in figure 1. It was observed that Fe had the maximum concentration (6.300mg/kg, 830.280mg/kg, 1450.350mg/kg, 1462.480mg/kg, and 6.321mg/kg in samples RY1, RY2, RY3, RY4 and RY5 respectively), Cd had the least concentration (0.092mg/kg, 0.148mg/kg, 0.164mg/kg, 0.158mg/kg and 0.160mg/kg in RY1, RY2, RY3, RY4 and RY5 respectively also). The observed trends in the various samples are as follows: Fe > Mn > Zn > Cr > Ni > Pb > Ca > Co > Cu > Cd for sample RY1, Fe > Mn > Pb > Zn > Ni > Cr > Co > Ca > Cu > Cd for sample RY2, Fe > Mn > Cr > Zn > Pb > Ni > Co > Cu > Ca > Cd for sample RY3 while Fe > Mn > Cr > Zn > Pb > Ni > Co > Cu > Ca > Cd and Fe > Mn > Cr > Zn > Pb > Co > Ca > Cu > Ni > Cd are for RY4 and RY5 respectively. The observed trend in the metal mean concentrations of the various soil samples 30cm depth was Fe > Mn > Cr > Zn > Pb > Ni > Co > Ca > Cu > Cd.

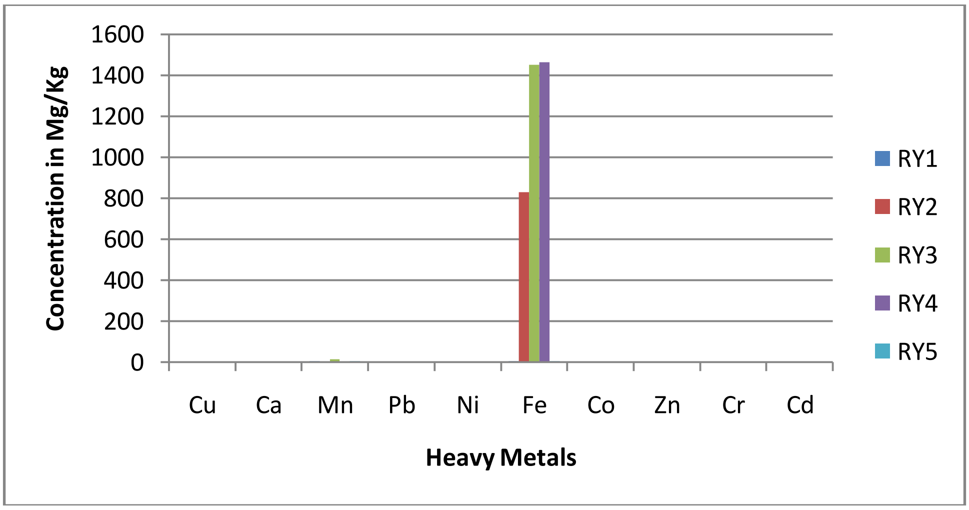

Figure 1: Total Metal Concentration for Soil 30cm Depth.

Figure 1 shows the mean metal concentrations with Fe having the most elevated concentration in almost all the soil sample and Ca being the next with Cd having the least concentration in almost all the soil samples.

Table 3: Percentage Total Metal Concentration 30cm Depth

Sample code	Cu	Ca	Mn	Pb	Ni	Fe	Co	Zn	Cr	Cd
RY1	2.529	5.585	23.323	6.398	6.827	28.149	5.326	13.007	8.445	0.411
RY2	0.044	0.075	0.479	0.250	0.166	98.493	0.139	0.176	0.160	0.018
RY3	0.055	0.021	1.100	0.183	0.114	97.900	0.094	0.231	0.292	0.011
RY4	0.057	0.019	0.309	0.105	0.103	98.849	0.085	0.207	0.254	0.011
RY5	3.345	4.046	23.962	5.880	2.212	28.417	5.606	11.783	13.986	0.719

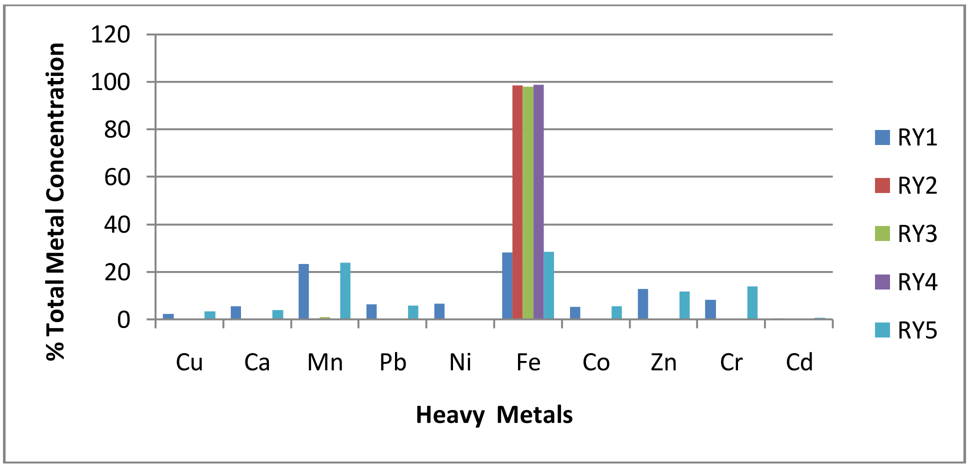

Figure 2: Percentage Total Metal Concentration of Soil 30cm Depth

The fractional concentration of Cu in the soil 30cm depth is as presented in table 4. Here much of the copper was associated with the residual fraction (F6) with a mean value of 0.387mg/kg. Cu was not detected in samples RY3 and RY4 at the water soluble fraction. The observed trend in the range of concentration of copper was F6 > F2> F5 > F3 > F4 > F1. The %BAF of Cu in all the samples followed the trend RY1 > RY4 > RY5 > RY2 > RY3. The mean %BAF is 37.281 and so was generally low for most of the samples.

Table 4: Fractional Concentration of Cu in the Various Soils 30cm Depth (mg/kg).

Sample code	F1	F2	F3	F4	F5	F6	Total	Mean	BAF	%BAF
RY1	0.011 ±0.001	0.081 ±0.001	0.180 ±0.000	0.099 ±0.003	0.136 ±0.004	0.212 ±0.002	0.719	0.090	0.272	50.464
RY2	0.001 ±0.003	0.096 ±0.000	0.137 ±0.000	0.082 ±0.002	0.144 ±0.001	0.382 ±0.093	0.842	0.140	0.234	27.791
RY3	ND	0.050 ±0.004	0.120 ±0.000	0.078 ±0.003	0.225 ±0.001	0.648 ±0.003	1.121	0.187	0.170	15.165
RY4	ND	0.407 ±0.003	0.128 ±0.000	0.045 ±0.000	0.117 ±0.001	0.360 ±0.003	1.057	0.176	0.535	50.615
RY5	0.029 ±0.001	0.550 ±0.000	0.151 ±0.002	0.110 ±0.003	0.550 ±0.005	0.333 ±0.008	1.723	0.287	0.730	42.368
Total	0.041	1.184	0.716	0.414	1.172	1.935	5.462	0.910	1.941	186.403
Mean	0.008	0.237	0.143	0.083	0.234	0.387	1.092	0.182	0.388	37. 281

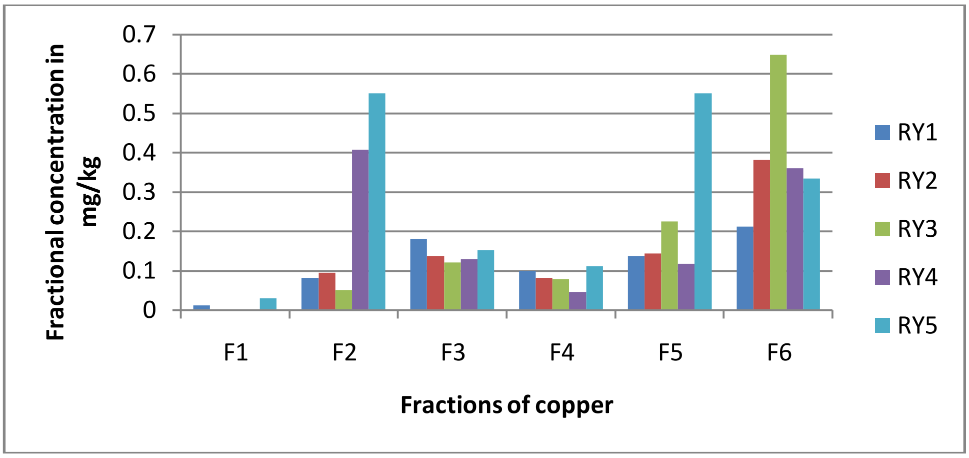

Figure 3: Fractional Concentration of Cu in the Various Soils 30cm Depth (mg/kg).

Represented in table 5 is the fractional concentration of Ca in soil sample 30cm depth. Sample RY2 had the highest concentration of Ca (18.900mg/kg) in the fraction and the least was recorded in sample RY3 (0.008mg/kg) in the carbonate fraction though undetectable in sample RY4 at the carbonate bound fraction and so also it is in samples RY3 and RY4 at the oxidizable fraction.

Table 5: Fractional Concentration of Ca in the Various Soils 30cm Depth (mg/kg).

Sample code	F1	F2	F3	F4	F5	F6	Total	Mean	BAF	%BAF
RY1	6.770 ±0.046	7.880 ±0.019	0.222 ±0.032	1.268 ±0.081	0.923 ±0.004	0.322 ±0.002	17.385	2.898	14.872	85.545
RY2	9.382 ±0.295	10.857 ±0.084	1.172 ±0.016	2.442 ±0.059	0.579 ±0.006	0.250 ±0.026	24.682	4.114	21.411	86.747
RY3	4.599 ±0.052	18.900 ±0.085	0.008 ±0.008	0.309 ±0.012	ND	0.338 ±0.008	24.154	4.026	23.507	97.321
RY4	12.096 ±0.058	5.212 ±0.080	ND	0.905 ±0.009	ND	0.326 ±0.019	18.539	3.090	17.308	93.360
RY5	8.966 ±0.049	9.221 ±0.088	0.962 ±0.001	0.668 ±0.006	0.323 ±0.021	0.216 ±0.019	20.356	3.393	19.149	94.071
Total	41.813	52.070	2.364	5.592	1.825	1.452	105.116	17.519	96.247	457.044
Mean	8.363	10.414	0.473	1.118	0.365	0.290	21.023	3.504	19.250	91.409

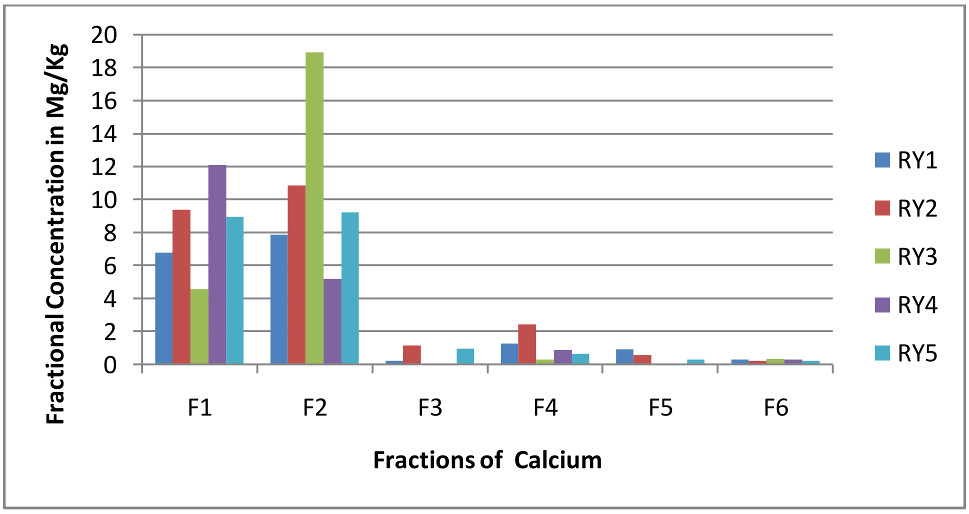

Figure 4: Fractional Concentration of Ca in the Various Soils 30cm Depth (mg/kg).

The exchangeable fraction recorded the meanest value (10.414mg/kg) and the residual fraction had the least (0.290mg/kg). The observed trend in the mean concentration of Ca in the various fractions was F2 > F1 > F4 > F4 > F5 > F6. From the table, it can be observed that the %BAF of all samples are very high and so we can infer that Ca is very bioavailable in the studied area. This is also supported by the low values recorded in the residual fractions (F6) of Ca. Figure 4 shows that Ca fractionated more in the water soluble and the exchangeable fractions (F1 and F2).

Table 6: Fractional Concentration of Mn in the Various Soils 30cm Depth (mg/kg).

Sample code	F1	F2	F3	F4	F5	F6	Total	Mean	BAF	%BAF
RY1	0.121 ±0.012	0.819 ±0.010	0.925 ±0.003	1.321 ±0.008	1.668 ±0.012	2.661 ±0.006	7.515	1.253	1.865	24.817
RY2	0.153 ±0.009	0.589 ±0.011	0.966 ±0.019	0.937 ±0.012	1.012 ±0.033	1.653 ±0.038	5.310	0.885	1.708	32.166
RY3	0.262 ±0.001	0.416 ±0.010	1.018 ±0.017	1.214 ±0.011	1.176 ±0.100	2.826 ±0.036	6.912	1.152	1.696	24.537
RY4	0.120 ±0.003	1.976 ±0.027	0.669 ±0.017	0.677 ±0.022	0.911 ±0.003	2.718 ±0.064	7.071	1.179	2.765	39.103
RY5	0.216 ±0.016	1.233 ±0.012	0.923 ±0.031	1.102 ±0.021	0.988 ±0.023	2.311 ±0.003	6.773	1.129	2.372	35.021
Total	0.872	5.033	4.501	5.251	5.755	12.169	33.591	5.597	10.406	155.644
Mean	0.174	1.007	0.900	1.050	1.151	2.434	6.716	1.119	2.081	31.129

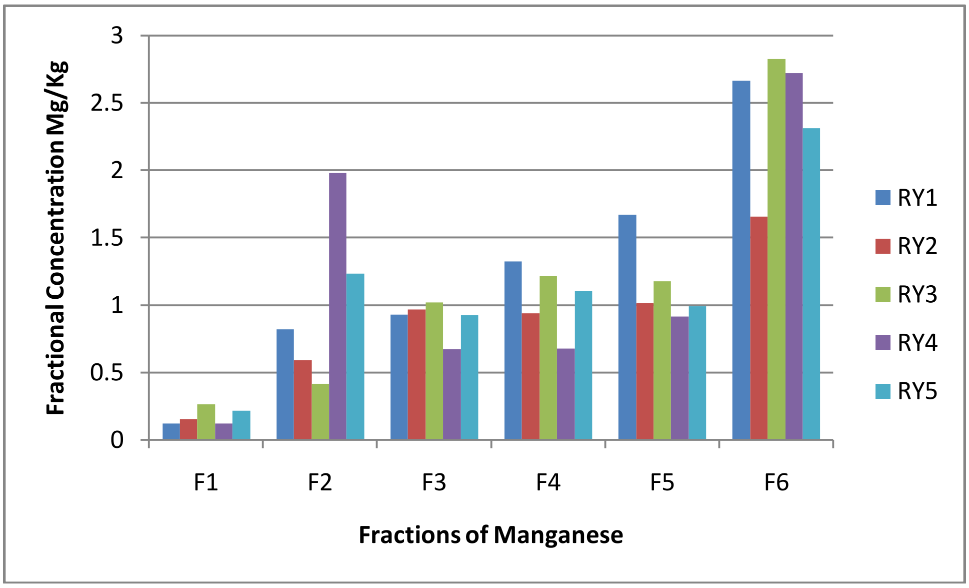

Figure 5: Fractional Concentration of Mn in the Various Soils 30cm Depth (mg/kg).

The fractional concentration of Mn showed that Mn concentration was most in the residual fraction with a mean value of 2.434mg/kg, and least in the water soluble fraction (0.174mg/kg). The observed trend in the mean concentration of Mn in the various fractions is F6 > F5 > F4 > F2 > F3 > F1 (Table 6). Also the observed trend in the %BAF of the samples is RY4 > RY5 > RY2 > RY1 > RY3. We can infer that the Mn in the studied area fractionated more in the residual and so are from geochemical sources.

Table 7: Fractional Concentration of Pb in the Various Soils 30cm Depth (mg/kg).

Sample code	F1	F2	F3	F4	F5	F6	Total	Mean	BAF	%BAF
RY1	ND	0.042 ±0.002	0.204 ±0.014	ND	ND	0.802 ±0.066	1.048	0.175	0.246	23.473
RY2	ND	ND	0.048 ±0.019	ND	ND	0.265 ±0.008	0.313	0.052	0.048	15.335
RY3	ND	ND	0.178 ±0.006	ND	ND	0.756 ±0.029	0.934	0.156	0.178	19.058
RY4	ND	0.804 ±0.002	0.208 ±0.034	ND	ND	0.667 ±0.018	1.679	0.280	1.012	60.274
RY5	ND	0.542 ±0.011	0.062 ±0.008	0.006 ±0.002	ND	0.523 ±0.016	1.133	0.189	0.604	53.310
Total	0.000	1.388	0.700	0.006	0.000	3.013	5.107	0.851	2.088	171.423
Mean	0.000	0.278	0.140	0.001	0.000	0.603	1.022	0.170	6.418	34.285

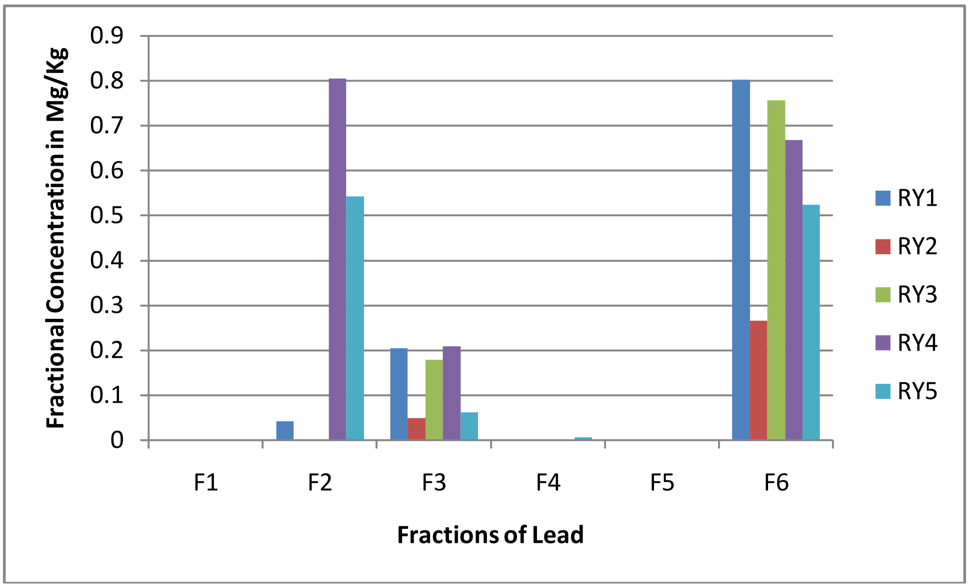

Figure 6: Fractional Concentration of Pb in the Various Soils 30cm Depth (mg/kg).

Table 7 showed that Pb was undetectable in the water soluble and the oxidisable fraction in all the samples. It was also undetectable in the reducible fraction except in sample RY5. The residual fraction had the meanest concentration of Pb (0.603mg/kg) and the least in reducible fraction (0.001mg/kg). The observed trend was F6 > F2 > F3 > F4 > F5 > F1. This suggests that most Pb in the studied area is from geochemical sources. The bioavailability of Pb is generally low except for sample RY4 and RY5 were the %BAF is slightly above 50%.

Table 8: Fractional Concentration of Ni in the Various Soils 30cm Depth (mg/kg).

Sample code	F1	F2	F3	F4	F5	F6	Total	Mean	BAF	%BAF
RY1	0.043 ±0.003	0.136 ±0.006	0.418 ±0.004	1.989 ±0.003	0.609 ±0.006	0.638 ±0.005	3.833	0.639	0.597	15.575
RY2	0.037 ±0.001	0.115 ±0.008	0.206 ±0.003	0.035 ±0.006	0.057 ±0.002	0.642 ±0.013	1.092	0.182	0.358	32.784
RY3	0.018 ±0.001	0.094 ±0.002	0.210 ±0.005	0.045 ±0.001	0.070 ±0.003	0.982 ±0.011	1.419	0.237	0.322	22.692
RY4	0.033 ±0.008	0.507 ±0.006+	0.218 ±0.009	0.020 ±0.000	0.069 ±0.000	0.859 ±0.011	1.706	0.284	0.758	44.431
RY5	0.039 ±0.001	0.124 ±0.009	0.328 ±0.008	0.309 ±0.003	0.810 ±0.008	0.724 ±0.005	2.334	0.389	0.491	21.037
Total	0.170	0.976	1.380	2.398	1.615	3.845	10.384	1.731	2.526	136.519
Mean	0.034	0.195	0.276	0.480	0.323	0.769	2.077	0.346	0.505	27.304

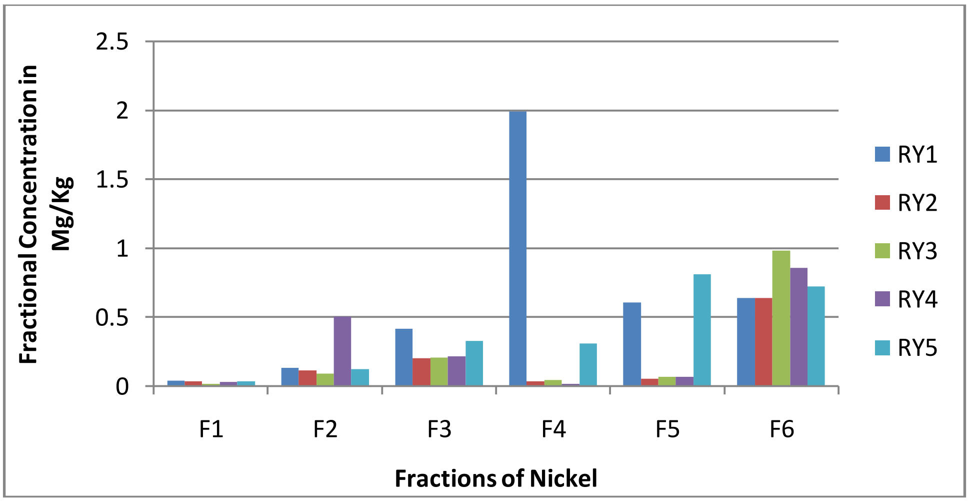

Figure 7: Fractional Concentration of Ni in the Various Soils 30cm Depth (mg/kg).

Ni recorded its highest concentration in the residual fraction were the mean concentration is 0.769mg/kg and the least in the water soluble fraction (Table 8). The trend in the mean concentration of the various fractions of Ni is F6 > F4 > F5 > F3 > F2 > F1. Considering the %BAF, it can be inferred that the non-bioavailable fractions is higher than those of bioavailable fraction since the % BAF of all the samples were below 50%, and the mean %BAF is 27.304.

Table 9: Fractional Concentration of Fe in the Various Soils 30cm Depth (mg/kg).

Sample code	F1	F2	F3	F4	F5	F6	Total	Mean	BAF	%BAF
RY1	0.200 ±0.010	8.900 ±0.023	7.400 ±0.556	5.300 ±0.096	12.300 ±0.112	5.400 ±0.014	39.500	6.583	16.500	41.772
RY2	ND	8.837 ±0.037	13.062 ±0.012	31.941 ±0.045	76.839 ±0.085	270.480 ±0.042	401.159	66.860	21.899	5.459
RY3	ND	8.103 ±0.052	21.714 ±0.013	102.039 ±0.129	14.694 ±0.090	717.060 ±0.076	863.610	143.935	29.817	3.453
RY4	ND	279.300 ±0.169	69.237 ±0.044	45.171 ±0.044	203.040 ±0.156	360.150 ±0.196	956.898	159.483	348.537	36.424
RY5	0.600 ±0.019	7.500 ±0.085	9.500 ±0.001	7.500 ±0.065	2.000 ±0.121	7.700 ±0.015	34.480	5.800	17.600	51.044
Total	0.800	312.640	120.913	191.951	308.873	1360.790	2295.967	382.661	434.353	138.152
Mean	0.160	62.528	24.182	38.390	61.775	272.159	459.194	76.532	86.870	27.630

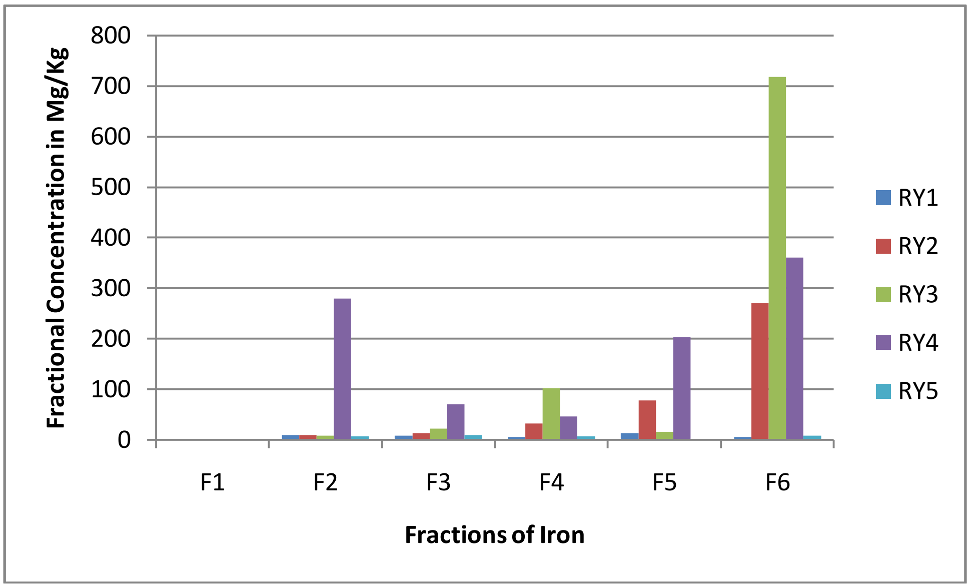

Figure 8: Fractional Concentration of Fe in the Various Soils 30cm Depth (mg/kg).

The residual fraction had the most concentration of Fe with a mean value of 272.159mg/kg while the least was found in the water soluble fraction (0.160mg/kg) (Table 9). This indicates a high level of non-bioavailable fractions of Fe and so may be from geochemical sources. The %BAF of Fe were generally low (below 50%) for all the samples except for RY5 which was 51.044%. Fe was not detectable in samples RY2, RY3 and RY4 in the water soluble fractions.

Table 10: Fractional Concentration of Co in the Various Soils 30cm Depth (mg/kg).

Sample code	F1	F2	F3	F4	F5	F6	Total	Mean	BAF	%BAF
RY1	0.016 ±0.001	0.079 ±0.002	0.216 ±0.002	0.025 ±0.001	0.015 ±0.000	0.778 ±0.001	1.130	0.188	0.311	27.547
RY2	ND	0.070 ±0.002	0.143 ±0.002	ND	0.007 ±0.002	0.526 ±0.010	0.746	0.124	0.213	28.552
RY3	0.018 ±0.006	0.090 ±0.000	0.224 ±0.001	0.025 ±0.001	0.051 ±0.002	0.930 ±0.028	1.338	0.223	0.332	24.141
RY4	0.010 ±0.000	0.504 ±0.013	0.275 ±0.003	0.007 ±0.003	0.054 ±0.002	0.785 ±0.005	1.635	0.273	0.789	48.257
RY5	0.013 ±0.003	0.086 ±0.002	0.179 ±0.001	0.005 ±0.001	0.029 ±0.002	0.852 ±0.002	1.164	0.194	0.278	23.883
Total	0.057	0.829	1.037	0.062	0.156	3.871	6.012	1.002	1.923	152.380
Mean	0.011	0.166	0.207	0.012	0.031	0.774	1.201	0.200	0.384	30.476

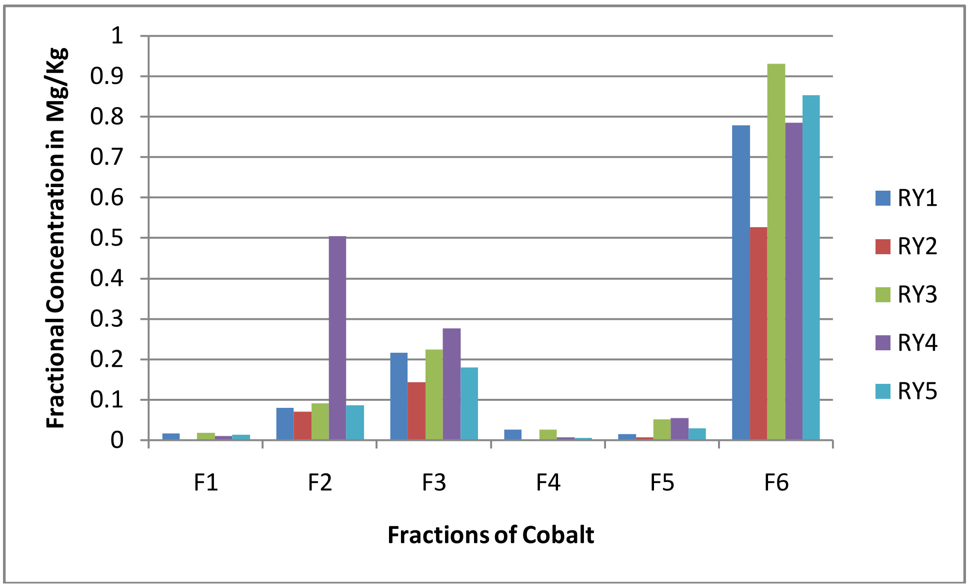

Figure 9: Fractional Concentration of Co in the Various Soil 30cm Depth (mg/kg).

Co was not detectable at the water soluble and reducible fractions in sample RY2 and the meanest concentration was recorded in the residual fraction (0.774mg/kg) (table 10), while the least mean was in the water soluble fraction (0.011mg/kg). The %BAF of Co was also generally low as the value for the samples were below 50%.

Table 11: Fractional Concentration of Zn in the Various Soil 30cm Depth (mg/kg).

Sample code	F1	F2	F3	F4	F5	F6	Total	Mean	BAF	%BAF
RY1	0.662 ±0.000	0.216 ±0.001	0.266 ±0.004	0.320 ±0.005	0.420 ±0.002	7.985 ±0.003	9.869	1.645	1.144	11.592
RY2	0.077 ±0.004	0.246 ±0.006	0.249 ±0.001	0.344 ±0.014	0.370 ±0.009	7.098 ±0.001	8.384	1.397	0.572	6.823
RY3	0.104 ±0.006	0.314 ±0.000	0.423 ±0.011	0.402 ±0.023	0.481 ±0.009	9.975 ±0.011	11.699	1.950	0.841	7.189
RY4	0.012 ±0.006	6.594 ±0.004	0.328 ±0.001	0.189 ±0.009	0.341 ±0.006	12.475 ±0.004	19.939	3.323	6.934	34.776
RY5	0.650 ±0.002	0.333 ±0.001	0.966 ±0.003	0.237 ±0.006	0.384 ±0.002	8.726 ±0.005	11.296	1.883	1.949	17.254
Total	1.505	7.703	2.232	1.492	1.996	46.259	61.187	10.198	11.440	77.634
Mean	0.301	1.541	0.446	0.298	0.399	9.252	12.237	2.040	2.288	15.527

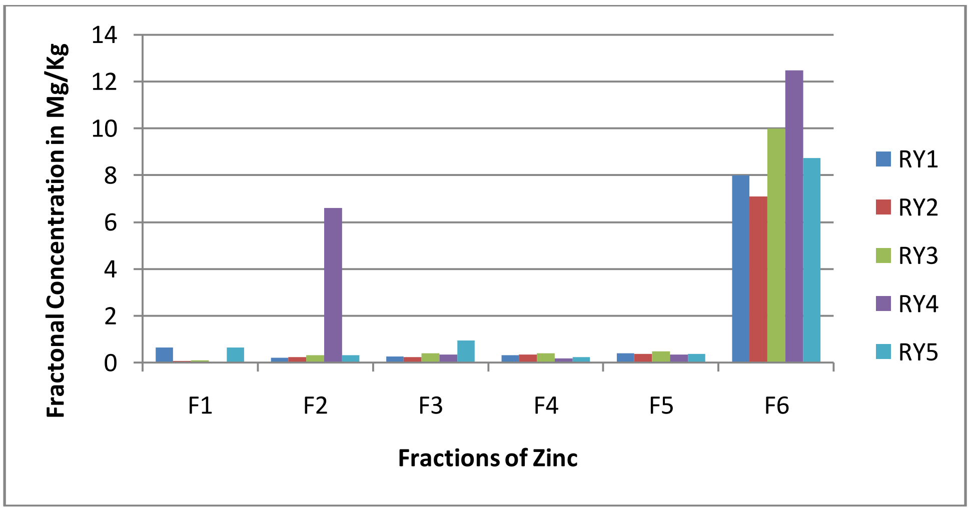

Figure 10: Fractional Concentration of Zn in the Various Soil 30cm Depth (mg/kg).

Sample RY4 had the highest value of %BAF (34.776%) while the least was recorded in sample RY2 (Table 11). The trend in the mean concentration of Zn in the various fractions was F6 > F2 > F3 > F5 > F4 > F1 while the trend in the %BAF of Zn in the various soil samples is RY4 > RY5 > RY1 > RY3 > RY2. This shows that Zn fractionated more in the residual fraction and sample 4 (RY4) recorded the most mean concentration.

Table 12: Fractional Concentration of Cr in the Various Soil 30cm Depth (mg/kg).

Sample code	F1	F2	F3	F4	F5	F6	Total	Mean	BAF	%BAF
RY1	0.032 ±0.002	0.072 ±0.001	0.192 ±0.003	0.199 ±0.003	0.244 ±0.002	0.491 ±0.014	1.230	0.205	0.296	24.065
RY2	ND	0.031 ±0.002	0.100 ±0.036	0.095 ±0.018	0.228 ±0.013	0.656 ±0.016	1.110	0.185	0.131	11.802
RY3	0.037 ±0.043	0.087 ±0.012	0.207 ±0.029	0.264 ±0.032	0.415 ±0.004	1.066 ±0.006	2.076	0.346	0.331	15.944
RY4	0.076 ±0.017	0.793 ±0.017	0.308 ±0.019	0.180 ±0.002	0.513 ±0.007	1.036 ±0.032	2.906	0.484	1.177	40.502
RY5	0.060 ±0.003	0.063 ±0.002	0.156 ±0.003	0.211 ±0.005	0.316 ±0.002	0.568 ±0.005	1.374	0.229	0.279	20.306
Total	0.205	1.046	0.963	0.949	1.716	3.817	8.696	1.449	2.214	112.619
Mean	0.041	0.209	0.193	0.190	0.343	0.763	1.739	0.290	0.443	22.524

Table 12 present the partitioning of Cr in the soil samples 30cm depth. The highest mean concentration of Cr was recorded in the residual fraction (F6) with the value 0.763mg/kg while the least was found in the water soluble fraction (0.041mg/kg). Road 4 (RY4) had the most %BAF and the least was recorded in road 2 (RY2). The trend in the %BAF of Cr in the various soil samples was RY4 > RY1 > RY5 > RY3 > RY2 and the observed trend in the mean fractional concentration of Cr was also F6 □ F5 □ F2 □ F3 > F4 > F1.

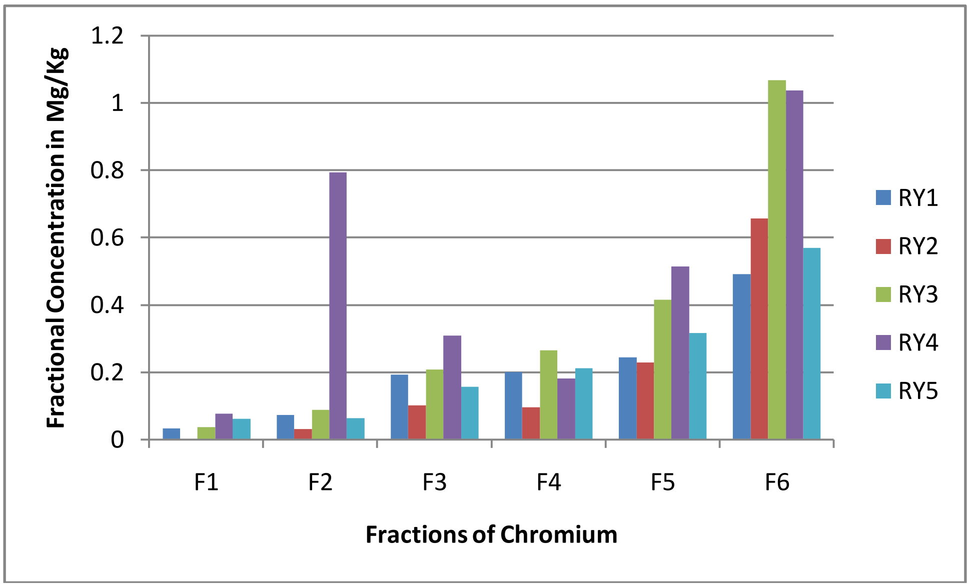

Figure 11: Fractional Concentration of Cr in the Various Soil 30cm Depth (mg/kg).

Table 13: Fractional Concentration of Cd in the Various Soil 30cm Depth (mg/kg)

Sample code	F1	F2	F3	F4	F5	F6	Total	Mean	BAF	%BAF
RY1	ND	0.016 ±0.001	0.046 ±0.002	ND	ND	0.006 ±0.000	0.068	0.011	0.062	91.176
RY2	ND	0.033 ±0.002	0.032 ±0.007	ND	ND	0.068 ±0.003	0.133	0.022	0.065	48.872
RY3	ND	0.011 ±0.001	0.043 ±0.001	ND	ND	0.103 ±0.002	0.157	0.026	0.054	34.395
RY4	ND	0.056 ±0.004	0.036 ±0.007	ND	ND	0.071 ±0.000	0.163	0.027	0.092	56.442
RY5	ND	0.051 ±0.000	0.041 ±0.000	ND	ND	0.009 ±0.001	0.010	0.017	0.092	91.089
Total	0.000	0.167	0.198	0.000	0.000	0.257	0.622	0.104	0.365	321.974
Mean	0.000	0.033	0.040	0.000	0.000	0.051	0.124	0.021	0.073	64.395

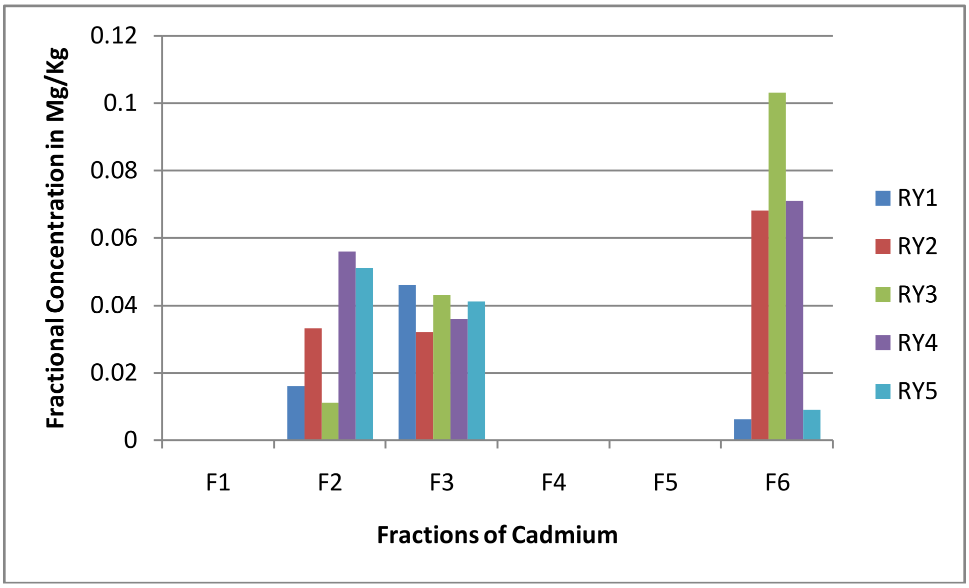

Figure 12: Fractional Concentration of Cd in the Various Soil 30cm Depth (mg/kg).

From the fractional concentration of Cd in the various soil sample (Table 13), we observe that Cd fractionated more in the residual fraction were it had the highest mean concentration of 0.051mg/kg. Cd was not detectable by the FAAS (Analyst 200) used at the water soluble fraction, reducible and the oxidisable fractions for all the samples. Road 1 (RY1) had the highest % BAF (91.176%). The trend for the percentage bioavailable fractions of Cd in the various roads was Y1 > RY5 > RY4 > RY2 > RY3 while the observed trend in the mean concentration of Cd was F6 > F3 > F2 > F1 > F4 > F5.

Table 14: Percentage Bioavailability of Metal Concentration in the Soil 30cm Depth.

Sample code	Cu	Ca	Mn	Pb	Ni	Fe	Co	Zn	Cr	Cd
RY1	50.464	85.545	24.817	23.473	15.575	41.772	27.547	11.592	24.065	91.176
RY2	27.791	86.747	32.166	15.335	32.784	5.459	28.552	6.823	11.802	48.872
RY3	15.165	97.321	24.537	19.058	22.692	3.453	24.141	7.189	15.944	34.395
RY4	50.615	93.360	39.103	60.274	44.431	36.424	48.257	34.776	40.502	56.442
RY5	42.368	94.071	35.021	53.310	21.037	51.044	23.883	17.254	20.306	91.089
GT	186.403	457.044	155.644	171.45	136.519	138.152	152.380	77.634	112.619	321.974
GM	37.281	91.409	31.129	34.290	27.304	27.630	30.476	15.527	22.524	64.395

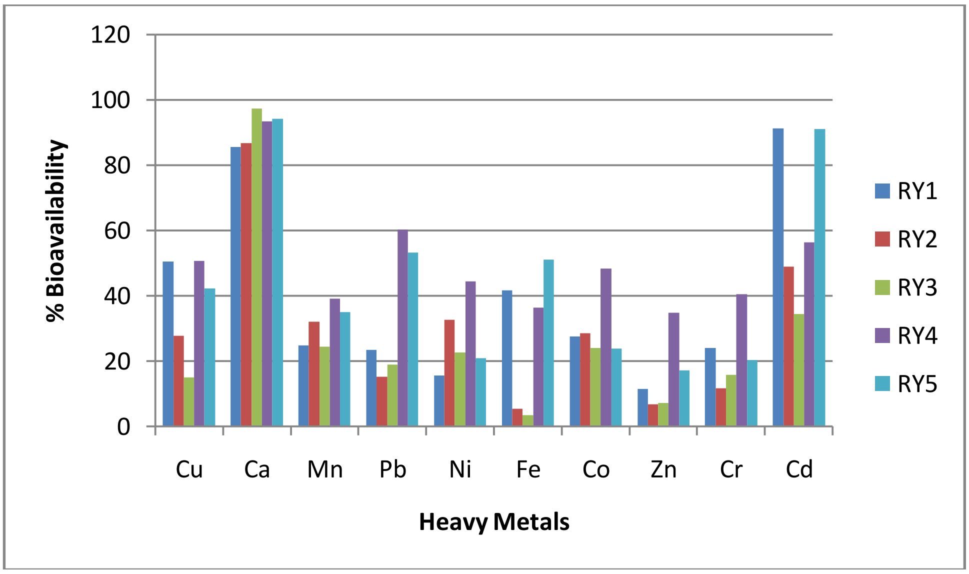

Figure 13: Percentage Bioavailability of Metal Concentration in the Soil 30cm Depth.

The percentage bioavailability (Table 14) shows that Ca had the highest concentration of bioavailable fractions which is found in road 3 (97.321%) and the least was recorded also in sample RY3. Ca also had the most ground mean (91.409%) and Zinc recorded the least value of the ground mean. The trend in the percentage bioavailability of the various heavy metals was as follows: RY1 – Cd > Ca > Cu > Fe > Co > Mn > Cr > Pb > Ni > Zn, RY2 – Ca > Cd > Ni > Mn > Co > Cu > Pb > Cr > Zn > Fe, RY3 – Ca > Cd > Mn > Co > Ni > Pb > Cr > Cu > Zn > Fe, RY4 – Ca > Pb > Cd > Cu > Co > Ni > Cr > Mn > Fe > Zn, RY5 – Ca > Cd > Pb > Fe > Cu > Mn > Co > Ni > Cr > Zn. The trend for the ground mean for the various heavy metals was Ca > Cd > Cu > Pb > Mn > Co > Fe > Ni > Cr > Zn.

The higher the %BAF, the higher the availability of the metal for organism's uptake and so the more harmful it is to the organism because of the level of exposure. This is true according to J.J.K Erwin (2006). In this case Ca is the most available metal in the studied area.

In the correlations of the various fractions of the soil samples 30cm depth, it was positive in the correlation of Zn and Cu at the water soluble fraction, positive between Ni and Mn, Ni and Zn, Ni and Cr, Cd and Cu, Cr and Zn also at the exchangeable fraction. At the carbonate fraction, it was only positive between Cu and Ni, Ca and Pb, and between Cr and Co. the correlation was also positive in the case of Co and Fe at the reducible fraction and none at the oxidisable fraction but positive between the following metals ate the residual level: Mn &, Fe & Co, Cr & Fe, Zn & Cu, Co & Cr as well as in Zn & Cd

IV. Conclusion

The speciation of heavy metals in Owerri industrial layout showed that most of the metals considered had the highest abundance in the Residual fraction. This indicates that the metals were immobile. Ten metals were considered and Cu, Co, Cr, Zn, Cd, Pb, Ni, Mn and Fe were found mostly abundant in the Residual fraction of the sequential extraction. This shows that soil in the environment was not likely to be polluted by these metals. Ca was found to be highly abundant in the Exchangeable fraction, indicating that it could be easily released to the environment from soil. It was also likely to be of high toxicity in the environment though it is not a heavy metal. Comparing these results obtained with the results of that reported by Abugu, et al (2012), it showed that the concentration of the heavy metals considered in the 30cm depth were higher than the soil surface samples. This shows that there is a serious leaching of these heavy metals under investigation. The results of the speciation have given the present status of metal pollution and the potential pollutants in Owerri industrial area.

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