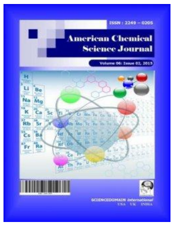

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Partitioning of Some Heavy Metals in the Soil along the Effluent Channels of JEZCO Plastic Industry Ekwulobia, Anambra State, Nigeria

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Authors' contributions

This work was carried out in collaboration between all authors. Author PACO designed the study and wrote the protocol while author HOA performed the statistical analysis and wrote the first draft of the manuscript. Authors AGE and UCU managed the analyses of the study. Author AGE managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

The partitioning of some selected heavy metals in soil samples along the effluent channels of JEZCO Plastics industry Ekwulobia was investigated. The pH of the soils had average value of 8.07 and moisture content of 5.22%. The results revealed total metal concentration range of 0.13 mg/kg to 16.49 mg/kg among the metals –Cd, Cr, Pb, Ni, Cu, Co, Zn,Mn, Fe and Ca. Cadmium (Cd) had the lowest metal concentration with a value of 0.15 mg/kg and iron (Fe) had the highest metal concentration with a value of 14.62 mg/kg. The observed trend for total metal concentration was Fe > Mn > Ca > Pb > Cu > Ni > Co > Zn > Cr > Cd. The computed bioavailability of the metals followed the trend: Ca > Mn > Cu > Pb > Ni > Co > Cr > Zn > Cd > Fe. The heavy metal partitioning showed that the highest and lowest concentration of the metals Fe, Mn, Pb, Cr, Cu, Ni, Co and Zn, were found in the residual and water soluble forms respectively, except for Ca which had its highest concentration in the carbonate bound form, and the lowest concentration in the water soluble

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fraction. The highest concentration of Cd was found in the residual fraction and lowest was found in the water soluble fraction. Comparison with NESREA standard also revealed low contamination level of the metals, and there was no mean significant difference to conclude there was heavy metal pollution of the environment.

Keywords: Speciation; discharge; channels; soil; fractions; digestion.

1. INTRODUCTION

Risk assessment of potential environmental toxicants and remedial measures are essential to preserve the health of the people and the life of nature for the future. Total metal content of soils is useful for many geochemical applications but often the speciation (bioavailability) of these metals is more of an interest agriculturally in terms of what is biologically extractable [1]. Speciation is defined as the identification and quantification of the different, defined species, forms, or phases in which an element occurs [2]. and is essentially a function of the mineralogy and chemistry of the soil sample examined [3]. Quantification is typically done using chemical solutions of varying but specific strengths and reactivity to release metals from the different fractions of the examined soil [4]. In terms of bioavailability, various species of metals are more biologically available in the ecosystem [5]. Bioavailability and the mobility of metals are also related to each other, then higher the concentration of mobile toxic metals (Cu, Pb, Cd, and Al) in the soil column which increases the potential for plant uptake, and animal/human consumption [6,7].

Heavy metals take part in biogeochemical cycles and are not permanently fixed in soils; therefore, assessment of their distribution in soils is a key issue in many environmental studies [8]. Heavy metals are included in soil minerals as well as bound to different phases of soil particles by a variety of mechanisms, mainly absorption, ion exchange, coprecipitation, and complexation. Moreover, soil properties such as contents of organic matter, carbonates, oxides as well as soil structure and profile development influence the heavy metal mobility [9].The knowledge of the binding of metals with the different soil phases and components is of major interest to assess the connections with other biotic and abiotic elements of the environment [10]. Nevertheless, as Cabral and Lefebvre indicate, the metal speciation is a more complex task that determination of total metal contents [11]. Hence this work bothers on assessing the risk levels of some selected heavy metals in the effluent discharge ways of Jesco industrial complex as well as the impact of these industries in terms of discharge of heavy metals to the environment. Already, much have been said and heard about the discharge of industrial effluents, the subsequent environmental pollution and Federal Ministry of Environment regulations for treatment of industrial effluents before discharge. The levels or concentrations of the target metals are to be ascertained from the soil along the effluent discharge ways of the industries through analytical procedures of digestion and leaching for a very good understanding of the total metal concentration as well as the speciation patterns.

2. MATERIALS AND METHODS

2.1 List of Apparatus

The following instruments were used: pH meter (Jenway 3505 model), centrifugation machine and AAS machine (*Analyst* 200 flame spectrophotometer).

2.2 List of Reagents

1 M Sodium acetate, 0.04 M hydroxylamine hydrochloride, 25%v/v Acetic acid, 0.02 M Nitric acid, 30% Hydrogen peroxide, Hydrochloric acid, 3.2 M Ammonium acetate, Hydrofluoric acid, 1M Boric acid, Deionised water, Aqua regia. All reagents used were made by Sigma-Aldrich.

2.3 Preparation of Reagents [3]

2.3.1 1 M sodium acetate (CH_3COONa)

35 g of NaOAc powder was weighed into 500 ml volumetric flask, dissolved with deionized water and made up to the mark. A pH of 5 and 8.5 respectively were obtained by adjustment with Acetic acid.

2.3.2 0.04 M hydroxylamine hydrochloric acid ($NH_2OH.HCl$) in 25% v/v acetic acid

1.39 g of $NH_2OH.HCl$ was weighed into a 500 ml volumetric flask, dissolved with 25% v/v HOAc (i.e. 75 ml Acetic acid in 175 ml of water) and made up to mark with deionised water.

2.3.3 0.02M HNO_3

With a percentage purity of 69 and specific gravity of 1.42, some 1.4 ml of the stock HNO_3 was taken and dissolved to a 1000 ml flask of deionised water and made up to mark.

2.3.4 3.2M ammonium acetate CH_3COONH_4 in 20% v/v HNO_3

64.8 g of NH_4OAc was weighed into a 250 ml flask, dissolved with 20% v/v HNO_3 and made up to mark.

2.3.5 30% H_2O_2

2 ml of a 35% H_2O_2 commercial stock was dissolved in 98 ml of deionised water to obtain a 100 ml solution of 30% H_2O_2. A pH of 2 was obtained by adjustment with HNO_3.

2.4 Sampling and Sample Pretreatment

Soil samples were collected with plastic containers and packed in polythene bags and taken to laboratory immediately for digestion and sequential extraction fractionation. Partial aeration was performed and appropriate particle size was obtained using 1.5 mm nylon sieve. In collecting the samples, a distance of 20 meters apart was maintained, and a total of 6 soil sample points were taken along the industry discharge channels. Samples were collected in rainy season (April to August). Fig. 1 is the map of the industry location.

2.5 pH Determination

Approximately 5 g of the soil samples was taken and equilibrated for 30 minutes in thoroughly washed and dried beakers containing 20 ml of deionised water. The pH values were determined using pH meter, Jenway 3505 model, and recorded.

2.6 Moisture Content

Approximately 5 g of the wet soil samples was taken in a beaker and placed in the oven for 24 hrs. The weights taken, W_1, weights after heating, W_2, moisture content and percentage moisture were recorded.

2.7 Sample Digestion for Total Metal Analysis

Approximately 2 g of the soil sample was placed into a Teflon container and digested by addition of 5 ml HF and 5 ml aqua regia, and heating on a water bath for one and half hours. After cooling, fresh volumes of HF and aqua regia, 5 ml each, was added and digested again for another one and half hours heating on the water bath. Finally, 20 ml volume of saturated boric acid (H_3BO_3) was added on cooling after the final digestion process to complex the residual hydrofluoric acid (HF) which would otherwise attack glass wares. Filtration of the samples was done with Whatman No.1 filter paper and the solution made up to 50 ml mark.

2.8 Sequential Extraction of Heavy Metals

2.8.1 Water soluble fraction

To 2 g of soil sample, 10 ml of deionised water was added in a 50 ml Teflon centrifuge tubes and agitated for 30 minutes before centrifugation and decantation into the sample bottles for storage. Subsequent series of washing with 10 ml of deionised water was done to make up to 50 ml mark of the sample bottles [3].

2.8.2 Exchangeable fraction

To the residue from previous leach, 8 ml of 1M sodium acetate (NaOAc pH 8.5) was added and agitated for one hour at room temperature before centrifugation and decantation. The residue was washed with deionised water and 4 ml of aqua regia added to the liquid sample taken for analysis before making up to 50 ml mark of the sample bottles with deionised water [3].

2.8.3 Carbonate-bound fraction

To the residue from previous leach, fresh 8 ml 1 M sodium acetate solution (adjusted to pH 5 with acetic acid) was added and agitated for one hour at room temperature before centrifugation and decantation. The residue was washed with deionised water while 4 ml aqua regia was added to the liquid sample taken for analysis and made up to mark with deionised water [3].

2.8.4 Fe-Mn oxide fraction (reducible)

To the residue from previous leach, 20 ml 0.04 M $NH_2OH.HCl$ in 25% v/v acetic acid was added and agitated periodically in boiling water bath for 5 hours. The residue was washed with deionised water after centrifugation and decantation. The liquid sample obtained for analysis was added 4 ml of aqua regia and made up to the mark [3].

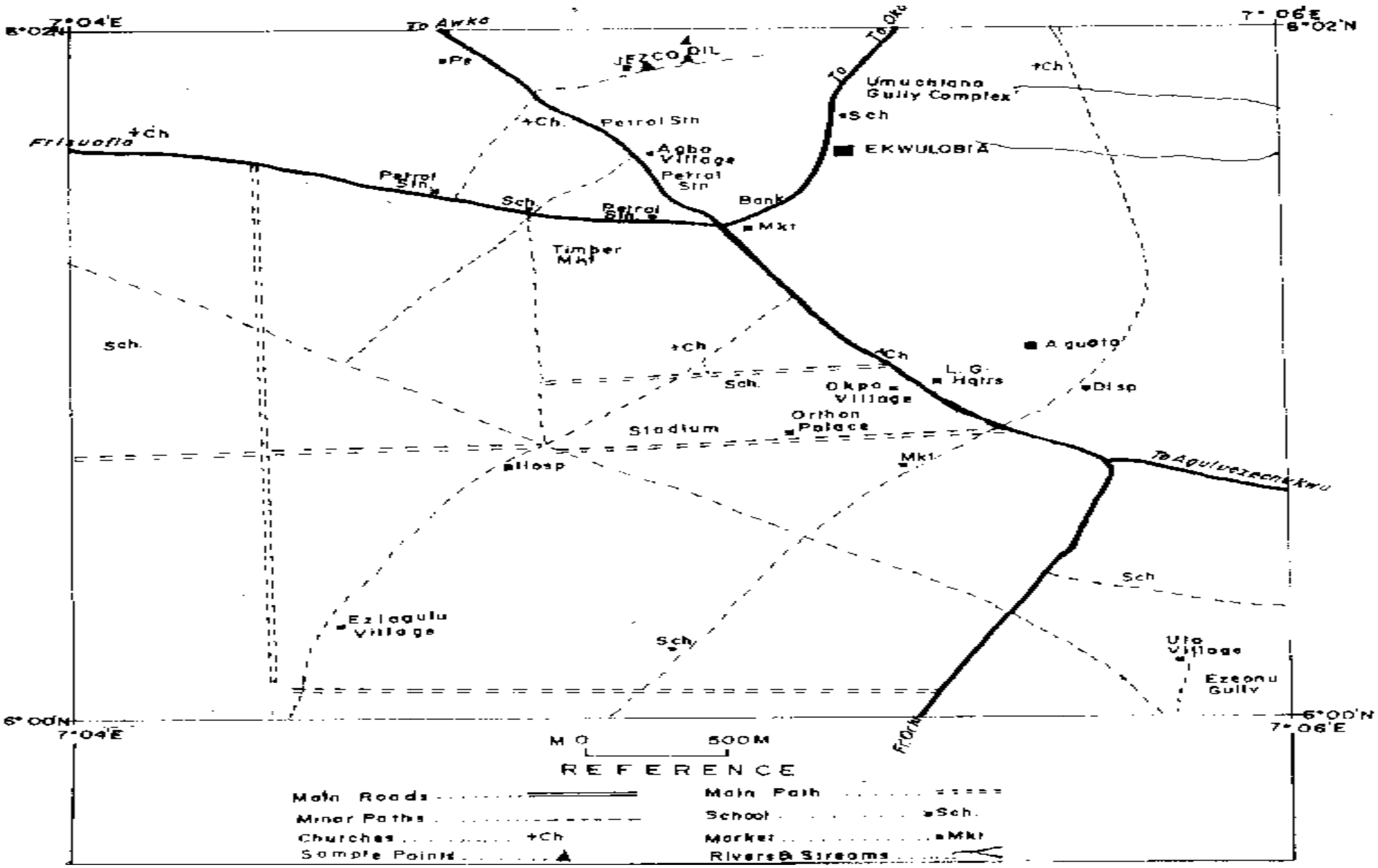

Fig. 1. Map of Ekwulobia showing JEZCO location and sampling point

2.8.5 Organic and sulfide fraction (oxidizable)

To the residue from previous leach, 3 ml 0.02 M HNO_3 and 5 ml of 30% H_2O_2, which has been adjusted to pH 2 with HNO_3, was added and agitated periodically in hot water bath (85^oC) for 2 hours. This was followed by addition of 3 ml H_2O_2 (pH 2) and periodic agitation in the hot water bath for another 3 hours. After cooling to room temperature, 5 ml of 3.2 M ammonium acetate in 20%v/v HNO_3 was added finally and agitated at room temperature for 30 minutes before centrifugation and decantation to obtain the liquid sample for analysis. The residue was washed with deionised water and 4 ml aqua regia was added to the liquid sample for analysis before making it up to mark in the sample bottles [3].

2.8.6 Residual fraction

To the residue from previous leach, 5 ml HF and 5 ml aqua regia was added to digest it. This was heated in a hot water bath for 2 hours. Centrifugation was followed by decantation and deionised water was used to make up to the mark [3].

All through the exercise, double portions of the normal reagent volumes were used for the 2 g of soil fractionated. And all the stored supernatant solutions obtained for all the fractions, as well as a blank, were instrumentally analyzed for the selected metals concentration using *Analyst 200* model of AAS machine.

3. RESULTS AND DISCUSION

The mean pH value for soil samples within the vicinity of JEZCO was 8.07, with average moisture content of 5.22% (Table 1). With a pH range between 7.5 and 8.5, it may be said that the soils are between neutrality and slightly alkaline. The metals bound to acid soluble or carbonates may remain attached to the soil pending pH change to acidity, as imminent change in pH of the soil due to an external influence, or changes in redox or other favorable conditions, would increase the level of some metal concentration in the soil solution/moisture available for absorption into biota.

The influence of rain and steady inflow of waste water contributed to the significant moisture content of the soil; hence with favorable conditions, absorption of the metals together with the moisture into biological tissue would take effect; or the evaporates may well transport the metals through the atmosphere and then breathed in air.

3.1 Total Metal Concentrations in Soil

The results from the total digestion of soils to determine its total metal concentration are presented in the tables below (Table 2). The results revealed a concentration range of 0.13 – 16.49 mg/kg of the soils among all the metals, Fe > Mn > Ca > Pb > Cu > Ni > Co > Zn > Cr > Cd was observed. The values are presented in the Table 1.

In determining the contamination status of soils or sediments, the contamination factor (C_f) or enrichment ratio (ER) and the degree of contamination (C_d) are used. The contamination factor is given by the equation:

C_f = (measured concentration/Background concentration) [12].

Where, Background values of metals used are that of the NESREA standards. The degree of contamination (C_d) was defined as the sum of all contamination factors. And C_f values for describing the contamination level are presented in Table 3.

The sample gave a contamination factor (C_f) < 1 for all the tested heavy metals and thus indicated low contamination (Table 4). When compared with the degrees of contamination, the complex constituted negligible pollution along the effluent discharge channels.

Table 1. Moisture content and pH values

Sample code	Weight taken (W_1) (g)	Weight after heat (W_2) (g)	Moisture content (g)	% moisture content	pH value
Plast 1	5.0060	4.5690	0.4370	9.56	8.5
Plast 2	4.3580	4.2080	0.1500	3.56	8.2
Plast 3	5.0300	4.9040	0.1260	2.56	7.5

Table 2. Total digestion of metals (mg/kg)

Sampling points	Cd	Cr	Ni	Pb	Co	Cu	Zn	Mn	Ca	Fe
Plast 1	0.139±0.001	0.158±0.007	1.279±0.016	1.611±0.012	1.086±0.012	1.058±0.005	0.387±0.006	8.977±0.108	5.480±0.051	15.720±0.247
Plast 2	0.156±0.002	0.150±0.013	1.329±0.022	2.641±0.001	1.120±0.030	1.739±0.004	0.786±0.019	0.950±0.002	0.449±0.008	11.680±0.001
Plast 3	0.158±0.009	0.178±0.034	1.240±0.009	1.908±0.043	1.113±0.008	1.087±0.023	0.612±0.028	6.032±0.059	1.772±0.059	16.470±0.138
Total	0.453	0.486	3.848	6.16	3.319	3.884	1.785	15.959	7.701	43.87
Mean	0.15	0.16	1.28	2.05	1.10	1.29	0.59	5.31	2.56	14.62

Table 3. C_f values for levels of contamination

Contamination factor (C_f)	Level of contamination
$C_f < 1$	Low contamination
$1 \leq C_f \leq 3$	Moderate contamination
$3 \leq C_f \leq 6$	Considerable contamination
$C_f < 6$	Very high contamination

Table 4. Contamination factor values for the soils studied

Sample location	Enrichment Ratio (ER) or Contamination factor (C_f)									Degree of contamination
	Cd	Cr	Ni	Pb	Co	Cu	Zn	Mn	Ca	
JEZCO	0.050	0.002	0.018	0.013	0.022	0.013	0.001	-	-	0.119

Table 5. Fractional concentration of cadmium (mg/kg)

Sampling points	Water soluble fraction (F1)	Exchange-able fraction (F2)	Carbonate bound (F3)	Fe-Mn oxide fraction (F4)	Organic and sulfide (F5)	Residual fraction (F6)	Total	Mean	BAF	% BAF
Plast 1	0.002±0.002	0.065±0.001	0.075±0.007	0.028±0.002	0.039±0.002	0.159±0.005	0.368	0.06	0.142	38.586
Plast 2	0.028±0.002	0.029±0.002	0.028±0.002	0.003±0.001	0.003±0.002	0.121±0.002	0.156	0.03	0.029	18.589
Plast 3	0.024±0.000	0.032±0.003	0.036±0.001	0.011±0.005	0.006±0.002	0.247±0.002	0.274	0.05	0.044	16.058
Total	ND	0.126	0.139	0.02	0.036	0.527	0.798	0.14	0.215	73.233
Mean	ND	0.04	0.04	0.006	0.01	0.17	0.26	0.04	0.07	24.14

The speciation result for Cd showed that the residual fraction was highest; and the other forms in which it was associated were the Fe-Mn oxide bound and organic/sulfide, with exchangeable and carbonate being the second highest concentration of the metal (Fig. 2). The metal was not detectable in the water soluble fraction, and may be interpreted as having a small concentration of the whole lot in the carbonate and exchangeable forms, which can only be bioavailable when there is a decrease in pH, increased salt concentration or any favorable condition in the soil; otherwise the metal was strongly bound in the residual form, an indication that anthropogenic contribution was slight.

Table 6 showed the fractional concentration of chromium in mg/Kg.

With a very high concentration of Cr in the residual fraction, especially when compared with the others, it may be said that the metal was less bioavailable at Jezco effluent channels (Fig. 3). However, the metal was quite bioavailable and mobile too when compared in terms of the water soluble fraction.

It may be said that the greater part of the total concentration of Ni was associated with the residual form; which showed that the remaining part of the metal, not so strongly tied up in the residual, constituted the lesser part of the total concentration of the metal. Considering the bioavailable fractions (water soluble, exchangeable and carbonate), it amounted to a low level of the metal afterall (Fig. 4). The observed trend for the metal speciation was F6 > F2 > F3 > F5 > F4 > F1. Anthropogenic contribution was slight and the overall concentration of the metal was low. However, considering a higher concentration of Pb, although not yet bad, when related to Pb standard, it became obvious that a closer attention was required for the metal.

The concentration of the metal available in the carbonate and the exchangeable was higher than that obtained in the residual as well as other fractions (Fig. 5). Yet the percentage bioavailability of the metal was low (34.10%). The metal was not detectable in the water soluble fraction. Co concentration was highest in the residual fraction followed by the exchangeable and the carbonate, which constituted the bioavailability of the metal.

It could be drawn that having a pH range of 7.5 and 8.5 may have likely affected the concentration of cobalt associated with the water soluble fraction (Table 9). The observed trend for the metal speciation was F6 > F2 > F3 > F5 > F4 > F1 (Fig. 6).

Apart from the highest concentration of Cu associated with the residual, the metal was observed to be highly bound to the exchangeable, and hence contributed to its increased bioavailability (Table 10). The concentration of the metal in the carbonate was next to that of exchangeable, then organic/sulfide and Fe-Mn oxide followed accordingly (Fig. 7). There was indication of anthropogenic contribution. The observed trend for the metal speciation was F6 > F2 > F5 > F3 > F4 > F1.

Zinc: The speciation of Zn in the soil of these industries is presented in Table 11.

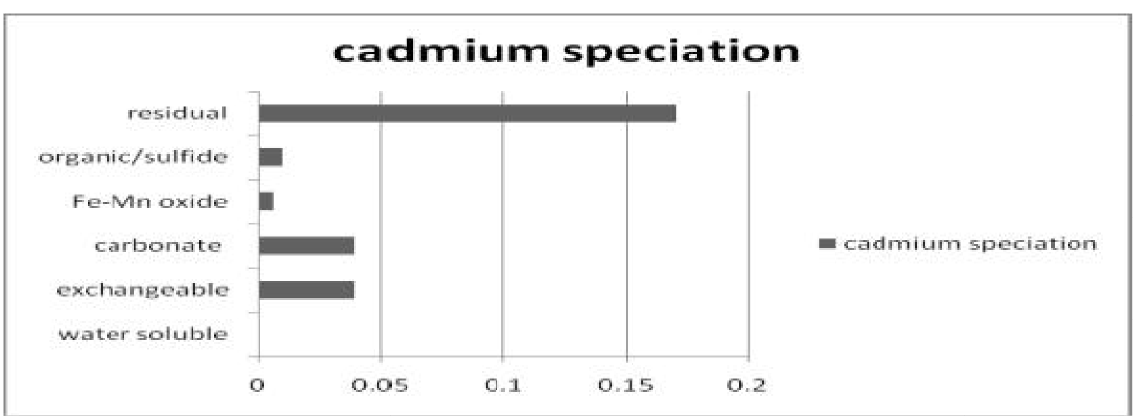

Fig. 2. Graphical presentation of cadmium speciation

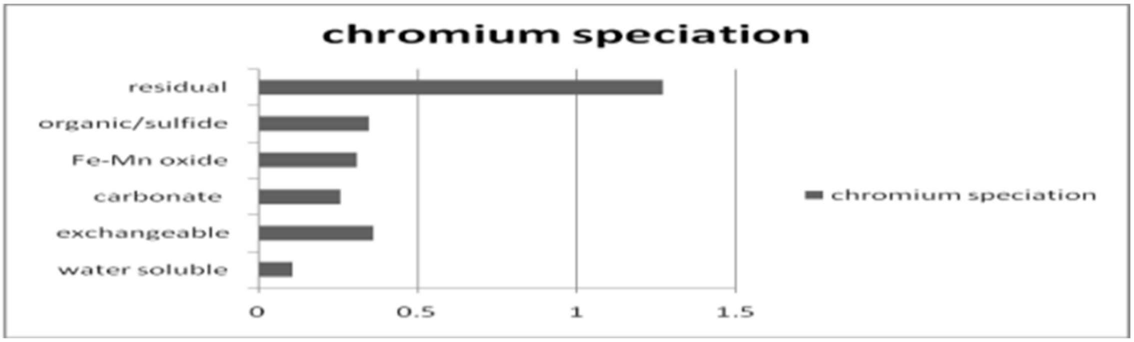

Fig. 3. Graphical presentation of chromium speciation

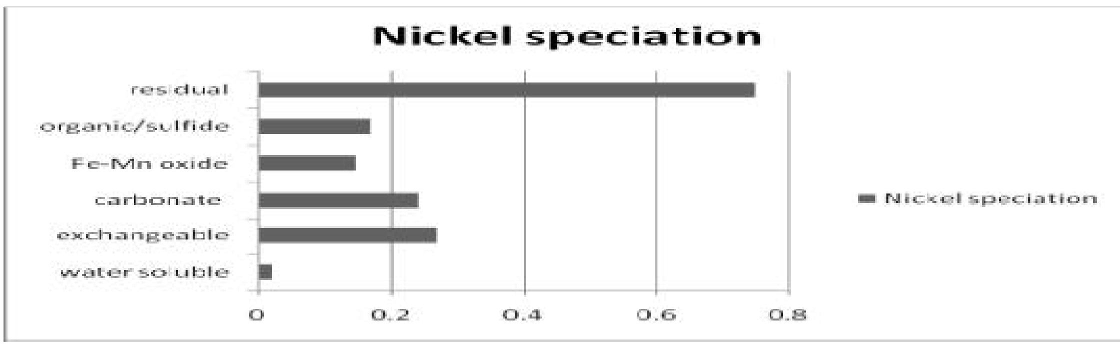

Fig. 4. Graphical presentation of nickel speciation

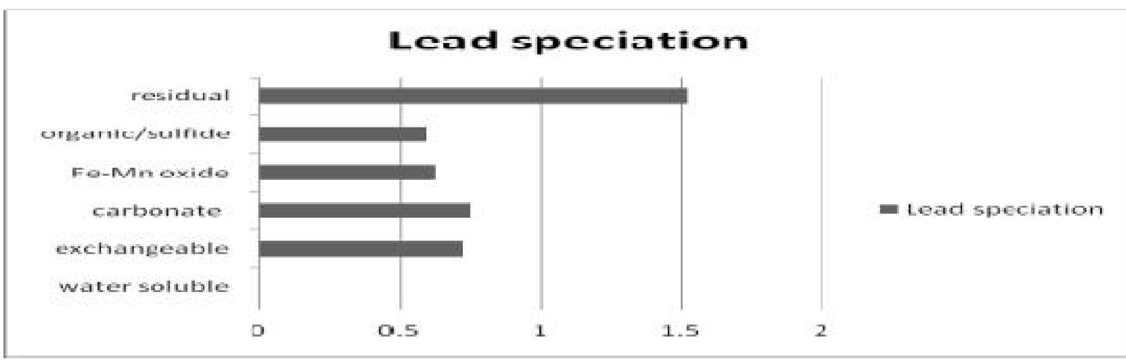

Fig. 5. Graphical presentation of lead speciation

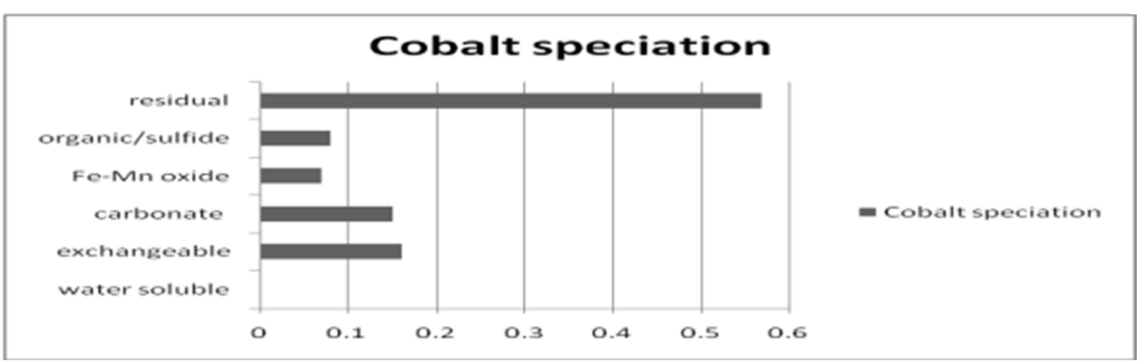

Fig. 6. Graphical presentation of cobalt speciation

Table 6. Fractional concentration of chromium (mg/kg)

Sampling points	Water soluble fraction (F1)	Exchange-able fraction (F2)	Carbonate bound (F3)	Fe-Mn oxide fraction (F4)	Organic and sulfide (F5)	Residual fraction (F6)	Total	Mean	BAF	% BAF
Plast 1	0.115±0.003	0.423±0.011	0.341±0.007	0.462±0.005	0.576±0.012	1.099±0.015	3.016	0.50	0.879	29.145
Plast 2	0.128±0.004	0.440±0.004	0.229±0.008	0.251±0.007	0.307±0.025	1.191±0.009	2.546	0.42	0.797	31.304
Plast 3	0.098±0.003	0.240±0.009	0.238±0.002	0.232±0.015	0.178±0.036	1.539±0.042	2.525	0.42	0.576	22.811
Total	0.341	1.103	0.808	0.945	1.061	3.829	8.087	1.340	2.252	83.26
Mean	0.11	0.36	0.26	0.31	0.35	1.27	2.69	0.44	0.75	27.75

Table 7. Fractional concentration of nickel (mg/kg)

Sampling points	Water soluble fraction (F1)	Exchange-able fraction (F2)	Carbonate bound (F3)	Fe-Mn oxide fraction (F4)	Organic and sulfide (F5)	Residual fraction (F6)	Total	Mean	BAF	% BAF
Plast 1	0.012±0.001	0.374±0.011	0.338±0.001	0.271±0.012	0.310±0.003	0.624±0.003	1.929	0.32	0.724	37.532
Plast 2	0.035±0.000	0.234±0.001	0.185±0.012	0.102±0.004	0.118±0.000	0.682±0.006	1.356	0.23	0.454	33.481
Plast 3	0.035±0.005	0.210±0.006	0.213±0.002	0.080±0.001	0.083±0.008	0.954±0.009	1.575	0.26	0.458	29.079
Total	0.082	0.818	0.736	0.453	0.511	2.260	4.860	0.810	1.636	100.092
Mean	0.02	0.27	0.24	0.15	0.17	0.75	1.62	0.27	0.54	33.36

Table 8. Fractional concentration of lead (mg/kg)

Sampling points	Water soluble fraction (F1)	Exchange-able fraction (F2)	Carbonate bound (F3)	Fe-Mn oxide fraction (F4)	Organic and sulfide (F5)	Residual fraction (F6)	Total	Mean	BAF	% BAF
Plast 1	0.029±0.016	0.813±0.014	0.808±0.010	0.742±0.002	0.745±0.014	0.995±0.007	4.074	0.68	1.592	39.077
Plast 2	0.053±0.008	0.806±0.026	0.779±0.007	0.727±0.016	0.598±0.012	1.503±0.261	4.360	0.73	1.532	35.138
Plast 3	0.071±0.013	0.545±0.008	0.676±0.001	0.410±0.001	0.448±0.003	2.085±0.009	4.093	0.68	1.150	28.098
Total	ND	2.164	2.263	1.879	1.791	4.583	12.527	2.09	4.274	102.313
Mean	ND	0.72	0.75	0.62	0.59	1.52	4.17	0.69	1.42	34.10

The speciation of Zn followed the same pattern with Cu. However, the metal was detectable in water soluble fraction which was absence in Cu (Fig. 8).

The Mn metal was evenly distributed among the other four forms outside residual and water soluble forms (Fig. 9).

There was higher concentration of Mn and that reflected in the increased bioavailability of the metal in the soil. The concentration of the metal observed in the water soluble indicated the metal's mobility in that vicinity (Table 12).

Table 13, indicated that there was virtually equal distribution of the Ca metal among the exchangeable, the carbonate, the Fe-Mn oxide and the organic/sulfide forms, with the highest concentration in the residual form. Anthropogenic activity was vivid as indicated by the speciation result (Fig. 10). This is in line with the results obtained by Abugu et al. 2013 [13,14].

The picture of the mobility of the Fe metal was shown by its detection in the water soluble form and the percentage bioavailability of the metal was highest for all the metals considered (Table 14). The observed trend for the metal speciation was F3 > F2 > F4 > F5 > F6 > F1 (Fig. 11).

The metal was quite distributed in all the forms considered. The water soluble had the lowest level of the metal, while the residual form retained the highest concentration of the metal in that soil. The mobility picture of the metal was shown by the fraction in the water soluble and the bioavailability of the metal was slightly elevated.

In general, heavy metals partitioning from the soils of effluent channels at Jesco Industry showed that the highest and lowest fractions for Fe, Mn, Pb, Cr, Cu, Ni, Co, and Zn are in the residual and water soluble fractions respectively, except for Ca which have carbonate bound fraction and water soluble as its highest and lowest forms, as well as Cd having residual and Fe-Mn oxide (reducible) fraction/ water soluble as its highest and lowest forms respectively. Again, in all the metals and the soil of the industries considered, an increased bioavailability and hence mobility would be enhanced by remobilization. Remobilization is mainly influenced by four types of chemical changes in soil and water, and they include the following:

- Increased salt concentrations whereby the alkali and alkaline earth cations can compete with the metal ions adsorbed onto solid particle. This is more obtainable for the exchangeable fractions.
- Decrease in the pH, which leads to dissolution of carbonates and hydroxides, and increased adsorption of metal cations due to competition with hydrogen ions (H^+). This is more obtainable in the carbonate forms.
- Changes in the redox conditions, usually in conjuction with a decrease in oxygen potential due to advanced eutropolication iron and manganese hydroxides are partly or completely dissolved, whereby part of the incorporated or adsorbed heavy metal load is being released. This is observed for the reducible fraction.
- Increased use of natural and synthetic complexing agents, which can form soluble complexes sometimes of high stability with heavy metals that are otherwise adsorbed to solid particles Omuku, [15].

In addition to these four processes, there are other biochemical transformation processes by which the heavy metals are either transferred from sediments to animals or plant organisms.

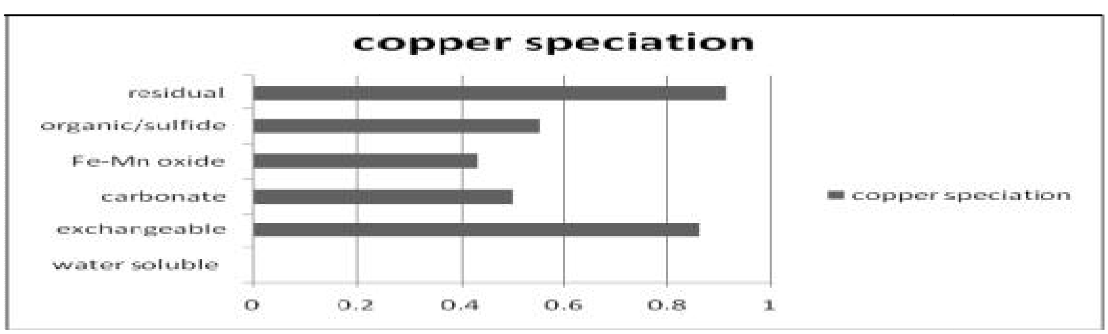

Fig. 7. Graphical presentation of copper speciation

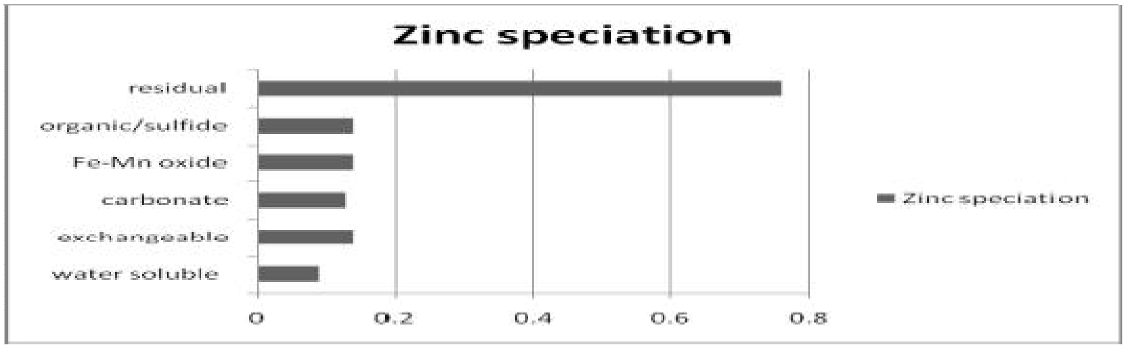

Fig. 8. Graphical presentation of zinc speciation

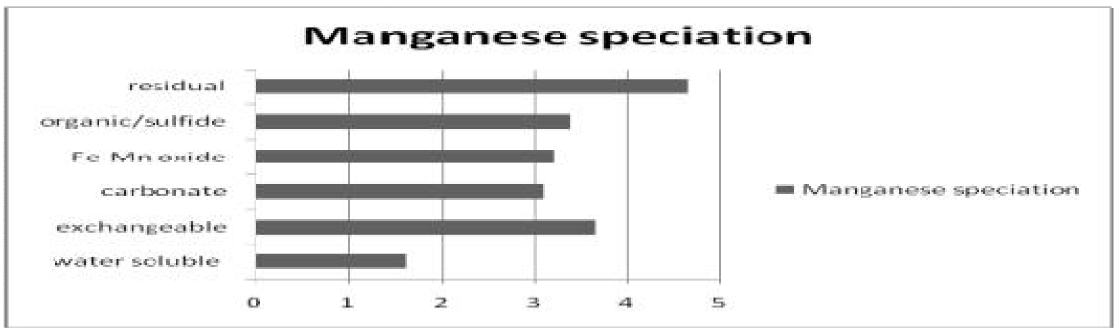

Fig. 9. Graphical presentation of manganese speciation

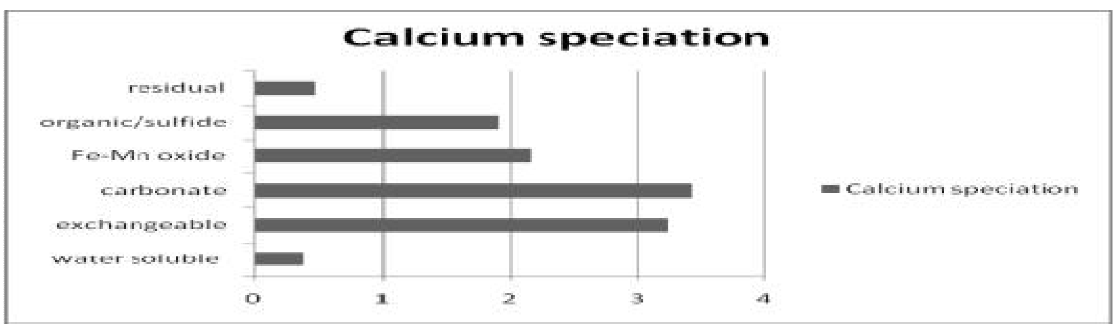

Fig. 10. Graphical presentation of calcium speciation

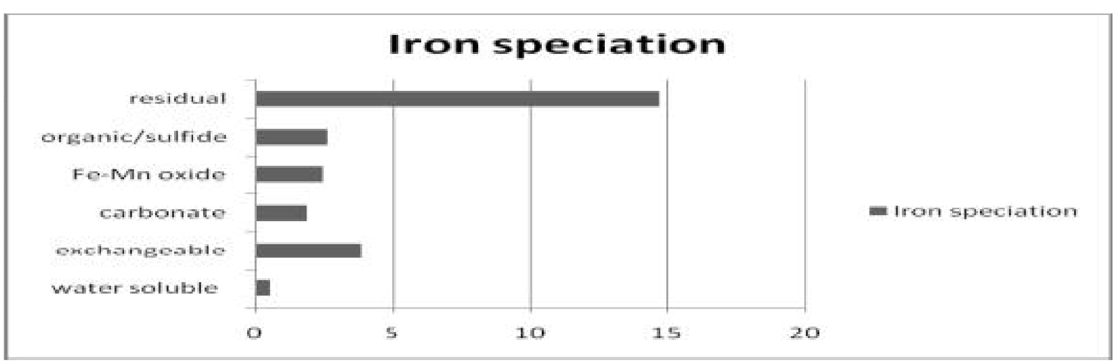

Fig. 11. Graphical presentation of Iron speciation

Table 9. Fractional concentration of cobalt (mg/kg)

Sampling points	Water soluble fraction (F1)	Exchange-able fraction (F2)	Carbonate bound (F3)	Fe-Mn oxide fraction (F4)	Organic and sulfide (F5)	Residual fraction (F6)	Total	Mean	BAF	% BAF
Plast 1	0.002±0.000	0.257±0.003	0.228±0.000	0.170±0.003	0.185±0.003	0.460±0.015	1.298	0.22	0.483	37.211
Plast 2	0.006±0.001	0.127±0.004	0.107±0.000	0.032±0.000	0.041±0.005	0.491±0.007	0.792	0.13	0.228	28.788
Plast 3	0.009±0.000	0.115±0.003	0.116±0.003	0.012±0.003	0.019±0.004	0.779±0.005	1.032	0.17	0.222	21.512
Total	ND	0.499	0.451	0.214	0.245	1.730	3.122	0.52	0.933	87.511
Mean	ND	0.16	0.15	0.07	0.08	0.57	1.04	0.17	0.31	29.17

Table 10. Fractional concentration of copper (mg/kg)

Sampling points	Water soluble fraction (F1)	Exchange-able fraction (F2)	Carbonate bound (F3)	Fe-Mn oxide fraction (F4)	Organic and sulfide (F5)	Residual fraction (F6)	Total	Mean	BAF	% BAF
Plast 1	0.024±0.004	0.632±0.006	0.522±0.006	0.417±0.008	0.488±0.010	1.082±0.004	3.117	0.52	1.130	36.253
Plast 2	0.008±0.001	0.609±0.021	0.504±0.015	0.642±0.037	0.717±0.001	0.772±0.015	3.236	0.54	1.105	34.147
Plast 3	0.036±0.003	1.344±0.004	0.499±0.007	0.258± 0.006	0.450±0.029	0.889±0.011	3.404	0.57	1.807	53.085
Total	ND	2.585	1.525	1.317	1.655	2.743	9.757	1.63	4.042	123.485
Mean	ND	0.86	0.50	0.43	0.55	0.91	3.25	0.54	1.34	41.16

Table 11. Fractional concentration of zinc (mg/kg)

Sampling points	Water soluble fraction (F1)	Exchange-able fraction (F2)	Carbonate bound (F3)	Fe-Mn oxide fraction (F4)	Organic and sulfide (F5)	Residual fraction (F6)	Total	Mean	BAF	% BAF
Plast 1	0.010±0.001	0.123±0.001	0.145±0.007	0.102±0.001	0.121±0.005	0.754±0.015	1.255	0.21	0.278	22.151
Plast 2	0.162±0.002	0.176±0.001	0.145±0.004	0.227±0.005	0.176±0.003	0.897±0.004	1.783	0.30	0.483	27.089
Plast 3	0.123±0.003	0.147±0.008	0.119±0.001	0.102±0.002	0.127±0.005	0.646±0.017	1.264	0.21	0.389	30.775
Total	0.295	0.446	0.409	0.431	0.424	2.297	4.302	0.72	1.15	80.015
Mean	0.09	0.14	0.13	0.14	0.14	0.76	1.434	0.24	0.38	26.67

Table 12. Fractional concentration of manganese (mg/kg)

Sampling points	Water soluble fraction (F1)	Exchange-able fraction (F2)	Carbonate bound (F3)	Fe-Mn oxide fraction (F4)	Organic and sulfide (F5)	Residual fraction (F6)	Total	Mean	BAF	%BAF
Plast 1	0.242±0.036	5.309±0.148	4.359±0.113	4.902±0.142	4.785±0.075	4.373±0.108	23.970	3.99	9.910	41.343
Plast 2	4.535±0.115	3.051±0.020	2.554±0.045	2.884±0.081	3.092±0.056	4.782±0.118	20.898	3.48	10.140	48.521
Plast 3	0.097±0.020	2.599±0.013	2.332±0.077	1.802±0.047	2.277±0.073	4.803±0.502	13.910	2.32	5.028	36.147
Total	4.874	10.959	9.245	9.588	10.154	13.958	58.778	9.79	25.078	126.011
Mean	1.62	3.65	3.08	3.19	3.38	4.65	19.59	3.26	8.35	42.00

Table 13. Fractional concentration of calcium (mg/kg)

Sampling points	Water soluble fraction (F1)	Exchange-able fraction (F2)	Carbonate bound (F3)	Fe-Mn oxide fraction (F4)	Organic and sulfide (F5)	Residual fraction (F6)	Total	Mean	BAF	%BAF
Plast 1	0.096±0.026	4.343±0.029	3.706±0.019	4.099±0.021	3.915±0.012	0.395±0.014	16.554	2.76	8.145	49.203
Plast 2	0.717±0.011	2.414±0.027	2.862±0.013	1.800±0.015	1.169±0.029	0.357±0.004	9.319	1.55	5.993	64.309
Plast 3	0.336±0.030	2.963±0.022	3.695±0.059	0.601±0.001	0.645±0.009	0.685±0.055	8.925	1.49	6.994	78.364
Total	1.149	9.72	10.263	6.500	5.729	1.437	34.798	5.80	21.132	191.876
Mean	0.38	3.24	3.42	2.16	1.90	0.47	11.59	1.93	7.04	63.95

Table 14. Fractional concentration of iron (mg/kg)

Sampling points	Water soluble fraction (F1)	Exchange-able fraction (F2)	Carbonate bound (F3)	Fe-Mn oxide fraction (F4)	Organic and sulfide (F5)	Residual fraction (F6)	Total	Mean	BAF	%BAF
Plast 1	0.733±0.021	4.488±0.164	2.640±0.033	3.486±0.203	3.428±0.007	13.28±0.144	26.589	4.43	6.395	24.051
Plast 2	0.700±0.033	6.061±0.006	2.061±0.048	2.238±0.017	2.489±0.060	16.85±0.097	30.399	5.07	8.822	29.020
Plast 3	1.723±0.195	1.025±0.006	0.919±0.030	1.630±0.043	1.907±0.042	13.95±0.038	21.154	3.53	3.667	17.334
Total	1.69	11.574	5.62	7.354	7.824	44.08	78.142	13.03	18.884	70.405
Mean	0.56	3.85	1.87	2.45	2.60	14.69	26.04	4.34	6.29	23.46

Table 15. Percentage bioavailability of metals

Sample code	Cd	Cr	Ni	Pb	Co	Cu	Zn	Mn	Ca	Fe
Plast 1	38.586	29.145	37.532	39.077	37.211	36.253	22.151	41.343	49.203	24.051
Plast 2	18.589	31.304	33.481	35.138	28.788	34.147	27.089	48.521	64.309	29.020
Plast 3	16.058	22.811	29.079	28.098	21.512	53.085	30.775	36.147	78.364	17.334
Total	73.233	83.260	100.092	102.313	87.511	123.485	80.015	126.011	191.876	70.405
Mean	24.41	27.75	33.36	34.10	29.17	41.16	26.67	42.00	63.95	23.46

Table 16. Water soluble fractions and the bioavailability fractions of metals

Metals (mg/2g)	Cd	Cr	Ni	Pb	Co	Cu	Zn	Mn	Ca	Fe
Sum of fractions	0.26	2.69	1.62	4.17	1.04	3.25	1.43	19.59	11.59	26.04
Bioavailable fraction	0.07	0.75	0.54	1.42	0.31	1.34	0.38	8.35	7.04	6.29
Water soluble fraction	ND	0.113	0.027	ND	ND	ND	0.098	1.624	0.383	0.563
%Bioavailability	24.41	27.75	33.36	34.10	29.17	41.16	26.67	42.00	63.95	23.46

ND = Not Detectable

3.2 Percentage Bioavailability

Having understood that the use of sequential extractions, although more time consuming, furnishes detailed information about the origin, mode of occurrence, biological and physicochemical availability, mobilization and transport of trace metals, consideration of the percentage bioavailability became necessary to have an adequate picture for adequate concern about the metals content of the soils considered. Bioavailability could mean the ready availability of elements for plant uptake, in which there exists potential effect to animals including man through the food chain. And recalling that the limiting step for elemental entry to the food chain, as discussed in the factors influencing bioavailability in soil, usually occur at the soil to the root; and this critical step usually depends on element concentrations in the soil pore solutions, which are controlled by local soil physical and chemical conditions including water content, pH and other factors, the percentage bioavailability was computed from the water soluble, exchangeable and carbonate fractions and presented in Table 15 above.

A close observation of the results revealed that iron with the highest concentration is the least bioavailable metal in the vicinity. Other metals with increased concentration (Table 16 above), like Ca, Mn and Cu, although showed significant bioavailability, are essential trace metals, which would otherwise draw alarming attention if it were to be Cd or Pb; and more so if readily leached into water. It would have been more serious if there was a significant concentration of these two most considered metals, Cd and Pb, in the water soluble fraction of their bioavailability; or more so when the concentration of the metals exceeded the permissible level for soils. A summary picture of the sum of fractions, bioavailable fractions and the water soluble fractions of the individual metals is presented in Table 16.

4. CONCLUSION

The levels of incidence of the considered metals in the soils studied are insignificant to conclude pollution of the environments.

There was significant level of anthropogenic contributions in the environments judging with the speciation results; but the risks are still below the tolerable range considering the standards presented in this work.

Iron, (Fe) being very significant in terms of pollution or concentration in the soil was the least bioavailable; secondly Fe is an essential element and therefore does not really connote the hazards sought for the environment, with respect to the presence of these industries. Finally the concentration of the selected heavy metal are not high enough to conclude that the activities of the industry is dangerous to the residents of the community putting into consideration the bioavailability of all the selected metals except for Ca which is an essential metal.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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