

Evaluating sediment metal pollution and risk indices efficiency in interpreting stream sediment pollution around abandoned barite mine sites, Southeastern Nigeria

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ABSTRACT

This study assessed the efficiency of sediment metal pollution and risk indices in interpreting sediment metal contamination associated with barite mining activities in parts of Oban Massif and Mamfe Embayment, Southeastern Nigeria. Results of the stream sediment analysis showed enhanced levels of As, Ba, Cu, Fe, Pb, and Zn relative to background values as contained in control samples and average shale values (ASV). In spite of the high concentrations of Ba and Fe, they have very low extraction rates ($ER < 10\%$) in sediment samples and are not major threat to the aquatic system. Evaluation of enrichment factor (EF), background enrichment index (BEI), pollution load index (PLI) and degree of contamination (CD) revealed varying degrees of sediment metal contamination ranging from low (Mn, Ni) to extreme (Ba, Pb). The ecological risk factor (Er) indicated that Al, Fe and Mn fell within the low risk category; Ni and Zn fell within low to moderate risk; Cr fell within low to considerable risk category; Ba and Cu fell within low to high risk while As and Pb fell within considerable to very high risk and high to very high risk categories respectively. The mean risk index (RI) ranked the mine sites in decreasing order of potential risk of sediment metal pollution as Nde> Alese> Iyametet> Okumuretet> Akpet 1=Ibogo. The significant positive correlation of extraction rates with Er (0.84) and RI (0.85) indicates that risk index is the most efficient method in interpreting sediment metal pollution in the study area.

INTRODUCTION

The abandoned barite mine pits and waste dump sites that have become landmarks in many parts of Oban massif and Mamfe Embayment (Southeastern Nigeria) are blocking farmlands and threatening to cause disease epidemics, flooding and stream sediment pollution. The abandoned mine pits and mine waste were generated by the mining of barite mineral in the area. The barite was mined and used as weighting agent in the drill mud, used in oil well drilling. (Akpeke 2008). At the exhaustion of the barite deposits, the mine spoils and mine pits were abandoned without proper demobilization. The pulverized rocks, consisting of fragments of barite, sulphides and host rocks, are potential pollutants of nearby stream sediments (Duruibe *et al.*, 2007; Siegel, 2002). Mine water was often drained from productive quarries into surrounding valleys. Also, runoff used to wash mine spoils scattered all over the mine dump sites into nearby streams (used for drinking, fishing and irrigation) and agricultural land.

Besides, rain water brings about flooding of surrounding lands by mine pond water into drainage basins. All these may bring contaminants directly or indirectly to the aquatic environment (Adamu and Nganje, 2010).

Sediments play an important role in overall geochemical cycle and they reflect the history of the drainage basin (Adamu, *et al.*, 2015; Ali *et al.*, 2015). In the past, stream sediments surveys were carried out to look for ore bodies that could be of economic importance (Rose, 1979). More recently however, the primary interest in stream sediments studies has shifted to assessing whether heavy metals have concentrated to dangerous levels in sediments (Agyarko, 2014; Casas *et al.*, 2003; Chakrapani, 2002; Nganje *et al.*, 2010). The shift in interest is borne out of the fact that sediments are regarded as both carriers and sinks for pollutants, including heavy metals, in the aquatic environment (Allen, 1993; Astron, 1998; Jain, 2004). Pollutants are bound efficiently by sediments but are also subject to partial release into the overlying water due to bioturbation and high flow regimes (Adaikpoh *et al.*, 2005). The pollutants, especially metal load, in a drainage system are transported partly in solution, part is carried as suspended sediments and some is moved as bed load. The pollutants in the first two phases are eventually precipitated onto the bottom sediments (Horsfall and Spiff, 2002). Pollutants in the sediments may be scavenged by bottom feeders and eventually enter the food chain or food web.

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However, high metal concentrations in sediments do not imply automatically that contamination has occurred, but may simply reflect the natural mineralogical composition of the parent geological material, the grain size and organic matter content of the host sediment (Adamu *et al.*, 2015; Jung, 2008; Klavins *et al.*, 2000; Siegel, 2002).

Sediment analysis is often included in environmental assessment studies because of the importance of sediments to the overall quality of aquatic systems (Allen, 1993; Bhattacharya *et al.*, 2006; Li *et al.*, 2007; Odor *et al.*, 1998). Trace elements, especially the so-called heavy metals, are among the most common environmental pollutants and their occurrence in waters and biota indicates the presence of natural or anthropogenic sources (Gonzalez *et al.*, 2006). The main natural sources of metals into the aquatic system are the weathering of soils and rocks, while the anthropogenic sources include industrial, agricultural, mining, construction, and commercial activities (Bonnet *et al.*, 2000; Karabassi *et al.*, 2006, 2007; Narayanan, 2009). Numerous studies have demonstrated that the concentrations of metals in suspended and bed sediments can be sensitive indicators of contaminants in hydrological systems (Casas *et al.*, 2003; Adamu and Nganje, 2010; Jain and Sharma, 2001).

Most studies on stream sediments quality compare their results with geochemical background values of heavy metals (from control/uncontaminated site, average crustal or shale values and national and international recommended acceptable values) (Agyarko *et al.*, 2014; Bhattacharya *et al.*, 2006; Boughriet *et al.*, 1992; Bryan and Langstone, 1992; Hwang *et al.*, 2009). The use of geochemical background as a criterion to assess the pollution status of sediment implies that all forms of a given metal have an equal impact on the environment; such an assumption is clearly untenable (Eggleton and Thomas, 2004). Besides, such pollution assessment does not consider multi-element impact, it is not comprehensive to non-scientist and does not give an overall quality of the environment. Pollution indices could however screen the potential for contamination with sediments to induce biological effects and identify the multi-element contamination potential resulting in the overall metal toxicity in the sediments. Pollution indices also attempt to summarize geochemical data into simple terms for reporting to the public and governments in a consistent and comprehensive manner. They also rank and prioritize the

contaminated areas or the contaminants for comparison and further investigations of pollution status of sediments.

A lot of studies abound in the literature on the development and application of index methods for sediment quality assessment. Such work include Ankley *et al.* (1996) Lee *et al.* (2005), Karabassi *et al.* (2006), Li *et al.* (2006), Adekola and Eletta (2007), Gonzalez-Nasrabadi *et al.* (2010), Botsou *et al.* (2012), Iwuoha *et al.* (2012), Adamu *et al.* (2015), and Odukoya *et al.* (2016). The pollution indices could be grouped into three; (1) contamination indices – compares with results measured elsewhere ie regional or global values, (2) background enrichment indices – compares with background levels from the study area and (3) ecological Risk Indices – compares with quality national and international guidelines or permissible limits. It is worth noting that pollution index values only reveal the disturbance status of metal levels in stream sediments relative to the background (control or average shale values, ASV, in this study) and do not represent the pollution or quality of the sediments in the strict sense. Risk assessment is a better tool used in evaluating the quality status of the sediments (Adamu *et al.*, 2015).

The preliminary report (Adamu *et al.*, 2015) has provided the base-levels of heavy metals for the stream sediments, assessed their contamination status and their dispersion trends as well as controls without which unsafe practices can compound the problem of heavy metal dispersion and water quality deterioration. Unfortunately, the report was rather complex and was not comprehensive to the indigenes and the government. The present study evaluates the degree of stream sediment contamination by barite mining activities in the study area using pollution indices and ecological risk factors and attempts to summarize geochemical data into simple terms for reporting to the public and governments in a consistent and comprehensive manner. The study also compares the efficiency of the sediment pollution indices using the extraction rates of elements with 0.1M HCl.

Study area

The study area lies between latitudes 05°30' - 06° 10'N and longitudes 08° 00' - 08° 50'E and covers parts of the Oban Massif and the Mamfe Embayment, Southeastern Nigeria (Fig.1). It is situated within the subequatorial climate of Nigeria with a total annual rainfall of between 180 and 200cm. The annual temperature varies between 25 and 30°C (Iloeje, 1999). The area experiences

two seasons; the wet season which lasts from April to October and the dry season which lasts from November to March. The mean humidity drops from 80% in the rainy season to as low as 60% in the dry season.

The relief of the study area varies from the low-lying northern fringes in the sedimentary areas to high elevations towards Oban Massif in the south. The elevation ranges from 100m in the Mamfe Embayment in the north to more than 500m above sea level in the Oban Massif in the south (Fig.1). The area is drained by the Cross River with major tributaries being Udip, Udam, Ukong, Bogai, Lakpoi, Okwo and Okpon Rivers, and many perennial streams which take their rise from Enugu escarpment and the Cameroon highlands. These rivers and streams join obliquely to form a network of dendritic drainage system.

The geology of the study area falls within parts of the Precambrian Basement Complex of Oban Massif and that of the Cretaceous sediments of Mamfe Embayment (Fig.1). 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 (Olade, 1976; Rahman *et al.*, 1981; Ekwueme, 1995). Overlying the Oban Massif is the Albian Mamfe Formation (Asu River Group), the oldest formation within the 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. The shales are often carbonaceous and pyritic which indicates that the sediments were deposited under a poorly oxygenated shallow water environment of restricted circulation, an indication of low energy environment (Petters *et al.*, 1987).

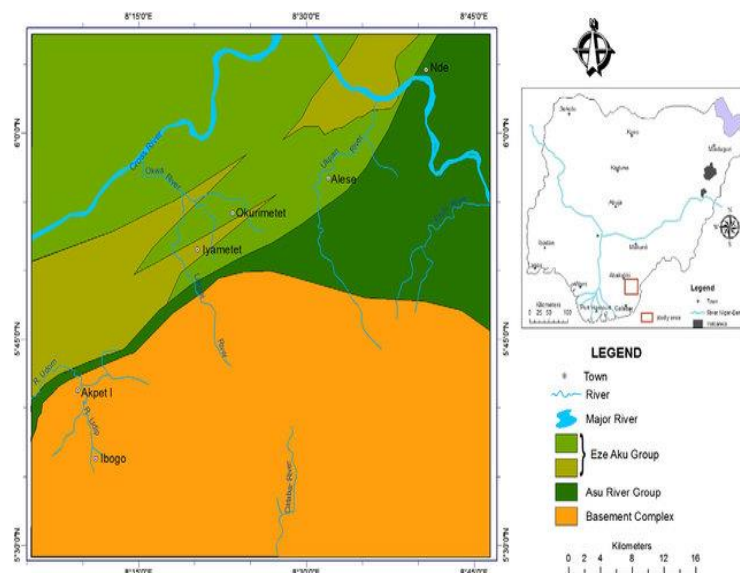


Fig. 1 Simplified geological map of the study area showing location of the abandoned mine sites. Insert: Map of Nigeria showing location of study area (After Adamu *et al.*, 2015).

The Mamfe Formation (Asu River Group) is succeeded by the middle Cenomanian- Turonian Eze-Aku Formation. This geologic formation covers the northern flanks of the study area and consists of shallow water grayish shale and siltstone with interbedded sandstone and limestone intercalations. Rocks of the Eze-Aku Formation are texturally similar to those of Asu River Group and could have been deposited under similar conditions of oxygen-deficient, low energy water (Petters *et al.*, 1987). The geologic sketch map of the area of study and rock distributions is shown in Fig.1.

MATERIALS AND METHODS

Stream sediment samples were taken from 30 sampling sites around six (6) abandoned barite mine sites in parts of the Precambrian basement complex of Oban massif (with 2 mine sites; Akpet 1 and Ibogo) and the Cretaceous sediments of the Mamfe embayment (with 4 mine sites; Nde, Alese- underlain by sandstones and, Iyametet and Okumuretet- underlain by shales) (Fig.1). At each of the 6 abandoned mine sites, 4 surface stream sediment samples were collected within and downstream of each mine site giving a total of 24 samples. A fifth set of surface sample was collected upstream of each abandoned barite mine site to serve as control, giving additional 6 samples. About 1kg of sample collected at each sampling site was put in a polyethylene bag and

properly labeled. The samples were immediately sealed and stored at 4°C until their arrival at the laboratory.

In the laboratory, the surface stream sediment samples were dried for 12 hours in an oven, disaggregated in an agate mortar and homogenized. The samples were then sieved and the particle size less than 63 microns, which retains metals, was chosen for analysis (Nasrabadi *et al.*, 2010. Details of sample digestion and analysis are presented in Adamu *et al.* (2015). In order to determine the mobile phase (dissolved and weakly adsorbed) of metals, partial extraction by 0.1M HCl, a scheme modified from Davidson *et al.* (1994), was adopted for the surface stream sediment samples. The modified scheme makes it possible to separate the acid soluble/mobile phase from the more structurally complex mineral-bound contaminants which are not bioavailable. The results of the analysis were reported in dry weight basis.

Furthermore, the precision evaluation of three different sediment metal pollution indices namely enrichment factors (EF), background enrichment index (BEI) and ecological risk index (RI) was carried out. The relationship among the indices in accordance with the extraction rate of metals from the sediments was analyzed using the Pearson correlation coefficient in the environment of SPSS 11.0 software.

Enrichment factor

Enrichment factor (EF) was described as heavy metal concentration in surface sediment divide by the heavy metal concentration from average shale values (Eq 1):

$$EF = (C/B)_{\text{sample}} / (C/B)_{\text{background}} \quad (1)$$

Where C is the concentration of the potential toxic element and B is the concentration of the proxy element (Al, Fe or Li), (C/B) sample is the ratio of the concentration of the element of concern (C) to that of the normaliser (Al, Fe or Li) in the sediment sample and (C/B) background is the same ratio in a reference sample from a local site, uncontaminated core sediments, or regional or global average values. In the present study, average shale values were used as background values and Al as the proxy element. The EF values are classified into four groups for interpretation: EF < 1, low contamination; 1 ≤ EF < 3, moderate contamination; 3 ≤ EF < 6, considerable contamination; EF ≥ 6 extreme contamination

Pollution load index (PLI).

The pollution load index was calculated as the n^{th} root from the products of n EFs that were obtained at a location or place for all the metals. The PLI is expressed according to Hakanson (1980) as

$$PLI = (CF_1 * CF_2 * CF_3 * \dots * CF_n)^{1/n} \quad (2)$$

According to Ali *et al.* (2015) PLI < 1 indicates no pollution while PLI > 1 indicates pollution of the investigated site by heavy metals

Degree of contamination (CD). The degree of contamination was calculated after Hakanson (1980) as the average of all EFs that were obtained at a location or place for all the metals.

$$CD = (EF_1 + EF_2 + EF_3 + \dots + EF_n)/n \quad (3)$$

The terminologies for describing CD values after Hakanson (1980) are (i) low degree of contamination, CD < 7 (ii) moderate degree of contamination, 7 ≤ CD < 14 (iii) high degree of contamination, 14 ≤ CD < 21, and (iv) very high degree of contamination CD ≥ 21.

Background enrichment index (BEI)

As a simple measure to quantify metal accumulation resulting from possible contamination, data for the stream sediments samples are often subjected to computation of geo-accumulation index (I-geo). The I-geo has been widely applied in evaluating the degree of metal pollution in different environments (Forstner, 1990; Fan *et al.*, 2002; Li *et al.*, 2006, Adamu *et al.*, 2015) and is calculated using:

$$I\text{-geo} = \log_2 [C_n / (B_n \times 1.5)] \quad (4)$$

Where I-geo is the geochemical accumulation index, C_n is the concentration of metal in a stream sediment sample, B_n is the average crustal geochemical background value for concentration of element n in the crust or in fossil argillaceous sediment (the average shale values of Turekian and Wedephol (1961) and 1.5 is a normalizing factor for possible variations in the crustal/shale data. In the present study, metal levels from control site with similar lithology as the impacted area were used as B_n and the I-geo equation modified as:

$$BEI = \log_2 [C_n / (B_n)] \quad (5)$$

BEI values are classified into seven grades for interpretation after Muller, (1979): Class 0 (practically unpolluted), BEI ≤ 0; Class 1 (slightly polluted), 0 < BEI ≤ 1; Class 2 (moderately polluted), 1 < BEI ≤ 2; Class 3 (moderately to strongly polluted), 2 < BEI ≤ 3; Class 4 (strongly polluted), 3 < BEI ≤ 4; Class 5 (strongly to very strongly polluted), 4 < BEI ≤ 5; Class 6 (very strongly polluted), BEI > 5

$5 < \text{BEI} \leq 6$. In an attempt to summarize pollution indices into simple terms for reporting to the public and governments in a consistent and comprehensive manner BEI_{tot} values were calculated. BEI_{tot} is defined as the sum of BEI for all the trace elements obtained from the site.

$$\text{BEI}_{\text{tot}} = (\text{BEI}_1 + \text{BEI}_2 + \dots + \text{BEI}_n) \quad (6)$$

Ecological risk assessment

According to Hakanson (1980) the potential ecological risk (Er) and risk index (RI) of a given contaminant are defined respectively as

$$\text{Er} = \text{Tr} \cdot \text{Cf} = \text{Tr} \cdot (\text{C}_s / \text{C}_n) \quad (7)$$

$$\text{RI} = \sum \text{Er} \quad (8)$$

Where Er is the ecological risk factor, Tr is the toxic response factor for the given element, which mainly reflects the heavy metal toxicity level and the degree of environmental sensitivity to heavy metal pollution, Cf is the contamination factor, C_s is the measured concentration for heavy metal in this study, C_n is the reference value for the heavy metal, and RI is the risk index. The following Tr values were proposed by Hakanson (1980) for the respective elements and are adopted in this study Cd=30, As=10, Ni=5, Cu=5, Pb=5, Cr=2, Fe=1, Zn=1. The purpose of ecological risk assessment is to evaluate ecological effects of human activities through scientifically credible assessment (chemical assessment and individual bioassay) to protect and manage the environment (Odukoya et al., 2016). The method considers a variety of factors such as the multi-element synergy, toxicity level, concentration of pollutant and sensitivity of environment to heavy metal pollution, which are widely used in environmental risk assessment. The values of Er and IR are grouped into five and four grades respectively as proposed by Hakanson (1980) and reported by Jiao et al. (2015). (i) Grade A (Low Risk), $\text{Er} < 5$, $\text{RI} < 30$; (ii) Grade B (moderate risk), $5 \leq \text{Er} < 10$, $30 \leq \text{RI} < 60$; (iii) Grade C (considerable risk) $10 \leq \text{Er} < 20$, $60 \leq \text{RI} \leq 120$; (iv) Grade D (High Risk) $20 \leq \text{Er} < 40$, $\text{RI} > 120$; and (v) Grade E (Very High Risk) $\text{Er} \geq 40$.

RESULTS AND DISCUSSION

Total metal content

Table 1 presents the summary statistics of metal concentrations for each mine site as well as that for all sample locations. The table also contains background values from control sites, average crustal values (ACV) (Taylor, 1964) and the average shale values (ASV) (Turekian and Wedephol 1961). These are commonly used as

background values in sediment studies (Lopez-Sanchez et al., 1993; Jones and Turki, 1997; Datta and Subramanian, 1998). Details of the results are presented in Adamu et al. (2015). A comparison of the mean metal concentrations for all sample locations with ACV and ASV reveals that most of the samples from the abandoned barite mine dumpsites are polluted with As, Ba, Cu, Fe, Pb, and Zn. These results are understandable if we bear in mind that the study area is highly affected by the barite mining activities for tens of years. On the contrary, the samples studied had mean Al, Cr, Mn, and Ni values less than those for ACV and ASV, which indicated that the study area is not polluted in these elements. The most probable source of the metals with mean concentrations less than ACV and ASV is geogenic. The elemental concentrations varied widely among the mine dump sites with the highest mean concentrations of As, Ba and Pb associated with Nde mine, Zn with Okumuretet mine, Cu with Iyametet mine, Al, Cr and Ni with Akpet 1 mine, and Fe and Mn with Ibogo mine. These variations could be attributed to differences in geology, grade of the barite mineralization, associated gangue, age and environmental factors among the mine dump sites.

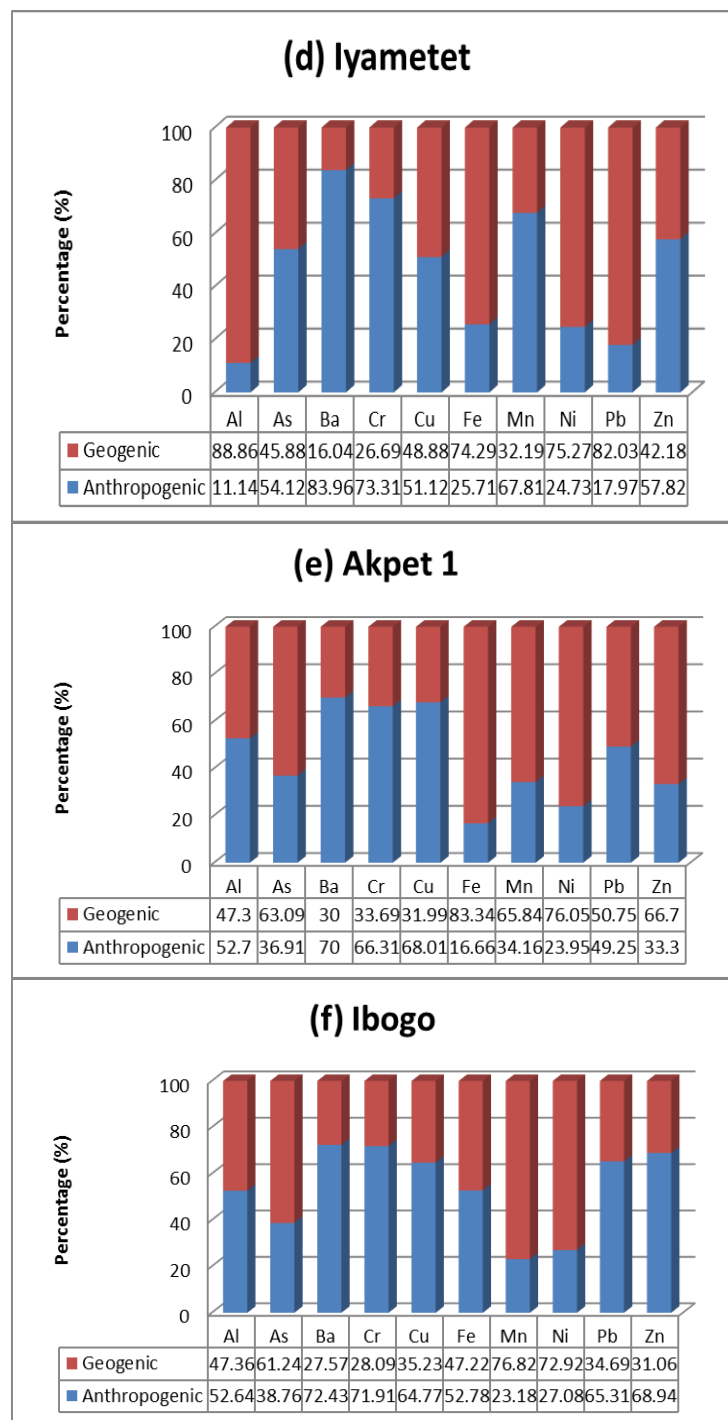
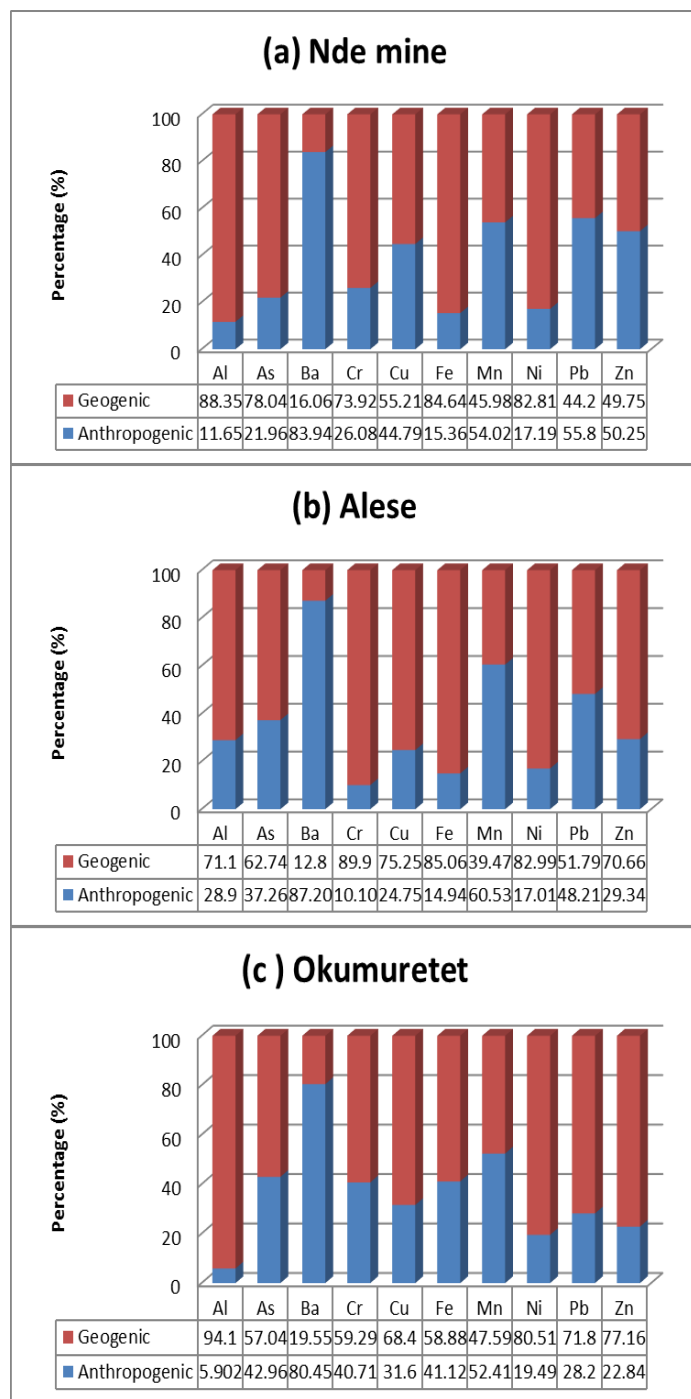


Fig. 2. Comparison of geogenic and anthropogenic inputs in the surface stream sediments for the different mine sites

The percentage anthropogenic portion of existing pollutants (difference between metal content in surface stream sediment sample from the mine and the control sites divide by total content x 100%) for each mine dump site is presented in figure 2 (a-f). The

figure shows random anthropogenic inputs of elements among the mine sites. The highest mean percentile anthropogenic portions of Al, Fe, Ni, Pb and Zn were associated with Ibogo mine, As, Cr and Mn with Iyametet mine, Cu with Akpet 1 mine and Ba with Alese mine. As expected, Ba was the most anthropogenically enriched metal whereas Fe, Al and Ni had the lowest percentile anthropogenic portions among the mine sites. Variability in percentile anthropogenic portions of elemental contents in the surface stream sediment samples among the mine dump sites could be due to differences in composition of sources, hydrodynamics and biogeochemical processes of individual stream (Cantwell et al., 2002).

Extraction rate (ER)

In order to quantify the association of metal concentrations with mobile sedimentary phase, the surface stream sediment were extracted by 0.1M HCl (Davidson et al., 1994) and analyzed for Al, As, Ba, Cr, Cu, Fe, Mn, Ni, Pb and Zn. The results of the extraction are presented in Table 2. Table 3 contains the extraction rate of the metals (metal concentration in mobile phase divided by the total metal content x 100%) computed from the mobile phase. High extraction rates are associated with ease of solubility and therefore high mobility (Siegel, 2002). Figures 3 and 4 compare the extraction rates between mine and control sites and presents extraction rates for the different mine sites respectively. The mean mobile phase of the metals for all sample locations (Table 2) followed the sequence Fe>Al>Ba>Pb>Zn>Cu>Mn>Cr>Ni>As similar to total metal contents (Table 1) and indicated proportionate extraction of metals by 0.1M HCl. The higher extraction rates of metals in the stream sediment samples from the mine sites relative to the control sites (Fig 3) indicated the impact of barite mining activities in the study area. The mean extraction rates of metals (Table 3) for all the mine sites and locations decreased in the order Pb>Cu>Zn>As>Ni>Mn>Cr>Fe>Al>Ba. This sequence was repeated at each mine site with only minor variations (Fig. 4). Table 3 further showed that Pb, Cu and Zn had the highest extraction rates. Arsenic, Ni and Mn showed moderate extraction rates. While Cr, Fe Al and Ba showed low extraction rates. This implies that Pb, Cu and Zn in the surface stream sediments are in forms that could be easily dispersed hydromorphically, As, Ni and Mn are less mobile while Cr, Fe, Al and Ba are relatively immobile

This sequence is most probably a reflection of variations in the binding strengths and solubility of the metals in an oxidized system (Eggleton and Thomas, 2004).

Table 1 Descriptive statistics of metal concentrations* in stream sediments of the different abandoned barite mines and all sample locations as well as control sites and average values used for assessing contamination levels

Mine site	Statistics	Al	As	Ba	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Nde (n=4)	Min	4.40	32.00	1130.00	22.00	68.00	5.70	320.00	30.00	252.00	202.00
	Max	5.60	52.00	4680.00	40.00	171.00	8.00	584.00	48.00	610.00	298.00
	Mean	4.80	39.75	3115.50	28.50	124.75	6.60	457.00	37.50	468.75	247.00
	SD	0.57	8.81	1606.17	8.06	49.04	0.99	112.30	8.23	152.54	43.95
	C1	4.20	30.00	370.00	20.00	60.00	5.50	200.00	30.00	185.00	120.00
Alese (n=4)	Min	5.20	20.00	1065.00	24.00	126.00	6.80	280.00	28.00	208.00	220.00
	Max	5.60	52.00	4550.00	32.00	180.00	9.20	570.00	40.00	620.00	306.00
	Mean	5.35	36.00	3075.25	27.00	149.00	7.85	435.00	32.00	461.00	258.25
	SD	0.19	13.47	1709.40	3.46	24.25	1.00	124.50	5.66	176.86	35.54
	C2	3.80	20.00	280.00	24.00	110.00	6.60	160.00	26.00	200.00	180.00
Okumuretet (n=4)	Min	4.80	11.00	524.00	12.00	53.00	7.20	196.00	7.00	165.00	230.00
	Max	6.20	50.00	4920.00	40.00	240.00	10.50	590.00	42.00	373.00	528.00
	Mean	5.43	27.50	2345.00	26.00	164.75	8.33	307.00	25.00	246.75	318.00
	SD	0.58	16.70	1846.99	14.05	82.21	1.49	189.18	14.76	94.68	140.69
	C3	5.20	15.00	250.00	16.00	120.00	4.80	120.00	24.00	160.00	220.00
Ivametet (n=4)	Min	4.20	22.00	1026.00	32.00	160.00	5.80	200.00	38.00	354.00	144.00
	Max	5.40	48.00	5000.00	44.00	244.00	10.00	560.00	44.00	406.00	530.00
	Mean	4.55	36.00	2548.00	38.00	210.50	7.70	297.50	40.00	379.00	293.25
	SD	0.57	12.11	1712.58	5.16	38.90	1.78	175.19	2.83	23.41	165.85
	C4	4.00	15.00	300.00	10.00	100.00	5.50	80.00	30.00	310.00	100.00
Akp1 (n=4)	Min	6.20	22.00	1025.00	120.00	66.00	6.60	256.00	42.00	140.00	148.00
	Max	10.80	40.00	4910.00	336.00	240.00	8.40	600.00	66.00	260.00	256.00
	Mean	8.35	33.50	2389.25	178.00	155.50	7.50	406.50	54.00	189.00	202.75
	SD	1.89	8.06	1780.36	105.45	71.26	0.77	155.21	9.93	56.23	45.09
	C5	3.80	20.00	500.00	50.00	40.00	6.20	240.00	40.00	90.00	130.00
Ibogo (n=4)	Min	6.80	26.00	598.00	110.00	30.00	6.60	365.00	36.00	104.00	160.00
	Max	10.00	40.00	5006.00	240.00	244.00	11.20	608.00	60.00	270.00	300.00
	Mean	8.40	33.50	2531.00	155.00	173.50	9.30	458.25	43.00	185.00	237.50
	SD	1.35	5.97	1826.85	58.02	97.34	2.13	104.75	11.49	69.21	57.95
	C6	3.90	20.00	400.00	40.00	30.00	4.20	340.00	30.00	57.00	70.00
All mines (n=24)	Min	4.20	20	524	20	30	5.70	196	25	104	144
	Max	10.80	52	5006	336	244	11.00	608	66	620	530
	Mean	6.17	34.79	2667.33	76.00	166.38	7.88	393.54	39.58	321.58	259.46
	SD	1.86	10.03	1579.56	79.04	59.80	1.58	146.88	10.65	156.17	93.57
	ASV	8.00	13.00	140.00	100.00	2.00	5.10	850.00	60.00	20.00	85.00
	ACV	8.20	1.80	425.00	100.00	5.00	5.60	950.00	75.00	12.50	70.00

*Concentrations in mg/kg (dry mass) except Al and Fe (%); n = Number of samples; C = Control; ASV = Average shale value (Turekian and Wedepohl, 1961) ; ACV=Average Crustal Values (Taylor, 1964)

Table 2 Mobile phase of metals* in the surface stream sediment samples of the study area

Mine site	Sample	Al	As	Ba	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Nde	L1	0.24	4.96	237.65	3.48	25.00	0.60	45.00	4.60	281.68	45.54
	L2	0.36	6.60	226.60	3.46	40.26	0.60	58.40	5.40	312.42	60.54
	L3	0.34	8.11	120.64	3.20	40.98	0.62	67.40	6.80	234.00	55.66
	L4	0.30	4.99	67.86	2.20	15.00	0.62	37.00	7.56	150.12	26.76
Alese	L5	0.32	6.60	226.65	2.20	50.00	1.02	62.43	3.13	264.86	47.90
	L6	0.34	7.12	248.43	2.40	32.64	0.80	44.00	4.20	230.00	40.58
	L7	0.36	5.60	124.89	4.54	35.99	0.82	35.00	5.80	280.96	30.00
	L8	0.33	3.62	60.34	3.00	38.05	0.62	26.23	5.00	130.62	38.42
Okumuretet	L9	0.36	4.02	101.04	3.22	44.78	1.00	44.24	5.68	186.50	130.32
	L10	0.38	4.00	262.24	3.66	52.50	1.02	35.40	3.80	108.80	37.78
	L11	0.38	7.20	110.44	2.40	54.66	0.82	26.54	2.98	120.00	30.94
	L12	0.31	3.75	32.82	2.60	38.68	0.62	23.00	2.98	100.24	50.66
Ivametet	L13	0.30	6.86	102.66	3.40	44.00	0.74	25.00	5.36	178.64	28.88
	L14	0.22	4.36	120.10	4.00	45.00	1.00	20.00	5.84	146.38	36.48
	L15	0.34	7.64	270.05	4.00	58.22	1.00	50.44	4.88	164.00	101.90
	L16	0.32	3.88	60.43	4.42	42.28	0.48	21.00	4.80	236.85	33.12
Akpet 1	L17	0.52	6.20	265.88	11.66	45.50	0.69	20.20	5.98	100.54	23.82
	L18	0.52	3.80	120.44	11.78	33.60	0.90	56.32	6.85	100.78	23.64
	L19	0.73	5.66	68.86	13.12	36.00	0.70	41.50	9.60	100.88	25.55
	L20	0.45	5.46	60.86	33.60	20.22	0.72	31.00	10.34	96.12	70.89
Ibogo	L21	0.52	3.96	126.50	14.00	60.13	1.00	40.00	4.00	42.94	28.67
	L22	0.70	5.12	128.27	12.00	61.00	0.88	36.60	4.80	95.98	50.50
	L23	0.60	5.68	270.44	12.00	50.00	0.82	60.80	3.76	121.62	60.00
	L24	0.38	5.43	40.10	23.22	7.90	0.56	40.50	11.26	60.76	30.80
Statistics	Min	0.22	3.62	32.82	2.20	7.90	0.48	20.00	2.98	42.94	23.64
	Max	0.73	8.11	270.44	33.60	61.00	1.02	67.40	11.26	312.42	130.32
	Nean	0.40	5.44	143.92	7.65	40.52	0.78	39.50	5.64	160.24	46.22
	SD	0.13	1.36	82.57	7.73	13.59	0.17	14.21	2.20	76.24	25.45

*Results of concentrations (mg/kg, except Al and Fe, %) measured in solution after extraction with 0.1M HCl

Table 3. Extraction rate (ER, %) of metals in the surface stream sediments within the different abandoned barite mine dump sites

Mine site	Sample	Al	As	Ba	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Nde	L1	5.00	14.17	5.08	8.70	25.00	9.23	9.00	15.33	56.00	20.70
	L2	6.50	16.50	5.50	12.36	23.54	10.53	10.00	16.88	51.22	20.32
	L3	7.73	15.60	4.76	14.55	25.61	7.75	15.90	17.00	45.88	20.77
	L4	6.82	15.60	6.01	9.17	22.06	10.00	11.56	15.75	59.57	13.25
Alese	L5	5.71	16.50	5.10	8.46	27.78	11.09	10.95	11.18	42.72	15.65
	L6	6.50	13.69	5.46	7.50	25.90	10.53	8.98	15.00	46.00	16.04
	L7	6.92	17.50	5.56	8.43	23.07	10.51	8.75	18.13	54.45	13.64
	L8	6.11	18.10	5.67	11.54	28.40	9.12	9.37	12.50	62.80	15.13
Okumuretet	L9	6.79	13.86	5.24	8.94	28.71	9.52	7.50	13.52	50.00	24.68
	L10	6.13	19.05	5.33	9.15	25.00	12.75	18.06	12.67	41.06	15.11
	L11	7.17	14.40	5.50	12.00	22.78	10.79	12.52	11.92	65.22	13.45
	L12	5.74	18.75	6.26	11.82	28.87	8.61	10.00	11.04	60.75	19.19
Ivametet	L13	5.56	15.60	5.28	10.63	27.50	10.57	12.50	14.11	45.81	12.24
	L14	5.24	14.53	5.41	9.09	22.50	12.50	9.09	13.27	39.99	13.87
	L15	7.73	15.92	5.40	11.11	23.86	10.00	9.01	12.84	40.39	19.23
	L16	7.62	17.64	5.89	11.05	17.76	8.28	10.00	12.00	66.91	23.00
Akpet 1	L17	6.19	16.32	5.42	9.72	27.74	8.85	7.89	14.24	48.34	16.09
	L18	6.50	17.27	5.08	8.92	22.11	10.71	9.39	13.17	38.76	12.31
	L19	6.76	14.15	5.50	10.58	15.00	10.61	9.02	14.55	68.16	11.88
	L20	7.26	16.06	5.94	10.00	30.64	10.00	10.00	18.46	68.66	27.69
Ibogo	L21	5.91	15.23	5.50	10.00	27.33	8.93	9.09	11.11	25.87	11.95
	L22	7.00	14.22	5.78	10.91	25.00	8.15	8.71	12.00	47.99	20.20
	L23	7.50	14.20	5.40	9.23	25.00	9.53	10.00	10.44	45.04	20.00
	L24	5.59	16.97	6.71	9.68	26.33	8.48	11.10	18.77	58.42	19.25
Statistics	Min	5.00	13.69	4.76	7.50	15.00	7.75	7.50	10.44	25.87	11.88
	Max	7.73	19.05	6.71	14.55	30.64	12.75	18.06	18.77	68.66	27.69
	Mean	6.50	15.91	5.53	10.15	24.90	9.88	10.35	13.99	51.25	17.32
	SD	0.79	1.59	0.41	1.58	3.55	1.27	2.42	2.47	10.98	4.35

According to Siegel (2002) the oxidation of some divalent metals (Zn, Cu) releases their soluble cations. However, the oxidation of Ba, As, Cr, Ni and Pb results to the formation of insoluble minerals such as carbonates and sulphates. While Al, Fe and Mn tend to form extremely stable oxidizes when exposed to air (Reible et al., 2002). This shows that the hydrogeochemical dispersion of metals in the surface environment depends largely on the compounds formed by oxidation. Hence, Cu and Zn, which form soluble carbonates or sulphates are labile. While the metals that form insoluble carbonates or sulphates or oxy/hydroxides tend to be relatively stable. It might be concluded that Pb in the study area was present in the form of exchangeable ions that are weakly adsorbed to sediments (Fan et al., 2002). This finding may suggest that the use of total metal concentration as a criterion to assess the potential effects of sediment concentration is untenable. This is because the use of total metal content in pollution assessment studies is based on the wrong assumption that all forms of a given metal have an equal impact. (Karbassi et al., 2007; Ma et al., 2000).

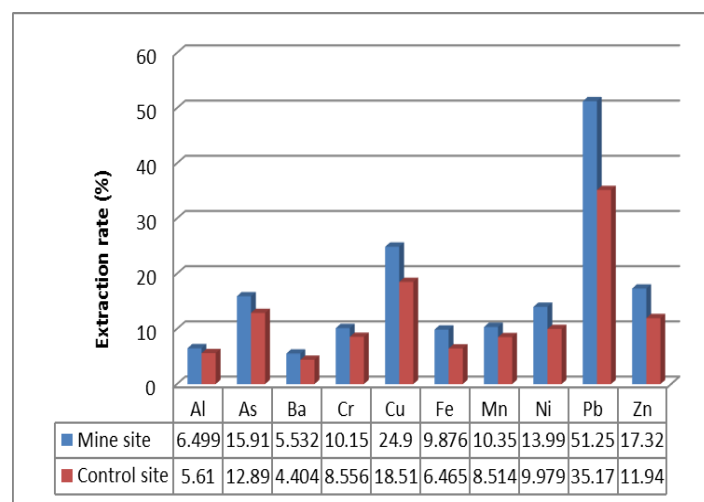


Fig. 3 Bar chart comparing extraction rates of metals from mine and control sites

Evaluation of indices efficiency

Enrichment factors (EF), Pollution load index (PLI) and Degree of contamination (CD)

The mean EF values for all the surface stream sediment samples at all locations (Table, 4) indicated varying degrees of metal contamination. The EF values grouped the metals into low contamination class (Mn, Ni), moderate contamination class (Cr,

Fe), considerable contamination class (As, Cu, Zn), and extremely contaminated class (Ba, Pb). However, these levels of contamination were milder and more variable when mean EF values of individual mine dump sites were used except for Ba, Pb and Mn. For instance the surface stream sediments showed low contamination of Cr, Mn and Ni at Nde and Alese, Cr and Mn at Okumuretet and Iyametet, and Mn and Ni at Akpet 1 and Ibogo mines. The surface stream sediments were extremely contaminated (EF>6) in As at Okumuretet, Ba and Pb at all mine sites, Cu at Iyametet, and Zn at Okumuretet and Iyametet.

The PLI values were >1 at all the sampling sites (Table 4) indicating that sediments within and downstream of mine dump sites were enriched in metals relative to the control sites. Such enrichment may be attributed to barite mining activities in the area. Other studies have also reported elevated metal levels in stream sediments impacted by mining activities (Adamu et al., 2015; Jiao et al., 2015; Adamu and Nganje, 2010; Franciskovic-Bilinski, 2005; Lee et al., 2005). The mean CD values obtained from the study classify the different abandoned mine sites into two groups; (i) abandoned mine dump sites with low degree of contamination $CD < 7$, Okumuretet, Akpet 1 and Ibogo and (ii) abandoned mine dump sites with moderate degree of contamination ($7 \leq CD < 14$), Nde, Alese and Iyametet. The CD values also showed that the degree of contamination of the different mine sites decreases in the order $Nde > Iyametet > Alese > Okumuretet > Ibogo \geq Akpet$ 1. The variations in the degree of contamination among the mine sites may be attributed to differences in lithology, mineralization, age and nature as well as distance of individual stream from mine dump site.

Background enrichment index (BEI)

The maximum BEI values of metals for all the sample sites (Table, 5) showed that the pollution levels of the stream sediments near abandoned barite mine sites varied from moderately polluted (Class 2, Al, As, Fe, Ni), moderately to strongly polluted (Class 3, Cr, Mn, Pb, Zn), strongly polluted (Class 4, Cu) to strongly to very strongly polluted (Class 5, Ba). The average BEI values indicated that pollution levels varied from practically unpolluted (Class 0) for various elements across the mine sites at Nde, Alese and Okumuretet (Cr, Ni), Iyametet (Ni), Akpet 1 (Ni, Zn), and Ibogo (Mn) to strongly polluted (Class 3) with respect to Ba at Nde, Okumuretet and Iyametet and Cu at Ibogo but only strongly to very

strongly polluted (Class 4) in Ba at Alese. The average BEI_{tot} values arranged the abandoned barite mine dump sites in order of decreasing metal pollution levels as Ibogo > Nde = Iyametet >

Akpet 1 > Okumuretet > Alese. This pollution sequence is different from that indicated by CD and explains why it is difficult to relay on any single index in sediment quality assessment.

Table 4. Summary statistics of aluminum normalized enrichment factor (EF), pollution load index and (PLI) and degree contamination (CD) for the different abandoned barite mine sites

Mine site	Statistics	As	Ba	Cr	Cu	Fe	Mn	Ni	Pb	Zn	PLI	Cd
Nde	Min	2.52	14.68	0.29	2.47	1.31	0.75	0.38	13.82	4.31	2.77	5.37
	Max	7.27	55.71	0.67	5.82	2.85	1.08	1.45	46.36	5.73	4.56	11.45
	Mean	4.67	36.33	0.41	4.13	1.94	0.98	0.82	36.42	4.84	3.90	9.39
	SD	1.96	17.22	0.18	1.51	0.70	0.15	0.46	15.18	0.68	0.84	2.73
Alese	Min	3.79	19.89	0.31	3.14	1.81	0.75	0.46	23.53	3.98	3.49	4.15
	Max	6.15	50.00	0.52	5.14	2.58	1.05	1.74	44.29	5.14	4.43	10.89
	Mean	4.59	34.97	0.42	4.11	2.08	0.89	0.86	36.49	4.53	3.97	8.48
	SD	1.07	14.90	0.10	1.01	0.36	0.15	0.60	9.00	0.48	0.39	3.16
Okumuretet	Min	3.85	12.48	0.40	3.53	3.13	0.41	0.39	26.29	7.73	3.65	3.21
	Max	10.99	159.74	1.82	19.09	6.98	1.15	2.27	60.23	13.37	11.33	7.74
	Mean	6.04	59.79	0.84	10.56	4.28	0.62	1.25	37.30	10.79	6.65	5.95
	SD	3.34	67.64	0.66	7.16	1.83	0.36	0.79	15.78	2.38	3.29	2.04
Iyametet	Min	1.40	22.55	0.58	5.82	1.85	0.43	0.51	17.27	5.05	3.36	6.72
	Max	8.79	85.03	1.23	14.65	4.66	1.32	1.83	48.33	14.85	8.17	13.45
	Mean	5.29	43.12	0.94	10.52	3.09	0.84	1.00	30.32	8.21	5.77	9.00
	SD	3.04	28.93	0.29	3.68	1.42	0.41	0.58	13.43	4.59	2.13	3.19
Akpet 1	Min	0.47	6.62	0.92	2.03	0.63	0.32	0.19	5.48	0.12	1.84	2.30
	Max	2.78	33.40	5.17	3.56	4.70	0.78	0.81	13.00	4.63	2.64	5.45
	Mean	1.60	17.05	2.14	2.94	2.91	0.51	0.42	9.79	2.07	2.31	3.86
	SD	1.11	11.68	2.03	0.65	1.84	0.19	0.27	3.15	1.88	0.37	1.31
Ibogo	Min	1.12	3.70	0.88	1.04	1.77	0.43	0.24	7.55	2.35	2.50	2.30
	Max	3.08	35.76	4.17	4.00	5.14	0.79	1.74	13.50	3.53	3.74	6.42
	Mean	2.00	16.77	1.91	3.24	3.26	0.57	0.78	9.52	2.93	2.94	3.88
	SD	0.84	13.56	1.52	1.46	1.51	0.15	0.66	2.72	0.56	0.56	1.77
Over all	Min	0.47	3.70	0.29	1.04	0.63	0.32	0.19	5.48	0.12	1.84	26.69
	Max	10.99	159.74	5.17	19.09	6.98	1.32	2.27	60.23	14.85	11.33	267.82
	Mean	4.03	34.67	1.11	5.91	2.93	0.74	0.85	26.64	5.56	4.26	82.45
	SD	2.53	32.37	1.18	4.54	1.47	0.29	0.57	15.97	3.70	2.14	53.52

Table 5. Summary statistics of background enrichment index (BEI) values of surface stream sediments for the different abandoned barite mine sites

Mine site	Statis	Al	As	Ba	Cr	Cu	Fe	Mn	Ni	Pb	Zn	BEItot
Nde	Min	0.07	-0.74	1.61	-0.91	0.18	-0.08	0.68	-0.91	-0.28	0.75	8.25
	Max	0.42	0.79	3.66	0.42	1.51	0.54	1.55	0.68	1.72	1.31	15.82
	Mean	0.19	0.17	2.88	-0.37	0.96	0.19	1.16	-0.20	1.09	1.02	11.49
	SD	0.16	0.65	0.93	0.65	0.62	0.27	0.37	0.70	0.92	0.26	3.16
Alese	Min	0.45	0.00	1.93	-0.26	-0.78	0.04	0.81	-0.53	-0.15	-0.32	4.86
	Max	0.56	1.38	4.02	0.42	0.71	0.48	1.83	0.62	1.63	0.77	11.19
	Mean	0.49	0.76	3.24	0.00	0.08	0.24	1.39	-0.01	1.04	0.31	7.85
	SD	0.05	0.58	0.99	0.33	0.67	0.18	0.44	0.50	0.81	0.46	2.80
Okurum	Min	-0.12	-0.45	1.07	-1.58	-1.18	0.58	0.71	-1.78	0.04	0.06	4.16
	Max	0.25	1.74	4.30	0.15	1.00	1.13	2.30	0.81	1.22	1.26	12.19
	Mean	0.06	0.66	2.83	-0.65	0.25	0.78	1.19	-0.21	0.55	0.44	8.52
	SD	0.15	0.92	1.33	0.86	0.99	0.24	0.74	1.12	0.54	0.55	3.40
Iyamet	Min	-0.07	-0.58	1.77	1.68	0.68	-0.14	1.32	-1.58	-1.01	0.53	8.25
	Max	0.43	1.68	4.06	2.14	1.29	0.86	2.81	0.55	0.39	2.41	15.82
	Mean	0.14	0.66	2.85	1.92	1.05	0.40	1.75	-0.43	-0.40	1.39	11.49
	SD	0.21	0.95	0.94	0.20	0.28	0.42	0.71	0.90	0.61	0.77	3.16
Akpet 1	Min	0.71	-2.32	1.04	1.26	0.72	0.09	-1.21	-1.74	0.64	-3.67	8.66
	Max	1.51	1.00	3.30	2.75	2.58	0.44	1.32	0.72	1.53	0.98	11.02
	Mean	1.11	-0.31	1.98	1.68	1.82	0.27	0.36	-0.90	1.02	-0.45	10.29
	SD	0.33	1.59	1.02	0.71	0.78	0.15	1.11	1.16	0.42	2.18	1.10
Ibogo	Min	0.80	-0.74	-0.42	1.46	0.00	0.65	-1.42	-0.91	0.87	1.19	8.46
	Max	1.36	1.00	3.65	2.58	3.02	1.42	0.60	1.00	2.24	2.10	16.60
	Mean	1.09	0.20	2.05	1.89	2.16	1.12	-0.15	0.19	1.62	1.73	13.52
	SD	0.23	0.86	1.74	0.49	1.44	0.35	0.88	0.80	0.58	0.38	3.53
Overall	Min	0.03	0.00	0.58	0.00	0.00	0.04	0.09	0.00	0.04	0.06	4.16
	Max	1.51	1.74	4.30	2.75	3.02	1.42	2.81	1.00	2.24	2.41	16.60
	Mean	0.52	0.78	2.68	1.16	1.17	0.52	1.19	0.37	0.97	0.95	10.31
	SD	0.47	0.48	1.06	0.82	0.92	0.40	0.71	0.26	0.64	0.63	3.11

Table 6. Comparison of ecological risk factor (Er) and risk index (RI) values for the different mine sites with their control sites

Mine	Statis	Al	As	Ba	Cr	Cu	Fe	Mn	Ni	Pb	Zn	RI
Nde	Min	0.55	24.62	8.07	1.10	6.80	1.12	1.07	2.50	63.00	2.38	112.21
	Max	0.70	40.00	33.43	2.00	17.10	1.57	1.95	4.00	152.50	3.51	241.13
	Mean	0.60	30.58	22.25	1.43	12.48	1.29	1.52	3.13	117.19	2.91	192.38
	SD	0.07	6.78	11.47	0.40	4.90	0.19	0.37	0.69	38.14	0.52	55.49
	C1	0.53	23.08	2.64	0.60	6.00	1.08	0.24	2.50	46.25	1.41	82.91
Alese	Min	0.65	15.38	7.61	1.20	12.60	1.33	1.30	2.33	52.00	2.59	98.48
	Max	0.70	40.00	32.50	1.60	18.00	1.80	1.90	3.33	155.00	3.60	245.89
	Mean	0.67	27.69	21.97	1.35	14.90	1.54	1.54	2.67	115.25	3.04	189.62
	SD	0.02	10.36	12.21	0.17	2.42	0.20	0.28	0.47	44.21	0.42	64.30
	C2	0.48	15.38	2.00	0.48	11.00	1.29	0.19	2.17	50.00	2.12	82.99
Okumuret	Min	0.66	15.38	3.74	1.00	13.40	1.41	0.71	2.08	41.25	2.71	82.59
	Max	0.78	38.46	35.14	2.00	24.00	2.06	1.97	3.50	93.25	6.21	159.86
	Mean	0.69	23.08	16.75	1.48	18.50	1.63	1.10	2.58	61.69	3.74	130.53
	SD	0.05	10.71	13.19	0.50	4.86	0.29	0.59	0.63	23.67	1.66	34.09
	C3	0.65	11.54	1.79	0.72	12.00	0.94	0.14	2.00	40.00	2.59	69.78
Iyametet	Min	0.53	16.92	7.33	1.60	16.00	1.14	0.74	3.17	88.50	1.69	145.74
	Max	0.68	36.92	35.71	2.20	24.40	1.96	1.87	3.67	101.50	6.24	212.91
	Mean	0.57	27.69	18.20	1.90	21.05	1.51	1.21	3.33	94.75	3.45	172.88
	SD	0.07	9.32	12.23	0.26	3.89	0.35	0.53	0.24	5.85	1.95	28.67
	C4	0.50	11.54	2.14	0.20	10.00	1.08	0.09	2.50	77.50	1.18	105.55
Akpet 1	Min	0.78	16.92	7.32	6.00	6.60	1.29	0.85	3.50	35.00	1.74	102.11
	Max	1.35	30.77	35.07	16.80	24.00	1.65	2.00	5.50	65.00	3.01	146.82
	Mean	1.04	25.77	17.07	8.90	15.55	1.47	1.36	4.50	47.25	2.39	124.41
	SD	0.24	6.20	12.72	5.27	7.13	0.15	0.52	0.83	14.06	0.53	18.95
	C5	0.48	15.38	3.57	1.00	4.00	1.22	0.28	3.33	22.50	1.53	51.76
Ibogo	Min	0.85	20.00	4.27	5.50	3.00	1.29	1.22	3.00	26.00	1.88	79.34
	Max	1.25	30.77	35.76	12.00	24.40	2.20	2.03	5.00	67.50	3.53	170.46
	Mean	1.05	25.77	18.08	7.75	17.35	1.82	1.53	3.58	46.25	2.79	124.99
	SD	0.17	4.59	13.05	2.90	9.73	0.42	0.35	0.96	17.30	0.68	37.84
	C6	0.49	15.38	2.86	0.80	3.00	0.82	0.47	2.50	14.25	0.82	40.57
All mines (n = 24)	Min	0.53	15.38	3.74	1.00	3.00	1.12	0.71	2.08	26.00	1.69	80.13
	Max	1.35	40.00	35.76	16.80	24.40	2.20	2.03	5.50	155.00	6.24	247.12
	Mean	0.77	26.76	19.05	3.80	16.64	1.54	1.37	3.30	80.40	3.05	156.69
	SD	0.23	7.72	11.28	3.95	5.98	0.30	0.44	0.89	39.04	1.10	48.75
Control (n = 6)	Min	0.48	11.54	1.79	0.20	3.00	0.82	0.09	2.00	14.25	0.82	40.57
	Max	0.65	23.08	3.57	1.00	12.00	1.29	0.47	3.33	77.50	2.59	105.55
	Mean	0.52	15.38	2.50	0.63	7.67	1.07	0.24	2.50	41.75	1.61	72.26
	SD	0.07	4.21	0.66	0.28	3.83	0.17	0.13	0.46	22.34	0.64	23.53

Table 7 Correlation among the extraction rate of metals in the stream sediments and different sediment pollution indices

	ER	BEI	Er	EF	CD	RI
ER	1.00					
BEI	0.44	1.00				
Eri	0.84*	0.22	1.00			
EF	0.13	-0.46	0.13	1.00		
CD	0.11	-0.34	0.12	0.97*	1.00	
RI	0.85*	0.16	0.99*	0.13	0.08	1.00

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

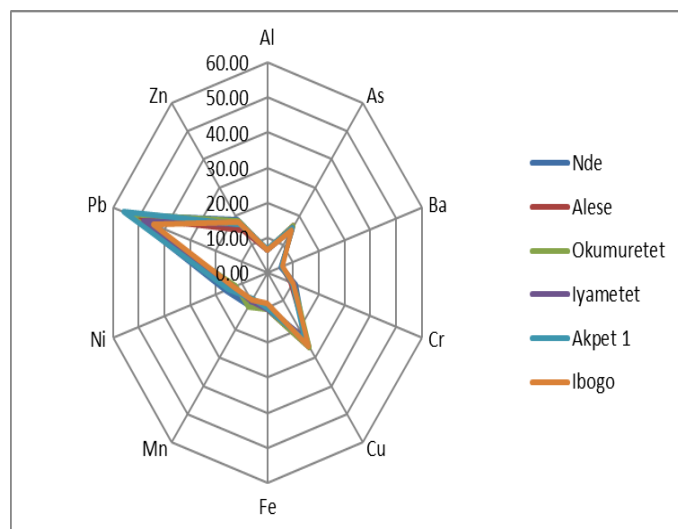


Fig. 4 Radar chart of extraction rates of metals for the different abandoned barite mine dump sites

Ecological risk assessment

The overall ecological risk factors (Er) of metals (Table 6) for the surface stream sediment samples indicated that Al (0.53-1.35), Fe (1.12-2.20) and Mn (0.71-2.03) fell within the low risk category for all the samples; Ni (2.08-5.50) and Zn (1.69-6.24) were within low to moderate risk, while Cr (1.00-16.80) fell within low to considerable risk category. Ba (3.74-35.76) and Cu (3.00-24.40) fell within low to high risk while As (15.38-40.00) and Pb (26.00-135) fell within considerable to very high risk and high to very high risk categories respectively. Potential ecological risk factor known as Risk Index (RI) ranged between 80.13 and 247.12 thus falling within the class of considerable to high risk. The potential ecological risk of sediments metal pollution was higher at the abandoned mine sites compared to the control sites at all the mine sites.

The average Er values indicated that potential ecological risk of sediment metal pollution varied across the abandoned barite mine dump sites (Table 6). The mean Er values indicated that Al, Cr, Fe, Mn Ni and Zn fell within the low risk category and Pb within the high risk category for all the mine sites. Arsenic fell within the considerable risk category across the mine sites except at Nde where it fell within the high risk category. Cu fell within the considerable risk category at all the mine sites but Iyametet where it fell within the high risk category. The decreasing order of potential risk of sediment metal pollution of the different mine sites based on mean RI values was Nde> Alese> Iyametet> Okumuretet> Akpet 1=Ibogo.

In order to find the correlation between the extraction rates of elements in stream sediments and the different sediment pollution indices, a correlation matrix was produced through SPSS11.0 software (Table 7). Table 7 revealed the weak and insignificant correlation between the extraction rates of elements and the sediments metallic pollution indices. Although BEI appeared to be more efficient in interpreting the anthropogenic metallic pollution in comparison with the EF and CD, it is also not capable enough to estimate the bioavailable risky metallic pollution in the sediments environment (Odukoya et al., 2016). This may be due to the similar fundamentals and concepts upon which these formulae are developed. Both EF and BEI formulae compare present concentration of metals to their background levels in shale and control respectively. In a specific area with its own geological background like the study area with naturally high concentration of some metals, a comparison with ASV may lead to biased conclusions regarding levels of anthropogenic contamination. However, BEI is also not enough to evaluate sediment quality because it is based on the wrong premise that all forms of a given metal have an equal impact on the environment. The significant positive correlation between ER with Er ($r=8.4$; $p \leq 0.01$) and RI ($r=0.85$; $p \leq 0.01$) illustrated that ecological risk factor/index is most efficient in the assessment of the stream sediment quality in the study area.

CONCLUSIONS

The surface stream sediments within abandoned barite mine dump sites in parts of Oban Massif and Mamfe Embayment are relatively polluted with As, Ba, Cu, Fe, Pb, and Zn with regards to average crustal and shale values. On the other hand, the low levels of Al, Cr, Mn and Ni relative to these background values indicated

that the major source for these elements is geogenic. The enhanced concentration of elements in the stream sediment samples from the abandoned barite mine dump sites relative to the control sites revealed the influence of barite mining. The high extraction of Pb, Zn and Cu as well as As suggested high mobility and exchange between the stream sediments and the water column. The rates of elements were higher in stream sediments from abandoned mines as compared to control sites.

An evaluation of enrichment factor (EF), degree of contamination (CD) and background enrichment index (BEI) revealed that the sediments had suffered varying degree of contamination ranging from low/slight to extreme/strongly contaminated. The sum of BEI for the elements at each sample location (BEI_{tot}) showed that the degree of sediment metal pollution at the mine sites decreased in the order $Ibogo > Nde = Iyametet > Akpet 1 > Okumuretet > Alese$. The ecological risk factor (Er) indicated that Al, Fe and Mn fell within the low risk category; Ni and Zn fell within low to moderate risk category; Cr fell within low to considerable risk category; Ba and Cu fell within low to high risk category while As and Pb fell within considerable to very high risk and high to very high risk categories respectively. The decreasing order of potential risk of sediment metal pollution of the different mine sites based on mean RI values was $Nde > Alese > Iyametet > Okumuretet > Akpet 1 = Ibogo$. The significant positive correlation between extraction rates (ER) of metals and Er, (0.84) indicates that Er is an efficient quality assessment method in this study.

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