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Assessment of Heavy Metal Contamination by Mine Dumps in Enyigba Lead/Zinc District, South Eastern Nigeria

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Abstract:
Nineteen {19} samples of mine waste dumps were collected from the lead/zinc mining areas 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 varied from fairly acidic to basic (4.8 - 11.6), resulting from the dissolution of the sulphide minerals in the waste dumps. The heavy metal mean trend indicates that As > Cd > Zn > Cu > Pb > Ni > Co. The variations observed indicate heavy metals contamination due to Pb-Zn mining operations in the area. Possible contamination by mine dumps 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, As show extremely high enrichment, Cd has significant to extremely high enrichment, Pb, Zn and Co show significant enrichment. The enrichment of Cu and Ni are moderate to low. The CF values for the dumps indicate the very high contamination factor for As and Cd, while the concentration for Pb and Zn are Cu, Co, Ni and Co show low contamination. These levels of contamination and values indicate that under the prevailing conditions and environmental regulations in Nigeria, the mining district would face major and hazardous discharges of these metals from the dumps into the soil and water sources, and needs remediation.

Keywords: *Mine waste dumps, partial leach test, enrichment/contamination factor, lead-zinc mine, Enyigba*

1. Introduction

The study area (Figure 1), 14 km southeast of Abakaliki, covered the Pb-Zn mining district of Enyigba and its surrounding villages of Ameka, Ameri and Ohankwu all in Ebonyi State, southeastern Nigeria. The major occupation of the people living in the area is farming and mining activities. The deposit of Pb-Zn sulphides (galena and sphalerite) in Nigeria have been known for a long time but have only been exploited in the past on a very small scale. The lead-zinc field covers over 48,000/sqkm in extent with lead-zinc mineralization at many centres. Deposits are localized in the Cretaceous sediments along 600/km long belt within the Benue Trough, a sediment filled intracratonic basin extending from Ishiagu (South of Abakaliki) Northeastward to Gombe (Farrington 1952, Olade, 1976, Akande et al. 1990; Orazulike 1994). The occurrence of lead–zinc in the Benue valley has attracted a lot of attention (Farrington, 1952; Olade and Morton, 1989). Mining of the ore has been carried out for a long time by both the natives, for local uses as cosmetics, and foreign companies, for export. Production of the ore started in the year 1925 but commercial production started in 1947 (Kogbe, 1989). Since the discovery of and mining of Pb-Zn deposits in Abakaliki and its environs in the early 1900s, not much data exist on the impact of their mining on the environment. 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. This study is to assess the levels of heavy metals distribution in rocks as may have resulted from leadzinc mining in the area.

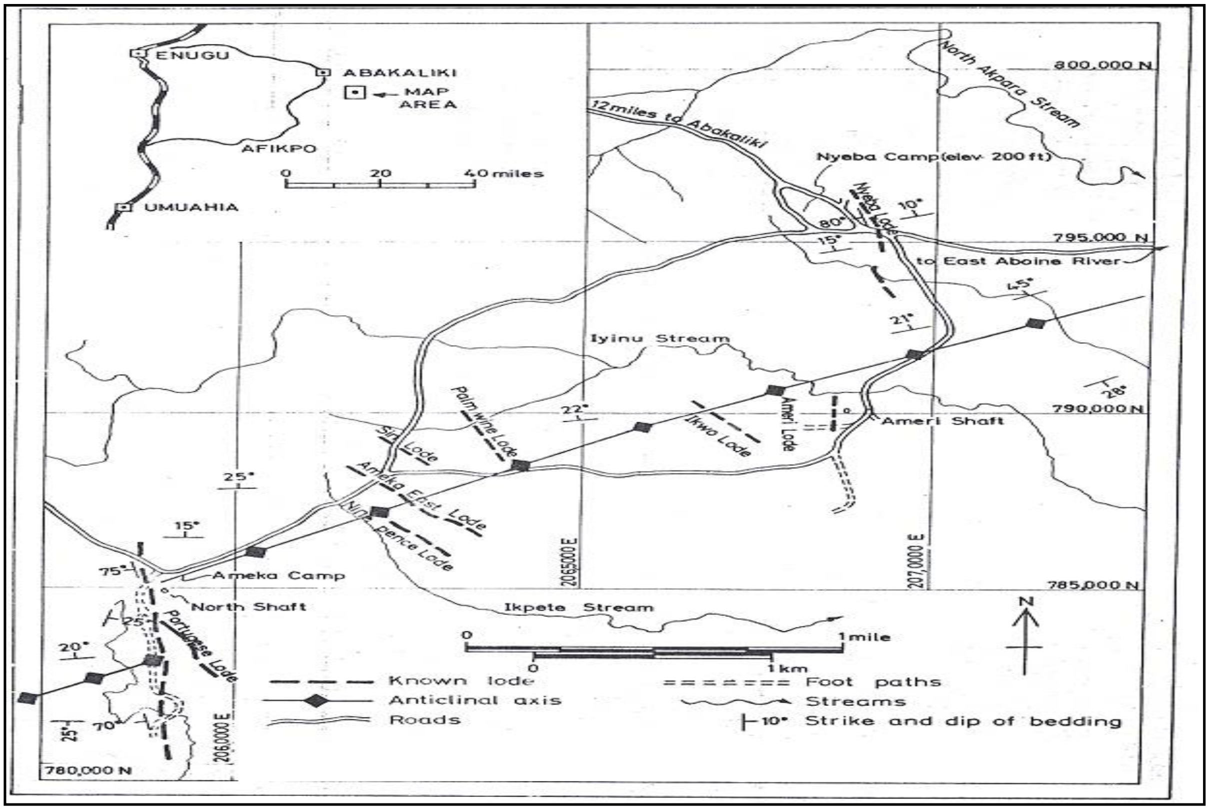

Figure 1: Geological map of lead-zinc deposits of Enyigba district, near Abakaliki, Lower Benue Trough. The area is underlain by Abakaliki shales (Modified from Orajaka, 1965).

2. Description of Study Area

In the study area, the topography is undulating plain alternating with running of ridges and hills from east to west. The plains are underlain by shale and some mudstones. The Enyigba, Ameri and Ameka are marked by undulating range of shale outcrops, which serves as the host for Pb-Zn mineral ore bodies. The whole area formed the "Abakaliki antichrionium" and generally underlain by shales. The area had about 60m as its highest elevation and 30m as its lowest elevation above sea level. The area falls within the tropical rainforest belt of South East Nigeria, and characterized by an average rainfall of 1750- 2000 mm per annum. The rainy season and dry season are the two major seasons that prevail in the area. The vegetation cover in Enyigba is controlled by its climatic condition. The highlands are characterized by drought resistance grasses, along stream and rivers. Among the vegetation includes economic mangoes trees, orange trees, and palm and coconut trees. The drainage system of the area is dendritic in pattern, which is a function of the lithology. The area is majorly drained by Ebonyi River. All the drainage systems flow eastward to join the Cross River somewhere outside the area.

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. The shales in some places are highly weathered and ferrugenized. The rocks are extensively fractured folded and faulted. From field observations, the rocks of the area consist of variably coloured shale and mudstone that has been imbedded by lead – zinc vein mineralization, baked intrusive shale as well as ironstone along veins. The ironstone occur as inter-beds within the shale and as vein filling. 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 have high concentration of these metals, the shale host are capable of retaining them from ancient sea (Nnabo et al. 2011).

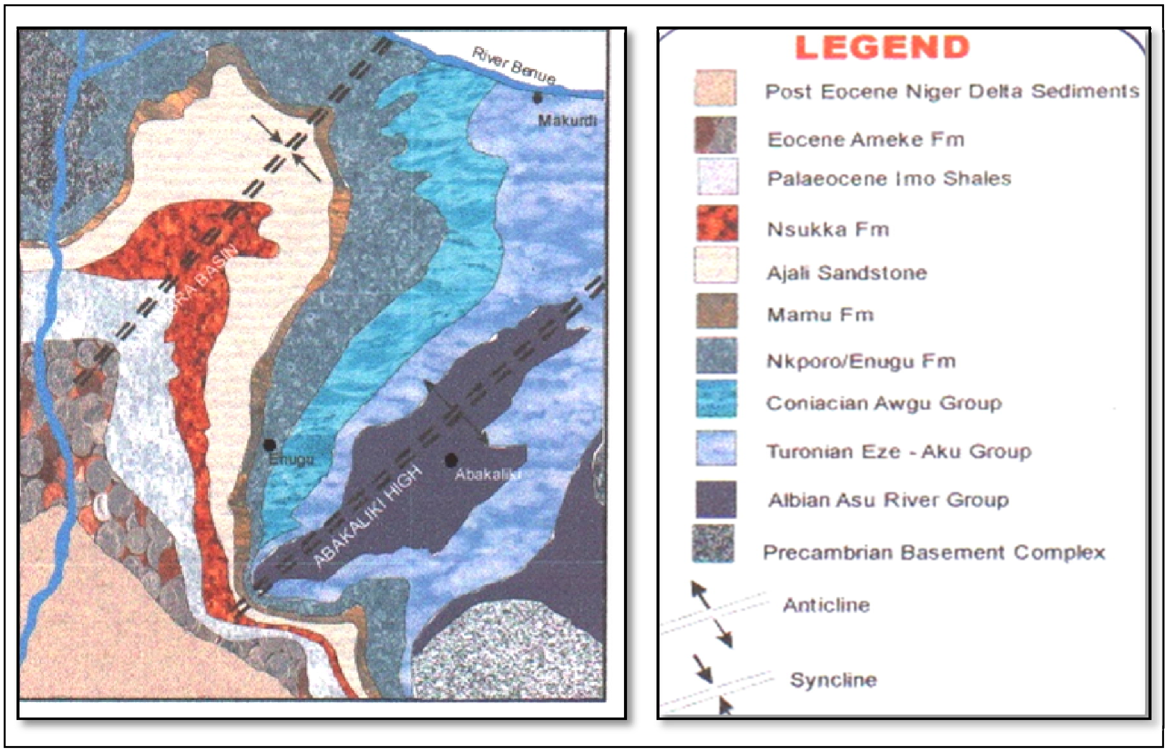

Figure 2: General geologic map of Southeastern Nigeria showing Abakaliki basin in the Lower Benue Trough (Modified after Hoque, 1977).

On-site work in the field included a brief description of the site, rock types, rock alterations and measurement or estimate of size of the dump pile, and the collection of a representative sample of the entire dump. The dump piles are generally of moderate size, 25m x 10m or more, and mostly covered with fine-grained red iron oxide materials possibly deposited from mine drainage **(Figure 3)**. They are coarse waste rock accumulations containing appreciable amounts of sulphides (sphalerite, siderite, chalcopyrite and galena), quartz and rock fragments (shale and mudstone). All of the mines and prospects of the project area are virtually polymetallic as many base metals are concentrated in these rocks even though the early miners emphasized lead or silver for economic reasons. Sphalerite, an ore of zinc, which is one of the potentially toxic metals of prime concern here, was not considered for economic and was not recovered by the miners. Significant amounts of zinc ore were found in the waste rock dumps, and may also be significantly present in water and soil of the project area.

This formation is considered essentially an impermeable unit, although secondary porosity can be locally important. This property can prevent the infiltration of large volumes of acid mine drainage to aquifers but enhances surface drainage of metal-rich leachates affecting the quality of effluent water. Samples of waste rock from mine dumps were collected from the abandoned Enyigba mining district, including Enyigba, Ameri, Ameka and Ohankwu areas where small-scale mining operations are still taking place (Figures 4 and 5).

Figure 3: A section of the mine dumps in the mine area composed of waste rock and minerals

Composite samples were randomly collected from subsites uniformly distributed over the top and sides of each dump pile and at each subsite dump rocks were collected from an area of 0.5 m^2 to a depth of 5 to 10 cm and mixed, and a portion of size of about 2 mm yielding 100 grams of materials was finally collected as representative samples. Coarse materials more than 4 cm in size were discarded during the collection. This form of representative sampling is the most important consideration in the characterization of the dump pile materials.

Figure 4: Mine dump material at Ameri mining site. It is composed mainly of weathered shale materials.

Figure 5: A mine waste dump at Ameka Ezza mining area. This is rich in black shales and vein (quartz) materials

3. Materials and Methods

Several techniques and scientific methods were employed to achieve and fulfill the aim and objectives of this research work. Unmined, mineralized, unmineralized and altered rock samples were collected from rock outcrops. The samples are typically composite chip samples collected at mining sites. Single grab samples were collected where compositing was not possible. A total of nineteen (19) dump samples were collected with their descriptions appropriately recorded (Figure 6). Rock samples were collected from each sampling point and were then crushed to get fine grain sizes. The choice of fine-grained material for this analysis is because higher metals concentration is generally found on smaller grain of rocks due to higher metals surface area to grain size ratio (Kabata-Pendias, 1995). A positive correlation usually exist between decreasing grain-size and higher metal concentration. Moreover this is to say that fine-grained sediments have a greater absorption surface area than coarser particles, especially clay minerals, Organic matter and Fe-Mn oxylydroxide complexes are able to absorb larger quantities of metal through cation exchange processes (Kabata-Pendias, 1995).

In the laboratory, the dump samples were reduced to about 0.5 cm fragments, crushed and then split. For each sample, an approximately 100g portion was pulverized with ceramic mortar and with pestle. The sample was grounded and then sieved until 100% passed an 80-mesh screen (< 180 µm). The sample was mixed to ensure homogeneity, and then served for chemical analysis. The remaining portion was archived for subsequent analysis. To ensure thorough cleanliness to avoid any level of cross-contamination, especially when ore-grade samples were prepared, a small amount of the next sample to be prepared was crushed and discarded with the crusher scrubbed out thoroughly prior to preparing the whole sample. The solid samples from outcrops were digested in the laboratory using the passive leach method that provides a measure of reactions in nature. In this method 100g of the samples was measured and placed in beaker with 200 ml of deionized water, stirred slightly and initial pH and temperature were measured. At 24 hours, the pH and temperature of the leach were again 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 (HNO3) to stabilize metal in solution. The leachate was sent for analysis. A total of nine elements were analysed for and they include As, Ca, Cd, Co, Cu, Mn, Ni, Pb and Zn.

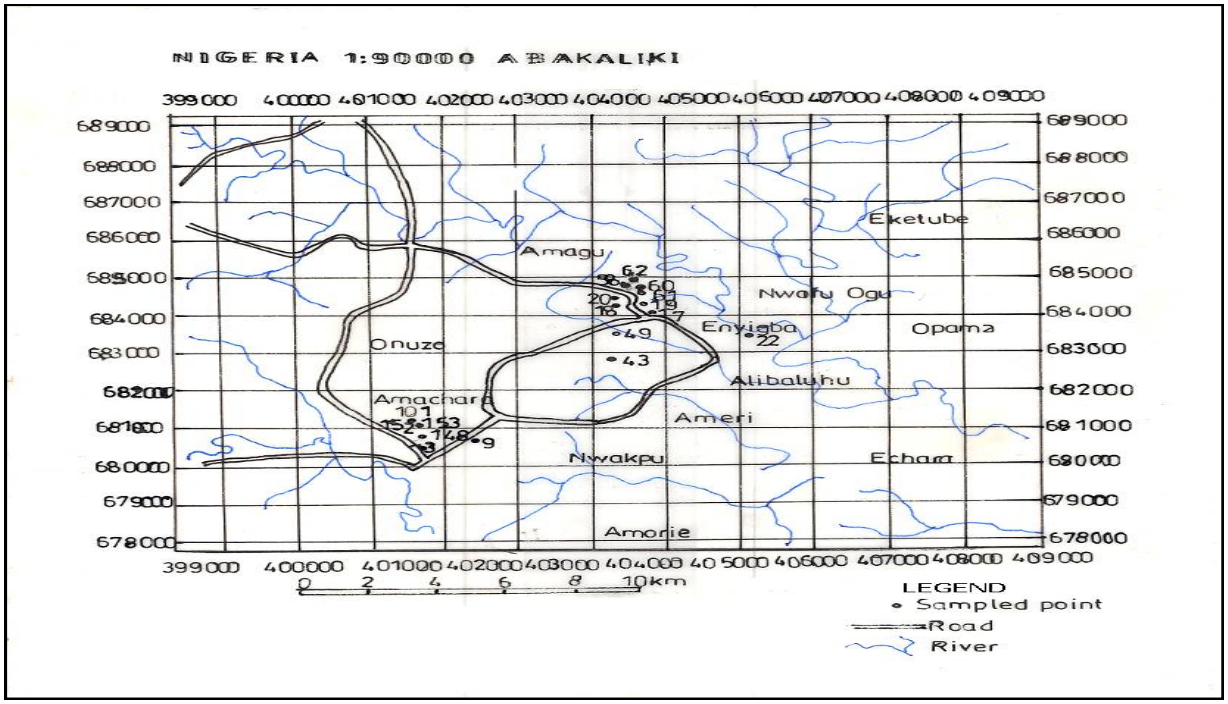

Figure 6: Location of Mine Dumps Samples Collected from Enyigba and its Environs. .

4. Results

For most of the mine dump samples (74%), the pH rose to higher values from a minimum pH of 4.3 to a maximum pH of 11.6. One of these remained very acid, PN/D/101 (4.1 – 4.8) while four remained fairly acidic with pH values ranging from 4.3 to 6.2. For the remaining 26% of the samples (5 samples) the pH values remained fairly constant. Three of these are in the neutral range from minimum pH value of 6.7 to a maximum.

S/No	Sample No	Initial pH	pH @ 24hr
1	PN/D/3	7.0	8.8
2	PN/D/9	4.3	6.2
3	PN/D/17	6.3	9.2
4	PN/D/18	7.8	11.6
5	PN/D/19	7.4	11.4
6	PN/D/20	6.4	8.1
7	PN/D/22	6.7	8.3
8	PN/D/26	5.0	5.7
9	PN/D/31	7.7	8.2
10	PN/D/43	5.1	6.2
11	PN/D/49	7.7	7.6
12	PN/D/58	7.7	7.4
13	PN/D/60	6.7	7.1
14	PN/D/61	5.9	6.8
15	PN/D/62	5.3	6.1
16	PN/D/101	4.1	4.8
17	PN/D/148	5.4	5.5
18	PN/D/152	6.1	7.4
19	PN/D/153	5.5	5.8

Table 1: Results of Leach tests of mine dump samples.

4.1. Mine Waste Dumps

Table 2 shows the results of the analysis of mine dump 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 concentration of each metal in all the locations are given in Figures 7-9.

Sample code	Location	Metal concentrations in mg/kg									
		As	Ca	Cd	Co	Mn	Cu	Ni	Pb	Zn	pH
PN/D/3	Ameka	81.60	410.60	2.64	7.90	180.40	36.00	1.06	18.42	**352.00**	8.8
PN/D/9	Ohankwu	184.42	**2424.0**	5.94	17.84	420.40	12.10	2.38	41.64	60.00	6.2
PN/D/17	Enyigba	190.10	556.20	6.12	18.40	403.20	12.12	2.46	42.92	236.40	9.2
PN/D/18	Enyigba	130.94	459.00	4.22	12.68	301.60	12.00	1.68	29.56	48.16	**11.6**
PN/D/19	Enyigba	209.60	467.60	6.80	20.28	480.60	ND	2.70	47.40	40.06	11.4
PN/D/20	Enyigba	73.20	1672.4	2.40	7.10	164.00	40.10	0.94	16.52	108.06	8.1
PN/D/22	Ameri	211.80	592.00	6.84	20.52	460.40	8.16	2.74	47.84	60.10	8.3
PN/D/26	Ameri	62.38	1680.2	2.02	6.04	142.80	52.06	0.80	14.08	168.00	5.7
PN/D/31	Ameri	228.20	2416.0	7.40	22.08	499.20	12.02	2.94	51.54	100.06	8.2
PN/D/43	Ameri	98.00	2230.0	**0.96**	**2.90**	**63.76**	**80.26**	**0.38**	**6.80**	196.18	6.2
PN/D/49	Ameri	**230.80**	604.20	**7.44**	**22.34**	519.80	**4.00**	**30.02**	**52.20**	56.00	7.6
PN/D/58	Ameri	226.40	**145.00**	7.30	21.90	**520.60**	**4.00**	2.92	51.20	32.06	7.4
PN/D/60	Ameri	193.60	1862.0	6.24	18.72	421.40	56.04	2.50	43.70	224.40	7.1
PN/D/61	Ameri	102.06	2044.0	3.30	9.88	211.00	32.00	1.32	23.04	108.00	6.8
PN/R/62	Enyigba	**41.06**	1858.4	1.32	3.96	81.28	36.06	0.52	9.26	136.04	6.1
PN/D/101	Ameka	219.40	2418.0	4.70	14.12	334.02	8.00	1.88	32.96	**8.16**	**4.8**
PN/D/148	Ohankwu	41.40	1860.60	1.34	4.00	81.40	36.10	0.52	9.38	132.04	5.5
PN/D/152	Ameka	141.12	724.80	4.60	13.66	322.00	32.16	1.82	32.02	132.16	7.4
PN/D/153	Ameka	150.06	568.00	4.84	14.52	340.40	28.06	1.94	33.88	108.06	5.8
Total		2816.14	24993	86.42	258.84	5948.26	501.24	61.52	604.36	2305.94	142.2
Mean		148.22	1315.42	4.55	13.62	313.07	27.85	3.24	31.81	121.37	7.48
Standard Deviation		65.96	805.52	2.20	6.59	154.20	20.32	6.37	15.38	82.97	1.80
Average Shale		10	$2.5.10^4$	0.3	20	850	50	80	20	90	
Average Crust		2.5	$6.4.10^4$	0.08	26.6	1000	27	59	11	72	
MPL (Kabata-Pendias, 1995).		20	--	0.5	50	--	100	30	20	300	

	Maximum concentration		Minimum concentration

Table 2: Concentration of mobile heavy metals in mine dumps from Enyigba and Environs.

From the Table 2, the metals showed the the following variations in concentration: manganese content varied from 63.76 to 520.6 mg/kg with an average value of 313.07 mg/kg (Figure 39*e*), arsenic ranged from 41.06 to 230.3 mg/kg with a mean value of 148.22 mg/kg (Figure 7), zinc varied from 8.16 to 352 mg/kg with a mean of 121.37 mg/kg; the concentration of lead varied from 6.8 to 45.4 mg/kg with an average value of 31.81 (Figure 8), copper ranged from 4 to 80.26 mg/kg with a mean of 27.85 mg/kg, cobalt varied from 2.9 to 22.34 mg/kg with average content of 13.62 mg/kg cadmium content ranged from 0.96 to 7.44 mg/kg with a mean value of 4.55 (Figure 9), and nickel content varied from 0.38 to 30.02 mg/kg with an average value of 3.24 mg/kg.
The concentration of calcium was high and demostrated an unusual variation from 145 to 2424 mg/kg with an average of 1315.42 mg/kg.

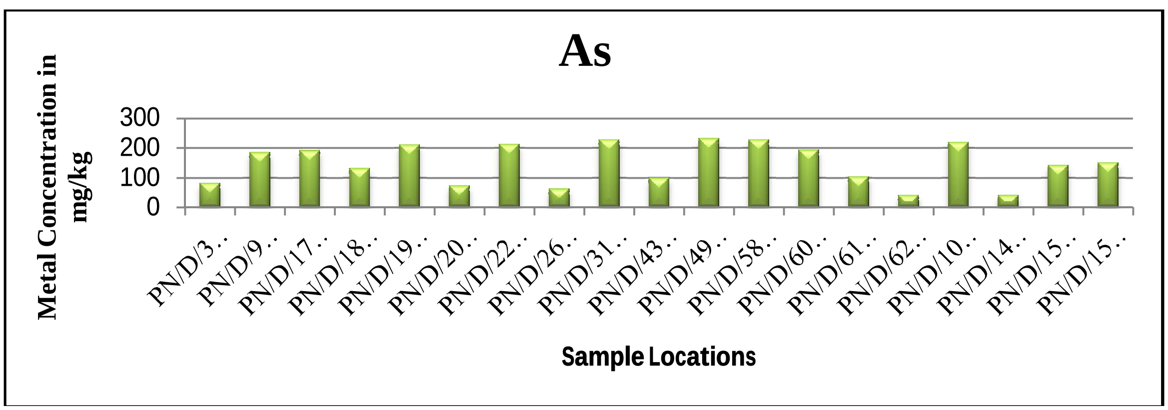

Figure 7: Concentration of Arsenic in Mine Dumps from Enyigba and Environs

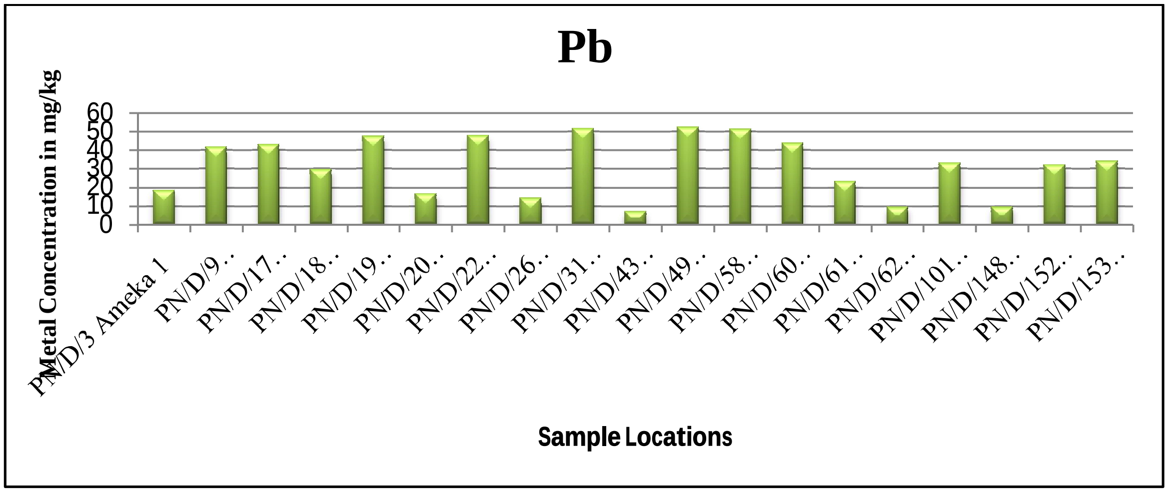

Figure 8: The concentration of Lead in Mine Dumps from Enyigba and Environs

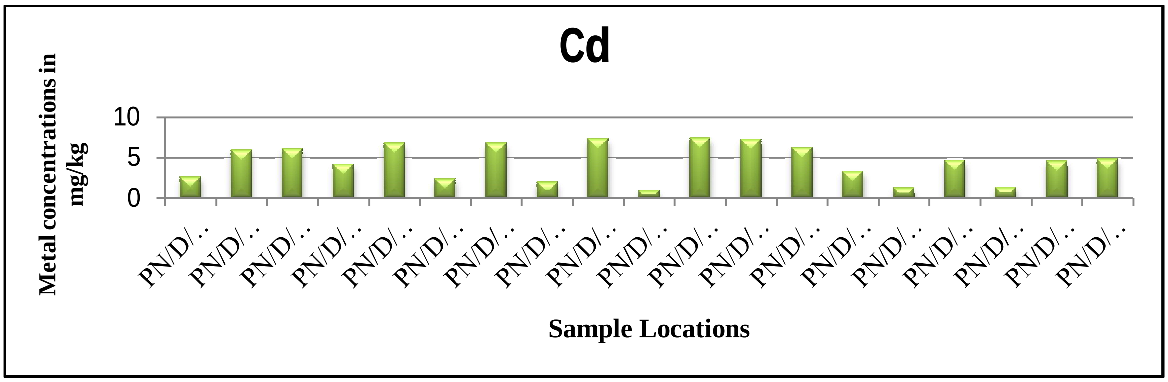

Figure 9: The concentration of Cadmium in Mine Dumps from Enyigba and Environs.

Enrichment Factor (EF)

The enrichment factor (EF) of heavy metals in mine dump samples was computed using a reference element characterized by low ocurrence variability. Manganese was used as the reference metal and the average shale (see **Table 2**) taken as the reference environment.

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

Where *Cn* is the concentration of the examined metal in the Enyigba and Environs, *Cref* is the mean content of the reference metal (Mn) in the mine dump of the Enyigba and Environs (313.07, Table 2), *Bn* is the content of the examined metal in the reference environment, *Bref* is the content of the refrence metal in the reference environment. The pollution conditions and health risk levels (Liao, 2006) based on enrichment factor are as shown on Table 3. The enrichment factors of the heavy metals in the mine dump samples are contained in Table 4 and are illustrated in Figure 10 - 13. Table 41 shows the calculated EF and HR levels of the heavy metals in the mine dumps.

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 3: Pollution condition and health risk (HR) level based on class of enrichment factor.

Sample No	Location	As	EF	Ca	EF	Cd	EF	Co	EF
PND3	Ameka	81.60	**26.07**	410.60	**0.04**	2.64	**24.1**	7.90	**1.26**
PND9	Ohankwu	**184.42**	**58.92**	2424.00	**0.26**	**5.94**	**54.22**	17.84	**2.85**
PND17	Enyigba	190.10	**60.73**	556.20	**0.06**	6.12	**55.86**	18.40	**2.94**
PND18	Enyigba	130.94	**41.83**	459.00	**0.05**	4.22	**38.52**	12.68	**2.03**
PND19	Enyigba	209.60	**66.96**	467.60	**0.05**	6.80	**62.07**	20.28	**3.24**
PND20	Enyigba	73.20	**23.39**	1672.4	**0.18**	2.40	**21.91**	7.10	**1.13**
PND22	Ameri	211.80	**67.67**	592.00	**0.06**	6.84	**62.44**	20.52	**3.28**
PND26	Ameri	62.38	**19.93**	1680.20	**0.18**	2.02	**18.44**	6.04	**0.96**
PND31	Ameri	228.20	**72.91**	2416.00	**0.26**	7.40	**67.55**	22.08	**3.53**
PND43	Ameri	98.00	**31.31**	2230.00	**0.24**	0.96	**8.76**	2.90	**0.46**
PND49	Ameri	230.80	**73.74**	604.20	**0.07**	7.44	**67.91**	22.34	**3.57**
PND58	Ameri	226.40	**72.33**	145.00	**0.02**	7.30	**66.64**	21.90	**3.50**
PND60	Ameri	193.60	**61.85**	1862.00	**0.20**	6.24	**56.96**	18.72	**2.99**
PND61	Ameri	102.06	**32.61**	2044.00	**0.22**	3.30	**30.12**	9.88	**1.58**
PND62	Enyigba	41.06	**13.12**	1858.40	**0.20**	1.32	**12.05**	3.96	**0.63**
PND101	Ameka	219.40	**70.10**	2418.00	**0.26**	4.70	**42.90**	14.12	**2.26**
PND148	Ohankwu	41.40	**13.23**	1860.60	**0.20**	1.34	**12.23**	4.00	**0.64**
PND152	Ameka	141.12	**45.09**	724.80	**0.08**	4.60	**41.99**	13.66	**2.18**
PND153	Ameka	150.06	**47.94**	568.00	**0.06**	4.84	**44.18**	14.52	**2.32**

Table 4: Enrichment Factor (EF) of Heavy Metals in Mine Dumps from Enyigba and Environs.

Sample No	Location	Cu	EF	Ni	EF	Pb	EF	Zn	EF
PND3	Ameka	36.00	**1.92**	1.06	**0.04**	18.42	**2.94**	352.00	**10.22**
PND9	Ohankwu	12.10	**0.64**	2.38	**0.08**	41.64	**6.65**	60.00	**1.74**
PND17	Enyigba	12.12	**0.65**	2.46	**0.09**	42.92	**6.86**	236.40	**6.87**
PND18	Enyigba	12.00	**0.64**	1.68	**0.06**	29.56	**4.72**	48.16	**1.40**
PND19	Enyigba	ND	---	2.70	**0.10**	47.40	**7.57**	40.06	**1.16**
PND20	Enyigba	40.10	**2.14**	0.94	**0.03**	16.52	**2.64**	108.06	**3.14**
PND22	Ameri	8.16	**0.43**	2.74	**0.10**	47.84	**7.64**	60.10	**1.75**
PND26	Ameri	52.06	**2.77**	0.80	**0.03**	14.08	**2.25**	168.00	**4.88**
PND31	Ameri	12.02	**0.64**	2.94	**0.10**	51.54	**8.23**	100.06	**2.91**
PND43	Ameri	80.26	**4.27**	0.38	**0.01**	6.80	**1.09**	196.18	**5.70**
PND49	Ameri	4.00	**0.21**	30.02	**1.07**	52.20	**8.34**	56.00	**1.63**
PND58	Ameri	4.00	**0.21**	2.92	**0.10**	51.20	**8.18**	32.06	**0.93**
PND60	Ameri	56.04	**2.98**	2.50	**0.09**	43.70	**6.98**	224.40	**6.52**
PND61	Ameri	32.00	**1.70**	1.32	**0.05**	23.04	**3.68**	108.00	**3.14**
PND62	Enyigba	36.06	**1.92**	0.52	**0.02**	9.26	**1.48**	136.04	**3.95**
PND101	Ameka	8.00	**0.43**	1.88	**0.07**	32.96	**5.27**	8.16	**0.24**
PND148	Ohankwu	36.10	**1.92**	0.52	**0.02**	9.38	**1.50**	132.04	**3.84**
PND152	Ameka	32.16	**1.71**	1.82	**0.06**	32.02	**5.12**	132.16	**3.84**
PND153	Ameka	28.06	**1.49**	1.94	**0.07**	33.88	**5.41**	108.06	**3.14**
Average Shale		50		80		20		90	

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 4 [contd]: Enrichment Factor of Heavy Metals in Mine Dumps from Enyigba and Environs.

From Table 4, arsenic showed extremely high enrichment in 12 locations with the highest value of 73.74 in PN/D/49 followed by PN/D/31 with 72.91, PN/D/58 with 72.33 and PN/D/101 with 70.1 (Figure 10).

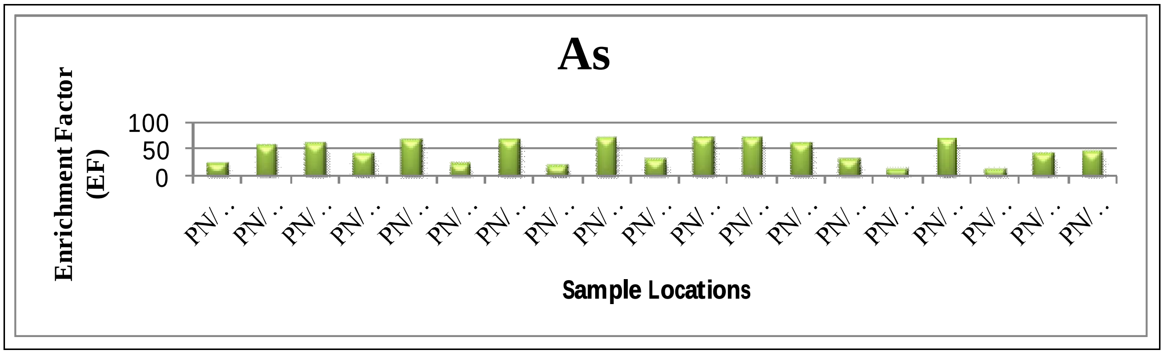

Figure 10: Enrichment Factor of Arsenic in Mine Dumps from Enyigba and Environs.

The enrichment of cadmium was extremely high in 11 locations with the highest value of 67.91 in PN/D/49, followed by sample PN/D/31 with a value of 67.55, PN/D/58 with 66.64 and PN/D/22 with 62.44 (Figure 11).

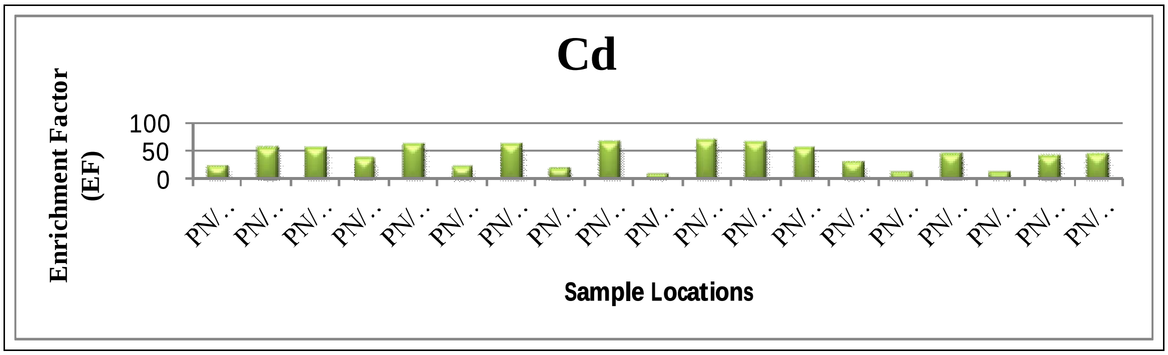

Figure 11: Enrichment Factor of Cadmium in Mine Dumps from Enyigba and Environs.

Lead had significant enrichment in 11 locations with the highest value of 8.34 got from sample PN/D/49 (Figure 12).
The concentration of zinc showed significant enrichment in four locations with the highest value of 10.22 in PN/D/3 (Figure 13).

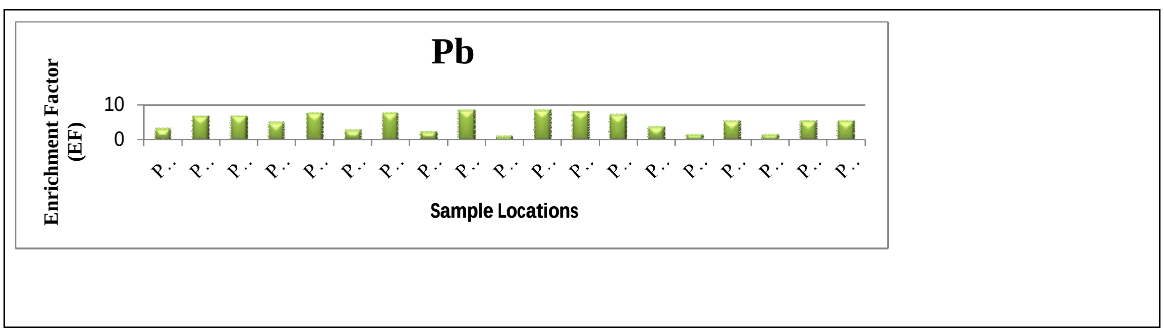

Figure 12: Enrichment Factor of Lead in Mine Dumps from Enyigba and Environs.

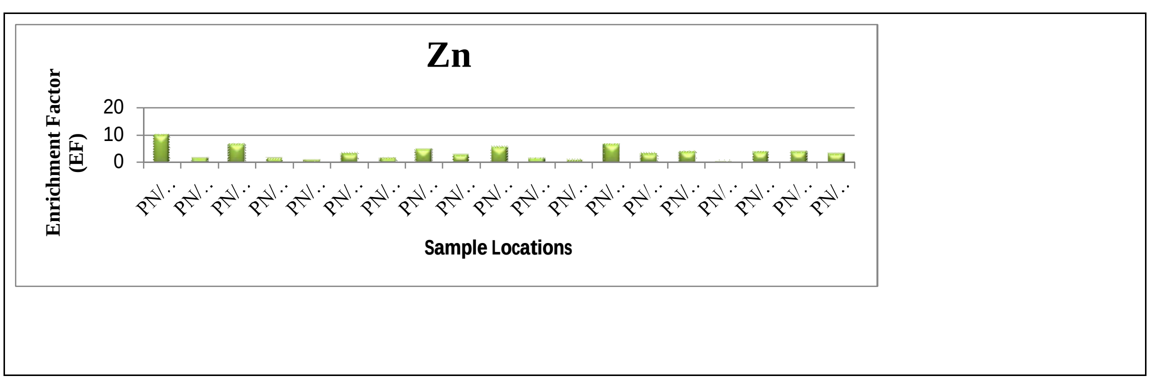

Figure 13: Enrichment Factor of Zinc in Mine Dumps from Enyigba and Environs

Based on enrichment factor, the health risk of As and Cd are both very high. For As, 63% of the samples (12) showed risk level of five. For Cd, 58% of the locations (11) showed health risk of five. Pb showed moderate pollution with risk level of three in 58% (11) of the locations. The risk levels of the other metals were very low (Table 5).

Sample Code	As		Cd		Co		Cu	
	EF	HR	EF	HR	EF	HR	EF	HR
PND3	26.07	4	24.1	4	1.26	1	1.92	1
PND9	58.92	5	54.22	5	2.85	2	0.64	0
PND17	60.73	5	55.86	5	2.94	2	0.65	0
PND18	41.83	5	38.52	4	2.03	2	0.64	0
PND19	66.96	5	62.07	5	3.24	2	---	---
PND20	23.39	4	21.91	4	1.13	1	2.14	2
PND22	67.67	5	62.44	5	3.28	2	0.43	0
PND26	19.93	3	18.44	3	0.96	0	2.77	2
PND31	72.91	5	67.55	5	3.53	2	0.64	0
PND43	31.31	4	8.76	3	0.46	0	4.27	2
PND49	73.74	5	67.91	5	3.57	2	0.21	0
PND58	72.33	5	66.64	5	3.50	2	0.21	0
PND60	61.85	5	56.96	5	2.99	2	2.98	2
PND61	32.61	4	30.12	4	1.58	1	1.70	1
PND62	13.12	3	12.05	3	0.63	0	1.92	1
PND101	70.10	5	42.90	5	2.26	2	0.43	0
PND148	13.23	3	12.23	3	0.64	0	1.92	1
PND152	45.09	5	41.99	5	2.18	2	1.71	1
PND153	47.94	5	44.18	5	2.32	2	1.49	1

Table 5: Enrichment factor (EF) and health risk (HR) of heavy metals in mine dumps.

Sample code	Ni		Zn		Pb	
	EF	HR	EF	HR	EF	HR
PND3	0.04	0	10.22	3	2.94	2
PND9	0.08	0	1.74	1	6.65	3
PND17	0.09	0	6.87	3	6.86	3
PND18	0.06	0	1.40	1	4.72	2
PND19	0.10	0	1.16	1	7.57	3
PND20	0.03	0	3.14	2	2.64	2
PND22	0.10	0	1.75	1	7.64	3
PND26	0.03	0	4.88	2	2.25	2
PND31	0.10	0	2.91	2	8.23	3
PND43	0.01	0	5.70	3	1.09	1
PND49	1.07	1	1.63	1	8.34	3
PND58	0.10	0	0.93	0	8.18	3
PND60	0.09	0	6.52	3	6.98	3
PND61	0.05	0	3.14	2	3.68	2
PND62	0.02	0	3.95	2	1.48	1
PND101	0.07	0	0.24	0	5.27	3
PND148	0.02	0	3.84	2	1.50	1
PND152	0.06	0	3.84	2	5.12	3
PND153	0.07	0	3.14	2	5.41	3

Table 5 [contd]: Enrichment factor and health risk (HR) of heavy metals in mine dumps.

EF is the Enrichment factor; HR is the Health Risk level (see Table 3).

4.2. Contamination Factor (CF)

The assessment of the contamination of the mine dump by heavy metals was also assessed using the contamination factor. It a calculation used to evaluate the potential risk of the heavy metals to the environment. It was carried using the equation:

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

Where C_{0-1}^{i} is the mean concentration of heavy metals in mine dumps and C_{n}^{i} was taken as the average concentration of the metals in Earth's crust as a reference value (see Table 2). Table 6 shows the contamination factors of the heavy metals and plotted in Figure 14. The four categories of contamination based on the calculation of contamination factor are as in Table 7.

As	CF	Cd	CF	Co	CF	Mn	CF	DC
148.22	**59.29**	4.55	**56.88**	13.62	**0.51**	313.07	**0.31**	
Cu	**CF**	**Ni**	**CF**	**Pb**	**CF**	**Zn**	**CF**	
27.85	**1.03**	3.24	**0.05**	31.81	**2.89**	121.37	**1.69**	**121.78**

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

Table 6: Contamination factors (CF) of heavy metals in mine dumps (mean values of metals in mg/kg).

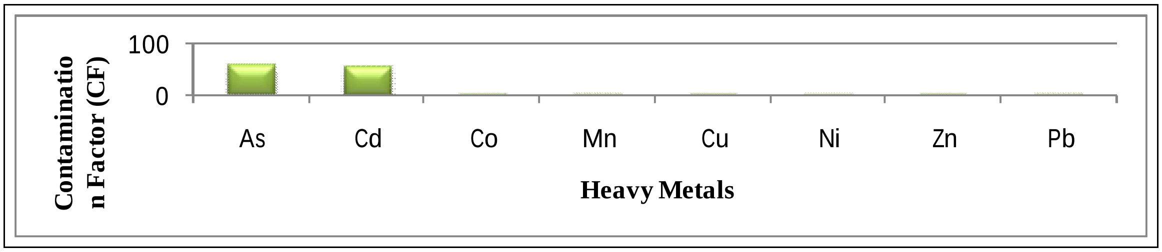

Figure 14: Contamination Factors of Heavy Metals in Mine Dumps from Enyigba and Environs.

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

Table 7: Categories of Contamination based on Contamination Factor

Table 6 and Figure 14 show that only the concentration of *As* and *Cd* are associated with very high contamination factors of 59.29 and 56.88 respectively

5. Discussion

The concentration of As in all the mine dump samples are above the maximum tolerable limits 6 mg/kg (Kabata-Pendias, 1984). High concentrations, for example, 230.8 mg/kg from Ameri, 219.4 mg/kg from Ameka and 209.6 mg/kg from Enyigba are up to 38 times more than the limit. The concentration of 184.42 mg/kg from Ohankwu is also more than the tolerable limit by over 30 times. The average value, 148.22 mg/kg is 25 times the maximum tolerable level (Table 8).

Heavy Metal	Present Study	MPL (Kabata-Pendias, 1984)	MPL (Kabata-Pendias, 1995).	No. of times > Permissible level	Level of Pollution
Arsenic	148.22	20	---	7.41	High
Cadmium	4.55	3	0.5	9.10	High
Cobalt	13.62	---	50	0.27	Low
Copper	27.85	100	100	0.28	Low
Nickel	3.24	30	100	0.11	Low
Lead	31.81	100	20	1.59	Moderate
Zinc	121.37	300	300	0.40	Low
Calcium	1315.42	---	---	---	---
Manganese	313.07	---	---	---	---

Table 8: Average concentration of mobile heavy metals in Mine Dumps compared with maximum permissible limits (MPL) established by Kabata-Pendias (1995) in mg/kg

Cadmium, commonly associated with sphalerite, varies between 0.96 and 7.44 mg/kg with an average value of 4.55 (±2.2) mg/kg. The concentrations of Cd from the area were above the tolerable limit of 0.5 mg/kg (Kabata-Pendias, 1995) with many of the locations from Ameri area. The high concentrations, for example, 7.44 and 7.40 mg/kg all from Ameri and 6.80 mg/kg from Enyigba are above the maximum permissible limits by more than 14 times the MPL. The total mobile content of Cd (86.42 mg/kg) is 173 times the permissible limit of 0.5 mg/kg while the average value, 4.55 mg/kg is 9 times the maximum tolerable level (Table 8). Cd is extremely toxic metal naturally associated with base metal deposits (Boussen et al. 2008; Antunes et al. 2008). Chon et al (2005) reported that Pb-Zn-Cu mines in Korea showed significant levels of Cd, Cu, Pb and Zn in mine dump soils from the mine wastes.

Lead contents are variable and ranged from 6.8 to 52.2 mg/kg with a mean value of 31.81 (±15.38) mg/kg with some of the contents above the maximum permissible limit of 20 mg/kg (Kabata-Pendias, 1995). The concentration of 52.2 from Ameri, 47.4 from Enyigba and 41.64 from Ohankwu are more than twice the maximum tolerable limit. while the average value of 31.81 mg/kg is 1.59 times the maximum tolerable level (Table 8). In Sambo base metal mine, Korea, elevated levels of Pb, Cd and Zn were found in mine wastes and this provided source of contamination of the nerarby water sources (Chon et al. 2005). Studies around metalliferous mining site in Wadi Faynan area (Jordan), indicated a significant heavy metal pollution with values of Pb at 375 and Cu at 55 mg/kg, which amounted to massive environmental pollution (Pyatt and Grattan, 2001).

The contents of nickel in mine dumps vary from 0.38 to 30.02 mg/kg with an average value of 3.24 (±6.37) mg/kg. It is only in Ameri that the concentration of 30.02 mg/kg of Ni was little above the maximum permissible limit of 30 mg/kg. while the average value of 3.24 mg/kg is below the maximum tolerable level (Table 8).

The distribution of copper in mine dumps is variable and range from 4 to 80.26 mg/kg with a mean value of 27.85 (±20.32) mg/kg. The contents of Cu in all dump samples were less than the maximum permissible limit of 100 mg/kg. while the average value, 27.85 mg/kg is less than the maximum tolerable level (Table 8). It is the mine wastes close to the mining area that are the sources of this metal (Gosar, 2000).

The content of zinc varies from 8.16 to 352 mg/kg with a mean value of 121.37 (±82.97) mg/kg. The highest concentration of Zn in mine dumps was obtained from Ameka part and the lowest value was also from Ameka and with pH values of 8.8 and 4.8 respectively (Table 2). The high zinc concentration was obtained in a quartz-rich dump with sphalerite and siderite (Table 2) and in which the Zn concentration of 352 mg/kg was more than the maximum tolerable limit of 300 mg/kg by 1.17 times. The total mobile content of Zn (2305.94 mg/kg) was 7.69 times MPL while the average value of 121.37 mg/kg is below the maximum tolerable level (Table 8).

The contents of cobalt ranges from 2.9 to 22.34 mg/kg with a mean value of 13.62 (±6.59) mg/kg. The content of Co in all the samples was below the maximum tolerable limit. while the average value of 13.62 mg/kg is below the maximum tolerable level (Table 8).

Mine dumps contain high levels of Pb, Cd, As, Cu and Zn and may be most important sources of pollution on earth (Mendoza et al. 2005; Nash, 2002; Nash, 2004; Liao et al, 2008; Salvareedy-Aranguren et al. 2008) and may have devastating environmental effects including water sources (Cotter and Brigden, 2006; Yoon et al. 2006). Water draining mine dumps can be directly toxic, causing damage to fish gills, and can also increase the solubility and toxicity of heavy metals such as Cd, As, Cu, Pb and Zn (Wenner and Miller, 2003; Johnston et al. 2008). Dumps from Pb-Zn mining in Slovenia resulted in multi-element contamination of the environment with Pb, Cd, As and Zn (Gosar, 2004). The seeps from Pb-Zn mine in Iglesiente district (Sardinia, Italy) show near neutral pH but with extremely high concentrations of Zn, Cd, As and Pb that were discharged into aquatic systems and soils (Cidu et al. 2005). The less mobile As and Pb concentrated in the uppermost part of the soil while the more mobile metals (Cd, Zn, Cu, Co) precipitated where the pH is more basic (Dorronsoro et al. 2002). One of the environmental problems of Zn mining is the release of Cd to the environment (Kim et al. 2001) and Cd, Pb and Zn represent coherent gropu of metals from the metallogenic point of view (Olade, 1987). In silver mines in Taxco, Mexico, hosted in hydrothermal veins with galena, sphalerite, chalcopyrite with native Ag, the resulting waste rock dumps was reported to have high concentrations of Cd, Cu, Ag, Pb and As with range of values of 0.005 – 19.2, 0.025 – 63, 0.025 – 0.655 and 0.10 – 1.79 mg/l respectively (Mendoza et al. 2005). These exceeded the background values for soils. The abandoned mine wastes from Jalta (Pb-Zn) mineralization in Northern Tunisia Metallogenic province were reported to contain extremely high level of toxic metals in agricultural soils around the wastes (Boussen et al. 2008), and this was the most important consequence of mining activities in the area. The Goliam Bukovets mining regions (NW Bulgaria), abandoned for decades, are now polluted with toxic metals such as As, Pb, Zn, Cd but the presence of carbonate minerals in wastes played an important role in attenuation of the effects of these toxic metals (Mladenova and Zlatev, 2004).

5.1. Enrichment Factor (EF)

Arsenic showed extremely high enrichment factor in many parts of the area (Table 4 and Figure 10). The health risk level varied from moderate to very high (see Table 3). Cd also had significant to extremely high enrichment factor in the area (Table 4, Figure 11). The health risk level was moderate to very high (see Table 5). Pb showed significant enrichment factor (Table 4, Figure 12) and health risk level that was moderate (Table 5).

Zn recorded minimal to significant enrichment factor (Table 4, Figure 13) and with health risk level that varied from minimal to moderate (Table 5). Co showed significant enrichment factor in the area (Table 4) and with generally low health risk level (Table 5). The enrichment factors of Cu, Ni and Ca were low, minimal or deficient (Table 4). Their health risk levels were also low or minimal or no contamination (Table 5).

5.2. Contamination Factor (CF)

Arsenic showed very high contamination factor and made significant contribution to the very high degree of contamination, DC (Table 6, Figure 14).

Cd in mine dumps also had very high contamination factor of 56.88 and with very significant contribution to the high degree contamination (121.78) of mine dumps by heavy metals (Table 6, Figure 14). The contamination factor of Pb was moderate and made moderate contribution to the degree of contamination, DC (Table 6, Figure 14).

The contamination factors of Cu, Ni and Co were low, and made low contribution to the degree of contamination, DC of mine dumps by heavy metals (Table 6, Figure 14). Zn had moderate contamination factor (1.69) in mine dumps (Table 6, Figure 14) and made low contribution to the degree of contamination, DC of 122.65.

6. Conclusion

High content of As in mine dumps was recorded in locations D49, D31 and D58 (from Ameri), D101 from Ameka, D22 from Ameri, D19 from Enyigba, D60 from Ameri, D17 from Enyigba, D9 from Ohankwu, and D153 from Ameka. Arsenic showed high enrichment factor, indicating very high contamination in locations D49, D31, D58, D101, D22, D19, D60 and D17, and with very high health risk level. Arsenic made significant contribution to high degree of contamination, DC. High Cd concentrations were obtained in locations D49, D31, D58 and D22 from Ameri; D19 from Enyigba, D60 from Ameri, and D17 from Enyigba.

Extremely high enrichment factor of Cd was obtained in locations D49, D31, D58 and D22 and with high health risk level of 5 while locations D19, D60, D17 and D9 had very high enrichment factor and health risk level of 4. All these indicate high level of contamination due to mining activities in the area. High Pb concentrations were obtained in locations D49, D31, D58 and D22 from Ameri; D19 from Enyigba, D60 from Ameri, D17 from Enyigba, and D9 from Ohankwu. Significant enrichment factor of Pb was obtained in locations D49, D31, D58, D22, D19 and D60 with moderate health risk level of 3. High concentration of Ni above the maximum tolerable level (MPL) was only obtained in location D49 from Ameri area. High concentration of Zn in mine dumps was obtained only location D3 from Ameka with a value of 352 mg/kg which is 1.17 times above the MPL of 300 mg/kg. This is where mining activities are currently taking place. Zn had significant enrichment factor in D3, D17, D60 and D43. Cobalt in mine dumps was very low with significant enrichment factor only in D49 from Ameri. The concentrations of Cu in mine dumps were below the maximum permissible level (MPL) and with low enrichment factor.

Cd and As had very high contamination factors of 56.88 and 59.29 respectively in mine dumps, and contributed to high contamination expressed by degree of contamination in D49, D31, D58 and D22. Pb had moderate contamination factor of 2.89. It contributed to high degree of contamination, DC. Cu had moderate contamination factor of 1.03 in mine dumps.. It contributed to high contamination expressed by degree of contamination, DC. Zn showed moderate contamination factor of 1.69.

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

The people of Abakaliki who are known producers of crops (mainly rice and yams) in southeastern Nigeria, would need a management plan against the transfer of metals from the dumps 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 crops from the area.

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