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HEAVY METALS DISTRIBUTION AND SPECIATION IN SOILS AROUND A MEGA CEMENT FACTORY IN NORTH-CENTRAL NIGERIA

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Abstract

Surface and sub-surface soils were sampled in the neighbourhood environment of an ultra-modern and largest cement factory in Nigeria. The five geochemical fractions investigated were exchangeable, carbonate, Fe-Mn oxide, organic matter and residual. All fractions were subsequently analyzed for lead (Pb), copper (Cu), zinc (Zn), manganese (Mn) and iron (Fe) using atomic absorption spectrophotometer. The average total metals concentrations (mg/Kg) in the surface soil were 1063.8± 261 for Fe, 30.29 ± 19.25 for Mn, 24.15 ± 21.69 for Cu, 15.08 ± 11.95 for Pb and 8.54 ± 3.18 for Zn. Relatively lower mean concentrations were measured in the sub-surface soil samples. The percent distribution concentration of the various metals in the residual fraction ranged from 0.23 to 69.48% for Pb, 0.85 to 75.30% for Cu, 36.02 to 83.86% for Zn, 12.97 to 44.04% for Mn and 18.11 to 57.25% for Fe. Factor analysis revealed that while Pb, Cu and Zn would majorly be of anthropogenic origin, Mn and Fe are mainly of natural origin. Pb was found to be the most mobile with mobility factor of 71.8% while Fe has the least mobility factor of 3.62%. Regression analysis ($r^2 = 0.71$) further showed that Cu is correlated with Pb. Soil pollution indices revealed that the surface soil is slightly contaminated in lead and zinc, and moderately contaminated in copper.

Key words: *Heavy metals speciation, Mobility factor, Soil pollution, Cement industry*

INTRODUCTION

The occurrence of heavy metals in soil can be of geogenic or natural and anthropogenic origins. The anthropogenic sources include mining, smelting, fossil fuel combustion and various industrial activities. Many researchers (Chandra *et al.,* 2005, Chen *et al.,* 2005, Fayun *et al.,* 2008, Olajire *et al.,* 2003) ascertained industrial activities to be the major source of soil heavy metals contamination.

One of the major challenges to human health and environmental quality is contamination of the environment by potential toxic element and this is of major concern to the environmental scientists (Olajire *et al.,* 2003, Sakan *et al.,* 2010). In particular, there is a very large set of health consequences from exposure to soil contamination depending on pollutant type, pathway of attack and vulnerability of the exposed population. Lead is especially hazardous to young children and for whom there is a high risk of developmental damage to the brain, while to all population kidney damage is a risk. Although many potential contaminants are required in trace amounts by plants for food production but they become hazardous when they occur in excess in the soil (Tokalioglue *et al.,* 2003).

Once there is an introduction of metal contaminants into the environment, it can exist in various chemical forms and the form in which these metals exists is much more important as the degree of metal toxicity has been closely related to their chemical forms (Eisler 1986, Evans 1989, Rubio and Rauret, 1996). Speciation studies are carried out by sequential extraction with reagents having different chemical properties. It provides information on the partition of metals into exchangeable, carbonate bound, Fe-Mn oxide-bound, organic matter-bound and residual fraction and this is the order of their chemical and biological availability (Olajire *et al.,* 2003).

The five fractions obtained by sequential extraction are not all available to plants,only the water soluble metals or those that participate in ion exchange reactions are usually available to plants (Kabala and Singh 2001) while those that are precipitated as carbonates, occluded in Fe, Mn and Al oxides or exists as complexes with organic matter are firmly bound; and this depends on physical and chemical properties of soil such as

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soil clay content, pH, organic matter and Fe-Mn oxide (Chuckwujingu 2007). A good number of researchers (Chuckwujingu 2007, Fayun *et al.*, 2008, Jaime *et al.,* 2003, Olajire *et al.,* 2003, Osakwe and Egbarevba 2008, Amanda and David 2010) have applied the sequential extraction procedure to river sediment, soil in the industrial zone areas, automobile waste dumps and municipal solid waste dump sites among others.

The particles of dusts which are emitted at every stage of cement production are numerous and differ based on their source of broadcast (Zerougi *et al.,* 2008) and hence their environmental impact calls for interest all over the world. The present study has been undertaken in order to evaluate the extent of pollution of soil around an ultra-modern and largest cement producing factory in Nigeria.

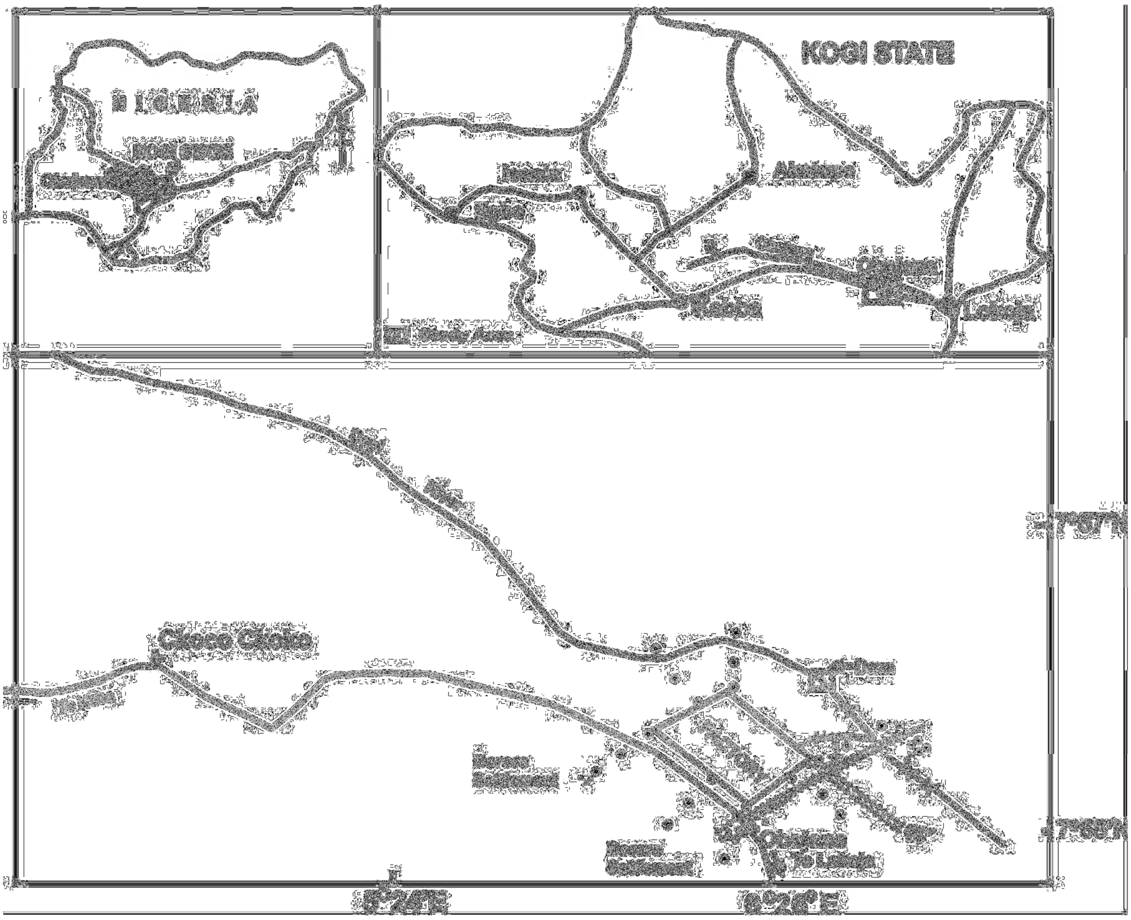

Figure 1: Map of the Study Area showing the sampling locations

Methodology

This study was carried out in the new urban settlement of Obajana town in the North-central state of Kogi in Nigeria. A total of 24 Soil samples were collected in November 2008 in a grid system around the cement factory as shown in Figure 1. At each wing, samples were collected by the perimeter fence (0 metre), 500m and 1km away from the perimeter fence of the factory. At each point, samples were taken at two depths i.e. 0-15 cm and 15-30 cm. Dirts in the sample were handpicked and the samples were air dried and grinded well to obtain fine particles. The soil was sieved through a 150μm plastic sieve to remove gravel-sized materials (Al-Khashman *et al.*, 2006). 5g of soil was accurately weighed and digested in a platinum crucible using a mixture of $HClO_4$ and HCl (Eletta, 2004), the digested sample was then dissolved with HCl, filtered and diluted to 50 cm^3 with distilled water in $50cm^3$ volumetric flasks. Metals were analyzed using Thermo-S4 atomic absorption spectrophotometer

Nine of the 24 samples were further subjected to sequential extraction following the Tessier's method (Tessier *et al.,* 1979). The details are briefly summarised below:

Fraction 1: $40cm^3$ 1.0 M $MgCl_2$ solution at pH of 7.0 was added to 5 g sample and was subjected to continuous agitation for two hours using Stuart flask shaker. This fraction gave the exchangeable metals.

Fraction 2: $40cm^3$ of 1.0M sodium acetate adjusted to pH 5 with glacial acetic acid was added to the residue obtained from fraction one and was subjected to continuous agitation for 6 hours using a shaking device. This fraction gave metals bounded to carbonates.

Fraction 3: The residue obtained from fraction two was leached with $100cm^3$ of $NH_2OH.HCl$ in 25% (v/v) acetic acid for 6 hours with occasional agitation. This gave metals bound to iron and manganese oxide**s.**

Fraction 4: The residue obtained from fraction 3 was leached with $15cm^3$ of 0.02M HNO_3 and $25cm^3$ of 30% H_2O_2 and was heated for 2 hours at 85 ^{0}C with intermittent agitation, then another $15cm^3$ portion of 30% HNO_3 solution was added and the mixture adjusted to pH 2 with concentrated trioxo nitrate V acid and heated at 85^0C for 3 hours with intermittent agitation. After cooling, $25cm^3$ of 3.2M ammonium acetate (NH_4Ac) in 20% (v/v) acetic acid was added to the mixture and was agitated continuously for 30 minutes at room temperature. This gave metals bounded to organic matter.

Fraction 5: The residue from fraction four was finally leached with $7.5cm^3$ $HClO_4$ and was shaken for 1 hour. This gave metals in the residual fraction.

A thermo S4 Atomic Absorption Spectrophotometer was used to analyse Pb, Zn, Cu, Mn and Fe in the digested samples.

Soil Pollution Index

Considering sample collection distance, soil pollution indices (SPI) for Pb, Cu and Zn were calculated for the top soil samples according to the formula given below (Sanka *et a*l., 1995):

$$\mathrm{SPI} = \frac{1}{n}\sum_{i=1}^{n} 100\,\frac{VSi}{LS}$$

Where VS is the metal concentration (mg/Kg) in the soil and LS is the maximum allowable concentration in soil.

Results and Discussion

Distribution of metals in soil samples

The range of concentrations, mean and standard deviations at 0-15cm and 15-30cm depths of Pb, Cu, Zn, Mn and Fe in the soil samples are presented in Table 1. In general, there is slight decrease in the mean concentration of all the metals examined vertically from upper to lower portions of the soil. Iron has the highest mean concentration followed by manganese, copper, lead and zinc in that order. There is wider variation in the concentration of metals. The concentrations for upper soil ranged from 659.6 to 1474.4 mg/kg for Fe, 1.11 to 74.48 mg/kg for Mn, 4.22 to 14.74mg/kg for Zn, 4.64 to 73.44mg/kg for Cu and 1.24 to 40.22mg/kg for Pb.

Highest concentrations of Pb and Cu were recorded at the east wall of the factory (E_0) by the major road passing through the front of the factory. The combustion of leaded gasoline by automobile usually leads to high concentration of Pb by the roadside (Olajire and Ayodele, 1997). A similar observation had been reported by Al-khashman and Shawabkeh (2006) in a separate study. Fayun *et al.,* 2008 in their study of an old and large industrial zone in North China also reported high level of Cu, Zn and Pb. Except for few locations, the concentration of the metals decreases generally with increasing depth in the soil samples examined. Many researchers have reported the same decrease in concentration as the depth increases (Chuckwujingu 2007, Fayun *et al.,* 2008, Osakwe and Egharevba 2008). The decreasing rate for all the metals was found to be very low (table I). This may signify that the heavy metal pollution did not stop at the top layer (0 – 15cm) but also penetrated vertically downward to reach the bottom layer (15 – 30cm). The rate of percolation however depends on the nature of the soil (King 2009).

Enrichment Factors In order to identify anthropogenic contributions of heavy metals to this environment, the enrichment factors for the various samples collected were calculated and summarized in Table 2. Considering the direction of wind flow and other sources of heavy metal pollution such as highways, E_{500m}FL was selected as the control. Pb enrichment was considerably high at all locations in all the soil with the highest values around the perimeter fence of the factory (E_0, W_0, S_0 and N_0). This was expected since these areas received particulates fallout from the factory as well as emissions from nearby highways. Few locations like N_{1km} and E_{1km} which are far away from the factory also have high Pb enrichment may be as a result of emissions from nearby highway. Cu also shows some significant enrichment at some point (N_{1km}, W_0, E_0, and E_{1km}). The fact that these points also have high Pb enrichment factor suggest that these metals could have the same origin. Mn and Fe exhibited very low enrichment factors in almost all the soil samples investigated compared with other metals. If an enrichment factor is greater than one, it indicates that the metal is more abundant in the soil relative to that found in the earth crust which indicates metal accumulation (Tokalioglu *et al.,* 2003). It is therefore evident that Pb, Cu and Zn have major anthropogenic inputs while Mn and Fe are mainly of natural origin.

Soil Pollution Index

The Canadian reference values for the maximum allowable limit for heavy metal in soil have been used (Dumitru *et al.*, 1994). These values expressed in mg/Kg are Pb (50), Cu (30) and Zn (50). The soil pollution indices calculated using the mean values for surface and subsurface soils for this environment are Pb: 0.26 and 0.30; Cu: 0.64 and 0.81; Zn: 0.16 and 0.17 respectively. According to the established contamination and pollution indices table (Dumitru *et al.,* 1994), the soil of this environment can be said to be slightly contaminated in lead and zinc, while it is moderately contaminated in copper. There are however few spots closest to the factory at the eastern part where the pollution indices were as high as 0.80 for Pb and 2.45 for Cu which suggested that these locations were moderately contaminated in Pb and moderately polluted in Cu.

Pearson correlation two tailed was conducted on all the soil samples. The results are shown in Table 3. The correlation was significant at $p < 0.05$ for Cu, Pb and Fe. Zn and Mn have no correlation with any of the metals and not even with each other. It is therefore most probable that Cu, Pb and Fe would have a common origin.

Factor analysis was also carried out using principal component analysis (PCA), Pb, Cu, Zn and Fe were found to have high loading in component 1 ranging from 0.3 to 0.91 whereas only Mn which was absent in component 1 was however loaded in component 2 with very high loading of 0.95. Using varimax rotation with Kaisier normalization, two components were also extracted with Pb, Cu, Zn and Fe having high loading in component one and Mn was the only extracted variable in component two. Cu was found to have the highest loading. The result indicates that while Pb, Cu, Zn and Fe could have common source (anthropogenic contribution), Mn has a different source (natural origin).

Chemical speciation of heavy metals in soil samples

In all the soil samples subjected to chemical speciation, Pb was found to be most associated with the residual fraction than all other fractions (Figure 2). Many researchers have reported varying concentrations of Pb in different fractions, Chuckwujindu (2007) reported high percentage concentration of Pb in the residual fraction, however, Olajire (2003) reported Pb to be most concentrated in the non-residual fraction while other researchers found Pb to be associated with organic matter fraction (Livette *et al.,* 1979, Tyler 1978). Sometimes the un-extracted Pb in fraction 3 (Fe-Mn oxide fraction) can be desorbed in organic matter fraction (Ryan *et al.,* 2002). The varying concentration of Pb in the different fractions could be attributed to varied nature of industrial activities.

In all the soil samples subjected to chemical speciation, Cu was found to be most associated with organic matter, Fe-Mn oxide and residual fraction (Figure 3). The dominance of Cu in the organic phase has also been reported by others (Chuckwujingu 2007, Olajire *et al.,* 2003, Osakwe and Egharevba 2008). The association of Cu with organic fraction may be due to high formation of organic – Cu complexes chiefly from agrochemicals (Olajire *et al.,* 2003). Cu has the lowest concentration in the exchangeable and carbonate bound fraction (Figure 3).

Zn was mostly associated with the residual fractions and the organic bound fraction (Figure 4). The strong association of Zn with residual and organic fraction was also reported by Fayun *et al.,* (2008) in soil collected around industrial zone. Zn has the lowest concentration in the carbonate, exchangeable and Fe-Mn oxide fractions (Figure 4).

In all the soil samples on which chemical speciation were conducted, manganese was found to be most concentrated in the residual fraction and Fe-Mn oxide fraction (Figure 5). This is in line with previous studies by some workers (Navas and Lindofer, 2003 ; Rico *et al.,* 2009).

Fe was found to be most concentrated in the residual fraction as well as in the organic and Fe-Mn oxide bound fractions to a lesser degree (figure 6) . This is consistent with the work of Navas and Lindhorfer (2003) where dominance of Fe in the residual fraction was also reported.

Conclusion

The concentrations of all the metals were found to decrease generally with increasing depth of the soil. Fe has by far the largest concentration followed by Mn, while Cu, Zn and Pb have the least and of the same order of magnitude. The results of this investigation also revealed the anthropogenic occurrence of Pb, Cu, Zn and partly Fe while Mn and Fe were mainly of natural origin. The soil pollution indices calculated using the mean values for surface and subsurface soils for this environment revealed that the soil was slightly contaminated in lead and zinc, and moderately contaminated in copper. Few spots closest to the factory at the eastern part were found to be moderately contaminated in Pb and moderately polluted in Cu. Pb exhibited the highest anthropogenic contamination followed by Cu and Zn. Pb is a highly toxic metal and therefore its environmental pollution should be taken seriously. Its bioaccumulation in plants and especially in human can lead to serious health challenges. Its emissions therefore should be minimized.

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TABLE 1 Total concentration of heavy metals in the soil samples
Mean, Standard deviation and range for the metal concentrations (mg/Kg) of 24 samples at two depths

Parameters	0-15cm			15-30cm		
	Mean	Std. dev	Range	Mean	Std. dev	Range
Pb	15.08	11.95	1.36 - 40.22	12.94	9.14	1.24 - 30.98
Cu	24.15	21.69	4.69 - 73.42	19.08	15.09	4.64 - 42.18
Zn	8.54	3.18	4.53 - 14.74	7.79	3.14	4.22 – 13.02
Mn	30.29	19.25	1.25 – 74.48	26.90	17.47	1.11 -68.43
Fe	1,063.83	261.00	660.40 – 1474.40	1,001.73	223.87	659.60 – 1311.70

Table 2 Enrichment factors for the heavy metals in the Soil

ELEMENT		Pb	Cu	Zn	Mn	Fe
N_o	0-15cm	10.434	3.676	1.968	2.444	0.697
	15-30cm	10.591	2.200	1.817	2.246	0.662
N_{500m}	0-15cm	8.380	1.360	1.145	1.026	0.909
	15-30cm	7.656	1.200	0.990	0.936	0.774
N_{1km}	0-15cm	23.831	7.081	1.996	1.589	0.536
	15-30cm	22.747	7.355	1.941	1.322	0.549
S_0	0-15cm	9.700	5.527	1.522	0.499	0.607
	15-30cm	8.046	5.462	1.007	0.440	0.554
S_{500m}	0-15cm	3.615	1.241	0.976	1.233	0.954
	15-30cm	3.442	0.990	0.820	1.184	0.911
S_{1km}	0-15cm	9.122	3.502	1.541	0.604	0.664
	15-30cm	9.700	2.816	1.170	0.569	0.623
W_0	0-15cm	16.413	9.041	2.867	0.533	0.773
	15-30cm	14.421	7.308	2.533	0.472	0.771
W_{500m}	0-15cm	3.101	1.698	2.304	0.505	1.074
	15-30cm	2.953	1.521	1.923	0.413	0.956
W_{1km}	0-15cm	2.911	1.490	2.208	1.159	0.892
	15-30cm	2.391	1.331	2.360	1.124	0.842
E_0	0-15cm	29.527	15.677	1.519	1.292	0.715
	15-30cm	17.781	8.992	1.716	0.867	0.685
E_{500m}	0-15cm	1.000	1.000	1.000	1.000	1.000
	15-30cm	0.913	1.037	1.002	0.989	0.951
E_{1km}	0-15cm	14.864	10.512	0.880	0.041	0.481
	15-30cm	13.525	8.587	0.868	0.036	0.481

Table 3: Two tailed Pearson correlation

Correlations

		PB	CU	ZN	MN	FE
PB	Pearson Correlation	1	.785**	.280	.165	-.518**
	Sig. (2-tailed)	.	.000	.054	.263	.000
	N	48	48	48	48	48
CU	Pearson Correlation	.785**	1	.154	-.090	-.600**
	Sig. (2-tailed)	.000	.	.297	.542	.000
	N	48	48	48	48	48
ZN	Pearson Correlation	.280	.154	1	.000	-.085
	Sig. (2-tailed)	.054	.297	.	.998	.566
	N	48	48	48	48	48
MN	Pearson Correlation	.165	-.090	.000	1	.043
	Sig. (2-tailed)	.263	.542	.998	.	.770
	N	48	48	48	48	48
FE	Pearson Correlation	-.518**	-.600**	-.085	.043	1
	Sig. (2-tailed)	.000	.000	.566	.770	.
	N	48	48	48	48	48

**. Correlation is significant at the 0.01 level (2-tailed).

Rotated Component Matrix [a]

	Component	
	1	2
PB	.871	.298
CU	.918	-4.16E-02
ZN	.307	.291
MN	-8.88E-02	.943
FE	-.789	9.469E-02

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.

a. Rotation converged in 3 iterations.

Component Matrix [a]

	Component	
	1	2
PB	.900	.192
CU	.907	-.151
ZN	.340	.252
MN	2.445E-02	.947
FE	-.772	.188

Extraction Method: Principal Component Analysis.

a. 2 components extracted.

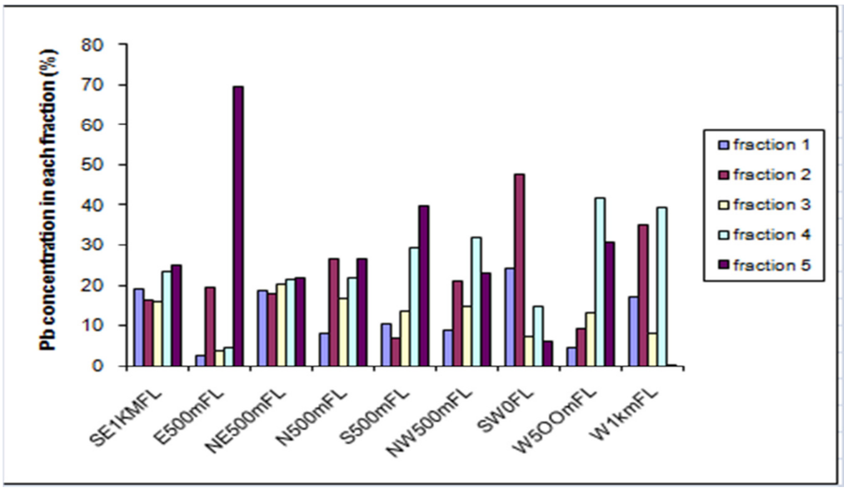

Figure 2 Percentage of total Pb associated with each of the five fractions for soil samples

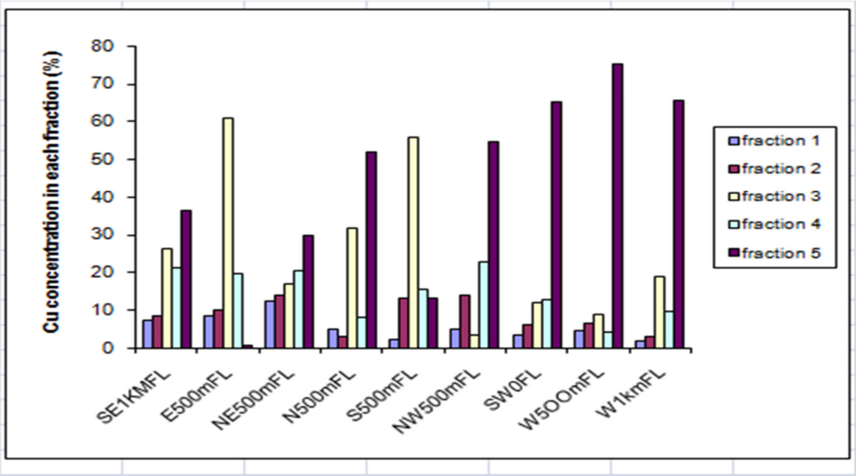

Figure 3 Percentage of total Cu associated with each of the five fractions for soil samples

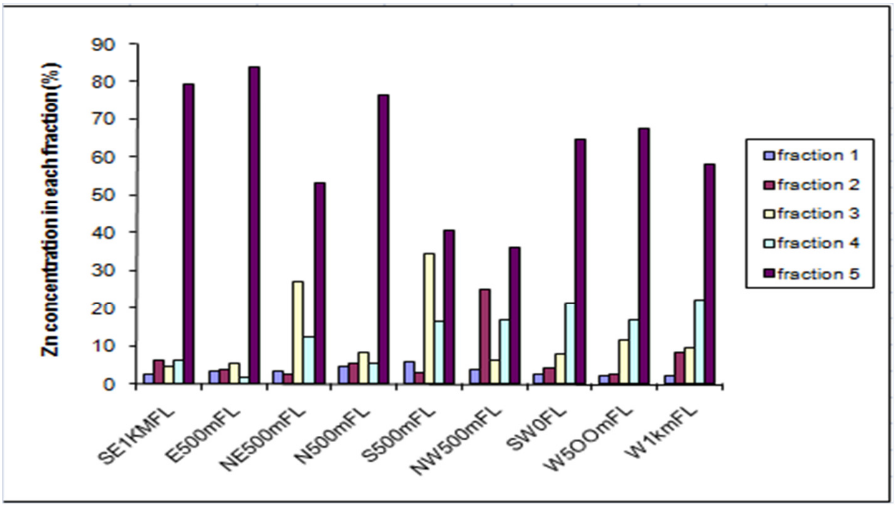

Figure 4 Percentage of total Zn associated with each of the five fractions for soil

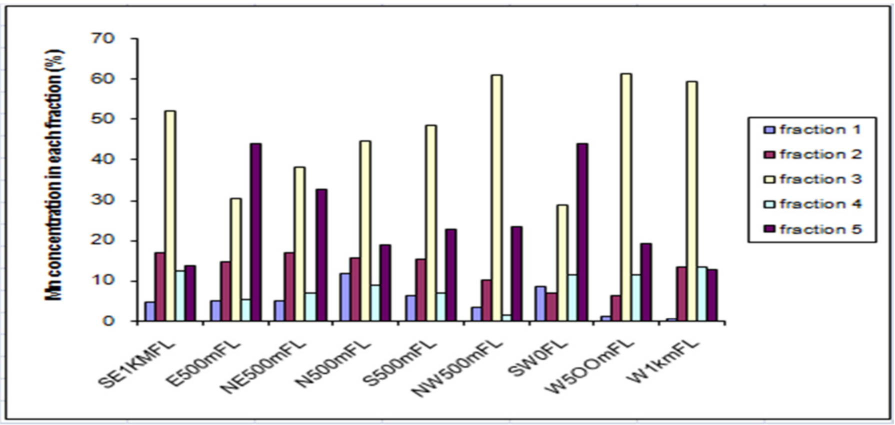

Figure 5 Percentage of total Mn associated with each of the five fractions for soil samples

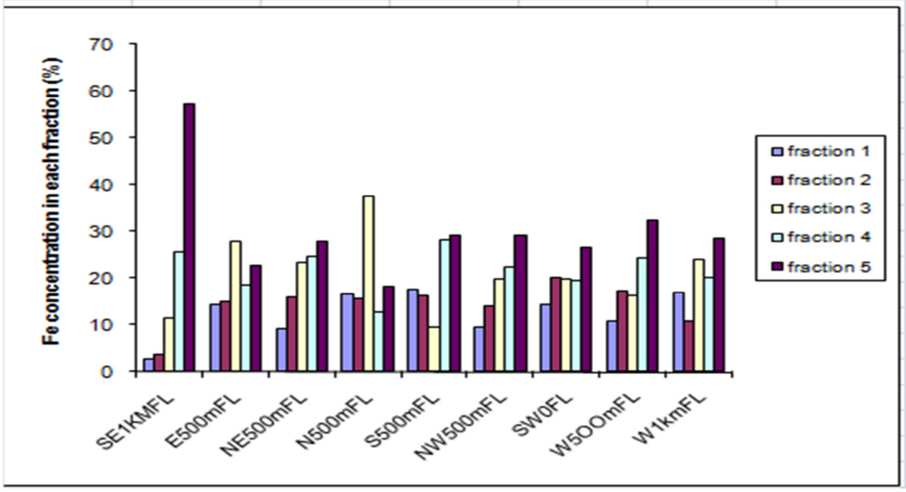

Figure 6 Percentage of total Fe associated with each of the five fractions for soil samples