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Assessment of Heavy Metal Contamination in Soils Around Lead (Pb)-Zinc (Zn) Mining Areas in Enyigba, Southeastern Nigeria

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Abstract: Mining activities have been undertaken for over 95 years in Enyigba area of southeastern Nigeria. In this area, thirty-six (36) trace metals including those that are essential for plant and animal nutrition have been analyzed from forty-nine (49) soil samples that were collected from three Pb-Zn mines. The aim of the analysis is to assess the level of contamination of the soils caused by mining activities. Potentially harmful elements which are commonly associated with Pb-Zn mines were of special interest. Such elements included Pb, Zn, As, Cd, Mn, Fe, Se, Sb, Cu and Bi. Generally, the samples analyzed showed elevated concentrations of Pb, Zn, Cd, Cu and Cr when compared with concentrations documented in the international agricultural soil standards. Geo-accumulation indices of soils that occur closer to the mines indicate moderate to extreme level of contamination in Pb and moderate levels in Cd. Enrichment factor (EF) showed very high enrichment to extremely high enrichment in Pb. Cd and Zn enrichment were found to be significant and moderate respectively. Conversely, the geo-accumulation indices for soil samples located away from the mines indicate moderate to heavy contamination in Pb but had moderate to significant enrichment in Cd and moderate in Bi and Cr. In general, soil quality all around the mines were found to have deteriorated as revealed by the pollution load index. Thus the results of this study call for immediate remedial measures to be initiated. In addition, miners and local communities living around the mines need to be enlightened about the dangers of exposure to these heavy metal contaminants.

Keywords: Heavy/trace metals, contamination, soils, Pb-Zn mining, Enyigba, southeastern Nigeria.

INTRODUCTION

Contamination of environments caused by heavy metal due to mining activities has become a global issue because of the potential health risks it poses to the local communities where the activities take place. The contamination of soils around mining localities can lead to the contamination of plants (food crops and grasses) grown on them. The contaminated food crops when consumed by humans and other animals can cause health hazards. A good number of researchers in various countries have carried out investigations to determine the concentrations of trace-metals that contaminate, with emphasis on harmful heavy metals in soils and sediments around mining areas of lead (Pb) and zinc (Zn). Regions that were investigated include Kirki region in NE Greece (Nikolaidis et al., 2010), southeastern Serbia (Djordjevic et al., 2014), Kosovska Mitrovica in Republic of Kosovo (Sajn et al., 2013), Cartagena-La Union mining district in SE Spain (Martinez-Martinez et al., 2013) and parts of China (Li et al., 2014). Knowing that large scale mining activity takes place in Africa, the International Geological Correlation Program (IGCP) in collaboration with Swedish International Development Agency (SIDA) approved two projects to address the environmental and health impacts caused by active and abandoned mines in sub-Saharan Africa. The projects were designated as project 594 and project 606. These two projects were undertaken during the year 2011 to 2014. With additional funding from UNESCO-SIDA, the scope of the IGCP Projects was expanded to include targeted mining sites in sub-Saharan African countries.

The Pb-Zn mining site in Enyigba area, which is geologically located within the lower Benue rift in south-eastern Nigeria and politically, in Ebonyi state of Nigeria, was one of the targeted sites (see Fig. 1). In this site, Pb-Zn ores occur in veins within slightly metamorphosed Albian

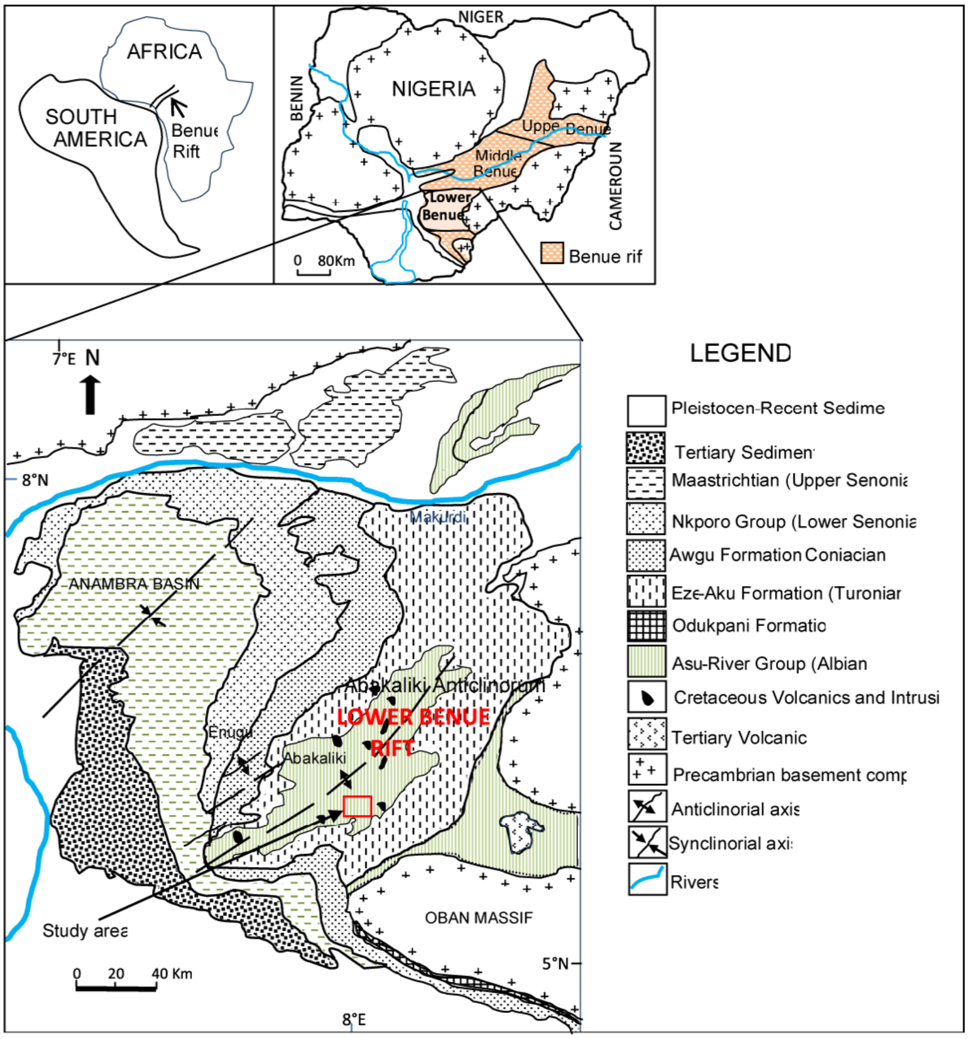

Fig.1. Geological map of Nigeria and location of the study area.

sedimentary rocks which are mainly black slates (Obiora and Umeji, 2004). The rocks essentially occur as NE-SW trending belt within the Benue rift. The ores in this belt are often associated with saline groundwater and mineralized igneous rocks. The mines in Enyigba area are located within Latitudes 6°10'40" N to 6°11'55" N and Longitudes 8°08' E to 8°09'E. The terrain is generally flat-lying with occasional small hills on which the mines are commonly located. The first recorded production of Pb-Zn ore was in 1925. Mining was abandoned in some of the mines during the civil war of 1966 to 1970 (Umeji, 2000). However, local mining continued intermittently within the "abandoned mines" after the civil war. The ore minerals exploited were mainly galena (PbS), sphalerite (ZnS), chalcopyrite ($CuFeS_2$) to some extent and bornite (Cu_5FeS_4). Azurite [$2CuCO_3Cu(OH)_2$], smithsonite ($ZnCO_3$) and cerussite ($PbCO_3$) are also found as products of supergenetic enrichment. The gangues associated with the main ores included siderite ($FeCO_3$), calcite ($CaCO_3$), pyrite (FeS_2), marcasite (FeS_2) and quartz (SiO_2) (Umeji, 2000; Obiora and Umeji, 2004). Waste material derived from mining activities were dumped in the nearby area where farmlands are located. Mine waters are pumped into these nearby farmlands, while natural surface drainage such as streams and rivers occur in the vicinity of the mines. Pb- Zn mines are known to be potential sources of harmful trace-elements such as Pb and Zn as well as other associated elements particularly, As, Cd, Mn, Fe, Se, Sb, Cu and Bi. Acid mine drainage that seeps through the dumped material contaminate soils and surface waters in the immediate vicinity (Nikolaidis et al., 2010; Obiora, 2012). These elements can be toxic to plants, animals and human beings when the elements are absorbed above recommended concentrations. Initially, there were scarce records of detailed studies that had been carried out to ascertain the extent of contamination of soils caused by mining activities in Enyigba.

The purpose of this study was to determine the concentration of heavy metals, trace elements including those that are essential for plant and animal nutrition. The study was carried around major abandoned Pb-Zn mines in the Enyigba area in order to assess the level of contamination that existed.

STUDY METHODOLOGY

Field Survey, Sampling Media, Methods and Procedure

Field survey was carried out on 1:15,000 scale around three major mines, namely: Ndinwanu Ishiagu Enyigba/ Ikwo (Ameka), Ishiagu Enyigba (Enyigba) and Alibaruhu mines. The first mine consisted of three elongated pits which trend N-S to 20° NNE-200° SSW. The mine length is 250 m and between 3 and 6 m in width and extended up to a depth of 10 m. The second mine consists of four elongated pits, three of which trend 345° NNW - 165° SSE to 325° NNW -145° SSE, with the fourth one trending 30° NNE-210° SSW. Lengths of the mines range between 30 and 90m, with widths between 5 and 8 m and extends to a depth of 15 m. The third mine consisted of two elongated pits which trend essentially 310° WNW - 130° ESE and 334° NNW - 154° SSE. The length for this pit ranged between 20 and 50 m while width varied between 3 to 7 m but depth was greater than 10 m. Sampling area around the mines varied from 500 square metres to 500 m x 300 m. The method and procedure adopted in the sampling was in accordance to the ones recommended by Kribek (2013) for the UNESCO-SIDA-sponsored Abandoned Mines Project in sub-Saharan African countries. Soil samples were collected mainly from farmlands in the vicinity of the mines (i.e. cultivated land). The sampling points were located at every one second (approximately 16 m) along the latitudes and longitudes (Fig. 2). Soil samples were collected mainly from top soils i.e. within 0 - 25 cm depth. A few samples from the sub-soils (within a depth of 50 to100 cm) at some locations were also collected in order to obtain information about enrichment or depletion between soil layers.

SAMPLE PREPARATION AND ANALYSIS

All the samples collected were air-dried over several days and subsequently homogenized in agate ball mill (particle size less than 0.063 mm). Altogether, 49 samples of soils were analyzed. The analyses were carried out by the Acme Analytical Laboratories (Vancouver) Ltd, Canada, using the Inductively Coupled Plasma, MassSpectrometer (ICPMS). Thirty- six (36) trace-elements, including those essential in plant and animal nutrition and harmful trace-elements commonly associated with Pb-Zn mines, were analysed.

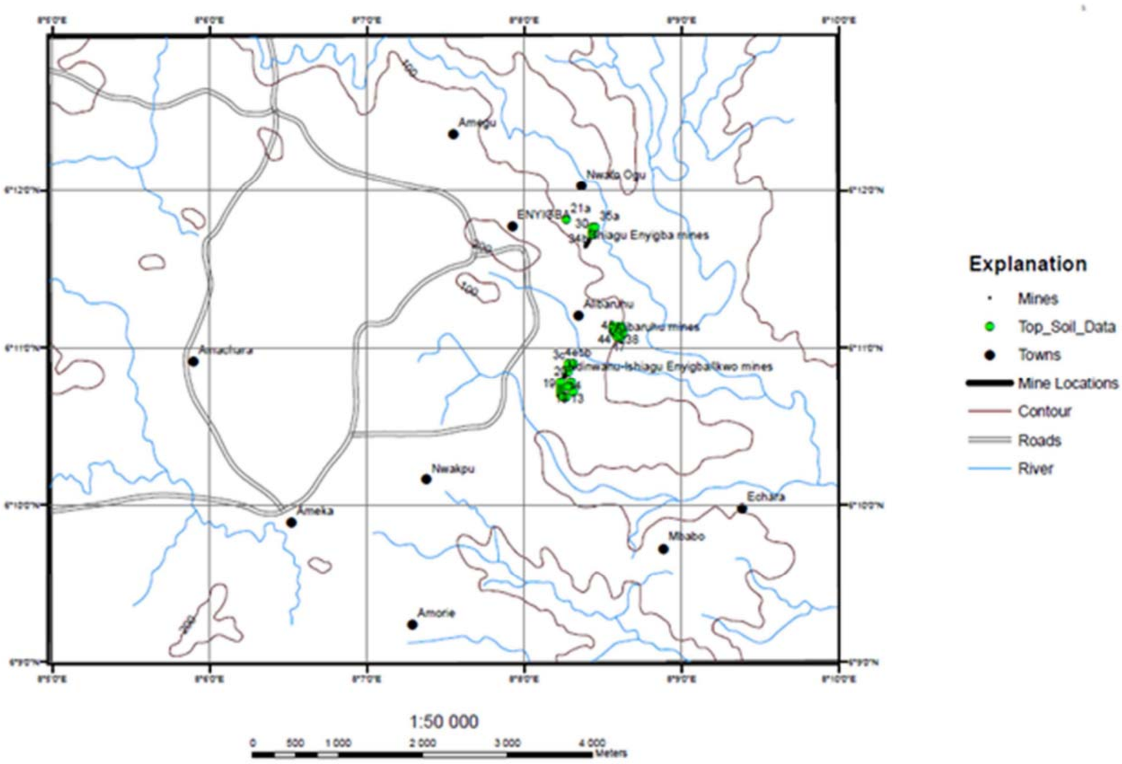

Fig.2. Topographic Map of Enyigba and the adjoining areas showing the locations of the mines and sampling points

RESULTS AND DISCUSSION

Statistical analysis of the 36 trace- elements in the soils that occur around the three major mines in the study area was carried out. The results are presented in Tables 1a, b.

Comparison of the mean concentrations of some of the potentially harmful elements which are common in Pb-Zn mining environments, namely: Pb, Zn, Cd, Cu, Cr, Se was done in accordance with international standards such as the Canadian Environmental quality guideline (1999) for agricultural soils. The results showed that Pb had values which greatly exceeded the guideline value of 70 mg/kg in all the soil samples which are either close to or away from all the three mines as shown in Table 2. The mean concentrations of trace element Zn was found to exceed the guideline value of 200 mg/kg for the soil samples collected closer to the Ameka mine only. The mean was 583.13 mg/kg for the samples closer and 442.5 mg/kg for samples away from the mine. The mean concentrations of element Cd exceeded the guideline value of 1.4 mg/kg only for the soil samples close to the Ameka mine. The mean was 3.45 mg/kg for samples collected close to the mine and 1.975 mg/kg for samples collected away from the mine. The mean concentration of Cu slightly exceeded the guideline of 63 mg/kg in the soil samples close to the Enyigba mines in which the mean was 63.7 mg/kg. The mean concentrations of Cr exceeded the guideline value of 64 mg/kg in all the soil samples around the Alibaruhu mines where the mean values were 87.56 mg/kg for samples collected closer to the mines and 95.33 mg/kg for samples collected away from the mines. The mean values of Se are generally below the guideline value of 1 mg/kg in the soil samples around all the mines, although five samples contained Se (1.2 to 1.3 mg/kg) which is slightly above the guideline value. When the data is compared with Clarke's values for the mean concentrations of the chemical elements in the upper continental crust as given by McLennan (2001), the mean concentrations of Pb, Zn, Cd exceed the Clarke's values of 17 mg/kg, 71 mg/kg, 0.1 mg/kg, respectively in all the mines. The mean concentrations of Cr (87.56 mg/kg and 95.33 mg/kg) exceeded the Clarke value of 83 mg/kg in the soil samples around the Alibaruhu mines only. The mean values of other heavy metals commonly associated with Pb-Zn mines such as Mo, Mn, Fe, Se, and Bi in the soil samples around the mines generally exceeded the Clarke values. The mean values of Mn and Fe are as shown in Table 3. They were found to exceed Clarke's values of 600 mg/kg and 35,000 mg/kg, respectively.

In a similar manner, the mean values of Sb are found to range from 0.3 to 0.43 mg/kg, which exceeded the Clarke value of 0.2 mg/kg. Mean values of Cu (63.7 mg/kg) and Bi (0.43 mg/kg) were higher than the Clarke's values of 25 mg/kg and 0.3 mg/kg, respectively as obtained in the soil samples close to the Enyigba mines only. However, the mean values of Mo are all below the Clarke's value of 1.5mg/kg in all the soil samples around all the mines (see also annexed Tables 1a and 1 b). The top soils compared with the sub-soils collected from the same locations, they were found to have a considerable depletion in Pb in the sub-soils whereas the other potentially harmful elements were either enriched or depleted.

Geo-accumulation indices (GI or I_{geo}) and Enrichment Factor (EF)

In order to assess contamination by comparing current and pre-industrial (mining) concentrations of heavy metals, geo-accumulation indices (GI or I_{geo}) is computed for the potentially harmful elements (Pb, Zn, As, Cd, Mn, Fe, Se, Sb, Cu, Bi).The ranges of the I_{geo} ,with their mean values, along with EF for soil samples close to the mines and those away from the mines are as presented in Tables 4a and 4b. The geo-accumulation index is computed using the following equation: $I_{geo} = log_2 [C_n/(1.5 \text{ x } B_n)]$, where ''$C_n$'' is the concentration of the element in the enriched samples and ''B_n'' is the background concentration of the element in the earth's crust, according to Martin and Meybeck (1979). The factor 1.5 is used to address possible variations due to lithogenic effects (Stoffers et al.,1986 as cited by Nikolaidis et al., 2010). The range of values for various degrees of contamination using geo-accumulation indices (I_{geo}) are as shown in Table 5.

The mean values of I_{geo} for the soils that occur closer to Enyigba and Alibaruhu mines indicated extreme contamination in Pb. At Ameka mine, the contamination was moderate to heavy in Pb and moderate in Cd. Bi values indicate levels that the soils are uncontaminated to moderately contaminated in all the mines. This was also in the case of Cu and Mn at the Enyigba and Alibaruhu mines. Conversely, the mean values of geo-accumulation indices for Pb in soil samples away from the mines indicated high contamination at Ameka and moderate to high contamination at Enyigba. The values for Cd indicated moderate contamination at Ameka and uncontaminated to moderately contaminated at Enyigba. Zn and Bi show uncontaminated to moderate contamination at Ameka, and Enyigba and Alibaruhu, respectively.

On the other hand, the enrichment factor (EF) is computed using the formula, $EF = (C_n/C_{ref})\text{sample}/(B_n/B_{ref})$ or $[(C_n/Fe)\text{sample}/(B_n/Fe)\text{background}]$ which was originally introduced by Buat-Menard and Chesselet (1979) as cited

Table 1a. Statistical analysis of the 36 trace-elements in the soil samples close to the three major mines in the study area

Mg/Kg	Ameka Mine								Enyigba Mine								Alibaruhu Mine								
	Min.	Max	Mean	Median	Std. Dev.	VC	Skewness	Kurtosis	Min.	Max	Mean	Median	Std. Dev.	VC	Skewness	Kurtosis	Min.	Max	Mean	Median	Std. Dev.	VC	Skewness	Kurtosis	Clarke's value
Mo	0.4	1.2	0.63	0.6	0.19	0.3	1.74	3.76	0.6	1	0.88	0.95	0.19	0.22	-1.66	2.62	0.7	2	1.39	1.5	0.44	0.31	-0.26	-1.12	1.5
Cu	12.7	28.1	17.72	16.4	3.86	0.22	1.11	0.79	27.2	104.6	63.7	61.5	31.99	0.5	0.39	1.06	19.4	33.6	23.42	21.8	4.86	0.21	1.57	1.51	25
Pb	40.7	7075.4	515.07	86.45	1481.29	2.88	4.21	18.48	265.3	4073.3	2509.7	2850.1	1807.85	0.72	-0.59	-2.57	434.9	3505.3	1048.26	704.3	964.9	0.92	2.55	6.8	17
Zn	56	7379	583.13	113.5	1502.86	2.58	4.38	20.2	117	214	163.25	161	51.92	0.32	0.04	-5.72	40	271	95.33	63	72.3	0.76	2.21	4.97	71
Ag	0.1	1.8	0.73	0.5	0.78	1.08	1.19	0.55	0.6	0.7	0.67	0.7	0.06	0.09	-0.93	<D.L	0.2	0.7	0.43	0.4	0.25	0.58	0.59		0.05
Ni	14.6	35.5	22.06	21.3	5.37	0.24	0.81	0.41	17.5	38.2	27.45	27.05	8.52	0.31	0.27	1.18	11.7	28.8	17.38	15.8	5.46	0.31	1.38	1.49	44
Co	10.3	35.5	20.98	19.8	6.56	0.31	0.64	0.38	15.9	37	23.45	20.45	9.55	0.41	1.43	1.74	5.7	30.9	20.94	20.5	7.68	0.37	-0.74	0.72	17
Mn	154	1853	787.96	806	529.05	0.67	0.51	-0.77	788	1713	1297.25	1344	465.62	0.36	-0.2	-4.79		2978	1391.33	1224	763.27	0.55	0.72	2.41	600
Fe	26800	55600	41529.17	40200	8314.97	0.2	0.17	-0.84	47100	85400	65175	64100	15732.85	0.24	0.4	1.41	10600	188400	124177.8	154800	66968.16	0.54	-0.88	-1.14	35000
As	0.6	4.7	1.51	1.3	0.82	0.54	2.71	9.83	1.5	5.1	3.28	3.25	1.52	0.46	0.09	-0.15	2.2	8.8	6.43	7.8	2.47	0.38	-0.9	-1.07	1.5
Au	0.5	1.3	0.8	0.6	0.44	0.54	1.63	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	0.5	0.6	0.55	0.55	0.07	0.13			0.0018
Th	3.6	7.6	5.69	5.7	0.95	0.17	-0.06	-0.05	5	9.1	6.58	6.1	1.76	0.27	1.46	2.74	4.9	8.4	7.17	7.6	1.07	0.15	-1.19	1.51	10.7
Sr	10	411	54	23.5	89.07	1.65	3.41	12.13	7	15	11.25	11.5	3.5	0.31	-0.32	-1.6	7	17	13.89	15	2.89	0.21	-1.97	4.49	350
Cd	0.1	20.7	3.45	0.7	6	1.74	2.33	4.93	0.2	0.5	0.4	0.5	0.17	0.43	-1.73	<D.L	0.1	1	0.43	0.2	0.49	1.14	1.65		0.1
Sb	0.1	0.8	0.43	0.4	0.35	0.81	0.42	<D.L	0.2	0.5	0.35	0.35	0.21	0.61	<D.L	<D.L	0.2	0.5	0.41	0.5	0.12	0.3	-0.89	-1.13	0.2
Bi	0.2	0.3	0.22	0.2	0.04	0.18	1.91	1.79	0.3	0.6	0.43	0.4	0.13	0.29	1.13	2.23	0.3	0.4	0.36	0.4	0.05	0.15	-0.27	-2.57	0.13
V	10	47	30.42	29.5	7.03	0.23	-0.23	3.06	19	49	28.75	23.5	13.67	0.48	1.85	3.56	16	94	66.22	78	29.92	0.45	-1.08	-0.34	107
Ca	600	3300	1395.83	1200	651.07	0.47	1.24	1.65	300	800	550	550	208.17	0.38	0	0.39	400	2700	1355.56	1200	650.21	0.48	0.94	1.76	30000
P	240	6500	2473.75	2550	1662.11	0.67	0.36	0.039	250	380	317.5	320	55.6	0.18	-0.22	-0.82	310	800	631.11	670	189.7	0.3	-1.08	-0.18	700
La	2	46	18.92	17.5	8.63	0.46	1.18	3.41	3	14	6.25	4	5.19	0.83	1.95	3.85	4	13	9.44	11	3.75	0.4	-0.72	-1.43	30
Cr	15	60	36.63	34.5	9.57	0.26	0.29	0.69	24	63	37	30.5	17.83	0.48	1.69	2.84	17	132	87.56	105	42.77	0.49	-0.96	-0.67	83
Mg	1100	3700	1825	1700	577.29	0.32	1.56	3.65	1100	2800	2175	2400	758.84	0.35	-1.41	1.79	200	2300	877.78	600	659.12	0.75	1.56	2	13300
Ba	129	4955	475	253.5	962.61	2.03	4.76	23.06	38	126	65.25	48.5	41.15	0.63	1.82	3.34	49	169	88.22	74	38.25	0.43	1.35	1.34	550
Ti	10	30	13.5	10	6.71	0.49	1.78	2.02	10	10	10	10	<D.L	<D.L	<D.L	<D.L	10	30	22.86	20	7.56	0.33	-0.6	-0.35	4100
Al	8000	22000	14604.17	13500	3341.37	0.23	0.67	0.4	9700	24100	15150	13400	6216.91	0.41	1.51	2.83	8400	17100	14333.33	15100	3021.16	0.21	-1.3	0.66	80400
Na	50	3330	720.42	305	853.89	1.19	1.67	2.69	30	50	45	50	10	0.22	-2	4	30	120	52.22	40	29.49	0.56	1.9	3.32	28900
K	400	1400	595.83	500	231.21	0.39	2.22	5.72	500	800	725	800	150	0.21	-2	4	400	700	522.22	500	120.19	0.23	0.57	-1.1	28,800
Hg	0.02	0.31	0.05	0.03	0.06	1.24	3.95	16.57	0.02	0.04	0.03	0.03	0.01	0.27	-1.33E-15	1.5	0.02	0.04	0.03	0.02	0.01	0.35	1.19	-0.45	NIL
Sc	3.7	6.8	5	4.8	0.84	0.17	0.48	-0.48	4.1	4.8	4.48	4.5	0.38	0.08	-0.06	-5.65	3.6	5	4.48	4.5	0.41	0.09	-1.08	2.04	14
Tl	0.1	0.5	0.15	0.1	0.12	0.79	2.74	7.94	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	0.1	0.1	0.1	0.1	0	0	<D.L	<D.L	NIL
S	1300	19900	7700	1900	10569.77	1.37	1.73	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	900	1200	1050	1050	212.13	0.2	<D.L	<D.L	NIL
Ga	3	9	6.17	6	1.4	0.23	0.19	0.68	5	11	7	6	2.71	0.39	1.81	3.48	4	12	9.22	10	3.07	0.33	-1.3	0.29	NIL
Se	0.5	0.7	0.62	0.6	0.08	0.12	-0.31	-0.1	0.5	0.8	0.67	0.7	0.15	0.23	-0.94	<D.L	0.6	1.3	1.01	1.2	0.32	0.32	-0.59	-1.85	NIL

D.L= Detective limit

Table 1b. Statistical analysis of the 36 trace-elements in the soil samples away from the three major mines in the study area.

	Ameka Mine								Enyigba Mine								Alibaruhu Mine								
Mg/Kg	Min.	Max	Mean	Med-ian	Std. Dev.	VC	Skew-ness	Kurto-sis	Min.	Max	Mean	Med-ian	Std. Dev.	VC	Skew-ness	Kurto-sis	Min.	Max	Mean	Med-ian	Std. Dev.	VC	Skew-ness	Kurto-sis	Clarke's value
Mo	0.5	1.1	0.875	0.95	0.26	0.3	-1.44	2.23	0.6	1	0.8	0.8	0.16	0.2	-2.04E-15	-1.2	1.2	1.6	1.37	1.3	0.21	0.15	1.29		1.5
Cu	10.6	36.2	22.2	21	10.84	0.49	0.58	0.22	18.5	35.8	24.88	24.3	6.58	0.26	1.46	2.69	20	22.9	21.37	21.2	1.46	0.07	0.51		25
Pb	36.8	4077.4	1103.6	150.1	1983.27	1.8	2	3.99	83.1	1204.7	331.16	114.5	489.41	1.48	2.21	4.91	158.8	438.6	271.23	216.3	147.77	0.54	1.44		17
Zn	123	1291	442.5	178	566.28	1.28	1.99	3.96	62	112	95.6	101	20.48	0.21	-1.44	1.98	56	121	80.33	64	35.44	0.44	1.63		71
Ag	0.3	0.3	0.3	0.3	<D.L	<D.L	<D.L	<D.L	0.3	0.3	0.3	0.3	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L		0.05
Ni	12.7	47.2	27.775	25.6	15.26	0.55	0.63	-1.2	20.3	36	29.76	30.9	6.6	0.22	-0.68	-0.95	15.9	18	16.97	17	1.05	0.06	-0.14		44
Co	10.9	32.9	25.75	29.6	10.07	0.39	-1.8	3.34	20.3	47.8	30.9	24	11.81	0.38	0.86	-1.4	14	21	16.93	15.8	3.64	0.21	1.27		17
Mn	175	3886	1353.75	677	1704.94	1.26	1.88	3.65	405	2143	1255.4	1338	628.19	0.5	0.13	1.2	559	949	772.33	809	197.57	0.26	-0.81		600
Fe	33500	80500	59425	61850	19511.26	0.33	-0.71	1.44	55400	92500	70420	60900	17092.31	0.24	0.66	-2.65	11600	102600	43200	15400	51476.99	1.19	1.72		35000
As	1.2	4.7	2.55	2.15	1.59	0.62	1.05	-0.079	1.4	3.2	2.32	2.2	0.73	0.32	0.02	-1.67	4.9	7.3	6.27	6.6	1.23	0.2	-1.13		1.5
Au	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	1.2	1.2	1.2	1.2	<D.L	<D.L	<D.L		0.0018
Th	3.6	5.9	4.6	6.95	1.06	0.23	0.52	-2.42	6.3	8.9	7.9	8.6	1.21	0.15	-0.71	-2.49	6.4	7.4	6.9	6.9	0.5	0.07	-1.60E-14		10.7
Sr	8	19	13.5	13.5	4.65	0.34	0	-0.43	8	26	14.8	8	9.34	0.63	0.63	-3.18	16	17	16.67	17	0.58	0.03	-1.73		350
Cd	0.1	6.1	1.975	0.85	2.79	1.41	1.84	3.45	0.4	0.4	0.4	0.4	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L		0.1
Sb	0.4	0.4	0.4	0.4	<D.L	<D.L	<D.L	<D.L	0.1	0.1	0.1	0.1	<D.L	<D.L	<D.L	<D.L	0.2	0.4	0.3	0.3	0.1	0.33	-1.90E-15		0.2
Bi	0.1	0.3	0.2	0.2	0.08	0.41	5.92E-16	1.5	0.3	0.4	0.36	0.4	0.05	0.15	-0.61	-3.33	0.3	0.3	0.3	0.6	<D.L	<D.L	<D.L		0.13
V	22	36	31.75	34.5	6.55	0.21	-1.91	3.69	19	51	36.8	32	13.59	0.37	-0.12	-1.68	65	84	72.33	68	10.21	0.141212	1.57		107
Ca	400	2700	1425	1300	1152.89	0.81	0.22	-4.66	100	9400	2280	700	3987.73	1.75	2.21	4.93	1200	2400	1666.67	1400	642.91	0.39	1.55		30000
P	180	420	280	260	105.83	0.34	0.86	-0.29	230	470	372	410	99.6	0.27	-0.76	-1.18	580	720	643.33	630	70.95	0.11	0.82		700
La	2	18	11.5	13	6.95	0.6	-1.07	0.88	3	12	8	10	4.18	0.52	-0.51	-2.96	11	12	11.67	12	0.58	0.05	-1.73		30
Cr	40	63	54.5	57.5	10.97	0.2	-0.93	-0.91	28	69	51	51	17.93	0.35	-0.23	-2.09	78	118	95.33	90	20.53	0.22	1.09		83
Mg	1200	8800	4000	3000	3622.15	0.91	0.94	-0.83	700	5600	2640	2200	1811.91	0.69	1.28	2.57	700	800	766.67	800	57.74	0.08	-1.73		13300
Ba	90	244	142.25	117.5	69.33	0.49	1.74	3.21	36	133	76	73	38.77	0.51	0.7	-0.26	66	89	76	73	11.79	0.16	1.07		550
Ti	10	10	10	10	<D.L	<D.L	<D.L	<D.L	10	10	10	10	<D.L	<D.L	<D.L	<D.L	20	20	20	20	<D.L	<D.L	<D.L		4100
Al	10500	29300	18200	16500	8838.55	0.49	0.64	-2.26	12100	26500	20120	20300	5505.63	0.27	-0.55	0.1	14600	18400	16100	15300	2022.37	0.13	1.5		80400
Na	50	80	62.5	60	15	0.24	0.37	-3.9	40	70	58	60	13.04	0.22	-0.54	-1.49	40	70	56.67	60	15.28	0.27	-0.94		28900
K	400	600	500	500	115.47	0.23	0	-6	400	1000	620	500	268.33	0.43	0.81	-1.54	400	600	500	500	100	0.2	0		28,800
Hg	0.02	0.16	0.07	0.03	0.08	1.12	1.7	<D.L	0.01	0.03	0.02	0.02	0.01	0.35	-5.55E-16	2	0.02	0.03	0.02	0.02	0.01	0.49	1.73		NIL
Sc	3.3	7.2	4.6	3.95	1.82	0.39	1.52	2	4.3	8.1	5.36	4.6	1.59	0.3	1.87	3.46	4.6	5.7	5	4.7	0.61	0.12	1.68		14
Tl	0.1	0.2	0.15	0.15	0.07	0.47	<D.L	<D.L	0.1	0.1	0.1	0.1	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L		NIL
S	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L		NIL
Ga	4	9	6.5	6.5	2.08	0.32	<D.L	0.39	5	11	8.8	9	2.49	0.28	-0.92	0.32	8	11	9.33	9	1.53	0.16	0.94		NIL
Se	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	0.6	1.4	0.97	0.9	0.4	0.42	0.72		NIL

D.L= Detective limit

Table 2. Concentration of Lead(Pb)

Mine name	Concentration(mg/KG)	
	Close to the mine	Far from the mine
Ameka	515.07	1,103.60
Enyigba	2,509	114.5
Alibaruhu	1,048.26	271.25

Table 3. Concentration of Maganese (Mn) and Iron (Fe)

Mine name	Concentration (mg/KG)			
	Close to the mine		Far from the mine	
	Mn	Fe	Mn	Fe
Ameka	787.96	41.529.17	1,353	59,425
Enyigba	1,297.25	65.175	1,297.25	70,420
Alibaruhu	1,391.33	124,177.80	772.33	43,200

in Nikolaidis et al. (2010) where C_n is the content of the examined element, C_{ref} (sample) is the content of the reference element, which is iron (Fe) in this study, B_n is the background value of the examined element and B_{ref} (sample) is the background value of the reference element. The background value used for Fe in this study is 35,900 mg/kg (Martin and Meybeck, 1979). From the computations, the mean values of the enrichment factors for the soil samples close to the mines show that they are extremely enriched in Pb at Enyigba, and Ameka and Alibaruhu, respectively. There is significant and moderate enrichment of Cd and Zn at Ameka. Mn, Bi, Cu, As, Sb, and Cr show minimal enrichment, with highest values of EF shown by Bi. The EF values for the soil samples away from the mines indicate that Pb is highly enriched at Ameka and has significant enrichment at Enyigba and Alibaruhu; Cd has significant enrichment at Ameka while there is moderate enrichment of Bi and Cr at Alibaruhu. Cu, Zn, Mn, As, and Sb show minimum enrichment in all the mines (see Table 6).

Table 4a. The ranges of geoaccummulation index (GI), with their mean values, alongside those for the enrichment factor (EF) for soil samples close to the mines

		Ameka Mine				Enyigba Mine				Alibaruhu Mine			
		Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD
Cu	GI	-1.92	-0.77	-1.46	0.3	-0.82	1.12	0.23	0.81	-1.31	-0.51	-1.06	0.27
	EF	0.35	0.64	0.49	0.08	0.36	1.79	1.17	0.6	0.12	2.23	0.5	0.69
Pb	GI	0.76	8.2	2.54	1.78	3.47	7.41	6.12	1.84	4.18	7.19	5.12	0.93
	EF	1.65	318.14	25.22	67.1	6.97	139.32	93.04	62.4	5.18	165.93	38.8	56.64
Zn	GI	-1.75	5.28	-0.03	1.78	-0.7	0.17	-0.28	0.47	-2.25	0.51	-1.25	0.83
	EF	0.2	41.8	3.68	8.57	0.4	0.97	0.74	0.25	0.09	1.62	0.46	0.56
Mn	GI	-2.81	0.78	-0.82	1.12	-0.45	0.67	0.19	0.55	-2.94	1.46	0.05	1.22
	EF	0.21	1.83	0.89	0.5	0.59	1.36	1.01	0.36	0.29	1.48	0.69	0.43
Fe	GI	-1.01	0.05	-0.4	0.29	-0.19	0.67	0.25	0.35	-2.34	1.81	0.81	1.4
	EF	1	1	1	0	1	1	1	0	1	1	1	0
As	GI	-4.3	-1.33	-3.11	0.63	-2.98	-1.22	-1.99	0.75	-2.43	-0.43	-1.01	0.72
	EF	0.05	0.43	0.16	0.07	0.14	0.35	0.23	0.1	0.2	1.71	0.49	0.5
Cd	GI	-1.58	6.11	1.68	2.4	-0.58	0.74	0.3	0.76	-1.58	1.74	-0.14	1.7
	EF	0.54	74.46	14.23	22.94	0.76	1.43	1.19	0.37	0.11	3.79	1.52	1.99
Sb	GI	-3.75	-0.75	-2.08	1.53	-2.75	-1.43	-2.09	0.93	-2.75	-1.43	-1.78	0.52
	EF	0.09	0.64	0.36	0.28	0.13	0.3	0.22	0.12	0.07	0.25	0.13	0.05
Bi	GI	0.037	0.62	0.14	0.22	0.62	1.62	1.08	0.41	0.62	1.04	0.85	0.22
	EF	0.99	2.06	1.48	0.28	1.29	2.53	1.84	0.51	0.49	7.82	1.66	2.35
Cr	GI	-2.83	-0.83	-1.59	0.41	-2.15	-0.76	-1.64	0.62	-2.65	0.31	-0.56	1.11
	EF	0.15	0.57	0.45	0.09	0.18	0.37	0.28	0.08	0.18	3.01	0.61	0.9

Table 4b: The ranges of geoaccummulation index (GI), with their mean values, alongside those for the enrichment factor (EF) for soil samples away from the mines.

		Ameka Mine				Enyigba Mine				Alibaruhu Mine			
		Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD
Cu	GI	-2.18	-0.41	-1.25	0.75	-1.38	-0.42	-0.98	0.36	-1.26	-1.07	-1.17	0.1
	EF	0.23	0.69	0.42	0.19	0.29	0.69	0.414	0.16	0.23	1.67	1.19	0.83
Pb	GI	0.62	7.41	3.32	2.89	1.79	5.65	2.87	1.6	2.73	4.19	3.36	0.75
	EF	1.39	113.65	32.49	54.2	2.02	46.44	12.228	19.18	9.59	23.14	18.62	7.82
Zn	GI	-0.63	2.76	0.48	1.54	-1.62	-0.77	-1.03	0.35	-1.77	-0.65	-1.33	0.6
	EF	0.74	4.53	1.8	1.83	0.29	0.57	0.398	0.11	0.15	1.17	0.83	0.59
Mn	GI	-2.63	1.85	-0.53	1.84	-1.42	0.99	0.03	0.89	-0.95	-0.19	-0.52	0.39
	EF	0.26	2.41	0.94	0.99	0.33	1.84	0.946	0.59	0.39	1.81	1.34	0.82
Fe	GI	-0.68	0.58	0.075	0.54	0.04	0.78	0.35	0.34	-2.21	0.93	-1.03	1.71
	EF	1	1	1	0	1	1	1	0	1	1	1	0
As	GI	-3.3	-1.33	-2.42	0.89	-3.08	-1.89	-2.41	0.48	-1.27	-0.7	-0.94	0.3
	EF	0.12	0.27	0.19	0.06	0.1	0.17	0.148	0.03	0.22	2.15	1.51	1.11
Cd	GI	-1.58	4.35	1.38	2.47	0.42	0.42	0.42	<D.L	<D.L	<D.L	<D.L	<D.L
	EF	0.3	13.6	5.43	6.07	1.23	1.23	1.23	<D.L	<D.L	<D.L	<D.L	<D.L
Sb	GI	-1.75	-1.75	-1.75	<D.L	-3.75	-3.75	-3.75	<D.L	-2.75	-1.43	-2.12	0.66
	EF	0.2	0.2	0.2	<D.L	0.07	0.07	0.07	<D.L	0.08	1.04	0.72	0.55
Bi	GI	-0.96	0.62	-0.065	0.66	0.62	1.04	0.87	0.23	0.62	0.62	0.62	0
	EF	0.69	1.4	0.94	0.31	1.19	1.9	1.45	0.28	0.81	7.14	4.44	3.27
Cr	GI	-1.41	-0.76	-0.99	0.31	-1.93	-0.63	-1.14	0.55	-0.45	0.15	-0.18	0.3
	EF	0.4	0.6	0.48	0.09	0.24	0.42	0.352	0.07	0.38	3.92	2.72	2.03

EF= ENRICHMENT FACTOR, GI= GEOACCUMULATION INDEX

Table 5. Description of geoaccumulation indices(after Muller, 1969)

Range	Description
GI ≤ 0	Uncontaminated
0 < GI < 1	Uncontaminated to moderately contaminated
1 < GI < 2	Moderately contaminated
2 < GI < 3	Moderately to heavily contaminated
3 < GI < 4	Heavily contaminated
4 < GI < 5	Heavily to extremely contaminated
GI ≥ 5	Extremely contaminated

Table 6. Categorization of enrichment (after Sutherland, 2000)

Range	Description
EF less than 2	Minimal enrichment
2 ≤ EF < 5	Moderate enrichment
5 ≤ EF < 20	Significant enrichment
20 ≤ EF < 40	Very high enrichment
EF ≥ 40	Extremely high enrichment

Table 7: Categorization of Contamination (after Hakanson, 1980)

Range	Description
CF less than 1	Low contamination
1 ≤ CF ≤ 3	Moderate contamination
3 ≤ CF ≤ 6	Considerable contamination
CF ≥ 6	Very high contamination

Contamination Factor (Cf) and Pollution Load Index (PLI)

Contamination factor (Cf) is also one of the parameters used in assessing the level of contamination of soils or sediments by various metals. Cf is given by C_mSample/ C_mBackground, where "C_m Sample" is metal concentration in sample and ''C_mBackground'' is background concentration of the metal. Contamination range is as shown in Table 7.

The ranges, mean values and standard deviation of contamination factors in the soil samples are presented in Table 8. Both soil samples collected close to the mines and those collected away from the mines are included. Contamination factor for Pb was found to be very high in all the mines. In Ameka mine, contamination caused by Cd and Zn levels indicate very high contamination to moderate contamination, respectively. Cf values for Mn are found to be moderate in all the mines. In Enyigba and Alibaruhu mines, Cf values for Cd are found to be moderate while values for elements Zn and Cr are moderate in Enyigba and Alibaruhu mines, respectively.

The Pollution Load Index (PLI) is a measure of the degree of overall contamination at a sampling site. It is given by PLI = $(Cf_1 \times Cf_2 \times Cf_3 \times .... \times Cf_n)^{1/n}$, where Cf is the contamination factor and "n" is the number of metals studied (Thomilson et al.,1980). In this study, eight metals which are common around Pb-Zn mines have been selected. They include Pb, Zn, Cd, Mn, Cu, As, Fe and Cr. The PLI provides a comparative means of assessing site quality and is given in Table 9.

The ranges, mean values and standard deviation of PLI around the three mines (Ameka, Enyigba and Alibaruhu) are greater than 1, with the highest values at the Ameka mine (Table 10). A graphical representation of PLI around the three mines is shown in Fig.3.The overall decrease in the degree of contamination of the soils by contaminants away from the mines is depicted in the maps (Fig.4).

CONCLUSION AND RECOMMENDATION

The trend in the variation of the concentrations of these elements away from the mines indicates that the contamination is directly related to mining activities in the

Table 8. The ranges, mean values and standard deviation of Contamination factors in the soil samples

CLOSE TO THE MINES	AMEKA MINE			ENYIGBA MINE			ALIBARUHU MINE		
	Range	Mean	SD	Range	Mean	SD	Range	Mean	SD
Cu	0.39-0.88	0.56	0.12	0.85-3.27	1.99	0.87	0.61-1.05	0.73	0.14
Pb	2.54-442.21	32.19	90.63	16.58-254.58	156.86	97.85	27.18-219.08	65.52	56.86
Zn	0.44-58.1	4.59	11.58	0.92-1.69	1.29	0.35	0.31-2.13	0.75	0.54
Mn	0.21-2.57	1.09	0.72	1.09-2.38	1.8	0.56	0.19-4.14	1.93	0.99
Fe	0.75-1.55	1.16	0.23	1.31-2.38	1.82	0.38	0.3-5.25	3.1	1.79
As	0.08-0.59	0.19	0.1	0.19-0.65	0.41	0.17	0.28-1.11	0.81	0.3
Cd	0.5-103.5	17.23	28.99	1-2.5	2	0.71	0.5-5	2.17	2.01
Cr	0.21-0.85	0.52	0.13	0.34-0.89	0.52	0.22	0.24-1.86	1.23	0.57

AWAY FROM THE MINES	AMEKA MINE			ENYIGBA MINE			ALIBARUHU MINE		
	Range	Mean	SD	Range	Mean	SD	Range	Mean	SD
Cu	0.33-1.13	0.69	0.29	0.58-1.12	0.78	0.18	0.63-0.72	0.67	0.04
Pb	2.3-254.84	68.98	107.35	5.19-75.29	20.7	27.36	9.93-27.41	16.95	7.54
Zn	0.97-10.17	3.48	3.86	0.49-0.88	0.75	0.14	0.44-0.95	0.63	0.23
Mn	0.24-5.4	1.88	2.05	0.56-2.98	1.74	0.78	0.78-1.32	1.07	0.22
Fe	0.93-2.24	1.66	0.47	1.54-2.58	1.96	0.43	0.32-2.86	1.2	1.17
As	0.15-0.59	0.32	0.17	0.18-0.41	0.29	0.08	0.01-0.92	0.52	0.38
Cd	0.5-30.5	9.88	12.07	<0.5-2	1	0	<D.L		
Cr	0.56-0.89	0.77	0.13	0.39-0.97	0.72	0.23	1.1-1.66	1.34	0.24

SD=Standard deviation

Table 9. Categorization of Pollution load index (after Thomilson et al., 1980)

Range	Description
PLI less than 1	Perfection
PLI = 1	Baseline level for pollutants present
PLI > 1	Deterioration of site quality

Table 10. Ranges, mean values and standard deviation of PLI around the three mines

	Ameka mine		Enyigba mine		Alibaruhu mine	
	A	**B**	**A**	**B**	**A**	**B**
Range	0.54-5.56	0.87-4.8	1.39-2.73	0.85-1.68	0.8-2.09	0.67-1.43
Mean	1.27	1.99	2.04	1.22	1.77	1.06
SD	1.06	1.64	0.62	0.28	0.39	0.31

A= Close to the mine, **B**= Away from the mine

PLI < 1 = Perfect; PLI= 1 = baseline levels of pollutants are present;
PLI > 1 = Detorioration of site quality (Thomilson et al 1980)

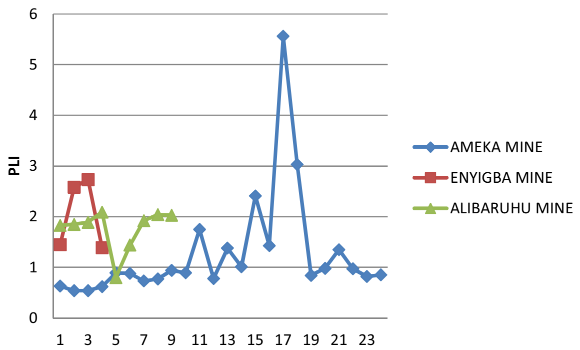

Fig.3. A graphical representation of Pollution Load Index (PLI) around the three mines, Ameka, Enyigba and Alibaruhu

study area. The major heavy metal, namely, Pb and Zn are the main components extracted from the mines while Cd is a by-product in the smelting/ refining of the Pb-Zn-Cu ores and also, by-product of acid mine drainage, as well as a common component of carbonaceous shales, which are the black slates in this study area (see The Center for Science in Public Participation Fact Sheets, 2003; Obiora, 2012). The element Cd can also occur in minor and trace concentrations in sphalerite (ZnS) and galena (PbS) in which it substitutes Zn and Pb in respective ores. Element Bi occurs in small amounts in galena (Deer, W. A. et al, 1966, p. 457 and 460). Cr, with mean values exceeding the guideline in some of the soil samples and EF indicating moderate enrichment, is an important component of black slates that are the host rocks (see Jeong, 2006). The moderate to extreme contamination in Pb and moderate contamination in Cd of the soils in the immediate environment of the mines as well as the significant to very high enrichment in Pb, significant enrichment in Cd, and moderate enrichment in Zn, Bi and Cr in soils are apparently responsible for poor yield of food crops close to the mines. Studies on plant growth have shown that high heavy metal concentrations in soils inhibit cytoplasmic enzymes and cause damage to the

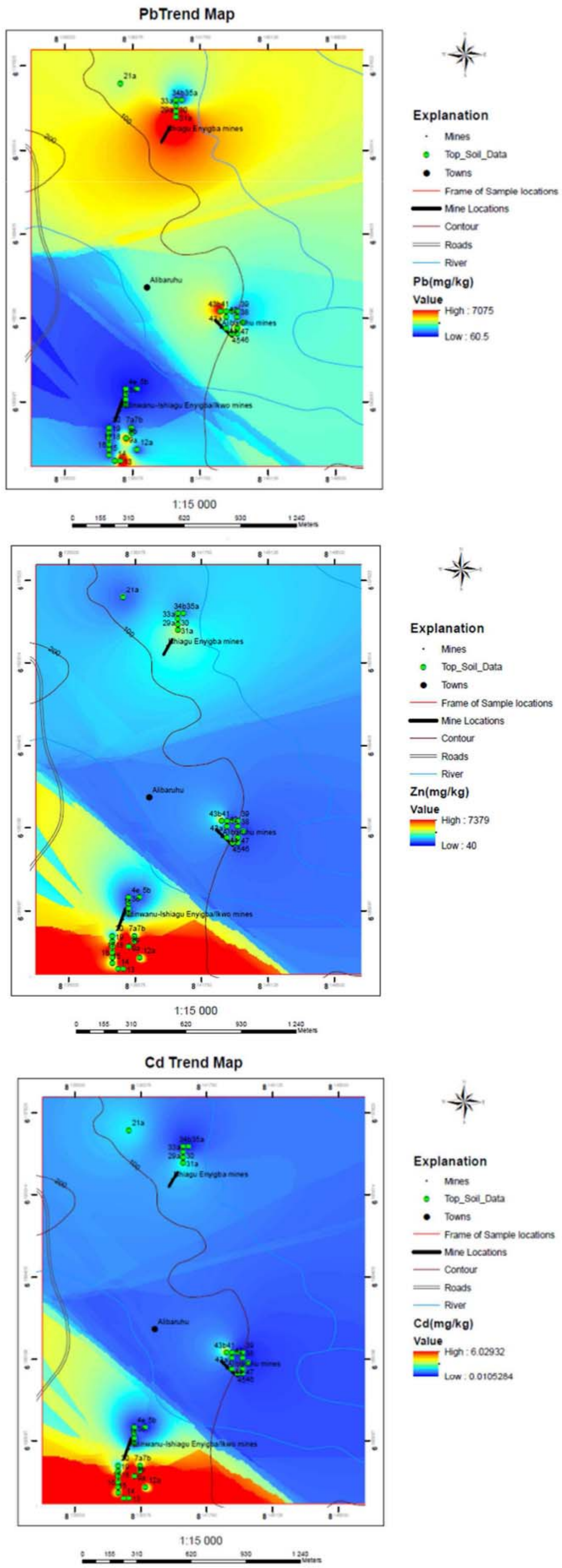

Fig.4. Geochemical maps of the major contaminants (Pb, Zn, Cd, Fe).

cell structure due to oxidative stress; it also causes the replacement of essential nutrients at the cation exchange sites of plants, thereby leading to a decline in plant growth (Chibuike and Obiora, 2014).

In general, mining activities which had lasted for over a period of 95 years in Enyigba area has adversely contaminated soils in the vicinity of the mines as indicated by the decrease in the intensity of contamination away from the mines.

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