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Partitioning Of Some Selected Heavy Metals In Okigwe Metropolis IMO State, Nigeria (Part I)

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Abstract:

The aim of this study was to assess the distribution patterns of heavy metal in Okigwe metropolis. Topsoil samples (10cm depth) were collected along the major roads within Okigwe metropolis during the rainy season (April to July). The total metal concentration for Fe was discovered to occur at elevated concentrations in virtually all the soil samples with the highest mean concentration (9.072mg/kg), while Zn had the least mean concentration (0.448mg/kg). The observed trend in the concentration of metals was Fe > As > Pb > Cd > Mn > Zn > Cr. Cr was the most bioavailable metal while As and Fe were the least bioavailable. The observed trend for the metal bioavailability was Cr > Pb > Cd > Mn > Zn > Fe = As. Since Cr and Pb are the most bioavailable heavy metals in the area, it means that they will affect the organisms around the area negatively especially Cr.

Key words: Heavy metal, bioavailability, concentration, distribution, soil

1.Introduction

In soils, there is a growing interest 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 (Ure, et al., 1995, Jonasson, 1977). Natural and anthropogenic environmental changes greatly influence the behaviour of metallic pollutants. The form in which they are associated with the environment can be altered by these environmental changes. Such external influences can include pH, temperature, redox potential, organic matter decomposition, leaching and ion exchange processes and microbial activity (Bendicho, et al., 2001). The determination of total heavy metals content in the soil environment is clearly important. However, the quantification of the heavy metal bioavailability fraction is equally if not more important as it is the bioavailable fraction, which determines the actual effective risk of the metals as a contaminant (Horonug, et al., 1993). Metal bioavailability is the degree to which that metal is available for the biotransformation processes in the soil plant system (Verloo, et al., 1995). Metals are varied in their tendency to adhere to the soil particles, a range of physicochemical processes dictate their mobility, availability and govern the behaviour and fate of such metal (Bate, et al., 1982). It is believed that the primary factor that determines the bioavailability of metals in the subsurface is their association with the solid phase. These factors influencing their bioavailability are focused primarily around physical and chemical sorption in the soil (Viets (1962). It has been established that the metal cations in the soil environment are found in recognizable successive chemical pools that are ranging from ions in soil solution to ions in soil crystal lattice which present a reduction in the degree of their availability (Gimeno, et al., 1996).

There is the need to have adequate information regarding the heavy metal pollution status of the major cities of the world, especially in the developing countries, since when living tissues are exposed to the toxicity of heavy metal portend a great danger to their health. This brings to the fore the need to determine the level of heavy metals which are continually being introduced to our God given environment. Metal partitioning gives information about the efficacy of their level of toxicity and also gives an insight about the likely origin or source to the environment.

2.Materials And Methods

2.1.Study Area

Figure 1 shows the map of Okigwe Metropolis. Okigwe is a commercial city in Imo State, Nigeria. This study focuses on eight major roads in Okigwe metropolis with considerable amounts of traffic that could significantly contribute to soil pollution. Okigwe lies between latitudes 5.483°N 7.55°E. The main vegetation of the area is hard soil mixed with various types of bush re-growth, grasses and creepers. The main arable crops are yam, cassava, rice, maize and vegetables alongside plantations of cocoa and oil palm that are also very common.

2.2.List Of Apparatus

Whatman Filter paper, Conical flasks, Water Bath, Dessicator, AAS machine, Syringe, Beakers, pH meter, Measuring cylinder, Flat bottom flask, Sample bottles, Oven, Heater, Electrical weighing balance, Fume cupboard, Electrical shaker, Sieve and plastic containers.

2.3.List Of Reagents

Perchloric acid (HClO₄), Magnesium chloride (MgCL₂), Deionized water, Concentrated Nitric acid (HNO₃), Acetic acid (CH₃COOH), Ammonium hydroxide (NH₄OH), Hydrogen peroxide (H₂O₂), Concentrated hydrochloric acid (HCl).

2.4.Sample Collection

The study area was divided into eight locations based on the major Roads/Streets in Okigwe Metropolis. These roads/streets are as follows: Market Road, Rev. Mann Street, Umuchima Road, Umu-Okpara Road, Agriga Road, Owerri Road Ogui Road and Ubahu Road. The locations were selected based on their closeness to the predominant activities of the inhabitants. Sampling spots were cleared of debris before actually sampling started. About 500 g of the soil samples were collected within a distance of 0-5 meters from the edge of the main road at each location and at a distance of 6 poles apart (about 30 meters). All soils collected were sampled at the surface (0 to 10 cm in depth) using a plastic scoop. The soil samples were kept in labelled polythene bags and taken to the laboratory for analysis. All soil samples were air-dried and ground to 2mm before chemical analysis was carried out.

2.5. Procedure For Total Heavy Metal Analysis

A 200um sieve was used to sieve the soil sample and approximately two grams of the air-dried ground soils samples in each case were placed in a 100ml Kjedahl digestion flask, which has been previously washed with nitric acid and distilled water. The samples were subjected to digestion with 20 ml of concentrated nitric acid (HNO₃) and concentrated Hydrochloric acid (Aqua Ragia in the ratio of 3:1) and was heated for about two hours. For complete digestion, a 10ml of Aqua Ragia was also added and heated for another one hour. The mixture was swirled gently and slowly at moderate heat on a digester, under a fume hood. The heating continued until dense white fumes appeared which was then digested for about 2hours, set aside to cool and diluted with distilled water. The mixture was filtered through Whatman filter paper into a 100cm³ volumetric flask, diluted to mark (Allen et al., 1974; Sahrawat et al., 2002). The filtrate was made up to 100ml mark with distilled water. Total concentration of the metals under investigation was determined by AAS (FS240AA Agilent model).

2.6. Sequential Extraction And Analysis

A thorough analysis of sequential extraction procedures has been made by Shiowatana et al., (2001) as reported hereafter. Sequential extraction to fractionate metals or other elements in solid materials (soils, sediments, sludge, solid wastes, etc.) into several groups of different leachability is widely employed to determine the distribution of metals in different phases. Although the procedures used are generally tedious and time consuming, the results furnish detailed information about the origin, mode of occurrence, bioavailability, potential mobility, and transport of the metals in natural environment. The technique is therefore widely used as a tool for the study of the origin and fate of metals in the environment. However, despite the fact that the development and use of sequential extraction schemes started in the early 1970s, uniformity in the procedures used is still lacking. In addition, problems of poor selectivity, redistribution during extraction, and the dependency of results on operating conditions have been frequently raised (Shiowatana et al. 2001). The most widely used sequential extraction schemes are those proposed by Tessier et al. (1979) and the Community Bureau of Reference (BCR) (Quevauviller, 1998). Tessier et al. (1979) procedure assumes that the chemical behaviour of a certain element is related to five fractions (listed according to an increasing difficulty in solubilisation).

2.7. Exchangeable Metal Fraction

1g of each soil sample was accurately weighed and was placed in a 100ml conical flask. The exchangeable fractions were gotten by adding 8ml of 1M MgCL₂ and agitation of 1 hour was done with the pH was adjusted to 7.0. The filtrate was labelled F1 after filtering the solution.

2.8. Carbonate-Bound/Acid Soluble Metal Fraction

Another 8ml of 1M NAOAC (CH₃C00Na) was added and was adjusted to pH of 5.0 this time around with HOAC (CH₃COOH) and also agitated for about 5 hours to determine the carbonate bound. This was called F2.

2.9.Fe-Mn Oxide/Reducible Metal Fraction

20ml of 0.04M Hydroxylamine hydrochloride (NH₂OH.HCL) in 25% HOAC was added and a temperature of about 96°C was attained with a continuous agitation for about 6 hours to determine the Iron/Manganese (Fe/Mn) oxide. The filtrate was tagged F3.

2.10. Organic And Sulfide/Oxidisable Metal Fraction

However, 3ml of 0.02M HNo₃ and 5ml of 30% H₂O₂ with pH of 2.0 were added and the solution was heated up to about $85^{\circ}C$ for 2 hours with a continuous agitation. An additional 8ml of 30% H₂O₂ was added and another temperature of about $85^{\circ}C$ was attained for 3 hours agitation to determine the organic bound that is F4.

2.11.Residual Metal Fraction

Digestion was done on the residue with $HCl-HNO_3 - HClO_4$ (per chloric acid) until all the total heavy metals are dissolved and the mixture was filtered. Metal analyses were conducted with atomic absorption spectrophotometer (FS240AA Agilent model) involving direct aspirations of the aqueous sample into an air-acetylene flame. Procedural blank samples were subjected to similar extraction method using the same amounts of reagents. Blank determinations of the elements were below the detection limits of the atomic absorption spectrophotometer labelled ND.

Samples	Cd	Mn	Pb	As	Cr	Fe	Zn	Ave. Metal
								Content
Market road	0.196	1.474	0.160	4.730	0.014	9.450	0.478	2.357
Umuchima road	0.162	1.467	0.080	6.900	ND	6.420	0.211	2.177
Umuokpara road	0.112	0.820	0.140	7.460	ND	9.370	0.212	2.588
Rev Mann street	0.172	1.302	0.152	ND	0.069	10.010	0.325	1.718
Ogui road	0.137	1.958	0.110	ND	ND	9.504	0.700	1.772
Ubahu road	0.158	1.139	0.100	9.620	0.134	8.841	0.290	2.897
Agriga road	0.158	0.840	0.180	7.400	0.175	9.011	0.208	2.567
Owerri road	1.195	2.100	2.900	ND	1.784	10.030	1.163	2.208
Iss 2008	10	6	4	4	6	10	6	
Mean	2.290	1.388	3.820	4.154	0.272	9.072	0.448	

3.Results And Discussion

 Table 1: Total Heavy Metal Concentration

 Nd = Not Detected

Table 1 shows the total heavy metal concentration of the eight major roads of Okigwe soil samples. From the table, the average values of the heavy metals decrease as follows Cr<Zn<Mn<Cd<Pb<As<Fe. The table also shows that Fe had the highest concentration in virtually all the sample while Cr had the lowest concentration in most of the samples. Some of the metals were undetectable by the spectrophotometer used such as As at Rev. Mann, Owerri and Ogui roads.



Figure 1: Total Metal Concentration

Figure 1 shows the Concentration of heavy metals for samples. It shows that Fe had the highest concentration followed by Arsenic while Cr, Cd and Pb had the lowest concentration in most of the samples. Table 2 shows the total heavy metal concentration of the eight major roads. From the table, we observe that Ubahu had the most metal concentration while Rev mann had the least.

Sampled Roads	Ave. Total Metal Conc. (mg/kg
Market	2.357
Umuchima	2.177
Umuokpara	2.588
Rev Mann	1.718
Ogui Road	1.772
Ubahu	2.897
Agriga	2.567
Owerri	2.208

Fraction	Cd	Mn	Pb	Cr	Fe	As	Zn
F1	0.174	0.223	0.016	0.035	1.996	1.950	0.102
F2	0.035	0.036	0.050	0.141	ND	ND	ND
F3	0.150	0.462	0.030	ND	ND	ND	0.100
F4	0.119	0.253	ND	0.035	ND	ND	0.101
F5	0.108	0.038	ND	ND	0.605	6.840	0.069
Mean	0.456	0.329	ND	ND	9.375	2.910	0.241

Table 3: Fractional Concentration Of Heavy Metals In Market Road Sample (Mg/Kg)

F1= exchangeable fraction,

F2 = Metals bound to carbonate,

F3 = metals bound to iron and manganese oxide,

F4 = metals bound to organic matter and F5 = residual metals.

Table 3 shows the sequential extraction of the metals in Market Road sample. From the table, Fe had the highest concentration while Pb had the least.



Figure 2: Fractional Concentration Of Heavy Metals In Market Road Sample In Mg/Kg

Figure 2 shows the heavy metal composition for samples collected from Market road. The metal with the highest concentration was Fe recorded in residual Fraction with small traces of As.

Fraction	Zn	As	Fe	Cr	Pb	Mn	Cd
F1	0.242	ND	ND	0.098	0.050	0.271	0.127
F2	0.041	ND	ND	0.115	ND	0.247	0.189
F3	0.355	4.890	5.434	ND	ND	1.150	0.070
F4	0.043	1.300	0.148	ND	ND	ND	0.265
F5	0.165	4.110	9.434	0.009	0.620	0.380	0.396
Mean	0.169	2.060	3.000	0.044	0.134	0.410	0.209

Table 4: Fractional Concentration Of Heavy Metals In Rev. Mann Road Sample In Mg/Kg

Table 4 shows the fractional concentration of heavy metals in the sample from Rev. Mann road. Fe had the highest value followed by As while Pb had the lowest metal average fraction.



Figure 3: Fractional Concentration Of Heavy Metals In Rev. Mann Road Sample (Mg/Kg)

Figure 3 describes the fractionating pattern of the selected heavy metals in Rev. Mann road.

Fraction	Cd	Mn	Cr	Pb	Fe	As	Zn
F1	0.084	0.281	ND	0.020	ND	ND	0.011
F2	0.137	0.676	0.392	0.030	ND	ND	0.165
F3	0.069	0.335	ND	ND	5.170	6.750	0.749
F4	0.133	ND	ND	ND	0.196	1.560	0.299
F5	0.377	0.838	0.249	ND	9.800	3.700	0.278
Mean	0.160	0.426	0.128	0.010	3.003	2.402	0.301

Table 5: Fractional Concentration Of Heavy Metals In Umuchima Road Sample (Mg/Kg)

Table 5 shows the Ubahu road fractionation pattern of the sample. From the table, Fe appears to have the highest value (9.800mg/kg) followed by As while Pb had the lowest average fraction.



Figure 4: Fractional Concentration Of Heavy Metals In Umuchima Road Sample (Mg/Kg)

Figure 4 describes the speciation pattern of the heavy metals for the samples collected from Umuchima road. Fe was found to have the highest concentration in the residual fraction, while the highest level of As was recorded in Fraction 3.

Fraction	Cd	Mn	Pb	Cr	Fe	As	Zn
F1	0.147	0.400	0.020	ND	ND	ND	0.011
F2	0.178	0.817	0.060	0.249	ND	ND	0.650
F3	0.127	0.822	0.070	0.045	ND	ND	0.396
F4	0.100	0.002	ND	0.107	ND	0.610	0.055
F5	0.477	0.649	0.010	0.105	9.509	4.740	0.268
Mean	0.206	0.538	0.032	0.102	1.900	1.070	0.258
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Table 6: Fractional Concentration of heavy metals in Umuokpara Road Sample (mg/kg)

Table 6 shows the Umuokpara road sample result. From the table, Fe appears to have the highest concentration followed by As while Pb had a negligible average fraction for the rainy season. The observed trend is as follows: Pb<Cr<Cd<Zn<Mn<As<Fe.



Figure 5: Fractional Concentration Of Heavy Metals In Umuokpara Road Sample (Mg/Kg)

Figure 5 shows the heavy metal composition of samples collected from Umuokpara road.

Fraction	Cd	Mn	Cr	Pb	Fe	As	Zn
F1	0.143	0.224	0.065	0.030	ND	ND	0.026
F2	0.209	0.714	0.008	0.050	ND	ND	0.225
F3	0.313	0.986	ND	0.040	5.006	2.250	0.249
F4	0.184	0.043	ND	ND	ND	0.430	0.074
F5	0.348	0.276	ND	ND	7.599	5.230	0.106
Mean	0.239	0.449	0.015	0.024	2.521	1.582	0.136

Table 7: Fractional Concentration Of Heavy Metals In Agriga Road Sample (Mg/Kg)

Table 7 shows the speciation pattern of Agriga road sample. Cr was undetectable at the F3, F4 and F5. So also it was for Pb except for F3. The observed trend was Cr < Pb < Cd < Zn < Mn < As < Fe.



Figure 6: Fractional Concentration Of Heavy Metals In Agriga Road Sample (Mg/Kg)

Figure 6 describes the fractionation patterns of the selected heavy metals in Agriga road.

Fraction	Cd	Mn	Pb	Cr	Fe	As	Zn
F1	0.217	0.292	0.220	ND	ND	ND	0.048
F2	0.136	0.916	0.500	0.080	ND	ND	0.357
F3	0.071	1.300	0.090	ND	7.438	1.160	0.389
F4	0.324	0.101	ND	ND	0.401	3.940	0.191
F5	0.389	0.110	0.050	ND	3.836	1.490	0.081
Mean	0.227	0.544	0.860	0.016	2.335	1.318	0.213

Table 8: Fractional Concentration Of Heavy Metals In Owerri Road Sample (Mg/Kg)

Table 8 shows the Fractional Concentration of heavy metals in Owerri Road Sample. Cr was only detectable at the carbonate fraction. Fe and As were undetectable at the exchangeable and carbonate fractions. The observed trend is Cr < Zn < Cd < Mn < Pb < As < Fe.



Figure 7: Fractional Concentration Of Heavy Metals In Owerri Road Sample (Mg/Kg)

Figure	7 illustrates the sequential	extraction of the heavy meta	als for the samples collected	ed at Owerri road.
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Fraction	Cd	Mn	Cr	Pb	Fe	As	Zn
F1	0.113	0.312	0.069	0.040	ND	ND	0.104
F2	0.149	0.300	0.073	ND	ND	ND	0.151
F3	0.078	0.373	ND	ND	5.210	0.910	0.154
F4	0.143	0.046	ND	0.080	0.361	3.250	0.078
F5	0.375	0.272	ND	ND	8.253	4.520	0.171
Mean	0.172	0.261	0.028	0.024	2.765	1.736	0.132

Table 9: Fractional Concentration Of Heavy Metals In Ogui Road Sample (Mg/Kg)

Table 9 shows the Fractional Concentration of heavy metals in Ogui Road Sample. Cr only occurred in the exchangeable and carbonate fractions only while the reverse was true for Fe and As. The observed trend is Pb<Cr<Zn<Cd<Mn<<As<Fe.



Figure 8: Fractional Concentration Of Heavy Metals In Ogui Road Sample (Mg/Kg)

Figure 8 illustrates the Fractional Concentration of heavy metals in Ogui Road Sample.

Fraction	Cd	Mn	Pb	Cr	Fe	As	Zn
F1	1.929	0.355	0.030	0.117	ND	ND	0.0153
F2	0.147	0.285	0.020	0.061	ND	ND	0.0319
F3	0.174	0.994	0.030	0.239	ND	ND	0.1829
F4	ND	0.010	ND	ND	0.087	3.430	0.0357
F5	0.399	0.323	ND	0.137	9.086	2.090	0.0963
Mean	0.530	0.393	0.016	0.111	1.834	1.104	0.0724

Table 10: Fractional Concentration Of Heavy Metals In Ubahu Road Sample (Mg/Kg)



Figure 9: Fractional Concentration Of Heavy Metals In Ubahu Road Sample (Mg/Kg)

Figure 9 illustrates Fractional Concentration of heavy metals in Ubahu Road Sample.

Sample	F1	F2	F3	F4	F5	Total	Mean	BAF	%BAF
Owerri road	0.217	0.136	0.071	0.324	0.389	1.137	0.227	0.353	31.047
Agriga road	0.143	0.209	0.313	0.184	0.348	1.195	0.239	0.352	29.456
Rev mann road	0.127	0.189	0.070	0.265	0.396	1.074	0.209	0.316	29.423
Ogui road	0.113	0.149	0.078	0.143	0.375	0.860	0.172	0.262	30.456
Ubahu road	1.929	0.147	0.174	ND	0.399	2.649	0.529	2.076	78.369
Umuchima Rd	0.084	0.137	0.069	0.133	0.377	1.630	0.326	0.163	10.000
Umuokpara road	0.147	0.178	0.127	0.100	0.477	1.029	0.206	0.325	31.584
Market road	0.174	0.035	0.150	0.119	0.108	0.586	0.117	0.209	35.666
Total	2.934	1.128	1.052	1.268	2.869	10.16	2.025	3.740	286.001
Mean	0.367	0.141	0.132	0.159	0.359	1.270	0.253	0.468	35.750
Umuchima Rd Umuokpara road Market road Total Mean	0.084 0.147 0.174 2.934 0.367	0.137 0.178 0.035 1.128 0.141	0.069 0.127 0.150 1.052 0.132	0.133 0.100 0.119 1.268 0.159	0.377 0.477 0.108 2.869 0.359	1.630 1.029 0.586 10.16 1.270	0.326 0.206 0.117 2.025 0.253	0.163 0.325 0.209 3.740 0.468	10.0 31.5 35.0 286. 35.7

Table 11: Fractional Concentration Of Cd (Mg/Kg).

Table 11 shows that Cd was only readily bioavailable in Ubahu road only (78%) even though the exchangeable fraction had the most mean concentration of Cd.



Figure 10: Fractional Concentration Of Cd

Sample	F1	F2	F3	F4	F5	Total	Mean	BAF	%BAF	
Owerri road	0.292	0.916	1.300	0.101	0.110	2.720	0.544	1.208	44.412	
Agriga road	0.224	0.714	0.986	0.043	0.276	2.245	0.449	0.938	41.782	
Rev mann road	0.271	0.247	1.150	ND	0.380	2.048	0.410	0.518	25.293	
Ogui road	0.312	0.300	0.373	0.046	0.272	1.305	0.261	0.612	46.897	
Ubahu road	0.355	0.355	0.994	0.010	0.323	1.965	0.393	0.710	36.132	
Umuchima road	0.281	0.676	0.335	ND	0.838	3.200	0.640	0.627	19.594	
Umuokpara rd	0.400	0.817	0.822	0.002	0.649	2.690	0.538	1.217	45.242	
Market road	0.223	0.036	0.462	0.253	0.038	1.012	0.202	0.259	25.593	
Total	2.358	4.061	6.422	0.455	2.884	17.185	3.437	6.089	284.945	
Mean	0.295	0.508	0.802	0.057	0.361	2.148	0.429	0.761	35.618	
Table 12: Engetional Concentration Of Mr. (Mc/Ka)										

Table 12: Fractional Concentration Of Mn (Mg/Kg).

From table 12, the %BAF of Mn for all the sampled roads are below average and so Mn is not potentially bioavailable.



Figure 11: Fractional Concentration Of Mn (Mg/Kg)

Figure 11 describes the fractional concentration of Mn for the samples. It shows that it fractionated more in the reducible fraction (F3).

sample	F1	F2	F3	F4	F5	Total	Mean	BAF	%BAF
Owerri road	0.220	0.050	0.090	ND	0.050	4.300	0.860	0.270	6.279
Agriga road	0.030	0.050	0.040	ND	ND	0.120	0.024	0.080	66.667
Rev mann road	0.050	ND	ND	ND	0.620	0.670	0.134	0.050	7.463
Ogui road	0.040	ND	ND	0.080	ND	0.120	0.024	0.040	33.333
Ubahu road	0.030	0.020	0.030	ND	ND	0.080	0.016	0.050	62.500
Umuchima road	0.020	0.030	ND	ND	ND	0.050	0.010	0.050	100.000
Umuokpara road	0.020	0.060	0.070	ND	0.010	0.160	0.032	0.080	50.000
Market road	0.016	0.050	0.030	ND	ND	0.096	0.019	0.066	60.750
Total	0.406	0.260	0.264	0.080	0.680	5.596	1.119	0.686	386.992
mean	0.051	0.033	0.033	0.010	0.085	0.699	0.139	0.086	48.374

Table 13: Fractional Concentration Of Pb (Mg/Kg).

Table 13 shows that the %BAF of Pb in all the samples is above average except for Ogui, Rev. Mann and Owerri Roads. This is an indication that lead may be a health issue for the residents of the area.



Figure 12: Fractional Concentration Of Pb (Mg/Kg)

F1	F2	F3	F4	F5	Total	Mean	BAF	%BAF
ND	0.080	ND	ND	ND	0.080	0.016	0.080	100.000
0.065	0.008	ND	ND	ND	0.075	0.015	0.073	97.333
0.098	0.115	ND	ND	0.009	0.222	0.044	0.213	95.946
0.069	0.073	ND	ND	ND	0.142	0.028	0.142	100.000
0.117	0.061	0.239	ND	0.137	0.555	0.111	0.178	32.072
ND	0.392	ND	ND	0.249	0.640	0.128	0.392	61.250
ND	0.249	0.045	0.107	0.105	0.510	0.102	0.249	48.823
0.035	0.141	ND	0.035	ND	0.211	0.042	0.176	80.412
0.384	1.074	0.284	0.142	0.500	2.435	0.486	1.503	615.836
0.048	0.135	0.036	0.018	0.063	0.304	0.061	0.188	76.979
	F1 ND 0.065 0.098 0.069 0.117 ND 0.035 0.384 0.048	F1 F2 ND 0.080 0.065 0.008 0.098 0.115 0.069 0.073 0.117 0.061 ND 0.392 ND 0.249 0.035 0.141 0.384 1.074 0.048 0.135	F1 F2 F3 ND 0.080 ND 0.065 0.008 ND 0.098 0.115 ND 0.069 0.073 ND 0.117 0.061 0.239 ND 0.392 ND ND 0.249 0.045 0.035 0.141 ND 0.384 1.074 0.284 0.048 0.135 0.036	F1 F2 F3 F4 ND 0.080 ND ND 0.065 0.008 ND ND 0.098 0.115 ND ND 0.069 0.073 ND ND 0.117 0.061 0.239 ND ND 0.392 ND ND ND 0.249 0.045 0.107 0.035 0.141 ND 0.035 0.384 1.074 0.284 0.142 0.048 0.135 0.036 0.018	F1 F2 F3 F4 F5 ND 0.080 ND ND ND 0.065 0.008 ND ND ND 0.098 0.115 ND ND 0.009 0.069 0.073 ND ND ND 0.117 0.061 0.239 ND 0.137 ND 0.392 ND ND 0.249 ND 0.249 0.045 0.107 0.105 0.035 0.141 ND 0.035 ND 0.384 1.074 0.284 0.142 0.500 0.048 0.135 0.036 0.018 0.063	F1 F2 F3 F4 F5 Total ND 0.080 ND ND ND 0.080 0.065 0.008 ND ND ND 0.080 0.065 0.008 ND ND ND 0.075 0.098 0.115 ND ND 0.009 0.222 0.069 0.073 ND ND ND 0.142 0.117 0.061 0.239 ND 0.137 0.555 ND 0.392 ND ND 0.249 0.640 ND 0.249 0.045 0.107 0.105 0.510 0.035 0.141 ND 0.035 ND 0.211 0.384 1.074 0.284 0.142 0.500 2.435 0.048 0.135 0.036 0.018 0.063 0.304	F1 F2 F3 F4 F5 Total Mean ND 0.080 ND ND ND 0.080 0.016 0.065 0.008 ND ND ND 0.080 0.016 0.065 0.008 ND ND ND 0.075 0.015 0.098 0.115 ND ND 0.009 0.222 0.044 0.069 0.073 ND ND ND 0.142 0.028 0.117 0.061 0.239 ND 0.137 0.555 0.111 ND 0.392 ND ND 0.249 0.640 0.128 ND 0.249 0.045 0.107 0.105 0.510 0.102 0.035 0.141 ND 0.035 ND 0.211 0.042 0.384 1.074 0.284 0.142 0.500 2.435 0.486 0.048 0.135 0.036 0.018 0.063 0.304	F1F2F3F4F5TotalMeanBAFND0.080NDNDND0.0800.0160.0800.0650.008NDNDND0.0750.0150.0730.0980.115NDND0.0090.2220.0440.2130.0690.073NDNDND0.1420.0280.1420.1170.0610.239ND0.1370.5550.1110.178ND0.392NDND0.2490.6400.1280.392ND0.2490.0450.1070.1050.5100.1020.2490.0350.141ND0.035ND0.2110.0420.1760.3841.0740.2840.1420.5002.4350.4861.5030.0480.1350.0360.0180.0630.3040.0610.188

Figure 12 shows that Pb fractionated more in the residual fraction (F5) for the Rev. Mann road sample.

Table 14: Fractional Concentration Of Cr (Mg/Kg).

Table 14 shows the fractional concentration of Cr. It shows that Cr is readily bioavailable in all the roads except for Ubahu, and Umuokpara roads since their %BAF are above average.



Figure 13: Fractional Concentration Of Cr (Mg/Kg)

Cr fractionated more in the carbonate fraction (F2) in almost all the samples (figure 13).

Sample	F1	F2	F3	F4	F5	Total	Mean	BAF	%BAF
Owerri road	ND	ND	7.438	0.401	3.836	11.675	2.335	0.000	0.000
Agriga road	ND	ND	5.006	ND	7.599	12.605	2.521	0.000	0.000
Rev mann road	ND	ND	5.434	0.148	9.434	15.016	3.000	0.000	0.000
Ogui road	ND	ND	5.210	0.361	8.253	13.825	2.765	0.000	0.000
Ubahu road	ND	ND	ND	0.087	9.086	9.170	1.834	0.000	0.000
Umuchima road	ND	ND	5.170	0.196	9.800	15.166	3.003	0.000	0.000
Umuokpara road	ND	ND	ND	ND	9.509	9.809	1.900	0.000	0.000
Market road	ND	ND	ND	0.605	9.375	9.980	1.996	0.000	0.000
Total	ND	ND	28.258	1.798	66.892	97.246	19.354	0.000	0.000
Mean	ND	ND	3.532	0.225	8.362	12.156	2.419	0.000	0.000

Table 15: Fractional Concentration Of Fe (Mg/Kg).

Table 15 shows that %BAF for all the samples are zero indicating that Fe is not bioavailable in the area. Figure 14 describes this in chart form.



Figure 14: Fractional Concentration Of Fe (Mg/Kg)

Sample	F1	F2	F3	F4	F5	Total	Mean	BAF	%BAF
Owerri road	ND	ND	1.160	3.940	1.490	6.590	1.318	0.000	0.000
Agriga road	ND	ND	2.250	0.430	5.230	7.910	1.582	0.000	0.000
Rev mann road	ND	ND	4.890	1.300	4.110	10.300	2.060	0.000	0.000
Ogui road	ND	ND	0.910	3.250	4.520	8.680	1.736	0.000	0.000
Ubahu road	ND	ND	ND	3.430	2.090	5.520	1.104	0.000	0.000
Umuchima road	ND	ND	6.750	1.560	3.700	12.010	2.402	0.000	0.000
Umuokpara road	ND	ND	ND	0.610	4.740	5.350	1.070	0.000	0.000
Market road	ND	ND	ND	6.840	2.910	9.750	1.950	0.000	0.000
Total	ND	ND	15.240	21.360	28.79	66.110	13.222	0.000	0.000
Mean	ND	ND	1.905	2.670	3.599	8.264	1.653	0.000	0.000

Table 16: Fractional Concentration Of As (Mg/Kg).

Table 16 shows the fractional concentration of As to be 0%BAF.



Figure 15: Fractional Concentration Of As (Mg/Kg)

Sample	F1	F2	F3	F4	F5	Total	Mean	BAF	%BAF
Owerri road	0.048	0.357	0.389	0.191	0.081	1.065	0.213	0.405	38.028
Agriga road	0.026	0.225	0.249	0.074	0.106	0.680	0.136	0.251	36.912
Rev mann road	0.242	0.041	0.355	0.043	0.165	0.847	0.169	0.283	33.412
Ogui road	0.104	0.151	0.154	0.078	0.171	0.660	0.132	0.255	38.636
Ubahu road	0.015	0.032	0.183	0.034	0.096	0.370	0.072	0.047	12.700
Umuchima road	0.011	0.165	0.749	0.299	0.278	1.503	0.301	0.176	11.709
Umuokpara road	0.011	0.650	0.396	0.055	0.268	1.290	0.258	0.661	51.240
Market road	ND	0.100	0.101	0.069	0.241	0.511	0.102	0.100	19.569
Total	0.457	1.621	2.576	0.843	1.406	6.926	1.383	2.178	242.206
Mean	0.057	0.203	0.322	0.105	0.176	0.866	0.173	0.273	30.276

Table 17: Fractional Concentration Of Zn (Mg/Kg).

From table 17, Zn was undetectable in the exchangeable fraction for the market road sample. The %BAF of Zn in all the samples where below average (50%) except for Umuokpara road.



Figure 16: Fractional Concentration Of Zn (Mg/Kg)

Sample code	As	Mn	Pb	Fe	Zn	Cr	Cd
Owerri Road	0.000	44.412	6.279	0.000	38.028	100.000	31.047
Agripa Road	0.000	41.782	66.667	0.000	36.912	97.333	29.456
Rev Mann Road	0.000	25.293	7.463	0.000	33.412	95.946	29.423
Ogui Road	0.000	46.897	33.333	0.000	38.636	100.000	30.456
Ubahu Road	0.000	36.132	62.500	0.000	12.700	32.072	78.369
Umuchima Road	0.000	19.594	100.000	0.000	11.709	61.250	10.000
Umuokpara Road	0.000	45.242	50.000	0.000	51.240	48.823	31.584
Market Road	0.000	25.593	60.750	0.000	19.569	80.412	35.666
GT	0.000	284.945	386.992	0.000	242.206	615.836	286.001
GM	0.000	35.618	48.374	0.000	30.276	76.979	35.750

Table 18: Percentage Bioavailability Of The Heavy MetalsGM = Ground Mean And GT = Ground Total

Table 18 and figure 17 shows that Cr had the highest percentage bioavailability (GM = 76.979) while Fe and As had the least ground mean of percentage bioavailability (0.000). The trend in the availability of the metals is as follows Cr > Pb > Cd > Mn > Zn > As = Fe.



Figure 17: Percentage Bioavailability Of The Metals

4.Conclusion

The study detailed the heavy metal concentrations of the eight major roads in Okigwe metropolis and from the concentration obtained for Cr, Zn, Cd, Mn, Pb, As, Fe, in the soil samples, Fe has the highest value when compared for the sequential extraction followed by As while Pb had the least value. Fe was above the international soil standard (2008) in Rev Mann, Ogui road, and Ubahu road and As was above the international soil standard (2008) in Market road, Umuchima road, Rev Mann, Ogui road, and Ubahu road, Agiriga road while other heavy metals were below the tolerance limit as proposed by the World Health Organization. It shows that Aside from occurring naturally in the environment, Arsenic can be released in larger quantities through volcanic activity, erosion of rocks, forest fires, and human activity. It can be concluded that, it is Cr that is most readily bioavailabe for all the samples while other heavy metals under consideration are not readily bioavailabe even though some of their fractional concentration may be very high. The ANOVA of the metal concentrations showed no significance different at P>0.05. In recommendation, there is need to carry out a similar research in the area during the dry season (September to March) to have a complete data for the partitioning of the selected heavy metals in Okigwe metropolis. This is on course and will form Part II of this paper.

5.References

- 1. Allen, E.S., H.M. Grimshaw, J.A. Parkinson and C. Quarmby, (1974). Chemical Analysis of Ecological Materials. Blackwell Scientific Publication, Oxford, London, pp: 18-432.
- 2. Bate, T.E. and Soon, Y.K. (1982). Chemical pools of cadmium, Nickel and Zinc in polluted soils and some preliminary indication of their availability to plants. Journal of soil science. 33(1):477-488.
- 3. Bendicho, C. and Lavilla, I. (2001). Applications of ultrasound-Assisted metal extractions. Encyclopedia of separation science, Academic Press, London. pp 17
- 4. Gimeno, G. and Andrew, V. (1996). Total content and extractable fraction of cadmium, cobalt, copper, nickel, lead and zinc in calcerous orchard soil Commun. Soil. Sci. Plant Anal. 27(13) :2633-2648.
- 5. Horonug, M. and Mench, M.J.D. (1993). Speciation and Bioavailability. Integrated soil and sediment Research: A basis for proper protection, Kluwer Academic Publishers, Hamer pp. 213-214.
- 6. Jonasson, I. R. (1977). Proceedings of the workshop on fluvial transport of sediment-associated nutrients and contaminants, held in Kitchen, Ontario, in October, 1976. pp 43-46
- 7. Quevauviller, P. (1998). Operationally defined extraction procedures for soil and sediment analysis. I. Standardization. Trends Anal Chem17:289 298.
- Sahrawat, K.L., Kumar, G.R. and Rao, J.K. (2002). Evaluation of triacid and dry ashing procedures for determining potassium calcium mangesium iron zinc manganese and copper in plant materials. Commun. Soil. Sci. Plant Anal., 33: 95-102.
- 9. Shcumacher, M. Meneses, S. Llobert, J.M. and Domingo, J.L. (1997). Trace elements pollution of soils; Bull. Env. Contamination and Toxicology, 59(1):211-231
- 10. Shiowatana, J., Tantidanai, N., Nookabkaew S., Nacapricha, D. (2001). A novel continuousflow sequential extraction procedure for metal speciation in solids, J. Environ. Qual. 30, pp. 1195–1205.
- 11. Tessier et al., (1979). Sequential extraction protocol for analysis of heavy metal speciation in soils and sediments.
- 12. Ure, A. M. Davidson, C. M. and Thomas R. P. (1995). Quality Assurance for Environmental Analysis, ed. Ph. Quevauviller, E.A. Maier and B/ Griepink, Elsevier, Amsterdam pp.505-523.
- 13. Verloo, M.G. and Tack, F.M.G. (1995). Chemical speciation and fractionation in soil and sediments heavy metal: A review Intern. J. Environ. And Chem, 59(3):225-238.
- 14. Viets, F.G. (1962). Chemistry and Availability of Micro-nutrients in soils. Journal of Agricultural and Food Chemistry 10:174-178
- 15. Young, S. and Jopony, M. (1994). The solid-solution equilibria of lead and cadmium in Polluted soils. European Journal of soil science 45(1): 89-70.