ASSESSMENT OF THE QUALITY OF SOIL PROFILES IN THE VICINITY OF ABANDONED BARITE MINES IN PARTS OF OBAN MASSIF AND IKOM-MAMFE EMBAYMENT, SOUTHEASTERN NIGERIA

C. I. Adamu

Department of Geology, University of Calabar, P.O. Box 3609 UPO, Calabar, Nigeria
E-Mail: adamuchristopher@yahoo.com Phone: 08057090987

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ABSTRACT

Soil samples were collected at depth intervals of 0-15, 15-30, 30-45 and 45-60 cm subsurface around selected abandoned barite mine dump sites in Oban massif and Ikom-Mamfe Embayment, south eastern Nigeria in order to assess the impact of barite mining activities on soil quality. The soils were characterized by lower clay fraction (<20%), pH range of 4.4-6.2, <4% organic matter content, cation exchange capacity of <12meq/100g, and elevated elemental levels relative to background concentration values. Physico-chemical parameters varied widely both within and among the dump. They decreased with depth in a given soil profiles except for Al, As, Co, Ni and Zn that showed random distribution with depth at some sites. Pollution of the soil profiles by metals were generally restricted to depths of 0-45cm except for As and Zn, Co, Cu, Pb and Ni which extended to 45-60 cm in the subsurface. These mobile metals pose potential contamination danger to aquifers. The absence of significant correlation ($p<0.05$) between the elements and the physical parameters of surface soils within mine dump sites is indicative of human influence due to barite mining. The significant correlations ($p<0.05$) among some heavy metals and between some metals with Al, Fe and Mn are suggestive of common sources and controls by hydrous oxides of Al, Fe and Mn respectively. The aluminum normalized enrichment factor and contamination/pollution index indicated different levels of enrichment and pollution. Cd, Cr, Ni, Fe and Mn show minimal enrichment and slight pollution at most sites. While Co, Pb and Zn display moderate enrichment and moderate pollution, Ba, Co and Cu show significant to very high enrichment and severe pollution and as very high enrichment and excessive pollution. These sites require remedial action before any development can proceed and nearby aquifers need to be monitored for heavy metal pollution.

Key words: Soil quality, Soil profile, Barite mines, Enrichment factor, Pollution index

INTRODUCTION

Abandoned barite mine waste dump sites that have become landmarks in many parts of Cross River State in Southeastern Nigeria are reducing the availability of farmlands and threatening to cause disease epidemics, flooding and groundwater pollution. The barite mine waste were generated from mining of the many mineralized barite veins and bedded deposits that occur in parts of the Precambrian Basement Complex of Oban Massif and the Cretaceous sediments of the east-west bifurcation of the lower Benue Trough (the Ikom-Mamfe Embayment) in a belt of over 200km long (Akpeke, 2008). Studies carried out on

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environmental impact of barite mining activities (Franciskovic-Bilinski, 2006; Nagaraju *et al.,* 2006; Adamu, 2011) revealed that barite mine waste dump sites are causes of environmental contamination. The impacts range from elevated levels of heavy metals, acidity and sulphates to changes in soil drainage and groundwater chemistry as well as damage to ecosystem (Duruibe *et al.*, 2007; Nagaraju *et al.*, 2006; Cheng and Broadbent,1981).

Most of the studies on soil pollution have focused on distribution of pollutants in topsoil and ecological risk assessment with little emphasis on subsurface soil profiles. In many cases the objectives of these studies have been concerned with the micronutrients (Fe, Mn, Zn, Cu, B, Mo, Cl) essential for the growth of plants and animals (Cox, 1995; Kabata-Psndias and Pendias, 2001; Siegel, 2002). Studies of heavy metal concentrations in the subsurface soils show that Mn, Ni and Cr that are sourced mainly from parent materials can accumulate to high levels in subsoil, whereas trace metals such as As, Cd and Pb whose main input into the soils is at the soil surface, through anthropogenic activities tend to accumulate in topsoil (DeHaan, 1993; Nolting *et al.*, 1999; Bhattacharya *et al.,* 2006; Romero *et al.,* 2007; Iwegbue *et al.,* 2010).

Environmental pollution from mining activities has continued to generate unpleasant implications for health and economic development in Nigeria (Chukwuma, 1995; Adamu, 2000). Shifting attention to agriculture increases the demand for arable which shall necessitate the use of contaminated sites in the future for either agricultural, residential, industrial or parkland purposes. However, in developing countries such as Nigeria, these potentially contaminated sites are used for projects without any form of assessment. There is the need to employ geoenvironmental studies to understand the relationship between lands use activities and environmental contamination. This is important in Nigeria and other developing nations, where environmental consideration usually takes a second place to economic growth. The main objectives of this study were (i) to determine some physico-chemical characteristics and the concentration of some metals in soil profiles around selected abandoned barite mine dumpsites in Oban massif and Ikom-Mamfe Embayment, and (ii) to assess the pollution status of the soil profiles. .

MATERIALS AND METHODS

Geological Setting

The study area lies between latitudes $05^{\circ}30'$ - 06° $10'$N and longitudes $08^{\circ}00'$ - 08° $50'$E (Figure1).

The elevation ranges from 100m in the Ikom- Mamfe Embayment in the north to more than 500m above sea level in the Oban Massif in the south. A dendritic system formed by the Cross River with major tributaries and many perennial streams drains the area.

The geology of the study area falls within parts of the Cretaceous sediments of Ikom-Mamfe Embayment and that of the Precambrian Basement Complex of Oban Massif (Figure1). Rocks of the Oban Massif are mainly phyllites, schists, gneisses and amphibolites. These are intruded by pegmatites, granites, granodiorites, tonalities, monazites and dolerites. Associated with these intrusives are charnockites which occur as enclaves in gneisses and granodiorites (Rahman *et al.*, 1981; Ekwueme, 1995). Overlying the Oban Massif is the Albian Mamfe Formation (Asu River Group), the oldest formation within the Ikom-Mamfe Embayment. The rocks of the formation comprise the continental arkosic sandstones, bluish grey/black to olivine brown shale and sandy shale, fine-grained micaceous calcareous sandstone and siltstone with limestone lenses (Petters, 1978). Detailed geology of the area is presented in Adamu (2011) and Adamu *et al. (*2015).

Method of Study

Soil samples were collected from six abandoned barite mine dump sites along the face of the mine pits. Four of the sites at Nde, Alese, Okumuretet and Iyametet are located in the Ikom-Mamfe Embayment and the other two, Akpet 1 and Ibogo are located in the Oban massif.

At each site, eight samples, comprising two sets of soil amples were collected at depth intervals of 0-15, 15-30, 30-45 and 45-60cm. Thus a total of 48 samples were obtained. Control samples were got about 500 m away from these sites

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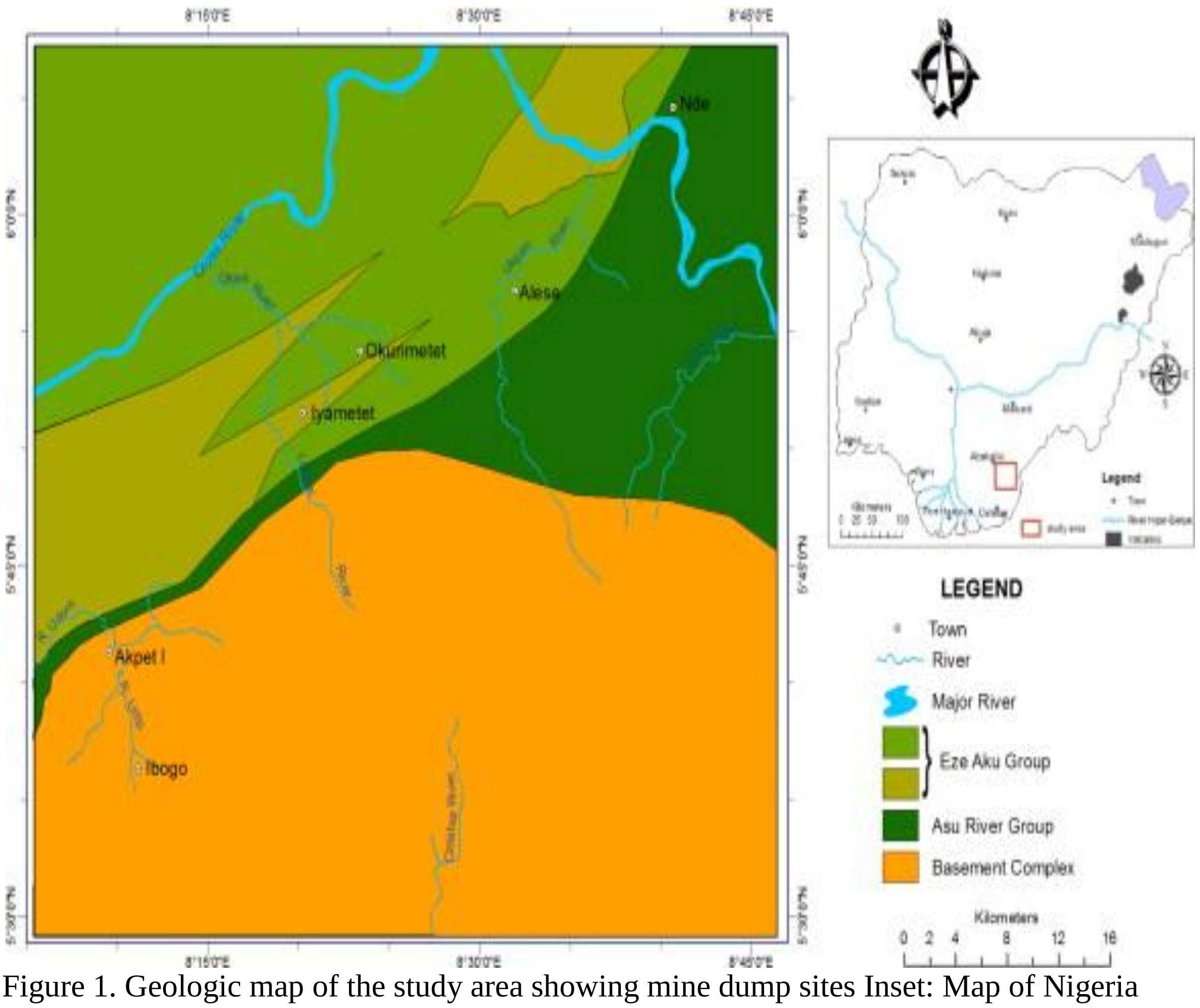

Figure 1. Geologic map of the study area showing mine dump sites Inset: Map of Nigeria showing location of study area.

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On reception in the laboratory, the samples were air-dried, sieved to pass a 2-mm mesh and stored at 4°C until required for analysis.The soil pH was measured in a 1:2 (v/v) ratio of soil and water suspension with a digital pH following the procedure of Radojevic and Bashkin (1999). Total organic matter content was estimated by loss on ignition (LOI) method. Cation exchange capacity (CEC) was determined as the sum of basic cation extractable by 1 M NH_4Ac and exchangeable acidity. Particle size distribution was determined by hydrometer method for silt and clay and dry sieving for sand fractions. For heavy metal determination, 1.0g of the soil sample was weighed into a 50-ml Teflon beaker and 10ml of aqua regia [8ml of 65% HNO_3 and 2 ml of 75% (v/v) $HClO_4$] was then added and digested at 130^0C for 2h. The digest was slowly evaporated until the white fumes of $HClO_4$ appeared. The digest was filtered and made up to 25 ml with high purity water. The sample solutions were analyzed for Al, As, Ba, Cd, Cu, Cr, Ni, Fe, Pb, Co and Zn using inductively coupled plasma mass spectroscopy (ICP-MS) model Perkin Elmer Elan 6000/9000 in the Acme Laboratory Limited, Vancover Canada. The results of the analyses were reported in dry weight basis.

Matrix matching, standard addition and background correction were used to overcome interferences. After every four determinations, blanks and certified reference material were also run to determine the precision and instrumental uncertainties. All sample runs were replicated and the coefficient of variation between replicate analyses was less than 5%. Recovery in spiked samples ranged from 90-95% (extractable heavy metals). Replicate analysis of reference standard material showed good accuracy with recovery rates for metals between 96% and 105%. Analar grade or its equivalent grade reagents were used throughout the work.

Enrichment factor

The enrichment factor (EF) of the metals in the soil profiles was qualified by the equation;

$$EF = (C_e/Al)\ Sample / (C_b/Al)\ Reference \quad (1)$$

Where C_e = the examined metal content in the soil sample; C_b = the examined metal content in the reference environment; Al= the reference element content.

A reference element is often a conservative one, such as Al, Fe, Me, Mn, Sc, T, etc. (Lee et al., 1998; Reimann and de Caritat, 2000; Bergamaschi *et al.*, 2002). Al is applied as a reference element in the present study because it is the least variable. It is pertinent to note that the enrichment factor is a convenient measure of geochemical trends and is used for comparisons between areas and over time. The enrichment factor gives an insight into differentiating an anthropogenic source from natural origin. An enrichment factor (EF) value close to 1 indicates crustal origin while values greater than 10, point to a non-crustal source (Yougming *et al.,* 2006). Five contamination categories (Table 1) are recognized based on enrichment coefficient values (Sutherland, 2000; Loska and Wiechula 2003). For ease of interpretation and understanding, the EF load (EFL) of all the elements at each sample location as the n^{th} root of the product of EFs at each location were determined from;

$$EFL = (EF_1 * EF_2 * \ldots EF_n)^{1/n} \quad (2)$$

Where n is the total number of elements.

Contamination/pollution index

The contamination/pollution index (CI/PI) values were computed following the method of Lacatusu (2000)

$$CI/PI = \text{Concentration of metal in soil}/\text{Target (Reference)value} \quad (3)$$

The targetvalues for maximum allowable concentrations of metals in soils (Table 2) were obtained using the Department of Petroleum Resources of Nigeria, DPR, (2002) values. The table also contains soil quality criteria from other countries for comparison. A CI/PI value greater than unitydefines a pollution range and a value less than unity define contamination range (Jung, 2008; Kabata- Pendias and Pendias, 2001). The significance of the CI/PI index is given in Table 3. The number of elements determined in a soil sample and their respective CI/PI value would influence the CI_{tot}/PI_{tot} value. The $CI_{to}t/PI_{tot}$ is defined as the nth root of the product of C1/P1 of all the elements at each sample location:

$$CI_{tot}/PI_{tot} = (CI_1/PI_1 * CI_2/PI * ......CI_n/PI_n)^{1/n} \quad (4)$$

RESULTS

Table 1: Contamination categories based on enrichment factor (EF) values

EF < 2	Deficiency to minimal enrichment
EF = 2-5	Moderate enrichment
EF = 5=20	Significant enrichment
EF = 20-40	Very high enrichment
EF > 40	Extremely high enrichment

Table 2: Soil quality standards for various metals

	Metal assessment criteria					Remediation criteria			Other related studies[c]			
Element	DPR	DTV	AEIL	GAV	CEQC	A	R/P	C/I	1	2	3	4
Al	-	-	-	71000*	-	-	-	-	-	5500	-	-
As	-	29	-	10	29	-	-	-	-	37	-	-
Ba	2000	160	-	625	625	-	-	-	2130	19400	-	-
Cd	0.8	0.8	3	3	0.5	4	4	8			1.5	4
Cr	100	100	400	400	20	750	250	800	215	384		200
Co	20	20	60	20		100*			18	60		20
Cu	36	36	100	100	30	150	100	500	72	128	35	20
Ni	35	35	60	60	20	150	100	500	240	48	61	137
Pb	85	85	600	600	25	375	500	100		718	83	40
Zn	146	140	20	600	60	600	500	1,500	52	1720	54	171
Fe	5000			38000	-	-				4600	26000	15000

DPR=Department of Petroleum Resource target values, Nigeria; DTV=Dutch Target Values; AEIL=Australian Ecological Investigation Levels; GAV=Global Average Values (Lindsay,1979); CEQC=Canadian Environmental Quality Criteria
A Agricultural purposes, R/P residential/parkland, C/I industrial /commercial
1 Nagaraju et al. (2006), 2 Franciskovic-Bilinski (20006), 3 Ofulume et al. (2004)
4 Nganje et al. (2010)

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Table 3: Classification of contamination/pollution index (CI/PI) values

`value	Contamination/pollution level
< 0.1	Very slight contamination
0.10-0.25	Slight contamination
0.26-0.50	Moderate contamination
0.51-0.75	Severe contamination
0.76-1.00	Very serve contamination
1.1-2.0	Slight pollution
2.1-4.0	Moderate pollution
4.1-8.0	Severe pollution
8.1-16.0	Very severe pollution

Correlation analysis

Statistical analyses using the product coefficient of correlation between physico-chemical parameters were used to determine the possible sources, the relationship between the metals and the possible factors controlling their distribution in the soil profiles. The Pearson (or product moment) correlation analysis was used in estimating the degree of relationship between constituent variables in soil profile samples. Computations were done using SPSS software package.

Physical parameters

Results of the physical parametersof the soil profiles from the dump sites (MS) and control sites (CS) are presented in Tables 4 and 5 respectively. The sites are designated as follows; Nde=ND, Alese=AL, Iyametet=IY, Okumuretet=OK, Akpet 1=AK, Ibogo=IB

The sand fraction is the predominant particle size at all depths from both the mine dump and the control sites (sand > 60%). It decreased with depth while the silt and clay fractions increased with depth. The soil profiles at AK and IB developed over basement rocksat all depths were most sandy followed by ND and AL underlain by sandstonesand lastly by the mine sites OK and IY underlain by shale rock. Expectedly, silt, clay, organic matter and cation exchange capacity decreased in the reverse order (shale > sandstone > basement rock). The spatial variations in particle size distribution indicate different sources and processes of soil formation. Generally, clays are fine grained and layered with large surface area to weight ratio. All these characteristics enable them to absorb large amount of water in their layers as well as to hold and exchange cations on their surfaces (Siegel, 2002).

The pH of the soil profiles from both mine and control sites decreased with increasing depth, varying from 4.2 at the depth of 45-60 cm at IB mine to 6.2. in the surface soil (0-15cm) at IY mine site. Data indicates that the soils are more acidic at the abandoned mine sites compared to the control sites. The probable cause of acidity in the soil profiles is due to dissolved CO_2 from decay organic matter and respiration of organisms in the soil (Jung, 2008) in addition to the oxidation of the mine waste materials, especially the sulphides. (Lee, 2005). pH is very critical for most element mobility which is relatively low when the pH is around 6.5-7.0. With the exception of Mo, Se and As, the mobility of metals decreases with increasing pH because of the formation of insoluble hydroxide, carbonate and organic complexes (Cox, 1995; Siegel, 2002).

Table 4: Some physico- chemical characteristics of soil profiles of mine dump sites

Site	Depth (cm)	Sand (%)	Silt (%)	Clay (%)	pH	OM (%)	CEC meq/100
Nde	0-15	86.8	7.2	6	5.8	3	6.4
	15-30	70.1	20.3	9.6	6.1	3.4	8.7
	30-45	67.48	22.4	10.12	5.8	3.6	10.8
	45-60	60.47	32.22	7.31	5.6	3.3	9.9
Alese	0-15	84.96	8.97	6.07	5.4	2.9	5.8
	15-30	77.52	10.78	11.7	6	3.3	10.2
	30-15	72.66	18.83	8.51	5.3	3.6	10.6
	45-60	65.55	26.63	7.82	5	3.8	13.18
Ivametet	0-15	77.47	10.52	12.01	5.2	3.2	12.2
	15-30	72.51	10.91	16.58	5.8	3	10.7
	30-45	74.68	14.2	11.12	5.4	3.2	10.2
	45-60	66.64	20.21	13.19	5	3.6	11.4
Okumuretet	0-15	67.82	16.06	16.12	6.2	3.4	8.4
	15-30	68	13.28	18	6	2.6	3.3
	30-45	64.33	16.57	19.1	4.6	2.9	3.7
	45-60	61.72	27.73	10.55	5.3	2	3.2
Akpet1	0-15	90.34	5	4.66	6	1.6	3.2
	15-30	85.36	10.44	4.2	5.5	2.3	8.6
	30-45	75.68	12.86	11.46	5.6	2.1	5.7
	45-60	68.26	17.22	14.52	5.3	1.6	2.6
Ibogo	0-15	90.2	5.64	4.16	5.2	2.3	3.6
	15-30	80.51	8.99	10.5	4.4	1.9	2.9
	30-45	76.72	10.14	13.14	4.6	2.5	10.14
	45-60	64.8	23.87	11.33	4.2	4.3	23.87

Table 5: Some physico-chemical characteristics of soil profile of the control sites

Site	Depth (cm)	Sand (%)	Silt (%)	Clay (%)	pH	OM (%)	CEC meq/100g
Nde							
	15-30	76.34	9.34	14.66	6.30	4.40	23.70
	30-45	70.48	17.44	12.08	5.80	3.60	10.80
	45-60	66.74	18.91	14.38	6.00	3.20	11.00
Alese	0-15	82.16	8.56	9.28	6.40	5.40	32.80
	15-30	73.26	9.65	17.09	6.20	4.40	21.20
	30-45	68.43	16.38	15.19	5.80	3.80	12.60
	45-60	70.55	20.67	8.76	5.40	4.00	16.18
Iyametet	0-15	79.57	9.32	11.11	5.60	6.80	36.20
	15-30	72.24	12.46	15.30	5.40	4.90	28.70
	30-45	70.68	13.43	15.89	5.40	5.20	30.20
	45-60	67.44	24.21	8.85	5.80	3.20	11.40
Okurumetet	0-15	65.82	16.04	18.14	6.40	6.00	33.40
	15-30	66.00	15.60	18.40	6.20	4.80	23.30
	30-45	64.33	18.75	16.10	5.80	3.90	12.70
	45-60	61.74	24.33	13.93	5.40	3.00	9.20
Akpet 1	0-15	89.14	5.00	5.66	6.10	4.40	23.20
	15-30	80.36	7.44	12.20	6.10	3.80	10.60
	30-45	74.38	15.76	9.86	5.60	3.10	9.70
	45-60	62.26	16.12	21.62	5.60	2.60	5.30
Ibogo	0-15	84.00	7.64	8.36	6.20	4.30	22.60
	15-30	77.21	9.32	13.48	5.80	3.90	12.90
	30-45	70.72	10.14	19.14	4.60	3.50	10.20
	45-60	63.20	20.87	15.93	4.20	3.60	13.80

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The organic matter content (OM) ranges from 1.0 - 4.3% atthe dump sites to 2.6 – 6.8% atthe control sites. The relatively lower OM values could be attributed to the removal of vegetation prior to mining. There is no pattern in the variation pattern of organic matter and cation exchange capacity (CEC) with depth in both sites. The cation exchange capacity is directly related to the capacity of adsorbing heavy metals, since the adsorption behavior depends on the combination of the soil properties and the specific nature of the chemical element (Kabata-Pendias and Pendias 2001).

Heavy metal distribution

The vertical distribution of metals in the soil profiles are presented in Tables 6 and 7. Since there are no known soil quality criteria in Nigeria for the solid mineral mining sector, the results were compared with the Nigerian Department of Petroleum Resources (DPR, 2002) target and intervention values.

The standard deviation values of the heavy metals showed their significant variability in concentrations with depths and sites, generally declining with depths. However, some metals (Al at Iyametet; As at Ibogo; Co at Nde, Okumuretet, Ibogo; Ni at Apet, Ibogo; Zn at Iyametet) first increased before decreasing with depth. The latter trend reversed for Al, AS and Zn at Nde; Al, Ba, Fe, Ni and Zn at Alese; As, Fe and Ni at Okumuretet, As and Ni at Iyamtet; Co at Akpet; and AS and Zn at Ibogo.This variability is most probably associated with soil physico-chemical characteristics, geogenic variations of parent rocks, differences in soil forming processes and nature of anthropogenic supplies (Adamu and Nganje, 2010).This distribution conforms to other studies of down profile heavy metal concentrations (DeHaan, 1993; Nolting et al., 1999; Bhattacharya et al., 2006; Romero et al., 2007; Iwegbue et al., 2010). They explained that heavy metals that are sourced mainly form parent materials accumulate to high levels in subsoil, while metals whose main input into the soils is at the soil surface, through human activities, concentratein the topsoil.The higher concentrations of metals in soils profiles at the mine sites in comparison with that of the control sites, except for Al and Fe, indicate that barite mining activities have contributed enhanced amounts of metals to the soil environment. The concentrations of Al and Fe in soil profiles around were consistent with average global values (Alloway, 2005) Thismay be attributed to their abundances in the crust and indicates that their main source is geogenic with minimal contribution from barite mine dumps.

The concentrations of aluminumranged in the soil profiles at all depths between 3,800 mg/kg at Nde site and 12,000 mg/ kg at Akpet and Ibogo. The higher value fall within the basement area and most probably indicate more unstable aluminosilicates in the rocks compared to the sedimentary area. Aluminum is not essential for life, and is now widely regarded as a toxic element hence excess of Al may interfere with phosphate metabolism (Cox, 1995).

The highest concentration of arsenic (As) of 316 mg/kg was observed at the 15-30cm depth of Okumureetet whereas the lowest concentration of 180mg/kg was found in Iyametet at 30-45cm depth. These concentrations were higher than the average global value of 10 mg/kg (Alloway, 2005). Arsenic is a highly toxic element at high concentration as it interferes with the function of enzymes. Acute poisoning causes severe gastro-enteritis, and long term effects of small doses include loss of hair and skin lesions (Christensen, 1995).

The concentrations of barium (Ba) fell between 976 and 11,446 mg /kg with highest concentration in the top section of Akpet and the lowest concentration at 45-60cm of Nde which are significantly ($p<0.05$) higher than levels from the control sites. The concentrations exceed the DPR (2002) target value of 2000 mg /kg except the concentration at 30-45cm depth of Okumuretet. The most probable source of the Ba in the soil is leaching from the mine waste dumps. Barium is not essential to most life, although crystals of barite are found in some aquatic organisms, which exploit the high density to cause them to sink or as gravitational sensor to orient them (Narayanan, 2009).

Copper (Cu) ranged between 62 and 402 mg/kg and decreased with depth. These concentrations are significantly ($p<0.05$) higher than levels from the control sites and exceed the target value of 35 mg /kg in soils (DPR, 2002) which is indicative of contamination by mine wastes. Copper is an essential trace element in life as a component of metalloenzymes. However, it is toxic to many micro-organisms and also toxic to animals at high doses (Siegel, 2002).

The highest concentration of lead (Pb) of 1344 mg/kg was obtained at the 0-15cm depth at Okumuretetwhereas the lowest concentration of 88mg/kg was found in Alese at 45-60cm depth. These are higher than the DPR target (85mg/kg) and intervention (530mg/kg) values in soils, except at Okumuretet (all depths) and Akpet (30-60cm depth) where concentrations were within intervention values. Lead is a toxic element and a common cause of anemia, anorexia, abdominal pains, and loss of coordination as well as impairment in children (Cox, 1995).
The concentrations of Cd observed in the surface soil at abandoned mine sites at Nde, Alese and Iyametet exceeded the DPR target value (0.8mg/kg) but below the intervention value (17mg/kg) in soils. This indicates that the surface soil from mine sites underlain by shales and sandstones are contaminated with Cd.

The highest value (196mg/kg) of chromium (Cr) decreased at 0.15cm in Iyametet mine to the lowest value of 28mg/kg at 45-60cm depth of Okumuretet. There are higher values reported for contaminated sites in Nigeria and other parts of the world (Nganje et al., 2010). The main sources of chromium in these soil profiles include geogenic and the mine wastes.
The concentrations of nickel (Ni) at all sites and depths ranged between 45mg/kg and 170 mg /kg which are higher than concentrations in soil profile of the control sites and the DPR target value of 35mg/kg. Only the levels of Ni at the top soil of Iyametet and 30-45cm depth at Ibogo exceeded the CCME (1999) stipulated value for agricultural purposes. Nickel is an essential element to animals but fairly toxic to many plant species and also carcinogenic at high doses (Cox, 1995).

The concentrations of nickel (Ni) at all sites and depths ranged between 45mg/kg and 170 mg /kg. These are higher than the DPR target value of 35mg/kg. Only the levels of Ni at the top soil of IY and 30-45cm depth at Ibogo exceeded the CCME (1999) stipulated value for agricultural purposes. Nickel is an essential element to animals but fairly toxic to many plant species and also carcinogenic at high doses (Cox, 1995). Cobalt (Co) whose value fell between 20 mg/kgand160 mg/kg)also exceeded the permissible limits.
The concentrations of iron (Fe) in the soil profiles of the mine dump ranged between 2,100 and16, 700 mg /kg, with the highest concentration at the top section of Ibogo mine. The concentrations of Fe in the soil profiles at 0-15cm, 15-30cm and 30-45cm (except at Nde and Iyametet) sections exceeded the DPR target value except at 45-60cm for all the soil profiles, other than

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at Ibogo which were below the DPR target value.

The concentration of zinc (Zn) fell between 224 mg/kg at 45-60cm depth of Akpet mine and 956 mg/kg at 0-15cm of Alese mine in all sites and depths. These are in exceedance of DPR target value of 140mg/kg in soils for Zn, but lower than the intervention value of 720mg/kg.

However, the concentrations of manganese which ranged between 124 and 912 mg /kg are within the DPR target of 850 mg /kg at all sites except the concentration at 0-15cm depth in of Alese mine dump site. These concentrations are also significantly ($p<0.05$) higher than levels from the control sites. This is indicative of soil enrichment by the abandoned barite mine dump wastes

Generally, levels of concentrations of metals observed in the present study were similar in trend to values reported in Croatia (Franciskovic-Bilinski, 2006) and India (Nagaraju et al., 2006) The mean concentrations of all depths in the mine sites were significantly ($p<0.05$) higher than levels in the control profiles, which is indicative of soil contamination in the metals the abandoned barite mine dump wastes. The major sources of iron in these sites include country rocks, mineralized veins and barite dump wastes.

Variations among mine dump sites

Comparing the elemental levels in soil profile at Nde with DPR (2002) target and intervention values, and the Canadian soil remediation criteria (CCME, 1999) for agricultural and residential/parkland purposes revealed that Co, Ni, Pb and Zn at all depths; Cd and Cr at top soil; Cu (0-45 cm depth); and Fe (0-30cm depth) were higher than target values. While the concentrations of Pb (0-15 cm) and Zn (0-30 cm); Co (0-60cm), Cu (0-45cm), Pb (0-30 cm), and Zn (0-30cm, 45-60cm); and Co (0-60cm), Pb (0-15cm) and Zn (0-60cm) clearly require intervention and remediation in order to use the sites for agricultural and residential purposes. This indicates that the soils at Nde are polluted with Co, Cu, Pb and Zn. The elemental levels in soil profiles at AL were generally higher than target value at most sections. While the concentrations of Ba (0-15cm), Pb (0-30, 45-60 cm) and Zn (0-30 cm); Co (0-45cm), Cu (0-30cm), Pb (0-15 cm), and Zn (0-60cm); and Co (0-30cm), Cu (0-30cm) and Pb (0-15cm) were higher than intervention values, and for agricultural and residential/parkland uses respectively. The calculated enrichment factors (EF) and CI/PI values of the soil profile at Alese indicate pollution in As, Co, Cu, Pb and Zn. However, the pollutions at both Nde and Alese were restricted to 0-30cm depth except for As and Zn that extend to 60cm depth.

The concentrations of Cu, Ni, Pb and Zn at all depths; Al at top soil; Co and Fe in soil profiles at OK were higher than taarget values. While the concentrations of Ba, Zn Co, Cu, Pb, and Zn (and Co, Cu, Pb and Zn were higher than intervention, agricultural andresidential/parkland values respectively. The soil profile at Okumuretet is polluted in Ba, Co, Cu, Pb and Zn which is restricted to 0-45cm depth except for As and Pb that extends to 60cm depth. The concentrations of all the studied elements at most sections in the soil profile at Iyametet were higher than target values. However, only the concentrations of Ba (0-30cm); Co (0-15cm), Ni (0-15cm), Pb (0-30 cm), and Zn (0-30cm and 45-60cm); and Cu (0-30cm), Ni (0-30cm), Pb (0-15cm) and Zn (0-60cm) were higher than all regulatory limits. The calculated enrichment factors (EF) and CI/PI values further revealed that the soil profile at Iyametet mine showed very high enrichment and excessive pollution in As, moderate to significant enrichment and slightly to very severe pollution in Ba, Cd, Co, Cu, and Ni. However, the pollution is restricted to 0- 30cm depth except for As and Zn that extend to 60cm depth.

In the abandoned mine dump sites located on the basement complex (Akpet and Ibogo), the concentrations of most elements in the soil profiles showed elevation in comparison to average crustal values and the control site. The concentrations of all the studied elements, except Cd and Mn, at most sections at both mine sites were higher than target values. However, only the concentrations of Ba (0-30cm) and Pb (0-15cm); Co (0-60cm), Cu (0-45cm), Pb (0-30 cm), and Zn (0-15cm); and Co (0-15cm and 30-45cm), Cu (0-60cm), Ni (0-30cm), Pb (0-15cm) and Zn (0-30cm) were higher than intervention, agricultural and residential/ parkland permissible values, respectively. This indicates that the soil profiles at AK and IB are polluted in As, Ba, Co, and Cu. The heavy metals that need close monitoring against groundwater pollution are Co and Zn at Nde, As and Zn at Alese and Iyametet; As and Pb at Okumuretet; As, Co, Cu and Zn at Akpet and As, Cu, Ni, Zn at Ibogo.

The quality of the soil profiles was evaluated using levels of heavy metals, aluminum normalized enrichment factors (EFs) and contamination/pollution indices (CI/PI). The calculated EF values showing the distribution of each element's EF value are shown in Tables 8 and 9 for the mine and the control sites respectively, and were interpreted according to the scheme provided in Table 1. Similarly, the calculated contamination/pollution index (CI/PI) values are shown in Tables 10 and 11 for the mine and the control sites respectively and were interpreted according to the scheme provided in Table 3.

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Table 6: Elemental composition (in mg/kg) of soils in profiles from the abandoned sites

Location	Depth (cm)	Al	As	Ba	Cd	Co	Cr	Cu	Fe	Ni	Mn	Pb	Zn
Nde	0-15	5200.00	296.00	10750.00	1.60	64.00	123.00	272.00	11900.00	100.00	410.00	654.00	894.00
	15-30	4400.00	290.00	4672.00	0.80	72.00	96.00	206.00	6300.00	72.00	334.00	420.00	804.00
	30-45	3800.00	187.00	2012.00	0.02	42.00	84.00	154.00	3400.00	96.00	204.00	255.00	567.00
	45-60	4000.00	266.00	976.00	0.00	56.00	62.00	102.00	2600.00	45.00	124.00	173.00	604.00
	Mean	4350.00	259.75	4602.50	0.61	58.50	91.25	183.50	6050.00	78.25	268.00	375.50	717.25
	SD	619.14	50.20	4384.02	0.76	12.79	25.42	72.69	4211.49	25.38	128.26	212.19	157.23
Alese	0-15	5600.00	210.00	7200.00	2.20	160.00	190.00	286.00	11200.00	66.00	912.00	504.00	956.00
	15-30	5200.00	220.00	3183.00	0.06	68.00	102.00	236.00	5800.00	64.00	884.00	247.00	924.00
	30-45	4600.00	226.00	994.00	0.00	48.00	65.00	148.00	6200.00	56.00	724.00	128.00	634.00
	45-60	4600.00	230.00	1016.00	0.00	38.00	35.00	96.00	3200.00	68.00	495.00	88.00	866.00
	Mean	5000.00	221.50	3098.25	0.57	78.50	98.00	191.50	6600.00	63.50	753.75	241.75	845.00
	SD	489.90	8.70	2920.91	1.09	55.75	67.18	85.48	3342.65	5.26	191.35	187.42	145.52
Okumuretet	0-15	8300.00	280.00	11378.00	0.04	36.00	92.00	284.00	10300.00	94.00	736.00	1344.00	636.00
	15-30	7200.00	316.00	5774.00	0.01	40.00	66.00	126.00	4400.00	68.00	582.00	905.00	484.00
	30-45	6700.00	256.00	1768.00	0.00	52.00	32.00	102.00	5400.00	62.00	433.00	383.00	409.00
	45-60	5800.00	278.00	1674.00	0.00	22.00	28.00	78.00	3800.00	76.00	224.00	148.00	356.00
	Mean	7000.00	282.50	5148.50	0.01	37.50	54.50	147.50	5975.00	75.00	493.75	695.00	471.25
	SD	1042.43	24.84	4571.57	0.02	12.37	30.26	93.09	2957.90	13.90	218.27	535.99	121.74
Iyametet	0-15	8600.00	240.00	10980.00	2.31	46.00	196.00	114.00	9800.00	154.00	760.00	498.00	678.00
	15-30	9200.00	220.00	5642.00	1.20	38.00	122.00	101.00	4700.00	140.00	600.00	285.00	712.00
	30-45	8200.00	180.00	2111.00	0.60	20.00	84.00	86.00	4500.00	96.00	346.00	192.00	539.00
	45-60	8000.00	280.00	1394.00	0.40	32.00	63.00	62.00	2100.00	120.00	286.00	112.00	606.00
	Mean	8500.00	230.00	5031.75	1.13	34.00	116.25	90.75	5275.00	127.50	498.00	271.75	633.75
	SD	529.15	41.63	4378.66	0.86	10.95	58.51	22.32	3239.73	25.21	221.43	166.58	77.09
Akpet 1	0-15	12000.00	249.00	11446.00	0.02	82.00	230.00	320.00	10400.00	102.00	625.00	625.00	654.00
	15-30	9000.00	302.00	6775.00	0.00	46.00	148.00	260.00	7400.00	122.00	482.00	382.00	532.00
	30-45	8000.00	284.00	2345.00	0.00	54.00	108.00	222.00	4800.00	134.00	326.00	254.00	243.00
	45-60	8000.00	276.00	1212.00	0.00	48.00	68.00	113.00	3600.00	94.00	196.00	168.00	224.00
	Mean	9250.00	277.75	5444.50	0.01	57.50	138.50	228.75	6550.00	113.00	407.25	357.25	413.25
	SD	1892.97	22.04	4665.80	0.01	16.68	69.19	87.08	3017.17	18.29	186.40	198.98	213.59
Ibogo	0-15	12000.00	246.00	11230.00	0.17	58.00	242.00	402.00	16200.00	126.00	780.00	767.00	996.00
	15-30	10000.00	211.00	5640.00	0.00	64.00	180.00	330.00	7200.00	130.00	560.00	497.00	630.00
	30-45	8000.00	228.00	2135.00	0.00	38.00	94.00	172.00	6200.00	170.00	462.00	287.00	440.00
	45-60	7000.00	218.00	2104.00	0.00	40.00	67.00	112.00	5100.00	124.00	320.00	156.00	640.00
	Mean	9250.00	225.75	5277.25	0.04	50.00	145.75	254.00	8675.00	137.50	530.50	426.75	676.50
	SD	2217.36	15.20	4301.55	0.09	12.96	80.24	134.87	5089.45	21.81	193.32	266.80	232.03

Table 7: Elemental composition (mg/kg) of soil profile samples of the control sites

Location	Depth(cm)	Al	Fe	As	Ba	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
Nde	0-15	5500.00	4000.00	21.00	456.00	BDL	16.00	90.00	30.00	250.00	12.00	120.00	60.00
	15-30	6400.00	2800.00	18.00	297.00	0.02	18.00	84.00	22.00	128.00	16.00	66.00	60.00
	30-45	3600.00	2400.00	15.00	233.00	0.02	20.00	64.00	20.00	194.00	28.00	54.00	64.00
	45-60	4400.00	2200.00	12.00	212.00	0.04	24.00	76.00	20.00	204.00	40.00	34.00	78.00
	Mean	4975.00	2850.00	16.50	299.50	0.03	19.50	78.50	23.00	194.00	24.00	68.50	65.50
	SD	1228.48	806.23	3.87	110.42	0.01	3.42	11.24	4.76	50.31	12.65	36.78	8.54
Alese	0-15	6500.00	5000.00	18.00	412.00	0.01	22.00	136.00	48.00	210.00	18.00	60.00	80.00
	15-30	5400.00	4000.00	22.00	370.00	0.02	26.00	130.00	26.00	180.00	34.00	36.00	120.00
	30-45	4600.00	3000.00	20.00	265.00	0.03	24.00	56.00	18.00	190.00	40.00	26.00	140.00
	45-60	4200.00	3000.00	14.00	224.00	0.04	30.00	34.00	13.00	220.00	42.00	19.00	160.00
	Mean	5175.00	3750.00	18.50	317.75	0.03	25.50	89.00	26.25	200.00	33.50	35.25	125.00
	SD	1014.48	957.43	3.42	87.91	0.01	3.42	51.65	15.46	18.26	10.88	17.91	34.16
Okumuretet	0-15	5400.00	3700.00	28.00	172.00	0.03	13.00	36.00	20.00	86.00	64.00	40.00	120.00
	15-30	5300.00	3200.00	14.00	180.00	0.02	14.00	23.00	22.00	88.00	42.00	32.00	140.00
	30-45	4800.00	2600.00	12.00	176.00	0.04	22.00	30.00	16.00	98.00	55.00	35.00	142.00
	45-60	4500.00	2200.00	10.00	132.00	0.03	20.00	24.00	10.00	118.00	49.00	27.00	180.00
	Mean	5000.00	2925.00	16.00	165.00	0.03	17.25	28.25	17.00	97.50	52.50	33.50	145.50
	SD	424.26	660.18	8.16	22.24	0.01	4.43	6.02	5.29	14.64	9.33	5.45	25.05
Iyametet	0-15	3600.00	2800.00	31.00	354.00	0.01	20.00	103.00	30.00	240.00	67.00	60.00	90.00
	15-30	3600.00	3000.00	16.00	364.00	0.01	18.00	100.00	28.00	200.00	32.00	52.00	100.00
	30-45	3000.00	1600.00	13.00	335.00	0.02	20.00	65.00	30.00	230.00	44.00	40.00	102.00
	45-60	3200.00	1300.00	14.00	238.00	0.01	26.00	49.00	28.00	260.00	55.00	30.00	134.00
	Mean	3350.00	2175.00	18.50	322.75	0.01	21.00	79.25	29.00	232.50	49.50	45.50	106.50
	SD	300.00	850.00	8.43	57.77	0.01	3.46	26.54	1.15	25.00	14.98	13.20	19.07
Akpet 1	0-15	4600.00	5000.00	19.00	720.00	BDL	5.00	130.00	12.00	440.00	40.00	36.00	70.00
	15-30	5000.00	6000.00	21.00	440.00	BDL	14.00	114.00	18.00	360.00	44.00	30.00	80.00
	30-45	4200.00	5000.00	16.00	339.00	0.01	20.00	92.00	16.00	300.00	57.00	32.00	84.00
	45-60	3400.00	4000.00	12.00	224.00	0.02	16.00	88.00	12.00	280.00	60.00	28.00	96.00
	Mean	4300.00	5000.00	17.00	430.75	0.02	13.75	106.00	14.50	345.00	50.25	31.50	82.50
	SD	683.13	816.50	3.92	212.07	0.01	6.34	19.66	3.00	71.88	9.74	3.42	10.75
Ibogo	0-15	4400.00	8000.00	15.00	270.00	0.01	20.00	200.00	18.00	398.00	50.00	31.00	60.00
	15-30	3600.00	6000.00	18.00	304.00	BDL	24.00	160.00	16.00	300.00	32.00	30.00	70.00
	30-45	2800.00	5000.00	18.00	396.00	BDL	27.00	115.00	14.00	280.00	34.00	25.00	80.00
	45-60	2200.00	4000.00	20.00	196.00	0.01	32.00	57.00	12.00	260.00	54.00	20.00	90.00
	Mean	3250.00	5750.00	17.75	291.50	0.01	25.75	133.00	15.00	309.50	42.50	26.50	75.00
	SD	957.43	1707.83	2.06	82.98	0.00	5.06	61.42	2.58	61.22	11.12	5.07	12.91

DISCUSSION

Enrichment factors (EF) and Contamination/pollution indces (CI/PI) indicatethat Cd, Fe and Mn as well as > 90% of Cr and Ni have enrichment factors of less than 2 at all sites and depths,

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suggesting that their main source is geogenic. The minimal enrichment was attributed to soil forming processes including adsorption and co-precipitation by hydrous iron and manganese oxides and clay minerals (Kabata-Pendias and Pendias, 2001). On the other hand, all of As, Ba, 79% of Co, 87.5% of Cu, 58% of Pb, 42% of Zn have enrichment factors higher than 2 at all sites and depths. These were considered to originate mainly from mine dumps. The barite in the study area occurs in association with sulphide minerals including galena (PbS), sphalerite (ZnS) and chalcopyrite ($CuFeS_2$) (Akpeke, 2008). The oxidation of the barite and sulphide minerals from the mine dumps would havereleased the incorporated heavy metals into the soil (Nagaraju et al., 2006, Ezeh et al., 2008; Adamu and Nganje, 2010). In contrast, the EF values from the control sites generally ranged from less than 2 (i.e. deficiency to minimal enrichment range) to between 2 and 5 (i.e. moderate enrichment range). The moderate enrichment of metals in soil profiles of the control sites was attributed to natural weathering of mineralized barite and sulphide veins. It could also be due to adsorption and co-precipitation by hydrous iron and manganese oxides and clay minerals (Kabata-Pendias and Pendias, 2001; Adamu and Nganje, 2010). It appears, therefore, that EF can also be an effective tool to differentiate a natural origin from an anthropogenic source in this study. The mean EF values decreased in the order of As > Ba> Cu > Co > Zn > Ni > Pb > Cr > Mn > Fe > Cd which can also be seen as the degree of order of their overall contamination of the soils of the dump sites. The EF values decreased with increasing depths at all sites such that the 0-15 cm depth showed the highest enrichment for all metals relative to other depths except for As, Co, Fe, Ni and Zn that did not show consistent patterns. The EFs values of As, Ba,Co and Cu at depths of 0-15cm and 15-30cm, As, Ba and Cu at 30-45cm depth and only As at 45-60cm depth in some profiles indicated "significant enrichment" to "extremely high enrichment". In general, the soil profiles of the abandoned mine sites showed varying degrees of enrichment with As in the "extremely high enrichment" to "significant enrichment" ranges, Ba in the "very high enrichment" and "significant enrichment" ranges, Co, Cu and Ni in the "deficiency to minimal enrichment" and "significant enrichment" ranges, Cr, Pb and Zn in the "deficiency to minimal enrichment" and "moderate enrichment" ranges. However Cd, Fe and Mn at all sites and depths have enrichment factors less than 2 (i.e. in the deficiency to minimal enrichment range).

The contamination/pollution index (CI/PI) indices show a general decrease in values with the depths of profiles. The indices indicated that the barite sites fitted into the "very slight contamination" to "severe pollution" ranges, with Cd, Cr, Mn, Pb and Zn in the "slight pollution ranges", Ba, Co, Cu, Fe, and Ni in the "moderate pollution" to "very severe pollution" ranges. However, As at all sites and depths fitted into the "excessive pollution" range. Because of possible occurrence of synergy among metals even at low concentrations, the index values defining only the pollution range were summed to obtain values of multiple heavy metal pollution for each site and depth.

The values of multiple pollution index with heavy metals in soil profiles of the mine sites (Table 7) indicate that the degree of pollution for the top soil follow the order: Alese> Ibogo > Iyametet >Nde > Akpet > Okumuretet with significant contributions from As, Cu, Ba and Co. The CI_{tot}/PI_{tot} values for the 15-30cm, 30-45cm and 45-60cm depths follow the orders: Iyametet> Nde> Ibogo > Alese> Akpet > Okumretet; Iyametet> Ibogo> Akpet> Nde> Alese> Okumuretet; and Iyama>

Nde>Ibogo>Akpet >Alese >Okumretet respectively. This implies that groundwater at Iyama is probably most vulnerable and that at Okumuretet, it is least vulnerable to heavy metal pollution from abandoned barite mine dumps respectively.

The CI/PI values of soil profiles from the control sites were generally less than 2 (indicating very slight contamination to slight pollution) except for As and Mn with CI/PI at some sites that fitted into the severe to very severe pollution ranges. The pollution of soil profiles in the control sites by heavy metals was attributed to natural weathering of mineralized barite and sulphide veins. The values of multiple pollution indexes with heavy metals in soil profiles of the control sites were less than 0.25 indicating very slight contamination.

Association of metals and soil parameters

The correlation patterns of the metals at the surface soil horizon in the mine dumps showed no significant relationship with soil physiochemical characteristics which is suggestive of anthropogenic input (Table 12). The significant negative correlations of Co (r = -0.50) and Cu (r = -0.60) with clay contents, and Al (r = -0.70), Cr (r = -0.56), and Ni (r = -0.51) with organic matter contents indicates that these metals are more subject to retention on surface soils with low clay and organic matter contents. This is contrary to the findings of Kabata-Pendias and Pendias (2001), Hwang et al., (2005), Elueze et al., (2009), Nganje et al., (2010), and Adamu and Nganje (2010) among others. These unexpected associations could be attributed to the impact of the barite mining activities on soil chemistry of the study area. As expected, the correlation patterns of the metals at the surface soil horizon in the control samples showed significant positive relationships with soil properties (Table13) which is suggestive of natural input of metals (Cox, 1995; Siegel, 2002).

Significant correlations exist among the metals in the surface soil horizons at both the mine dumps and the control sites. In the mine dump sites, the significant positive correlations that exist for: Ba and Ni with Al, Mn; Pb and Zn with Fe; and Mn with Zn can be explained by environmental and geochemical controls involving the fixation of the heavy metals by hydrous oxides of Al, Fe and Mn. While the significant correlations among the other metals most probably reflect a common source (anthropogenic input). The major sources of these metals are the mine waste dumps containing barite, sulphide minerals and rock fragments exposed to the atmosphere. The significant positive correlations among the metals in the control sites suggest common lithogenic source (Cr and Mn), geochemical controls (Al and Fe with Cr, Mn and Pb) or influence of barite and Pb-Zn mineralization (Ba, Pb and Zn with Cd, Cr, Cu and Mn).

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Table 8: Enrichment factor (EF) values of soil profiles from the sites

Site	Depth	**Fe**	**As**	**Ba**	**Cd**	**Co**	**Cr**	**Cu**	**Mn**	***Ni***	**Pb**	**Zn**	**EFL**
Nde	0-15	40.42	29.36	0.73	4.37	1.68	9.28	0.43	1.82	0.66	2.98	4.07	3.20
	15-30	46.80	15.08	0.43	5.81	1.55	8.31	0.27	1.55	0.63	2.26	4.32	2.71
	30-45	34.94	7.52	0.01	3.92	1.57	7.19	0.17	2.39	0.45	1.59	3.53	1.57
	45-60	47.22	3.46	0.01	4.97	1.10	4.53	0.12	1.07	0.26	1.02	3.57	1.16
Alese	0-15	26.63	18.26	0.93	10.14	2.41	9.07	0.37	1.12	1.36	2.13	4.04	3.29
	15-30	30.04	8.69	0.03	4.64	1.39	8.06	0.21	1.17	1.42	1.12	4.21	1.79
	30-45	34.88	3.07	0.01	3.70	1.00	5.71	0.25	1.15	1.31	0.66	3.26	1.30
	45-60	35.50	3.14	0.00	2.93	0.54	3.70	0.13	1.40	0.90	0.45	4.46	0.82
Okumuret	0-15	23.95	19.47	0.01	1.54	0.79	6.07	0.23	1.07	0.74	3.83	1.81	1.43
	15-30	31.16	11.39	0.01	1.97	0.65	3.11	0.11	0.89	0.68	2.97	1.59	1.15
	30-45	27.13	3.75	0.01	2.76	0.34	2.70	0.15	0.88	0.54	1.35	1.44	0.91
	45-60	34.03	4.10	0.02	1.35	0.34	2.39	0.12	1.24	0.32	0.60	1.45	0.83
Iyametet	0-15	19.81	18.13	0.64	1.90	1.62	2.35	0.21	1.70	0.74	1.37	1.87	1.89
	15-30	16.98	8.71	0.31	1.47	0.94	1.95	0.10	1.44	0.54	0.73	1.83	1.26
	30-45	15.59	3.66	0.17	0.87	0.73	1.86	0.10	1.11	0.35	0.55	1.56	0.92
	45-60	24.85	2.47	0.12	1.42	0.56	1.38	0.05	1.42	0.30	0.33	1.79	0.81
Akpet 1	0-15	14.73	13.54	0.03	2.43	1.36	4.73	0.16	0.80	0.44	1.23	1.29	1.21
	15-30	23.82	10.69	0.01	1.81	1.17	5.13	0.15	1.28	0.45	1.00	1.40	1.12
	30-45	25.21	4.16	0.01	2.40	0.96	4.93	0.11	1.59	0.34	0.75	0.72	0.92
	45-60	24.50	2.15	0.01	2.13	0.60	2.51	0.08	1.11	0.20	0.50	0.66	0.66
Ibogo	0-15	14.56	13.29	0.03	1.72	1.43	5.95	0.25	0.99	0.54	1.51	1.96	1.39
	15-30	14.98	8.01	0.02	2.27	1.28	5.86	0.13	1.23	0.47	1.18	1.49	1.17
	30-45	20.24	3.79	0.01	1.69	0.83	3.82	0.14	2.01	0.48	0.85	1.30	0.96
	45-60	22.11	4.27	0.01	2.03	0.68	2.84	0.14	1.68	0.38	0.53	2.16	0.91

Table 9: Enrichment factor (EF) values of soil profiles for the control sites

Location	Depth (cm)	**Fe**	**As**	**Ba**	**Cd**	**Co**	**Cr**	**Cu**	**Mn**	***Ni***	**Pb**	**Zn**	**EFL**
Nde	0-15	0.14	2.71	1.18	-	1.03	1.16	0.97	0.38	0.21	0.52	0.26	1.22
	15-30	0.08	2.00	0.66	0.01	1.00	0.93	0.61	0.17	0.24	0.24	0.22	1.18
	30-45	0.12	2.96	0.92	0.00	1.97	1.26	0.99	0.45	0.74	0.36	0.42	1.23
	45-60	0.12	2.51	0.89	0.03	2.51	1.59	1.04	0.50	1.11	0.24	0.54	1.24
	0-15	0.14	3.91	1.31	0.01	2.31	2.31	1.15	0.38	0.80	0.21	0.71	1.26
Alese	15-30	0.19	3.91	1.31	0.01	2.31	2.31	1.15	0.38	0.80	0.21	0.71	1.27
	30-45	0.13	3.38	0.90	0.02	2.03	0.95	0.76	0.38	0.90	0.15	0.79	1.24
	45-60	0.16	2.92	0.94	0.03	3.13	0.71	0.68	0.54	1.17	0.13	1.11	1.25
	0-15	0.13	3.68	0.45	0.01	0.85	0.47	0.66	0.13	1.12	0.18	0.53	1.21
Okumuretet	15-30	0.11	1.91	0.49	0.01	0.96	0.31	0.75	0.14	0.76	0.15	0.64	1.18
	30-45	0.11	1.85	0.54	0.02	1.70	0.46	0.62	0.18	1.13	0.18	0.73	1.20
	45-60	0.09	1.58	0.42	0.02	1.58	0.38	0.39	0.22	1.03	0.14	0.95	1.19
	0-15	0.15	6.11	1.40	0.01	1.97	2.03	1.48	0.56	1.76	0.39	0.59	1.29
Iyametet	15-30	0.16	3.16	1.44	0.01	1.78	1.97	1.38	0.46	0.84	0.34	0.66	1.26
	30-45	0.11	3.30	1.70	0.02	2.54	1.65	1.90	0.69	1.49	0.34	0.86	1.28
	45-60	0.08	3.11	1.06	0.01	2.88	1.09	1.55	0.68	1.63	0.22	0.99	1.27
	0-15	0.20	2.93	2.22	0.01	0.39	2.01	0.46	0.80	0.82	0.19	0.36	1.24
Akpet 1	15-30	0.22	2.98	1.25	0.01	0.99	1.62	0.64	0.60	0.83	0.14	0.38	1.23
	30-45	0.22	2.70	1.15	0.01	1.69	1.56	0.68	0.60	1.28	0.18	0.47	1.24
	45-60	0.22	2.51	0.94	0.01	1.67	1.84	0.63	0.69	1.67	0.19	0.67	1.24
	0-15	0.34	2.42	0.87	0.01	1.61	3.23	0.73	0.76	1.08	0.17	0.32	1.25
Ibogo	15-30	0.31	3.55	1.20	0.01	2.37	3.16	0.79	0.70	0.84	0.20	0.46	1.27
	30-45	0.33	4.56	2.01	0.01	3.42	2.92	0.89	0.84	1.15	0.21	0.68	1.29
	45-60	0.34	6.45	1.27	0.01	5.16	1.84	0.97	0.99	2.32	0.22	0.97	1.32

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Table 10: Contamination/Pollution index (CI/PI) values of metals at the mine dump sites

Location	Depth (cm)	Al	As	Ba	Cd	Co	Cr	Cu	Fe	Ni	Mn	Pb	Zn	CI/PI*tot*
Nde	0-15	0.73	29.60	5.38	2.00	3.20	1.23	7.56	2.53	2.86	0.48	1.23	1.24	2.40
	15-39	0.62	29.00	2.34	1.00	3.60	0.96	5.72	1.34	2.06	0.39	0.79	1.12	1.74
	30-45	0.54	18.70	1.01	0.03	2.10	0.84	4.28	0.72	2.74	0.24	0.48	0.79	0.91
	45-60	0.56	26.60	0.49	0.01	2.80	0.62	2.83	0.55	1.29	0.15	0.33	0.84	0.68
Alese	0-15	0.79	21.00	3.60	2.75	8.00	1.90	7.94	2.38	1.89	1.07	0.95	1.33	2.65
	15-30	0.73	22.00	1.59	0.08	3.40	1.02	6.56	1.23	1.83	1.04	0.47	1.28	1.41
	30-45	0.65	22.60	0.50	0.00	2.40	0.65	4.11	1.32	1.60	0.85	0.24	0.88	0.00
	45-60	0.65	23.00	0.51	0.00	1.90	0.35	2.67	0.68	1.94	0.58	0.17	1.20	0.00
Okumuretet	0-15	1.17	28.00	5.69	0.05	1.80	0.92	7.89	2.19	2.69	0.87	2.54	0.88	1.83
	15-30	1.01	31.60	2.89	0.01	2.00	0.66	3.50	0.94	1.94	0.68	1.71	0.67	1.18
	30-45	0.94	25.60	0.88	0.01	2.60	0.32	2.83	1.15	1.77	0.51	0.72	0.57	0.88
	45-60	0.82	27.80	0.84	0.01	1.10	0.28	2.17	0.81	2.17	0.26	0.28	0.49	0.67
Iyametet	0-15	1.21	24.00	5.49	2.89	2.30	1.96	3.17	2.09	4.40	0.89	0.94	0.94	2.45
	15-30	1.30	22.00	2.82	1.50	1.90	1.22	2.81	1.00	4.00	0.71	0.54	0.99	1.80
	30-45	1.15	18.00	1.06	0.75	1.00	0.84	2.39	0.96	2.74	0.41	0.36	0.75	1.21
	45-60	1.13	28.00	0.70	0.50	1.60	0.63	1.72	0.45	3.43	0.34	0.21	0.84	1.05
Akpet 1	0-15	1.69	24.90	5.72	0.03	4.10	2.30	8.89	2.21	2.91	0.74	1.18	0.91	1.92
	15-30	1.27	30.20	3.39	0.01	2.30	1.48	7.22	1.57	3.49	0.57	0.72	0.74	1.39
	30-45	1.13	28.40	1.17	0.01	2.70	1.08	6.17	1.02	3.83	0.38	0.48	0.34	1.04
	45-60	1.13	27.60	0.61	0.01	2.40	0.68	3.14	0.77	2.69	0.23	0.32	0.31	0.77
Ibogo	0-15	1.69	24.60	5.62	0.21	2.90	2.42	11.17	3.45	3.60	0.92	1.45	1.38	2.58
	15-30	1.41	21.10	2.82	0.01	3.20	1.80	9.17	1.53	3.71	0.66	0.94	0.88	1.51
	30-45	1.13	22.80	1.07	0.01	1.90	0.94	4.78	1.32	4.86	0.54	0.54	0.61	1.09
	45-60	0.99	21.80	1.05	0.01	2.00	0.67	3.11	1.09	3.54	0.38	0.29	0.89	0.92

Table 11. Contamination/Pollution index (CI/PI) values of metals in soil profiles of the control sites

Location	Depth(cm)	Al	Fe	As	Ba	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
Nde	0-15	0.08	0.11	2.10	0.91	0.00	0.80	0.90	0.75	0.29	0.16	0.40	0.20
	15-30	0.09	0.07	1.80	0.59	0.01	0.90	0.84	0.55	0.15	0.21	0.22	0.20
	30-45	0.05	0.06	1.50	0.47	0.01	1.00	0.64	0.50	0.23	0.37	0.18	0.21
	45-60	0.06	0.06	1.20	0.42	0.01	1.20	0.76	0.50	0.24	0.53	0.11	0.26
Alese	0-15	0.09	0.13	1.80	0.82	0.00	1.10	1.36	1.20	0.25	0.24	0.20	0.27
	15-30	0.08	0.11	2.20	0.74	0.01	1.30	1.30	0.65	0.21	0.45	0.12	0.40
	30-45	0.06	0.08	2.00	0.53	0.01	1.20	0.56	0.45	0.22	0.53	0.09	0.47
	45-60	0.06	0.08	1.40	0.45	0.01	1.50	0.34	0.33	0.26	0.56	0.06	0.53
Okumuretet	0-15	0.08	0.10	2.80	0.34	0.01	0.65	0.36	0.50	0.10	0.85	0.13	0.40
	15-30	0.07	0.08	1.40	0.36	0.01	0.70	0.23	0.55	0.10	0.56	0.11	0.47
	30-45	0.07	0.07	1.20	0.35	0.01	1.10	0.30	0.40	0.12	0.73	0.12	0.47
	45-60	0.06	0.06	1.00	0.26	0.01	1.00	0.24	0.25	0.14	0.65	0.09	0.60
Iyametet	0-15	0.05	0.07	3.10	0.71	0.00	1.00	1.03	0.75	0.28	0.89	0.20	0.30
	15-30	0.05	0.08	1.60	0.73	0.00	0.90	1.00	0.70	0.24	0.43	0.17	0.33
	30-45	0.04	0.04	1.30	0.67	0.01	1.00	0.65	0.75	0.27	0.59	0.13	0.34
	45-60	0.05	0.03	1.40	0.48	0.00	1.30	0.49	0.70	0.31	0.73	0.10	0.45
Akpet 1	0-15	0.06	0.13	1.90	1.44	0.00	0.25	1.30	0.30	0.52	0.53	0.12	0.23
	15-30	0.07	0.16	2.10	0.88	0.00	0.70	1.14	0.45	0.42	0.59	0.10	0.27
	30-45	0.06	0.13	1.60	0.68	0.00	1.00	0.92	0.40	0.35	0.76	0.11	0.28
	45-60	0.05	0.11	1.20	0.45	0.01	0.80	0.88	0.30	0.33	0.80	0.09	0.32
Ibogo	0-15	0.06	0.21	1.50	0.54	0.00	1.00	2.00	0.45	0.47	0.67	0.10	0.20
	15-30	0.05	0.16	1.80	0.61	0.00	1.20	1.60	0.40	0.35	0.43	0.10	0.23
	30-45	0.04	0.13	1.80	0.79	0.00	1.35	1.15	0.35	0.33	0.45	0.08	0.27
	45-60	0.03	0.11	2.00	0.39	0.00	1.60	0.57	0.30	0.31	0.72	0.07	0.30

Table 12: Correlation matrix of surface soil of the dump sites

	Clay	**pH**	**OM**	**CEC**	**Al**	**As**	**Ba**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Ni**	**Mn**	**Pb**	**Zn**
Clay	1,00															
pH	-0.10	1.00														
OM	-0.15	-0.27	1.00													
CEC	-0.19	-0.35	0.77	1.00												
Al	0.02	-0.12	-0.70	-0.49	1.00											
As	-0.17	0.34	-0.27	-0.13	0.03	1.00										
Ba	-0.28	0.35	-0.47	-0.49	0.53	0.20	1.00									
Cd	0.09	0.35	-0.23	-0.34	-0.05	-0.11	0.46	1.00								
Co	-0.50	0.26	-0.07	-0.13	-0.06	-0.11	0.32	0.47	1.00							
Cr	-0.37	0.23	-0.56	-0.47	0.65	-0.14	0.78	0.41	0.52	1.00						
Cu	-0.60	0.09	-0.25	-0.26	0.44	0.05	0.69	0.05	0.54	0.77	1.00					
Fe	-0.46	0.13	-0.28	-0.32	0.46	0.03	0.87	0.40	0.47	0.80	0.82	1.00				
Ni	0.20	-0.20	-0.51	-0.16	0.63	-0.11	0.29	0.17	-0.24	0.43	0.16	0.22	1.00			
Mn	-0.14	0.20	-0.21	-0.29	0.29	-0.21	0.58	0.36	0.47	0.57	0.53	0.65	0.04	1.00		
Pb	-0.10	0.20	-0.32	-0.44	0.37	0.34	0.80	0.13	0.18	0.42	0.59	0.66	0.05	0.48	1.00	
Zn	-0.44	0.20	0.23	-0.04	-0.08	-0.26	0.46	0.45	0.47	0.45	0.45	0.56	-0.15	0.59	0.23	1.00

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Table 13 Correlation matrix of surface soil of control sites

	Clay	pH	OM	CEC	Al	Fe	As	Ba	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
Clay	1.00															
pH	-0.27	1.00														
OM	-0.12	0.32	1.00													
CEC	-0.18	0.36	0.95	1.00												
Al	-0.45	0.56	0.51	0.60	1.00											
Fe	-0.10	0.01	0.04	0.01	0.06	1.00										
As	0.03	0.19	0.64	0.51	0.18	0.19	1.00									
Ba	-0.28	0.38	0.11	0.13	0.18	0.30	0.33	1.00								
Cd	-0.11	-0.11	0.00	-0.04	0.04	-0.40	-0.27	-0.57	1.00							
Co	0.29	-0.48	-0.32	-0.33	-0.53	-0.08	-0.15	-0.45	0.09	1.00						
Cr	-0.12	0.42	0.01	0.03	0.08	0.74	0.23	0.58	-0.55	-0.10	1.00					
Cu	0.02	0.51	0.45	0.48	0.37	-0.15	0.25	0.22	-0.44	-0.01	0.19	1.00				
Mn	-0.26	0.07	-0.35	-0.34	-0.26	0.59	0.06	0.65	-0.53	-0.15	0.70	-0.17	1.00			
Ni	0.20	-0.33	0.00	-0.08	-0.40	0.09	0.10	-0.37	0.02	0.01	-0.26	-0.39	0.04	1.00		
Pb	-0.17	0.52	0.41	0.47	0.49	-0.36	0.31	0.33	-0.33	-0.32	0.12	0.57	-0.11	-0.56	1.00	
Zn	0.06	-0.27	0.00	-0.01	0.02	-0.44	-0.26	-0.53	0.50	0.24	-0.70	-0.20	-0.55	0.39	-0.44	1.00

The geochemical data showed that the soil samples within abandoned barite mine dump sites werecharacterized by lower clay, pH, organic matter content and cation exchange capacity, but enhanced elemental level relative to control site and background concentration values.

The concentrations of metals found in the soil profiles are suggestive of soil elemental enrichment above acceptable values of human health. Ba, Co and Cu showed significant to very high enrichment and severe pollution and As very high enrichment and excessive pollution. The lack of significant correlation between the elements and the soil physical parameters is indicative of human influence due most probably to barite mining. The decreasing order of pollution among the abandoned barite mine sites based on PI_{tot} is Alese > Ibogo > Iyametet > Nde > Akpet > Okumuretet. These lands may be faced with great environmental hazards including groundwater pollution. These sites require remedial action before any form of chosen development can proceed. Aquifers need to be monitored for heavy metal pollution.

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