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Heavy Metal Distribution and Contamination in Soils around Enyigba Pb-Zn Mines District, South Eastern Nigeria

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ABSTRACT
Twelve {12} soil samples were collected from the Pb – Zn mining district of Enyigba, Ameri and Ameka in the Abakaliki area of Ebonyi State, south-eastern Nigeria and analysed for As, Cd, Cu, Pb, Zn, Ni, Co, Mn, Ca and pH. The physico-chemical analyses show that pH is fairly acidic to neutral (5.3-7.0) resulting from the dissolution of the sulphide ore waste dump into the soil. The heavy metal mean trend indicates that As > Cd > Co > Mn > Cu > Ni > Pb > Zn. Ca is also high. The variations observed for the heavy metals suggest that both geologic and anthropogenic activities may be responsible for their distribution.
Soil contamination is assessed on the basis of enrichment factor (EF) and contamination factor (CF).
The results of enrichment factor (EF) show that using Mn concentration in the background value, Cd show extremely high enrichment, Cu, Pb and As have significant enrichment, while Co, Zn and Ni show moderate to low enrichment.
The CF values for the soils indicate very high contamination for Cd, high concentration for As while Pb, Cu, Co, Mn, Ni and Zn show moderate contamination.
Keywords: Soil Contamination, Partial Leach Test, Enrichment/Contamination Factor, Enyigba, Pb-Zn Mines

1. INTRODUCTION

Soil is the preeminent source of most biologically active trace elements such as Lead, Zinc, Cadmium, Arsenic, Nickel and Copper that reach man through plants and animals (Mitchell and Burridge, 1979). The trace element content of soil depends on the nature of its parent rocks and also the amount of sewage effluents, industrial wastes and fertilizer impurities entering the soil (Williams and David, 1976). Although fewer than 20 trace elements are required for the healthy growth of plants and animals (Mitchell and Burridge 1979), the excess concentration of these metals might be hazardous with negative health effects (Dickshroom et. al, 1979, Malini et. al; 1995, Underwood, 1971).

Extensive researches have been conducted to obtain data on the heavy elements distribution in soils from varieties of environments throughout the world, including urban areas (Odigi et. al; 2011; Zhongping et. al; 2011), highway road sides (Ihenyen 1998) rural areas in active and abandoned mining districts (Nnabo, 2011, Nnabo et al, 2011, Onyeobi and Imeokparia, 2014, Levy et al 1992, Rowan et. al; 1995, Navarro et. al; 2008) and in agricultural regions used for crops (Archer 1980, Loska et al, 2004).

It is generally known that rivers and related urban environments have been severely contaminated by heavy metals such as Cd, As, Pb, Cu and Zn) as a result of Pb/Zn historic and modern mining operations and industrial activities (Hudson – Edwards et. al; 2001, Miller et. al; 2004, Taylor et. al; 2010). Metal contamination that occurs as a result of mining characterized by elevated toxic metal concentrations and acid rock and mine drainage, continue several years after the cessation of mining activities. Heavy metal effluents from the weathering of the mineral deposits and mine dumps affect both the surface and underground water quality and soil. These levels of contamination in the area may lead to low agricultural production, and other biological communities if present at anomalously high level. The release of such contaminants to water sources and air can pose a significant threat to the environment and human health especially to people living around such environments (Taylor et. al; 2010).

Elevated concentrations of Cd, As and Pb in the environment are a particular issue in mining regions because of their documented deleterious human health effects (Nnabo, 2011, Taylor et. al; 2010) especially in young children who often place objects in their mouths resulting in dust and soil being ingested (Lanphear et. al; 1996) as well as being inhaled directly (Laidlaw and Filippelli 2008).

In Nigeria, only a few of such studies have been conducted and published (Egboka et al, 1993; Ajayi and Mombe-Shora, 1990; Ezeh et al, 2007; Nnabo et al, 2011; Adaikpoh et. al; 2005) particularly in the active and abandoned Pb – Zn mining district of Abakaliki, southeastern Nigeria, where the people are predominantly small-scale miners and rural farmers (Loska et al, 2004; Nnabo, 2011). However, there are documented studies involving soil and alluvium surveys and stream sediment geochemical surveys in relation to mineral exploration for Pb – Zn deposits (Ukpong and Olade 1979,). No much work has been undertaken to assess the impact of mining upon the local environment.

Since the discovery of and mining of Pb-Zn deposits in Enyigba and its environs in the early 1900s, not much data exist on the impact of their mining on the environment. This study is aimed at assessing the distribution and concentration of heavy metals in the soils around Enyigba-Ameka-Ameri and Ohankwu Pb – Zn

mining district, near Abakaliki and to determine the anthropogenic and/or geologic contribution to the enhancement of the heavy metals.

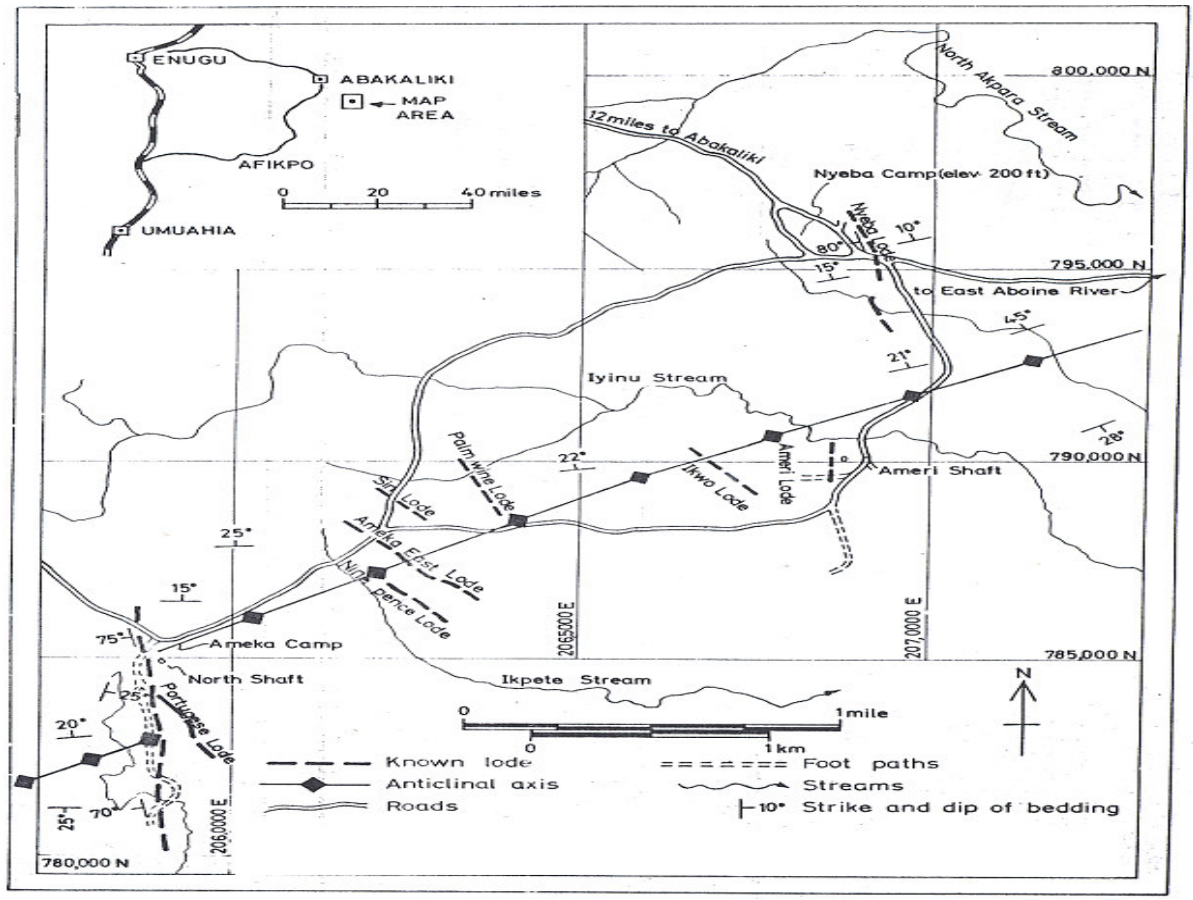

Figure 1. Geological map of lead-zinc deposits of Enyigba district, near Abakaliki, Lower Benue Trough. The area is underlain by Abakaliki shales (Modified from Orajaka, 1965).

2. GEOLOGY

The Enyigba, Ameri, Ameka and Ohankwu region is marked by undulating range of shale outcrops, which serve as the host for Pb-Zn mineral deposits. The area forms part of the "Abakaliki antichrionium" and generally underlain by the Abakaliki shales of the Asu River Group. The Abakaliki shale of lower Cretaceous age is exposed in the area. The sedimentary rocks are predominantly black calcareous (calcite-cemented) shale with occasional intercalation of siltstone (Figure 2). The shale formation belongs to the Asu-River Group of the Albian Cretaceous sediments. The Asu River Group which consists of alternating sequence of shales, mudstone and siltstone with some occurrence of sandstone and limestone lenses in some places and attains an estimated thickness of 1500 meters (Agumanu 1989, Farrington, 1952). Kogbe (1989) described the sediments as consisting of rather poorly-bedded sandy limestone lenses. Extensive weathering and ferruginization have generally converted the black shales to a bleached pale grey colour with mottles of red, yellow, pink and blue (Orajaka, 1965; Ukpong and Olade, 1979). The rocks are extensively fractured folded and faulted. The rocks of the area consist of variably coloured shale and mudstone that has been imbedded by lead – zinc vein mineralization, baked shale as well as ironstone along the veins. The vein mineralization is hosted within the dark shale (Nnabo et al. 2011). The geology and mineral resources are the major factors responsible for availability of the heavy metals in the area. While the sulphide mineralization has high concentration of these metals, the shale host rocks are capable of retaining them from ancient sea (Nnabo et al. 2011).

The Benue Trough Pb – Zn mineralization occupies a 600-km stretch of highly deformed Albian sediments from Abakaliki – Ishiagu (Ebonyi State) to Gwana (Gombe State) (Farrington 1952, Olade, 1976, Orazulike 1994, Fig..). The mineralization consists of a few occurrences of telethermal mississippi valley-type Pb – Zn deposits, localized as open – space fillings within steeply dipping fractures and veins associated with anticlinal structures (Abakaliki Anticlinorium) in shales. The sulphide deposits, principally galena and sphalerite, have been mined on and off for several decades (Offodile, 1989, Kogbe, 1989), with associated minor chalcopyrite, bornite, pyrite and quartz. Within the Abakaliki pyroclastics, disseminated pyritic sulphide

mineralization had been observed where the dominant mineral is pyrite with minor chalcopyrite and native copper. In the supergene zone, primary ores are replaced by secondary minerals such as cerussite, anglesite, smithsonite, pyromorphite and siderite.

In the Enyigba, Ameri and Ameka areas near Abakaliki, there is clear evidence of post-mineralization deformation (Nwachukwu,1972). Although the age of mineralization is not precisely known it is generally suggested that the lead/zinc lodes were developed at the end of Santonian folding (Wright, 1968; Nwachukwu, 1972). The Pb – Zn minerals show two habits, coarsely crystalline and granular. The granular varieties are extensively sheared, intensely striated and grooved. The area has a few scattered brine springs along the same axes as the mineralization.

The abandoned mines have their mine dumps left on the surface and the open cast mines were not filled up. These are likely to constitute environmental problems as a result of heavy metal build up in the soils, water and stream beds.

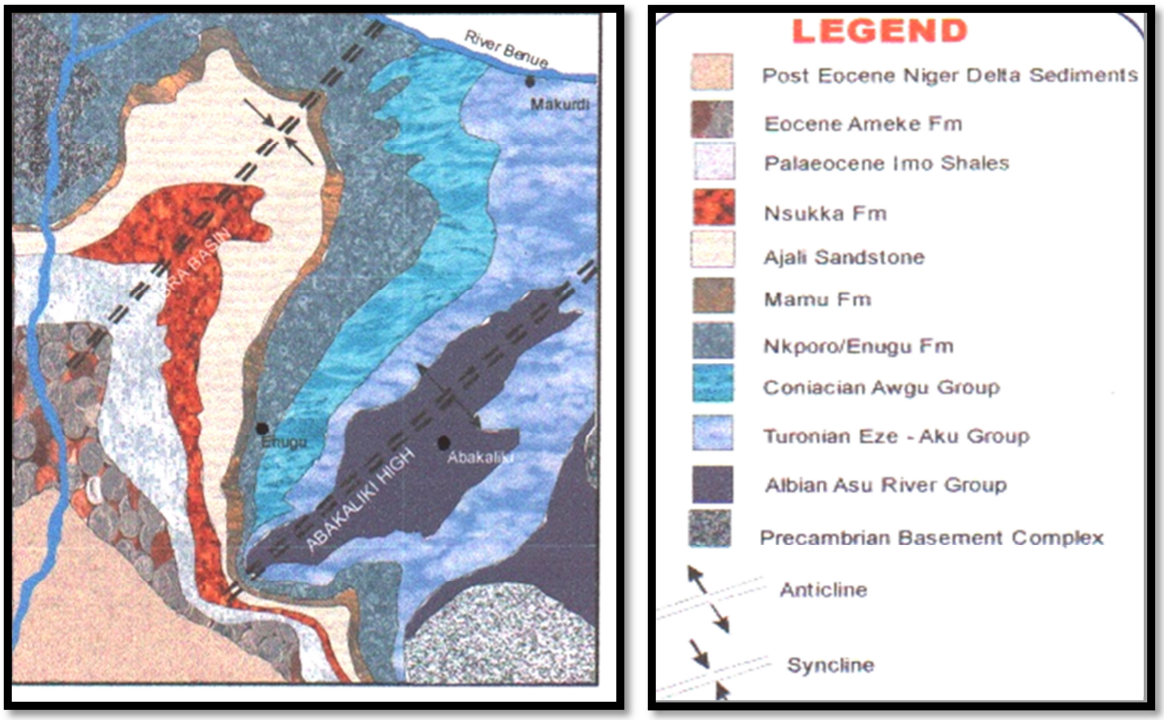

Fig. 2: General geologic map of Southeastern Nigeria showing Abakaliki basin in the Lower Benue Trough (Modified after Hoque, 1984).

3. MATERIALS AND METHODS.

Soil is the layer of unconsolidated particles derived from weathered rock, organic material, water and air that forms the upper surface over much of the earth and supports plant growth. The composition of the soil depends on the parent material, the original rock or bed rock from which the soil is derived. The climate and topography of the area, the organisms present in the soil, and the time over which the soil has been developing, also determine the composition of the soil. Soils are often classified in terms of their structure and texture. The structure refers to the way in which the individual soil particles are bound together to form aggregates. The structure types include platy, blocky, granular and crumbs. The texture of the soil denotes the proportion of the various particle sizes that it contains – sand, silt, clay and loam. Loams are generally the best agricultural soils as they contain a mixture of all particle sizes. The soil type in the project area is ferosol, which favours extensive growth of vegetation. It is heavily leached/weathered to reddish-brown coloured laterite and loam.

Twelve (12) soil samples were collected at different locations within the project area **(Figure 3)**. Some of the samples were collected around the mine dumps and others were sampled several metres away from the dumps, all within the derelict Enyigba mine area. Samples were taken from a depth of 20 to 30 cm with an auger. The GPS was used for the location of the sample points. The samples were collected in the wet season and they had to be sun-dried for one week. The dry soil samples were disaggregated and then homogenized by the use of agate mortar and pestle. The samples were sieved to obtain the required grain size of minus 80-mesh (<180 µm) fraction and minus 100-mesh (<150 µm) fraction by the use of sieves with stainless steel screens. The sieved fraction was pulverized to further reduce the drain size as required for geochemical analysis.

Solid soil samples were digested in the laboratory using the passive leach method that provides a measure of reactions in nature. In this method, 100 g of the sample was measured and placed in a beaker with 2000 ml of deionized water, stirred slightly and initial pH and temperature were measured. After about 20 hours, the upper part of the liquid was stirred slightly to mix the leachate solution. At 24 hours, the pH and temperature of the leachate were measured and a 60 ml aliquot was taken with a syringe and filtered. The leachate solutions were acidified with 5 drops of 1:1 ultrapure nitric acid (HNO_3) to stabilize metals in the solution – chiefly to minimize adsorption on the plastic bottle or formation of precipitates. The leachate was sent for analysis in a laboratory in Institute of Oceanography, University of Calabar. A total of nine elements were analysed and they include arsenic (As), calcium (Ca), cadmium (Cd), cobalt (Co), copper (Cu), manganese (Mn), nickel (Ni), lead (Pb) and zinc (Zn).

The behaviour of samples during the 24-hour tests was variable. In some samples the pH evolved to lower values during the 24 hours, and in some others, the pH rose to higher values reflecting acid consumption in reaction with minerals in these samples.

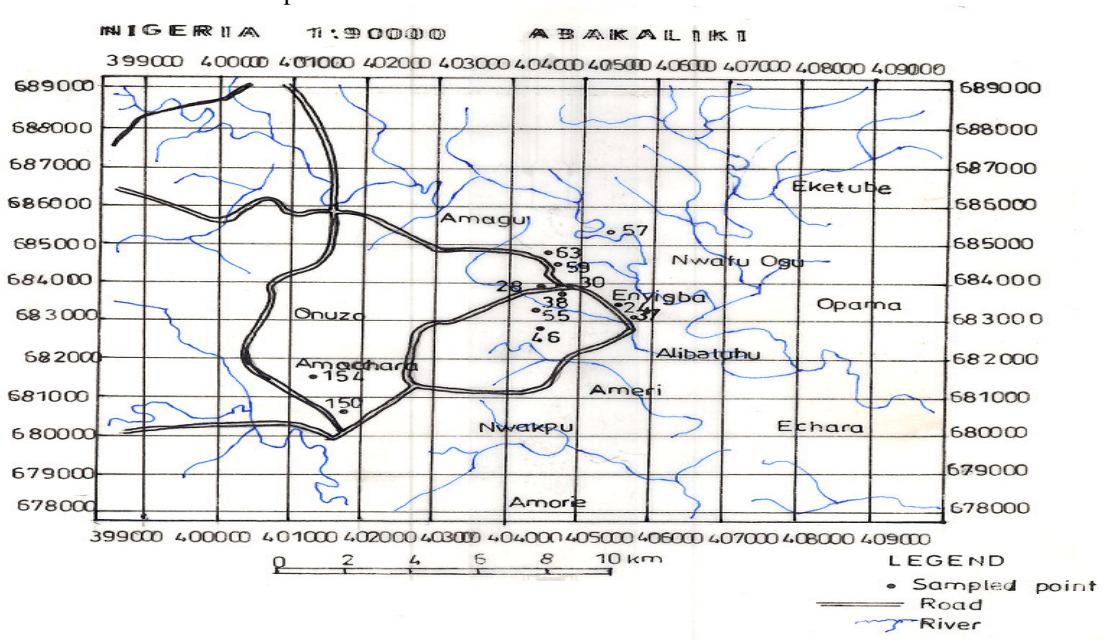

Figure 3. Location of Soil Samples Collected from Enyigba and its Environs.

4. RESULTS

In 66% of the soil samples (8 samples), the pH values evolved to lower values from 6.8 to 5.3 while in two samples (17%), the pH rose to higher values from 6.4 to 7.0. For the remaining two samples (17%) there was no significant change in the pH values and fairly acidic to neutral **(Table 1)**. Most of the materials created orange- to pale-yellow-coloured water, and a few were light-gray and some introduced little colour.

Table 1. Result of Leach tests on soil samples

S/No	Sample No	Initial pH	pH @ 24hr
1	PN/S/24	6.0	6.0
2	PN/S/28	6.8	6.1
3	PN/S/30	6.4	6.6
4	PN/S/37	6.7	7.0
5	PN/S/38	6.2	5.8
6	PN/S/46	6.5	5.9
7	PN/S/55	6.6	6.7
8	PN/S/57	6.5	6.2
9	PN/S/59	6.2	5.8
10	PN/S/63	6.3	6.0
11	PN/S/150	6.3	5.9
12	PN/S/154	5.6	5.3

Table 2 shows the results of the analysis of soil samples for their partial extractable heavy metals, representing mainly the mobile fractions of the nine metals..The maximum and minimum concentrations of each metal are also highlighted. There is the cluster of the maximum concentration of most of the heavy metals

around Ameri area. The concentrations of each metal in all the locations are given in Figures 4 - 6.

Table 2: Concentration of Mobile Heavy Metals in Soils from Enyigba and Environs.

Sample code	Location	Metals concentrations in mg/kg										
		As	Ca	Cd	Co	Mn	Cu	Ni	Pb	Zn		pH
PN/S/24	Enyigba 1	**nd**	**1925.70**	**0.24**	**0.70**	nd	**7.08**	**0.94**	nd	**2.45**		6.0
PN/S/28	Enyigba 2	9.23	9869.00	3.08	9.18	215.7	91.8	12.22	21.57	15.55		6.1
PN/S/30	Enyigba 3	nd	5306.00	0.66	2.00	**46.37**	19.90	2.64	nd	6.88		6.6
PN/S/37	Enyigba 4	nd	4809.00	0.61	1.80	nd	18.03	Nd	nd	6.24		7.0
PN/S/38	Enyigba 5	nd	5915.00	0.73	2.21	nd	86.50	Nd	nd	7.68		5.8
PN/S/46	Ameri	nd	3159.00	0.38	1.18	nd	69.52	Nd	nd	4.10		5.9
PN/S/55	Enyigba 6	**8.64**	9237.00	2.87	8.64	200.20	**160.17**	9.12	20.18	23.72		6.7
PN/S/57	Enyigba 7	nd	7432.00	2.31	6.95	162.22	34.08	9.26	**16.22**	24.10		6.2
PN/S/59	Enyigba 8	**16.02**	**17115.00**	**5.33**	**16.07**	**373.70**	19.30	**21.37**	**37.38**	**55.55**		5.8
PN/S/63	Enyigba 9	nd	9106.00	1.14	3.40	nd	44.88	Nd	nd	28.28		6.0
PN/S/150	Ohankwu	nd	5194.00	0.64	1.93	nd	91.80	Nd	nd	11.81		5.9
PN/S/154	Ameka	nd	4796.00	1.49	4.48	104.72	44.88	5.99	nd	6.73		5.3
Total		33.89	83863.70	19.48	58.54	1102.91	687.94	61.54	95.35	193.09		73.3
Mean		11.3	6988.64	1.62	4.88	183.82	57.33	8.79	23.84	16.09		6.11
Std.dev.		3.35	3847.48	1.45	4.37	102.43	42.54	6.30	8.06	14.48		0.44
Average Shale		10	2.5.104	0.3	20	850	50	80	20	90		
Average Crust		2.5	6.4.104	0.08	26.6	1000	27	59	11	72		
Normal Soil (Bowen, 1979)		6	--	0.1	8	--	30	15	14	90		

	Maximum concentration		Minimum concentration

From Table 2, Arsenic was detected in only three locations and ranged from 8.64 to 16.02 mg/kg with an average content of 11.3 mg/kg (Figure 4). Cadmium varied from 0.24 to 5.33 mg/kg with average value of 1.62 mg/kg (Figure 5). Cobalt ranged in concentration from 0.7 to 16.07 mg/kg with an average value of 4.88 mg/kg. The content of manganese, detected in six locations, ranged from 46.37 to 373 mg/kg with an average value of 183.82. Copper ranged from 7.08 to 160.17 and an average content of 57.33 mg/kg. Nickel ranged from 0.94 to 21.37 and an average value of 8.79 mg/kg and was detected in seven locations. Lead was detected in only four locations and varied from 16.22 to 37.38 with an average of 23.4 mg/kg (Figure 6) while zinc ranged from 2.45 to 55.55 mg/kg with an average value of 15.09 mg/kg.

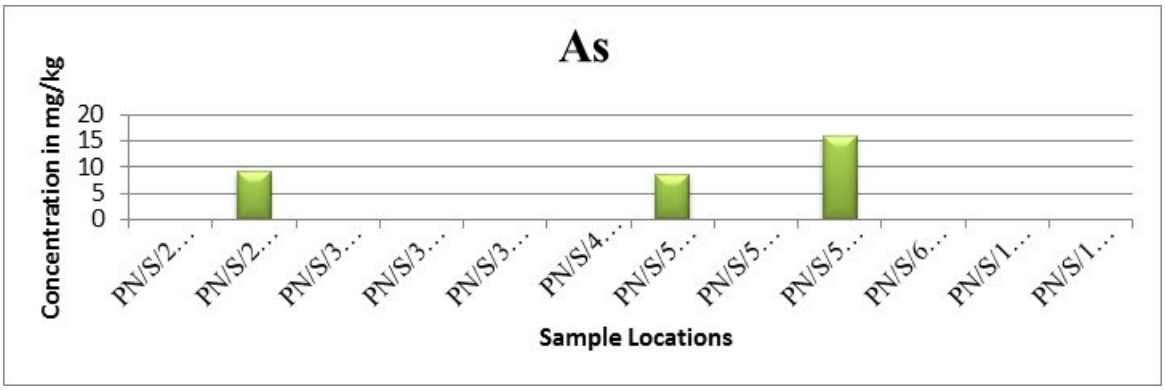

Figure 4 The Concentration of Arsenic in Soils from Enyigba and Environs.

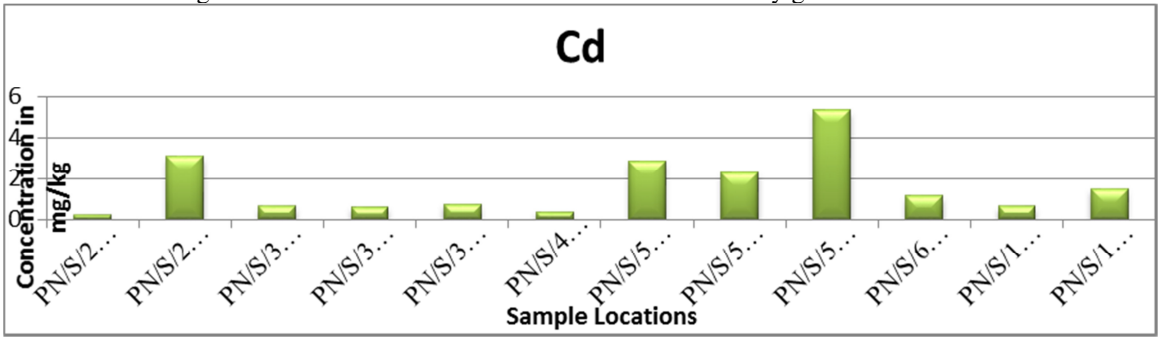

Figure 5. The Concentration of Cadmium in Soils from Enyigba and Environs.

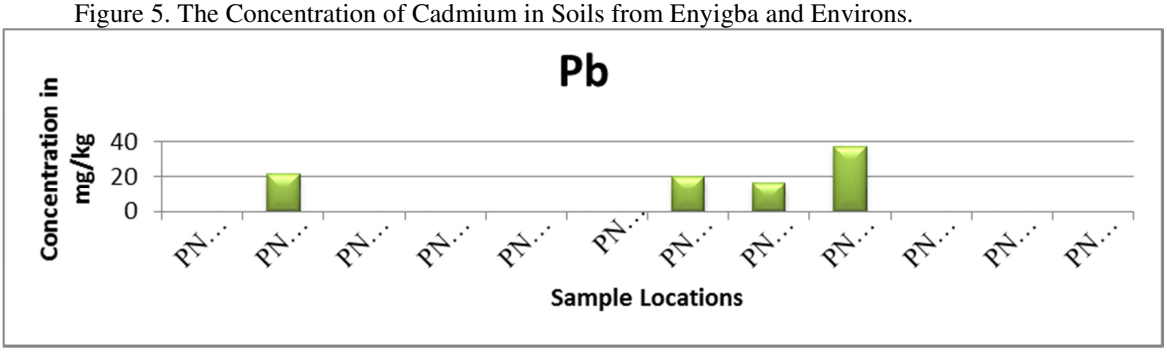

Figure 6. The Concentration of Lead in Soils from Enyigba and Environs.

Enrichment Factor (EF).

The enrichment factor (EF) was calculated based on the standardization of the tested element against the concentration of a reference metal (Kumar and Edward, 2009). In this work, Mn was used as the reference metal using the formula:

$$EF = \frac{Cn(sample)/Cref\ (sample)}{Bn\ (background)/Bref(background)}$$

Where **C***n* (sample) is the concentration of the examined element in the examined environment, **C***ref* (sample) is the content of the reference element in the examined environment (soil), **B***n* (background) is the content of the examined element in the reference environment and **B***ref* (background) is the content of the reference element in the reference environment. For this study, the average concentration of elements in shale (**Table 3**) was taken as the reference environment while C*ref* was taken as 183.82, the average manganese content of the analysed soil samples (see Table 2) of the Enyigba and Environs. Five contamination categories recognized on the basis of the enrichment factor are shown in Table 4. Table 5 shows the enrichment factors of the heavy metals analysed for in the soil samples of the Enyigba and Environs and the values are also depicted in Figures 7 - 10. The calculated EF and the corresponding health risk level (HR) are presented in Table 6.

Table 3. Compositional Estimates of the Crust and Shale (Average Crust and Shale) (in mg/kg)

Metals →	As	Cd	Co	Cu	Ni	Pb	Zn	Mn	Ca
Krauskopf (1979)**	1.8	0.15	22	50	75	12.5	70	1000	$4.1x10^4$
Wedepohl (1995)**	1.7	0.10	24	25	56	14.8	65	1000	$5.6x10^4$
Taylor & McLennan (1985, 1995**	1.0	0.10	29	75	105	8.0	80	1800	$7.4x10^4$
Gao et al (1998)**	3.1	0.08	24	38	46	15	81	1200	$4.9x10^4$
Rudnick & Gao (2003)**	2.5	0.08	26.6	27	59	11	72	1000	$6.4x10^4$
Krauskopf (1979)***	10	0.3	20	50	80	20	90	850	$2.5x10^4$

**Average Crust, ***Average Shal

Table 4. Contamination categories and health risk levels based on Enrichment Factor.

EF	**Pollution condition**	**Health Risk Level**
EF < 1	Deficient	0
EF = 1 - 2	Minimal	1
EF = 2 – 5	Low	2
EF = 5 – 20	Significant	3
EF = 20 – 40	Very high	4
EF > 40	Extremely high	5

Table 5. Enrichment Factors (EF) of Heavy Metals in Soils from Enyigba and Environs.

Sample Code	As	EF	Ca	EF	Cd	EF	Co	EF
PN/S/24	0.00	0	1925.70	**0.36**	0.24	**3.73**	0.70	**0.19**
PN/S/28	9.23	**5.02**	9869.00	**1.83**	3.08	**47.88**	9.18	**2.50**
PN/S/30	0.00	0	5306.00	**0.98**	0.66	**10.26**	2.00	**0.54**
PN/S/37	0.00	0	4809.00	**0.89**	0.61	**9.48**	1.80	**0.49**
PN/S/38	0.00	0	5915.00	**1.09**	0.73	**11.35**	2.21	**0.60**
PN/S/46	0.00	0	3159.00	**0.58**	0.38	**5.91**	1.18	**0.32**
PN/S/55	8.64	**4.70**	9237.00	**1.71**	2.87	**44.61**	8.64	**2.35**
PN/S/57	0.00	0	7432.00	**1.37**	2.31	**35.91**	6.95	**1.89**
PN/S/59	16.02	**8.72**	17115.00	**3.17**	5.33	**82.85**	16.07	**4.37**
PN/S/63	0.00	0	9106.00	**1.68**	1.14	**17.72**	3.40	**0.92**
PN/S/150	0.00	0	5194.00	**0.96**	0.64	**9.95**	1.93	**0.53**
PN/S/154	0.00	0	4796.00	**0.89**	1.49	**23.16**	4.48	**1.22**

Table 5 [*contd*]. Enrichment Factors (EF) of Heavy Metals in Soils of the Enyigba and Environs.

Sample Code	Cu	EF	Ni	EF	Pb	EF	Zn	EF
PN/S/24	7.08	**0.64**	0.94	**0.06**	0.00	---	2.45	**0.12**
PN/S/28	91.8	**8.32**	12.22	**0.74**	21.57	**5.87**	15.55	**0.77**
PN/S/30	19.90	**1.80**	2.64	**0.16**	0.00	---	6.88	**0.34**
PN/S/37	18.03	**1.63**	0.00	---	0.00	---	6.24	**0.31**
PN/S/38	86.50	**7.86**	0.00	---	0.00	---	7.68	**0.38**
PN/S/46	69.52	**6.30**	0.00	---	0.00	---	4.10	**0.20**
PN/S/55	160.17	**14.52**	9.12	**0.55**	20.18	**5.49**	23.72	**1.17**
PN/S/57	34.08	**3.09**	9.26	**0.56**	16.22	**4.41**	24.10	**1.19**
PN/S/59	19.30	**1.75**	21.37	**1.29**	37.38	**10.17**	55.55	**2.75**
PN/S/63	44.88	**4.07**	0.00	---	0.00	---	28.28	**1.40**
PN/S/150	91.80	**8.32**	0.00	---	0.00	---	11.81	**0.58**
PN/S/154	44.88	**4.07**	5.99	**0.36**	0.00	---	6.73	**0.33**

EF < 1	EF = 1 - 2	**EF = 2 – 5**	**EF =5 – 20**	**EF=20 – 40**	**EF> 40**
Deficient	Minimal	Low	Significant	Very high	Extremely high

Table 6. Enrichment factor and health risk of heavy metals contamination in soils.

Sample code	As		Cd		Co		Cu	
	EF	HR	EF	HR	EF	HR	EF	HR
PN/S/24	0	0	3.73	2	0.19	0	0.64	0
PN/S/28	5.02	3	47.88	5	2.50	2	8.32	3
PN/S/30	0	0	10.26	3	0.54	0	1.80	1
PN/S/37	0	0	9.48	3	0.49	0	1.63	1
PN/S/38	0	0	11.35	3	0.60	0	7.86	3
PN/S/46	0	0	5.91	3	0.32	0	6.30	3
PN/S/55	4.70	2	44.61	5	2.35	2	14.52	3
PN/S/57	0	0	35.91	4	1.89	1	3.09	2
PN/S/59	8.72	3	82.85	5	4.37	2	1.75	1
PN/S/63	0	0	17.72	3	0.92	0	4.07	2
PN/S/150	0	0	9.95	3	0.53	0	8.32	3
PN/S/154	0	0	23.16	4	1.22	1	4.07	2

Table 6 [*contd*]. Enrichment factor and health risk of heavy metals contamination in soils.

Sample code	Ni		Zn		Pb	
	EF	HR	EF	HR	EF	HR
PN/S/24	0.06	0	0.12	0	---	---
PN/S/28	0.74	0	0.77	0	5.87	3
PN/S/30	0.16	0	0.34	0	---	---
PN/S/37	---	---	0.31	0	---	---
PN/S/38	---	---	0.38	0	---	---
PN/S/46	---	---	0.20	0	---	---
PN/S/55	0.55	0	1.17	1	5.49	3
PN/S/57	0.56	0	1.19	1	4.41	2
PN/S/59	1.29	1	2.75	2	10.17	3
PN/S/63	---	---	1.40	1	---	---
PN/S/150	---	---	0.58	0	---	---
PN/S/154	0.36	0	0.33	0	---	---

EF is Enrichment Factor; HR is Health Risk level (See Table 7).

Table 5 shows that Cd had extremely high enrichment in three locations with the highest figure of 82.85 in sample PN/S/59, followed by PN/S/28 and PN/S/55 with values of 47.88 and 44.61 respectively (Figure 7).

Copper was significantly enriched in five locations with PN/S/55 having the highest value of 14.52 Figure 8). Lead showed significant enrichment in three locations with a maximum figure of 10.17 in PN/S/59 (Figure 9). Arsenic was significantly enriched in two locations with a maximum value of 8.72 in sample PN/S/59 (Figure 10). Co, Zn, Ni and Ca had low to deficient enrichment in all the samples (see Table 6).

Cd had extremely high pollution in three locations (25%) with health risk level of five. Cu had five samples (42%) showing health risk level of three (moderate pollution). Lead and arsenic showed similar pollution pattern. For Pb, 75% (three) of the samples had moderate pollution with health risk value three. For As, 67% (two) of the samples had moderate pollution with health risk value three. The pollution and health risk level for the other metals are very low (Table 6).

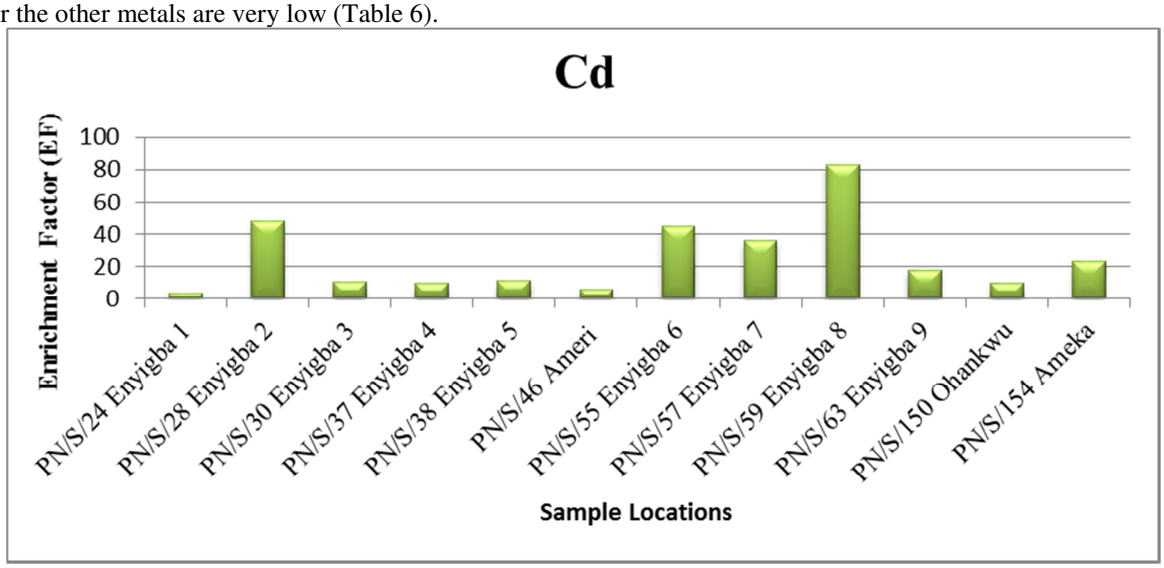

Figure 7. Enrichment Factor of Cadmium in Soils from Enyigba and Environs.

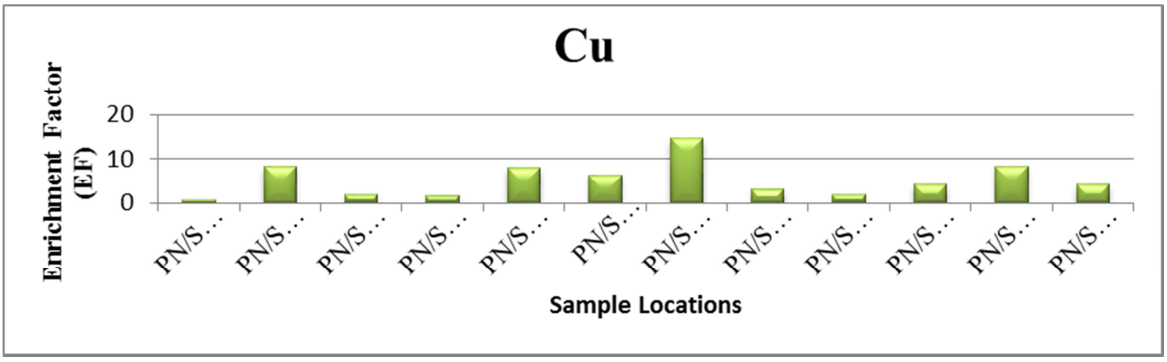

Figure 8 Enrichment Factor of Copper in Soils from Enyigba and Environs.

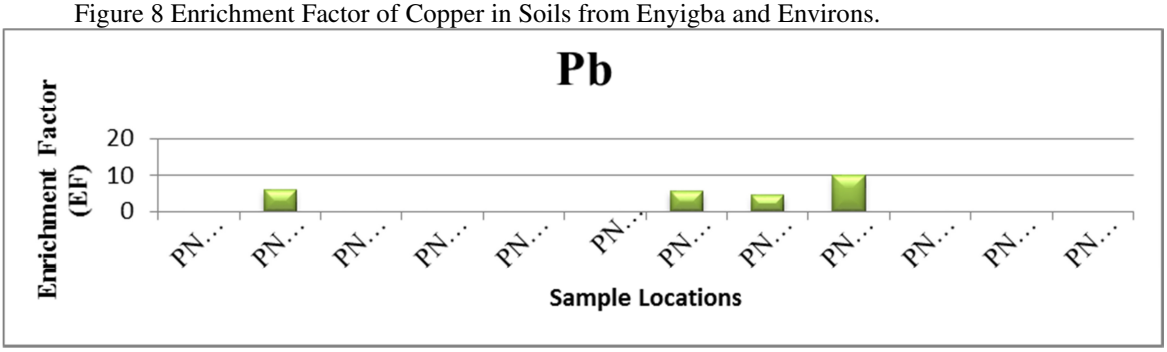

Figure 9. Enrichment Factor of Lead in Soils from Enyigba and Environs.

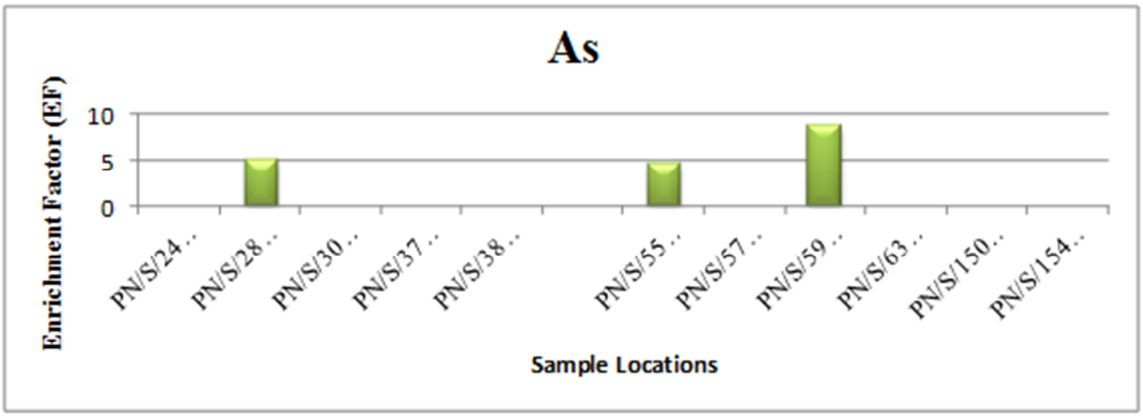

Figure 10. Enrichment Factor of Arsenic in Soils from Enyigba and Environs.

Contamination Factor (CF).

The assessment of contamination of the soils of Enyigba and Environs was also carried out using the contamination factor. This calculation was used to evaluate the potential risk of the heavy metals to the environment using the formula below (Kumar and Edward, 2009):

$$C_f^i = \frac{C_{0-1}^i}{C_n^i}$$

Where C_{0-1}^i is the mean concentration of metals from the soil sampling sites of the Enyigba and Environs (at least five) and C_n^i was taken as the average concentration of elements in the Earth's crust as a reference value (see **Table 3** Table 7 and Figure 11 show the contamination factors of heavy metals in rocks of the area. Four categories of contamination factor have been distinguished (Kumar and Edward, 2009; Table 8).

Table. 7. Contamination factors of heavy metals in soils from Enyigba and Environs.

As	CF	Cd	CF	Co	CF	Mn	CF	DC
11.3	**4.52**	1.62	**20.25**	4.88	**0.18**	183.82	**0.18**	
Cu	**CF**	**Ni**	**CF**	**Pb**	**CF**	**Zn**	**CF**	
57.33	2.12	8.79	**0.15**	23.84	**2.17**	16.07	**0.22**	**29.28**

< 1	1 - 3	3– 6	➢ 6
Low contamination factor	Moderate contamination factor	Considerable contamination factor	Very high contamination factor

Table 8. Categories of Contamination based on Contamination Factor

C_f^i	**Category of Contamination**
$C_f^i < 1$	Low contamination factor indicating low contamination
$C_f^i = 1 - 3$	Moderate contamination factor
$C_f^i = 3 - 6$	Considerable contamination factor
$C_f^i > 6$	Very high contamination factor

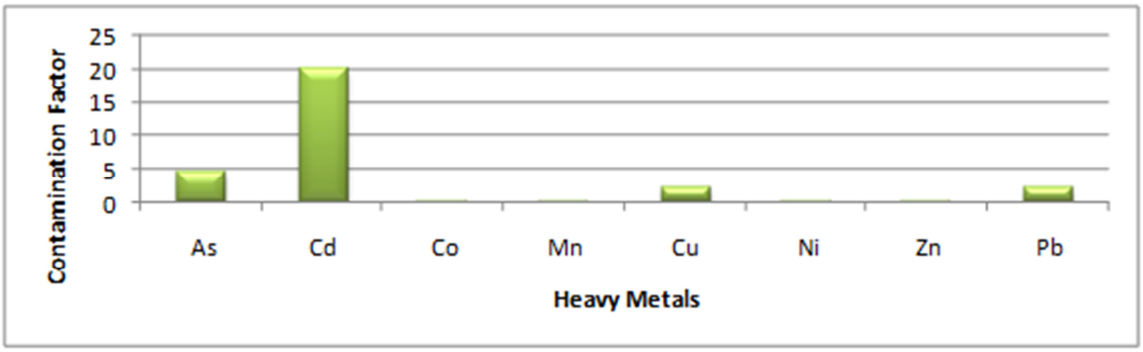

Figure 11. Contamination Factors of Heavy Metals in Soils from Enyigba and Environs.

Cadmium had the highest contamination factor of 20.25, followed by arsenic with a value of 4.52. The values for Pb, Cu, Co, Mn, Ni and Zn are very much lower, indicating low contamination (Table 7, Figure 11).

5. DISCUSSION

Distribution of Heavy Metals

Arsenic in the soil was detected in only three samples and varies from 8.64 to 16.02 mg/kg with an average value of 11.3 (±32.35) mg/kg. The three locations with concentrations of 16.02 mg/kg, 9.23 mg/kg and 8.64 mg/kg) all from Enyigba are 2.67, 1.54 and 1.44 times above the normal soil level of 6 mg/kg (Bowen, 1979) (Table 2). The highest value of 16.02 mg/kg was at pH of 5.8 while the lowest, 8.64 mg/kg was at pH of 6.7. Release of As is possible at wide range of pH. The average concentration of 11.3 mg/kg is also above the normal soil limit by 1.88 times (Table 9). Soils around the mines wastes generated from mining of Ba-Pb-Zn quartz veins at Segura area, central Portugal, was reported to have high contents of As, Pb and Zn (Antunes et al. 2008). Arsenic can be found in the environment in small concentrations, occurring in minerals, rocks and soils. Arsenic can be mobilized easily when it is immobile but due to human activities mainly through mining, naturally immobile arsenic have also mobilized and can get dispersed on many more locations than where they existed naturally. Arsenic in soils is highly mobile and once it is liberated it results in possible groundwater contamination (Plant and Raiswell, 1983).

Table 9. Average concentration of mobile heavy metals in soils compared with normal soil (Bowen, 1979) in mg/kg.

Heavy metal	Present study	Normal soil (Bowen, 1979)	No of times > normal soil	Level of pollution
Arsenic	11.3	6	1.88	Moderate
Cadmium	1.62	0.1	16.20	Very high
Cobalt	4.88	8	0.61	Low
Copper	57.33	30	1.91	Moderate
Nickel	8.79	15	0.59	Low
Lead	23.84	14	1.70	Moderate
Zinc	16.09	90	0.18	Low
Calcium	6988.64	15,000	0.47	Low
Manganese	183.82	---	---	---

Cadmium was detected in all the analysed soil samples, and ranged between 0.24 and 5.33 with a mean value of 1.62 (±1.45) mg/kg. The average content is 16.2 times above the normal soil composition of 0.1 mg/kg (Table 9). Some of the elevated concentrations, for example, 5.33 and 3.08 mg/kg both from Enyigba, and 1.49 mg/kg from Ameka are respectively 53.3, 30.8 and 14.9 times the normal soil level (Table 2). These localized high concentrations of Cd in the Enyigba area may be related to the vicinity of the highly oxidized ore zones (Bolucek, 2007). Cadmium waste streams from mining and mineral processing mainly end up in soils. Another important source of cadmium in the environment is through the production of phosphate fertilizers. Part of this enters the soil after fertilizer application while the rest enters surface water from dumps from fertilizer productions. The soils around Shileung Cu-Pb-Zn mine was reported to be severely contaminated where the mean concentrations of Cd, Cu, Pb and Zn were 10 to 100 times higher than those of the normal soils (Chon et al. 2005). And in Ceje area of Slovenia, concentration of heavy metals in soils exceeded the official limit where the content of Cd in soils was reported to be between 3 to 15 times above the normal soil average, a reflection of strong anthropogenic impact (Sajn and Gosar, 2008).

Cd present in soil is strongly adsorbed to organic matter and it can be extremely dangerous as their uptake through food will increase. Cd and As are the most hazardous because of their geochemistry and toxicological properties (Antunes et al. 2008). In Japanese soils, base metal mining activities are the main source of Cd contamination (Dudka and Adriano, 1999).

Mining may have contributed a high percentage of Cd to the soil as mining is the dominant anthropogenic activity in the area, as the main source of Cd contamination may be anthropogenic (Wang et al. 2008). Mining remains one the sources of Cd and other heavy metals to the environment (Dolenec et al. 2005; Kar et al. 2008; Wang et al. 2008; Sajn and Gosar, 2008). This can adversely affect the biota, including human around the mines area (Mendoza et al. 2005). The remaining may be from natural weathering of bedrock (shales) and the unmined sulphide ores. Many of the rocks samples in the study area are enriched in Cd with concentrations sucg as 16.23, 11.57, 10.38, 9.01 and 8.17 mg/kg (Nnabo, 2011). The concentrations of Cd in mine dumps are much lower, and ranged from 0.96 to 7.44 mg kg (Nnabo, 2011). In the soil samples, Cd concentration ranged from 0.24 to 5.33 mg/kg (Table 2). Cd in soil particularly elevated around Ameri mineshaft with content of 5.33 mg/kg, which is 53.3 times the normal soil level of 0.1 mg/kg. These concentrations may be relatively low but Cd is highly toxic even at low concentrations (Salvarredy-Aranguren et al. 2008).

Lead was detected in only four samples and its concentration range from 16.22 to 37.38 with a mean value of 23.84 (±8.06) mg/kg. This average content is 1.7 times the normal soil composition of 14 mg/kg (Table 9). The content of Pb within some Pb/Zn mining sites at Enyigba with values, 37.38, 21.57, 20.18 and 16.22 mg/kg were slightly above the normal soil composition of 14 mg/kg (Table 2). This indicates the low absorption capacity of the soils of the area (Mattigod and Page, 1983). Once lead enters the environment through natural and anthropogenic sources, it ends up in soils and surface water especially under slightly acidic conditions. The mining of sulphide ore in Stratoni area, Western Greece resulted in the mobility of the toxic metals in soils with the elevated contents of Pb, Cd and Zn with average concentrations of 1090, 6.2 and 878 mg/l respectively (Plakaki, 2006). In the Imcheon Au-Ag mineralization associated with galena and pyrite in quartz vein, the abandoned mine wastes was the source of contamination of the soils, water and sediments in the vicinity of mines by Cd, Cu, Pb and Zn to the level of 0.27, 1.90, 2.8 and 53.4 mg/l respectively (Jung, 2001). Also, in the Zlatna area of Carpathian Region of Romania, located in a region of polymetallic mining activities, the environment and particularly the soils were polluted by heavy metals including Pb, Cd, As, Cu and Zn (Lacatusu et al. 2001).

The contents of Cu in soils were variable from 7.08 to 160.17, with an average value of 57.33 (±42.54) mg/kg that is 1.91 times the normal soil composition (Table 9). Copper was detected in all the samples. Some of

the high concentrations, 160.17 mg/kg from Enyigba and 91.8 mg/kg from Ohankwu are above the normal soil level of 30 mg/kg by more than three to five times (Table 2). The health effects of Cu will be experienced mainly in the rock and soil environments. This is because when Cu ends up in soils it strongly adsorbs to organic matter and clay minerals, becomes immobile and hardly enters groundwater (Mattigod and Page, 1983).

The concentration of Ni in soil ranges between 0.94 and 21.37 with a mean of 8.79 (±6.3) mg/kg. It was only from Enyigba that the Ni content of 21.37 mg/kg was above the normal soil composition of 15 mg/kg by 1.42 times (Table 2). The low concentration of Ni was probably due to the relatively low mobility of the metal in alkaline environment (Cidu et al, 2005). This was obtainable in the Enyigba and Environs. Larger part of nickel compounds in the environment are adsorbed to organic matter in sediments or soil particles and thus become immobile. But high Ni concentrations are known to be associated with sandy soils and it can damage plants.

The distribution of zinc was as well variable, ranging from 2.45 to 55.55 and an average value of 16.09 (±14.48) mg/kg. The concentration of Zn in all the samples was below the normal soil composition of 90 mg/kg (Table 2). Zn, if in solution phase in soil would be highly attenuated through adsorption reactions thereby reducing its mobility (Mattigod and Page, 1983). while the average value of 16.09 mg/kg is below the normal soil level (Table 9).

Cobalt was detected in all the soil samples while nickel was recorded in only seven samples. The content of Co ranges from 0.7 to 16.07 with an average value of 4.88 (±4.37) mg/kg. The concentrations of Co, 16.07, 9.18 and 8.64 mg/kg all from Enyigba, were slightly above the normal soil standard of 8 mg/kg (Table 2). The low concentration of Co in some areas was probably due to the relatively low mobility of the metal in alkaline environment (Cidu et al, 2005). This was obtainable in the Enyigba and Environs. The areas with high Co concentrations are within the Pb/Zn mining area.

The mobile Co in the Enyigba and Environs will present health problems in the soil environment where the measured concentrations were found to be above the normal soil composition. Cobalt is widely dispersed in the environment and humans may be exposed to it by breathing air, drinking water and eating food that contains high Co. Cobalt in the environment reacts with other elements or adsorb on soil particles or water sediments. Cobalt may mobilize under acidic conditions but ultimately most Co will end up in soils and sediments.

Manganese is one of the most abundant metals in soils where it occurs as oxides and hydroxides. It occurs principally as pyrolusite (MnO_2) but nearly always present in sphalerite as solid solution and in pentlandite as impurity. However, the concentration of Mn in soils of Enyigba area had very low contamination factor (0.18) and made low contribution to the degree of contamination (Table 7, Figure 11). Manganese in the environment occurs in solids in soils and as particles in water. Mn is one of the toxic essential trace metals which are toxic when too high concentrations are present in human body.

The most important heavy metals with regards to potential hazards and their occurrence in contaminated soils are Cd, Cu, As and Pb (Table 9). Pb and Zn mining and other anthropogenic activities lead usually to the most severe agricultural soils contamination not only by Pb and Zn but also by As, Cd, Cu and Ni (Mattigod and Page, 1983; Dudka and Adriano, 1999; Wand et al 2008). In Upper Silesia (South Poland), metal contamination was mainly by active Pb-Zn mining and processing where soils in the area were contaminated with Cd, Pb and Zn with occasional high concentration of Cu in the ranges of 0.1-143, 4-8200 and 5-13250 mg/l for Cd, Pb and Zn respectively (Dudka and Adriano, 1999). The concentration of these toxic metals in soils of this area may have been derived from the mining activities in Enyigba and environs, weathering of the natural high background rocks (shales) and unmined Pb/Zn mineral deposits and occurrences. These metals are also highly enriched in the bedrocks and mine dumps (Nnabo, 2011; 2015). Sphalerite (ZnS) was the main source of Cd, As and Cu where they occur as trace metals. Kim et al. (2001) reported closed mines in South Korea as sources of heavy metals contamination of soils and crops in the mining areas. The concentrations of Cd, Cu, Pb and Zn exceeded the tolerable levels.

In a Pb-Zn mine in Hunan Province, China, the average contents of Zn, Pb, Cd, Cu and As in soils were 508.6, 384.8, 7.53, 356 and 44.6 mg/kg which are 5.3, 4.27, 15.06, 13.04 and 0.67 times those of the reference (Liao and Li, 2008). This is comparable to the situation in this study except the case of Zn in which the average is less than the normal soil composition. This was an indication that the soil was fairly polluted by the heavy metals.

Enrichment Factor (EF)

Cd had variable enrichment factor from moderate to extremely high enrichment (Table 5, Figure 6). Cd had moderate to high health risk level, indicating moderate to extremely high pollution in the area (Table 6).

The concentration of As in soils had significant enrichment factor (Table 5, Figure 9) and with significant health risk level (Table 6). This indicates significant contamination due to the mining activities in the Enyigba area. In Pb-Zn-Ag historical mining area of Prichard Creek in the northern Coeur d'Alene mining district (N. Idaho), the resultant enrichment of Pb, As, Zn, Cd, Co, Co, Mn and Hg in soil and sediments originated from the abandoned mines and waste rock dumps (Box et al. 2004). Here, the pH was consistently

observed to be neutral to alkaline (6.8 to 8.4), and the surface water and soil compositions attesting to significant amounts of carbonate rocks sufficient to naturally mitigate any acidity by mixing. There were, however, indications of elevated amounts of As that are mobile in weakly alkaline environments (Nash, 2004).

The concentrations of Cu and Pb in soils had significant enrichment factors and next to Cd (Table 5, Figures 7 and 8). The health risk level is also moderate (Table 6), implying significant contamination.
Co, Ni and Zn showed low to minimal enrichment factors (Table 5, Figures 53d, f and h) and low health risk levels, indicating minimal pollution levels (Table 6).

Contamination Factor (CF)
In soil Cd showed very high contamination factor of 20.25 and also made the most significant contribution to the degree of contamination expressed by DC (Table 7, Figure 11). But As, Cu and Pb showed significant contamination factors and also made contribution to the significant degree of contamination expressed by DC (Table 7, Figure 11).

Ni, Co and Zn had very low contamination factor (Table 7, Figure 11), and made low contribution to the degree of contamination expressed by DC.

6. CONCLUSION

High content of As in soil was recorded in locations S59, S28 and S55 (all from Enyigba) with significant enrichment factor of As in S59 and S28. The health risk level of As is moderate. High contents of Cd were obtained in locations S59, S28, S55 and S57 all from Enyigba and environs where intensive Pb-Zn mining activities took place. Extremely high enrichment factor of Cd were obtained from locations S59, S28 and S55 and with health risk level of 5. High contents of Pb were obtained in locations S59, S28, S55 and S57 all from Enyigba and environs. Pb had significant enrichment factor in location S59 and with moderate health risk level of 3. High contents of Cu were obtained in locations S55, S28 from Enyigba, S150 from Ohankwu, S38 from Enyigba, S46 from Ameri, S63 from Enyigba, S154 from Ameka, and S57 from Enyigba. These contents are several times more than the normal soil composition. Cu had significant enrichment factor in location S59 and with moderate health risk level of 3. High concentration of Ni above the normal soil composition of 15 mg/kg was obtained in locations S59 from Enyigba. High contents of Co above the normal soil composition of 8 mg/kg were recorded in S59, S28 and S55 from Enyigba, with low enrichment factors. The contents of Mn and Zn in soil were very low.

Arsenic showed significant contamination factor in soil and made contribution to significant contamination of the soil expressed by degree of contamination, DC. Cd had very high contamination factor in soils, and also contributed to the high degree of contamination (DC). Pb had moderate contamination factor in soil samples, and with anthropogenic input of 41%, and with significant contribution to high degree of contamination, DC of heavy metals in locations S59, S28, S55 and S57. Cu had moderate contamination factor, and with significant contribution to high degree of contamination, DC of heavy metals in locations S59, S28, S55 and S57.

The total concentration of all the mobile heavy metals in soils were above the normal soil composition based on Bowen (1979), and in the order Cd $\gg$ Cu>Co>Pb>As>Ni>Zn. The high values may indicate both geologic and anthropogenic orin. Many of the soil samples contained heavy metals at levels that could cause toxicity to the environment.

The main conclusion that can be drawn from this study is that the risk level of heavy metal leaching and groundwater contamination from the soil is very high with considerable likelihood of heavy metal transport by water percolating through the soils/mine waste since the dumping of the mine wastes.
According to the environmental quality criteria for soils, the Enyigba mining district would in future require remediation.

The people of Abakaliki who are known producers of rice and yams in southeastern Nigeria, would need a management plan against the transfer of metals into the ecosystem in order to alleviate the possible metal-related health problems. This can be done by reducing the solubility and concentration of metals in the soil to reduce metal intake through the consumption of contaminated forages and soil.

Approaches described by Alloway (1990) for the rehabilitation of Cd–polluted soils may apply to soils of the Enyigba district. Soil applications of $CaCO_3$ to increase soil pH to 6.5 or above would greatly reduce metal availability to plants due to decreased trace metal solubility at higher pH values (Zindall and Forster, 1976, Lindsay, 1979). Additional measure such as deep plowing to reduce metal concentrations at the soil surface would be needed to reduce metal intake by crops during cultivation.

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