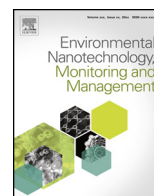




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Heavy metal contamination and health risk assessment associated with abandoned barite mines in Cross River State, southeastern Nigeria

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ABSTRACT

In the present investigation, the concentration of heavy metals (As, Ba, Fe, Hg, Mn, Ni, Pb, Zn) in pond and stream water samples near abandoned barite mines have been studied. The main objective of study was to appraise the degree of contamination and human risk assessment due to barite mining. Results showed that the average concentrations of Fe, Hg and Pb were above the required standard. This indicates anthropogenic inputs from barite mining activities. The mean concentrations of Ba, Hg, Mn, Ni, Pb and Zn were higher in pond water compared to stream water. Contamination index and Nemerow pollution index indicated contamination at some mine sites, while human health risk assessment indicated unacceptable risk (hazard index (HI) values > 1) for non-carcinogenic adverse health effect. The cancer risk of being exposed to Arsenic by drinking water from these sources did not exceed the acceptable risk of 1:10,000 for regulatory purposes.

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1. Introduction

In recent years, considerable attention has been shifted towards barite mining in Nigeria due to Federal Government's policy of using local raw materials. This resulted in many legal and illegal mining of barite, a major component used in the oil and gas industry in Nigeria. The mining and processing of barite generates vast quantities of mine rocks and mine tailings. Barite has been mined near communities in Cross River State (southeastern Nigeria). These abandoned mine sites constitute some of the largest barite mines in Nigeria. The occurrence and exploitation of barite potentially threatens nearby water resources due to leachate from the waste. Mine waste can generate elevated levels of sulphates, metals and acidity. Unless mine waste sites are protected from oxidation and metal release, these sites represent sources of environmental contamination and risk to human health (Suresh et al., 2007).

In the last few years, an industrial revolution has been noticed all over the globe. As a result of this rapid development, heavy metals have been discharged into the pristine environment. Thus

mining and release of heavy metals into the environment is one of the most important threats to their degradation, because most of these metals are very toxic to humans, especially when they exceed the maximum admissible values set by international organizations including WHO, EPA, etc. Recently, sediment quality has been used as an important indicator of pollution (Zarei et al., 2014) since they are considered as a major sink for various pollutants. In addition, sediments are normally mixtures of several components and they can play a significant role in remobilization of contaminants in aquatic systems and interactions between water and sediments (Zarei et al., 2014).

Generally, most studies on barite occurrence are focused on the geological, mineralogical and structural aspects (Boye, 1972; Whitehead and Macdonald, 1998; Adamu, 2000, 2011; Egeh et al., 2004; Akpeke, 2008; Oden, 2012) rather than environmental aspect. Besides, the process of barite prospecting was done in the area without due process and consideration to environmental management. In addition, these barite mines were abandoned without proper demobilization, remediation and restoration of the environment. Therefore, there is the need to carry out a geochemical study in abandoned barite mining areas in order to (i) document the effects of barite mining on potable water sources and (ii) consider the risk to human health by heavy metals through drinking water pathway. Besides, the inhabitants of these areas use water from ponds within the mine areas and nearby streams for their domestic and agricultural purposes.

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Environmental pollution from mining activities has continued to generate unpleasant implications for health and economic development all over the world (Adamu, 2000; Adiuku-Brown and Ogezi, 1991; Chukwuma, 1995). Despite the public and international agencies policy focus on this problem, the situation in Nigeria seems degenerating and therefore demands increased attention. So far, there are no clear formulated policies in Nigeria aimed at coordinating and monitoring the relationship between environmental management and sustainable development (NEST, 1995; Bell and Rusell, 2002). The objectives of this study were (i) to assess the level of heavy metals in ponds and streams within and near abandoned barite mining sites and (ii) appraise the degree of contamination and human risk assessment of the pond and stream water.

2. Study area description

2.1. Geographic setting

Six abandoned barite mine sites at Nde, Alese, Okumurutet, Iyametet, Akpet I and Ibogo (Cross River State, Nigeria, Fig. 1) were studied. These sites are located between latitudes 05°30'–06°10' North and longitudes 08°00'–08°50' East. The mine areas are situated within the subequatorial – climate zone of Nigeria with a total annual rainfall of between 1800 and 2000 mm, and annual temperature ranging from 25 to 30 °C (Iloeje, 1999). The relief of the study area varies from 100 m in the north to more than 500 m above sea level in the south. The area is drained by tributaries of Cross River (Fig. 1).

2.2. Geologic setting and barite mineralization

The geology of the study area falls within parts of the Precambrian Basement Complex, of Oban Massif and the Cretaceous sediments of Mamfe Embayment (Fig. 1). Rocks of the Oban Massif are mainly of igneous and metamorphic origin (phyllites, schists, gneisses, amphibolites, pegmatites, granites, granodiorites tonalities, monazites, dolerites, and charnockites; Rahman et al., 1981; Ekwueme et al., 1995). The basement rocks are overlain by sedimentary Ezillo Formation and Amaseri Sandstone (Eze Aku Group) and the Mamfe Formation (Asu River Group). The rock sequence of the Mamfe Formation consists of sandstones and mudstones, while the Ezillo Formation consists of shale with sandstone, siltstone and limestone intercalations. The Amaseri Sandstone overlying the Ezillo Formation is composed of shale, calcareous shale and sandstone (Ekwueme et al., 1995). The stratigraphic units are presented in Fig. 2.

In the area, barite mineralization occurs as veins and bedded deposits of over 200 km long trending in N-S and NE-SW directions (Oden, 2012). These deposits occur in association with sulphide, carbonate and Fe-Al-oxide minerals (Akpeke, 2008). The deposits are of hydrothermal type of mineralization, hosted in schists, phyllites, shales and sandstones (Adamu, 2000, 2011; Egeh et al., 2004; Akpeke, 2008). The mine sites at Nde, Alese, Okumurutet and Iyametet mines are located in the Mamfe Embayment Sedimentary basin, designated as Group I (GPI) in this study. The abandoned mine sites at Akpet I and Ibogo are located in the Precambrian age Oban massif crystalline basement and are designated as Group 2, GP 2 (Table 1).

2.3. Characteristics of mine sites

2.3.1. Sandstone area

The Nde abandoned mine is the largest of all the mines that was studied. The mine has an estimated area of 340,800 m² (Table 1). Nde area is dominated by sandstones. The depth of mine pits ranged from 5 to 20 m with widths of between 1 and 6 m (Adamu,

2011). Barite mining took place at Nde between 2000 and 2007 at an estimated production rate of 4,089,600 kg/annum (Table 1). The sediments at Nde consisted of silty sand. The site geology at Alese is similar to that of Nde, except that the shale and limestone are thicker with thinner sandstone beds. Two major barite veins were encountered at Alese with depth range of 15–40 m and width of between 2 and 6 m. The Alese mine area is approximately 140,000 m² in size with an estimated production capacity of about 1,680,000 kg/annum (Table 1). The sediments at Alese consisted of silty sand.

2.3.2. Shale area

The main lithologic unit at Okumeritet is black, baked, fractured shales that are intruded by dolerite sills. The barite vein here trends in north–south direction, while the mined area is approximately 15,000 m² in size with estimated production capacity of 180,000 kg/annum. Iyametet mine is situated at the break of hill slope near Lokpai River. The geology is similar to that of Okumeritet. The barite deposits at Iyametet trend in a north–south direction with an estimated area and production capacity of 11,250 m² and 135,000 kg/annum (Table 1).

2.3.3. Basement area

Akpet I lie within the Precambrian basement rocks. Gneiss, schist and granodiorite are the predominant rocks in the area covering an estimated area of 104,800 m². Ibogo mine constitutes the south most mine area occupying an estimated area of 68,700 m² with annual barite production of 824,400 kg/annum. Ibogo lies within the Precambrian Basement Complex, with schist, phyllite and pegmatite as the major rock types.

3. Materials and methods

3.1. Sampling and analysis

Water samples for analysis were obtained from ponds located within six abandoned barite mine sites and streams in the vicinity of these mine sites. In all, 60 water samples were collected comprising 12 samples from six mine ponds and 48 samples from six streams (12 water samples) and 8 samples from each adjoining stream near each mine site (48 samples) during two sampling campaign periods comprising wet (July 2009) and dry (February, 2010) seasons. Several analyses such as temperature, total dissolved solids (TDS), pH, and total suspended solids (TSS) were carried out on-site. All the samples were collected in low density polyethylene bottles and filtered in the laboratory through 0.45- μ m membrane. The water samples were preserved by acidifying to pH <2 with 0.5 ml concentrated HNO₃ acid for trace elements analysis.

Heavy metals contents were determined using inductively coupled plasma-mass spectrometry (ICP-MS) at Acme Laboratory Limited, Vancouver Canada. The statistical evaluations (descriptive statistics, correlation and factor analysis) were carried out using the computer software, STATISTICA®.

3.2. Assessment of environmental impacts

Water in the mine ponds and adjoining streams are used for drinking, domestic, fishing and irrigation purposes. It is worth noting in mine areas such as the present study area, inhabitants and animals are likely to accumulate potential toxic elements through ingesting mine tailings (Alloway, 1990; Azcue, 1999) and drinking of contaminated waters (Adamu, 2000; Adiuku-Brown and Ogezi, 1991) as well as feeding on fish from contaminated streams (Adamu, 2011). This may therefore have some health implications on the humans and animals through bioaccumulation and biomagnifications (Keller, 1981; Siegel, 2002). However, toxicological

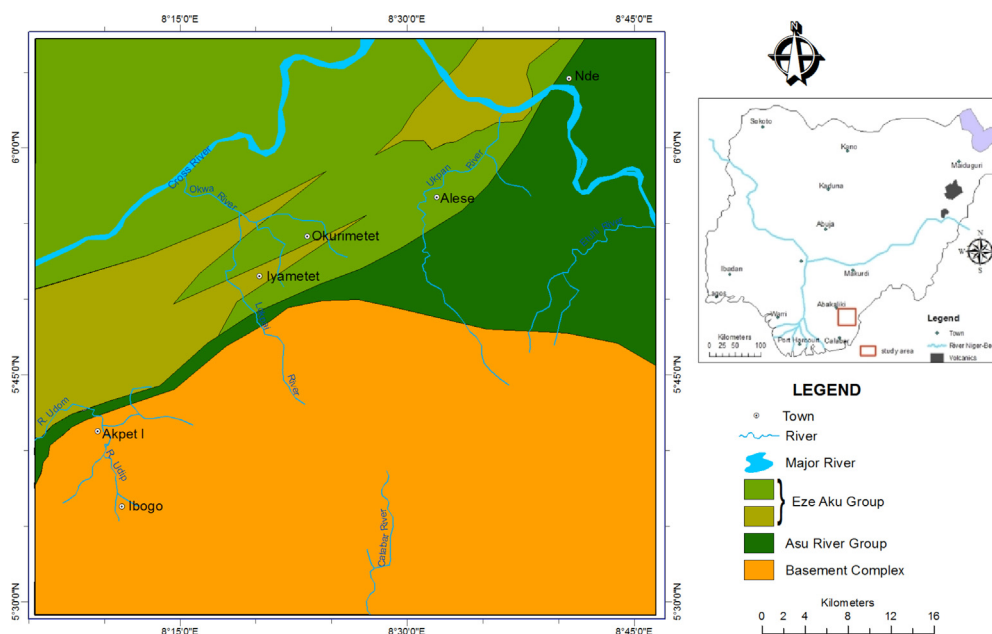


Fig. 1. Simplified geological map of the study area including mine sites.

Age	Basin	Group	Formation	Lithology	Igneous activity
Tertiary				Basalts	Emplacement of newer basalts
Santonian			Amaseri		Emplacement of dolerite, microgabbro & microdiorite
Coniacian	Ikom- Mamfe Embayment	Eze Aku	Sandstone	Calcaerous highly bioturbated sandstones	
Turonian			Ezillo	Marine shales	
Cenomanian		Asu River	Mamfe	Sandstones Siltstones Shales	
Albian					
Precambrian	Oban massif			Gneiss, phyllite, schist, amphibolites	

Fig. 2. Stratigraphic units of the Mamfe-Ikom Embayment.

Modified from Ekwueme et al. (1995).

Table 1

Physical characteristics of each abandoned mine site. Location of abandoned mine site on Fig. 1.

No.	Abandoned mine site location	Longitude East	Latitude North	Lithology	Basin	Formation	Group	Area (m ²)	Quantity (kg/annum)
1	Nde	8.608	6.053	Sandstone	Mamfe	Mamfe	GP 1 (sedimentary)	340,800	4,089,600
2	Alese	8.495	5.955	Sandstone	embayment	Mamfe		140,000	1,680,000
3	Okuremetet	8.392	5.895	Shale		Eze Aku		15,000	180,000
4	Iyametet	8.357	5.862	Shale		Eze Aku		11,250	135,000
5	Akpet I	8.147	5.627	Schist/Gneiss	Oban massif	Basement	GP 2 (basement)	104,800	1,257,600
6	Ibogo	8.090	5.650	Schist/Gneiss		Basement		68,700	824,400

Table 2
Wet and dry seasons heavy metal content in pond and stream water for the different barite abandoned mine sites (Location of mine sites are shown on Fig. 1).

Season	Barite mine site	Sample code	Sample type	Group	Longitude East	Latitude North	Wet							Dry								
							As	Ba	Fe	Hg	Mn	Ni	Pb	Zn	As	Ba	Fe	Hg	Mn	Ni	Pb	Zn
							mg/l															
	Nde	Mine site	Pond water	GP 1	8.608	6.053	0.002	0.01	1.2	0.02	0.4	0.03	0.92	0.3	0	0.11	0.52	0.001	0.36	0.004	3.03	1.7
		ND 1	Stream water	Sedimentary	8.590	6.054	0.013	0.4	0.8	0.03	0.44	0.001	0.03	0.32	0.001	0.25	2.62	0.001	0.14	0.004	0	0.13
		ND 2			8.595	6.060	0.014	0.3	0.6	0.03	0.46	0.002	0.03	0.2	0.001	0.11	2	0.001	0.26	0.003	0.01	0.7
		ND 3			8.600	6.066	0.018	0.2	0.5	0.2	0.5	0.001	0.04	0.08	0	0.3	1.6	0.001	0.42	0.002	0.008	0.06
		ND 4			8.608	6.072	0.01	0.104	0.34	0.01	0.53	0.002	0.03	0.01	0	0.12	1.14	0.002	0.01	0.003	0.012	0.02
	Alese	Mine site	Pond water		8.495	5.955	0.006	0.092	1.55	0.01	0.3	0.002	0.03	0.24	0.001	0.11	0.5	0.001	0.33	0.036	0.03	0.16
		AL 1	Stream water		8.508	5.967	0.004	0.058	0.96	0.01	0.12	0.006	0.02	0.01	0	0.2	1.14	0.002	0.02	0.002	0.48	0.01
		AL 2			8.506	5.959	0.005	0.27	0.03	0	0.13	0.002	0.01	0.2	0	0.2	1.2	0.003	0.02	0.003	0.06	0.02
		AL 3			8.501	5.949	0.001	0.06	1.2	0	0.03	0.002	0.01	0.18	0	1.2	0.22	0.002	0.03	0	0.01	0.01
		AL 4			8.494	5.943	0	0.051	0.8	0	0.01	0.002	0.02	0.16	0	1	0.55	0	0.02	0	0.02	0.01
	Okumeritet	Mine site	Pond water		8.392	5.895	0.005	0.27	0.03	0.01	0.13	0.003	0.22	0.06	0.001	0.12	3.12	0.001	0.34	0.002	0.03	0.13
		OK 1	Stream water		8.373	5.896	0.004	0.1	0.1	0.01	0.16	0.004	0.03	0.07	0.001	0.11	2.2	0.001	0.07	0.013	0.01	0.02
		OK 2			8.379	5.892	0.003	0.08	0.02	0	0.12	0	0	0.04	0.001	0.12	1.6	0.001	0.08	0.004	1.03	0.04
		OK 3			8.386	5.885	0.002	0.08	0.02	0	0.11	0	0.01	0.07	0.001	0.1	1.2	0.001	0.1	0.002	0.02	0.02
		OK 4			8.394	5.879	0.001	0.07	0.1	0	0.1	0.001	0.02	0.04	0.001	0.08	0.5	0.004	0.04	0.001	0.04	0.04
	Iyemetet	Mine site	Pond water		8.357	5.862	0	0.1	0.3	0.01	0.14	0.007	0.08	0.07	0.001	0.9	0.71	0.1	1.11	0.042	1.01	0.02
		IY 1	Stream water		8.343	5.847	0.001	0.103	0.4	0.01	0	0	0.04	0.03	0	0.71	4.7	0.004	0.41	0.003	0.08	0.04
		IY 2			8.352	5.849	0.001	0.1	0.43	0	0	0.002	0.03	0.02	0.003	0.15	0.7	0	0.03	0.01	0.04	0.02
		IY 3			8.364	5.850	0	0.094	0.05	0	0.12	0.001	0	0.01	0.005	0.21	0.66	0.001	0.03	0.001	0.02	0.02
		IY 4			8.375	5.848	0	0.074	0.04	0	0.02	0	0	0.05	0.003	0.05	0.6	0.001	0	0	0.03	0.01
	Akpet I	Mine site	Pond water	GP 2	8.090	5.650	0.01	0.5	0.43	0.04	0	0.002	0.02	0.24	0.002	0.62	3.6	0.001	0.3	0.006	0.01	0.7
		AK 1	Stream water	Basement	8.098	5.680	0	0.434	0.08	0.01	0.01	0.002	0	0.07	0.002	0.42	1.6	0	0.1	0.002	0.03	0.04
		AK 2			8.103	5.688	0.001	0.3	0.2	0.01	0.01	0	0	0.03	0.002	0.6	2	0.01	0.04	0.003	0.01	0.02
		AK 3			8.108	5.695	0.001	0.08	0.1	0	0	0	0	0.02	0.001	0.5	0.8	0	0.1	0.002	0.01	0.01
		AK 4			8.117	5.697	0	0.02	0.08	0	0.02	0	0	0.01	0	0.03	0	0	0.002	0.008	0.008	0.01
	Ibogo	Mine site	Pond water		8.147	5.627	0.008	0.364	0.45	0.02	0.13	0.003	0.02	0.17	0	2	0.07	0.02	0.2	0.005	0.06	0.88
		IB 1	Stream water		8.152	5.638	0	0.504	1.9	0.02	0.06	0.001	0	0.04	0	0.86	13.8	0.5	0.3	0.002	0.01	0.04
		IB 2			8.151	5.647	0.001	0.2	1.5	0.01	0.02	0.001	0	0.06	0.002	1.2	12	0.03	0.06	0.002	0.02	0.03
		IB 3			8.157	5.652	0.001	0.1	0.92	0.01	0.01	0	0.02	0.06	0.004	0	6.2	0.01	0.4	0.003	0.003	0.02
		IB 4			8.164	5.659	0	0.06	0.43	0.01	0.01	0	0	0.04	0.002	0.8	1.22	0.02	0.6	0.002	0.004	0.01

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investigation was not conducted on crops, human and animal tissues.

Contamination index here has been used to identify the enrichment of heavy metals with respect to the maximum admissible limit (MAL) standards (SON, 2007; WHO, 2008). Where there was a discrepancy between the SON (SON, 2007) and WHO (WHO, 2008) values, the average was computed (e.g. Mn = 0.3 mg/l and Ni = 0.045 mg/l). The contamination indexes for the potentially toxic elements (PTEs) in the pond and stream water have been calculated as in Eq. (1):

$$CI_z = [As_{ij}/0.01 + Ba_{ij}/0.7 + Fe_{ij}/0.3 + Hg_{ij}/0.001 + Mn_{ij}/0.3 + Ni_{ij}/0.045 + Pb_{ij}/0.01 + Zn_{ij}/3]/8 \quad (1)$$

where CI_z is contamination index and numerator determined concentration of As_{ij} , Ba_{ij} , Fe_{ij} , Hg_{ij} , Mn_{ij} , Ni_{ij} , Pb_{ij} and Zn_{ij} at each sampling site for wet and dry seasons (60 samples). The concentrations of elements are given in Table 2. Contamination index is classified as $CI > 5$ (contaminated), $CI 1-5$ (slightly contaminated) and $CI < 1$ (not contaminated).

To further determine the magnitude contribution of each metal to toxicity of the area, the single factor index (Nemerow pollution index, Yang et al., 2013) was applied. The single-factor pollution index can evaluate the pollution of single contamination and is used to establish water quality parameters. The Nemerow pollution index is widely applied to reflect the total pollution level and evaluate environmental quality. The Nemerow pollution index is calculated as follows:

$$P_{ij} = C_{ij}/S_{ij} \quad (2)$$

$$P_{ave} = 1/12 \sum P_{ij} \quad (3)$$

$$P_{ij} = \sqrt{1/2(P_{max}^2 + P_{ave}^2)} \quad (4)$$

where P is the Nemerow pollution index; P_{ij} is the pollution index of the i th potentially toxic element (PTE) in a particular water sample j ; C_{ij} is the measured concentration of the i th PTE in a particular water sample j and S_i is the required standard of the i th PTE (Yang et al., 2013). P_{max} and P_{ave} are respectively the maximum and average values of the pollution indices of all the PTE. P indicates the pollution gradation: $P \leq 1$, water has not been contaminated; $1 < P \leq 2$, water has been slightly contaminated; $2 < P \leq 3$, water has been moderately contaminated; $P > 3$ water has been severely contaminated.

3.3. Risk assessment

Risk assessment is a function of hazard and exposure and is defined as the process of estimating the probability of occurrence of an event and the probable magnitude of adverse health effects on human exposures to environmental hazards over a specified time period (NRC, 1983; Kolluru et al., 1996; Paustenbach, 2002; Wongsasuluk et al., 2014). According to Lee et al. (2005), risk assessment consists of hazard identification, exposure assessment, dose response (toxicity) and risk characterization. The health risk assessment of each potentially toxic metal is usually based

Table 3

The toxicity responses to heavy metals as the oral reference dose (RfD) and oral slope factor (SF).^a

Metals	Oral RfD (mg/kg/day)	Oral SF (mg/kg-day) ⁻¹
As	3.0×10^{-4}	1.5
Cd	5.0×10^{-4}	n.d.
Cr	3.0×10^{-3}	n.d.
Cu	4.0×10^{-2}	n.d.
Hg	3.0×10^{-4}	n.d.
Pb	3.5×10^{-3}	n.d.
Ni	2.0×10^{-2}	n.d.
Zn	0.3	n.d.

^a US EPA IRIS (2011) and n.d. means not determined.

on the quantification of the risk level and is expressed in terms of a carcinogenic or a non-carcinogenic health risk. Two toxicity risk indices reported are the slope factor (SF) for carcinogen risk characterization and the reference dose (RfD) for non-carcinogen characterization (Lim et al., 2008). These ones are shown in Table 3 for each PTE. The estimations of the magnitude, frequency and duration of human exposure to each PTE in the environment are reported as average daily dose, ADD (Siriwong, 2006) for each water sample as:

$$ADD_i = C_i \times IR \times ED \times EF/BW \times AT \quad (6)$$

where ADD is the exposure duration (mg/kg-day), C is the concentration of the contaminant in pond and stream water (mg/l), IR is the ingestion rate per unit time (L/day), ED is the exposure duration (years), EF is the exposure frequency (days/year), BW is body weight (kg), AT is the average time (years). The principal exposure factors that have been taken into account to carry out the risk assessment calculations are shown in Table 4.

The health risk from pond and stream water consumption was assessed in relation to its non-carcinogenic as well as carcinogenic effects based on the calculation of ADD estimates and defined toxicity for each PTE according to the following relationships. The non-carcinogenic was computed as:

$$\text{Hazard quotient(HQ)} = \frac{ADD}{RfD} \quad (7)$$

where ADD and RfD are in mg/kg-day. If HQ exceeds 1.0, there is unacceptable risk of adverse non-carcinogenic effects on health, while if $HQ < 1.0$, it is an acceptable level of risk (Lim et al., 2008). The risk assessments of a mixture of chemicals, the individual HQs are summed to form hazard index (HI):

$$\text{Hazard index(HI}_i) = \sum HQ_i \quad (8)$$

An $HI > 1$ means an unacceptable risk of non-carcinogenic effects on health, while $HI < 1$ means an acceptable level of risk (Lim et al., 2008).

The carcinogenic risk can be calculated as product of ADD (mg/kg-day) times the SF (mg/kg/day). An acceptable value is $\leq 1 \times 10^{-6}$, which means on average the probability is that approximately 1 per 1,000,000 will develop cancer as a consequence of the exposure (Lim et al., 2008). The risks of cancer are expressed in terms of the probability that one may develop cancer at a

Table 4

Input parameters to characterize the ADD value.

Exposure parameters	Symbols	Units	Value	Source
Concentration of water	C	mg/l	Table 6	This study
Exposure duration	ED	Years	30	US EPA (1977)
Exposure Frequency	EF	Days/Year	350	US EPA (1977)
Average time	AT	Years	52	World Bank (2014)
Body weight	BW	Kg	60	Wongsasuluk et al. (2014)
Ingestion rate	IR	L/day	2	EPA (2004)

given lifetime exposure level. The cancer risk probability is determined from the slope factor (SF) of the dose-response curve in the low-dose region where relationship between the exposure dose (measured in mg/kg BW/day) and response (measured in terms of developing cancer) is assumed to be linear. Mathematically, the SF denotes the probability of developing cancer per unit exposure level of mg/kg/day and its values may be obtained from the IRIS database (Lim et al., 2008) as presented in Table 3. The life time exposure level (ADD_{life}) is arrived by prorating the exposure incurred over the exposure duration over the expected life span. According to the IRIS database a slope factor has only been derived for As. Cancer risk is then calculated as follows (Kolluru et al., 1996; Wongsasuluk et al., 2014):

$$\text{Cancer risk} = \text{ADD}_{\text{life}} \times \text{SF} \quad (9)$$

4. Results and discussion

4.1. Overview of pond and stream water quality

Details of the sample locations and results for wet and dry seasons are presented in Table 2. The data show that each location was sampled twice to cover the different seasons. The summary descriptive statistics of physical parameters (Adamu et al., 2014) and trace elements for the pond and stream water for the entire study period are given in Table 5. The average temperatures for pond (PW) and stream (SW) water samples were 29.2° and 29.24°C, respectively. The pond and stream water were moderately acidic with mean pH values of 5.50 for pond water (PW) and 5.86 for stream water (SW). These mean pH values are not within recommended standard for drinking and domestic purposes of 6.5–8.5 (WHO, 2008). The total dissolved solids (TDS) ranged from 30 to 430 mg/l for PW and from 40 to 410 mg/l for SW. These values of TDS are within the stipulated standards of 1000 mg/l for drinking and domestic purposes (WHO, 2008). The mean values of colour/TSS were 154.08 Pt Co/95.54 mg/l for PW and 165.40Pt Co/259.28 mg/l for SW. High colour in SW relative to PW is due to the fact that PW are mainly from the mine site, while SW includes water from the mine sites in addition to activities. These activities include runoff from agricultural lands, bush burning areas, etc.

The mean values for colour for the different water types exceeded 15Pt Co, the standard value for water potability. Dissolved oxygen values were low (<5.0 mg/l) ranging from 2.0 to 4.6 mg/l for PW and from 1.2 to 5.0 mg/l for SW. The average value of hardness for the two water types were below <75.0 mg/l indicating soft water. The different water types are fresh with electrical conductivity (EC) and total dissolved solids (TDS) within the WHO (Yang et al., 2013) limits of 1400 µS/cm [EC] and 1000 mg/l [TDS] respectively for drinking and domestic use.

The abundance of the heavy metals on the average in the pond water was Fe > Ba > Pb > Zn > Mn > Hg > Ni > As, while for stream water the trend was Fe > Ba > Mn > Zn > Pb > Hg > Ni > As (Table 5). The trend is attributed to the different degree of exposure of rocks and different rates of weathering.

4.2. Seasonal variations of physical parameters and heavy metals

The descriptive statistics values of physical parameters (Adamu et al., 2014) and trace elements for the pond and stream water for different sampling seasons are presented in Table 6. The average temperature of the water samples in the dry season (DS) were higher compared to the wet season (WS). The high values of temperature for the dry season are consistent with atmospheric temperature during the sampling period and reflected local climatic conditions. The average values of colour were higher in the WS relative to the DS. This is due to the fact that high volume of surface

Table 5 Statistical summary of physical parameters^a and trace elements of pond and stream water.

Source	Parameter/statistics	Unit	Pond water				Stream water				WHO [20] ^a	SON [21] ^b	Average of WHO (2008) and SON (2007)
			Mean	Min	Max	SD	Mean	Min	Max	SD			
Temp	Temp	°C	29.200	28.600	30.000	0.445	29.243	28.000	30.000	0.484			
Colour	Colour	Pt Co	154.077	15.000	470.000	169.853	165.400	3.400	600.000	130.561			
pH	pH		5.502	5.000	6.000	0.421	5.864	4.800	7.000	0.495			
TDS	TDS	mg/l	156.231	30.000	430.000	110.533	151.304	40.000	410.000	94.539			6.5–8.5
EC	EC	µS/cm	229.000	52.000	600.000	153.479	216.500	56.000	520.000	124.737			500
TSS	TSS	mg/l	95.538	8.000	900.000	242.315	259.283	6.000	870.000	254.652			1000
DO	DO	mg/l	3.108	2.000	4.600	0.886	3.120	1.200	5.000	0.968			5
HT	HT	mg/l	14.573	2.300	57.480	14.106	19.244	0.500	112.750	28.133			
As	As	mg/l	0.003	0.010	0.003	0.003	0.002	0.000	0.018	0.004			0.01
Ba	Ba	mg/l	0.433	0.010	2.000	0.561	0.274	0.000	1.200	0.304			
Fe	Fe	mg/l	1.040	0.030	3.600	1.170	1.497	0.000	13.800	2.674			0.3
Hg	Hg	mg/l	0.020	0.001	0.100	0.028	0.020	0.000	0.500	0.077			0.001
Mn	Mn	mg/l	0.312	0.000	1.110	0.279	0.131	0.000	0.600	0.168			0.2
Ni	Ni	mg/l	0.012	0.002	0.042	0.015	0.002	0.000	0.013	0.002			0.02
Pb	Pb	mg/l	0.455	0.010	3.030	0.885	0.048	0.000	1.030	0.160			0.01
Zn	Zn	mg/l	0.389	0.020	1.700	0.488	0.066	0.010	0.700	0.112			0.3

^a Drinking and domestic use TDS – total dissolved solids, EC – electrical conductivity, TSS – total suspended solids, DO – dissolved oxygen, HT – hardness, SD – standard deviation.

^b Adapted from Baidi et al. (1996).

Table 6 Statistical summary of physical parameters^a and trace elements of pond and stream water for different seasons.^b

Source	Season	Statistics	Pond						Stream								
			Wet			Dry			Wet			Dry					
			Mean	Min	Max	SD	Mean	Min	Max	SD	Mean	Min	Max	SD			
Temp	°C	29.143	29.000	30.000	0.378	29.314	28.600	30.000	0.511	28.957	28.000	30.000	0.367	29.530	28.500	30.000	0.415
Colour	Pt Co	155.714	20.000	400.000	165.515	135.571	15.000	470.000	179.515	182.757	3.400	600.000	153.350	148.043	18.000	476.000	103.544
pH		5.429	5.000	6.000	0.535	5.460	4.700	6.000	0.410	5.826	5.000	7.000	0.491	5.903	4.800	6.800	0.506
TDS	mg/l	114.286	30.000	250.000	83.038	194.714	85.000	430.000	117.717	119.478	40.000	390.000	81.496	183.130	44.000	410.000	97.582
EC	µS/cm	158.857	52.000	380.000	115.942	301.000	161.000	600.000	148.017	178.130	56.000	500.000	115.636	254.870	66.000	520.000	124.000
TSS	mg/l	156.714	24.000	900.000	327.797	22.429	8.000	74.000	23.308	426.522	6.000	870.000	267.056	92.043	23.000	200.000	53.321
DO	mg/l	3.186	2.500	4.600	0.906	2.929	2.000	4.300	0.888	3.617	2.400	5.000	0.848	2.622	1.200	4.600	0.823
HT	mg/l	8.786	2.300	22.000	6.982	18.751	3.310	57.480	17.633	8.804	0.500	31.000	8.789	29.684	1.600	112.750	36.246
As	mg/l	0.005	0.000	0.010	0.004	0.001	0.000	0.002	0.001	0.003	0.000	0.018	0.005	0.001	0.000	0.005	0.001
Ba	mg/l	0.223	0.010	0.500	0.188	0.643	0.110	2.000	0.742	0.160	0.020	0.504	0.136	0.388	0.000	1.200	0.379
Fe	mg/l	0.660	0.030	1.550	0.584	1.420	0.070	3.600	1.525	0.483	0.020	1.900	0.514	2.510	0.000	13.800	3.493
Hg	mg/l	0.018	0.010	0.040	0.012	0.021	0.001	0.100	0.040	0.015	0.000	0.200	0.040	0.025	0.000	0.500	0.101
Mn	mg/l	0.183	0.000	0.400	0.143	0.440	0.200	1.110	0.333	0.125	0.000	0.530	0.172	0.137	0.000	0.600	0.168
Ni	mg/l	0.008	0.002	0.030	0.011	0.016	0.002	0.042	0.018	0.001	0.000	0.006	0.001	0.003	0.000	0.013	0.003
Pb	mg/l	0.215	0.020	0.920	0.354	0.695	0.010	3.030	1.209	0.014	0.000	0.040	0.014	0.082	0.000	1.030	0.223
Zn	mg/l	0.180	0.060	0.300	0.098	0.598	0.020	1.700	0.640	0.076	0.010	0.320	0.079	0.056	0.010	0.700	0.139

^a Adapted from Baldi et al. (1996).

^b See Table 5 for explanations on abbreviations.

runoff, which carries a of debris in the wet season compared to the dry season. This in addition, makes the water to be dirty, muddy with high sediment load. The average values of pH displayed acidic nature throughout the different sampling periods. Acidic nature of water is related to atmospheric and soil CO₂, decaying organic matter and composition of mine dump sites (Baldi et al., 1996). The water samples were characterized by low mineralization with total dissolved solids generally less than 1000 mg/l. TDS of the water samples were higher in DS. High TDS values in the dry season are attributed to the effects of evaporation in dry season and low values due to dilution in the wet season. Higher concentration of TSS were recorded in wet season, reflecting high discharge and draining of mine waste areas and ponds into the drainage systems of the abandoned barite mine areas.

The average concentrations of all the metals (As, Ba, Fe, Hg, Mn, Ni, Pb and Zn) were higher in pond water compared to stream water in wet season. Also the concentrations of Ba, Mn, Ni, Pb and Zn were higher in the pond water in dry season. On the other hand, Fe and Hg concentrations were lower in the dry season in pond water compared to stream water samples. As stated earlier, higher concentration of trace elements in the pond water indicates higher dissolution of minerals by pond water due to variations in geochemical parameters. The higher values in dry season could be attributed to the higher temperature leading to evaporation and concentration of ions in solution (Hem, 1985; Singh et al., 2005). On the other hand, lower concentrations of heavy metals obtained in wet season are attributed to the high surface runoff in the wet season leading to dilution and dispersion of trace elements (Maila et al., 2004).

4.3. Spatial variations of parameters

The statistical summary of physical parameters (Baldi et al., 1996) and heavy metals with respect to different geologic areas are given in Table 7. The average values of TDS/EC and most of the trace elements (As, Ba, Fe, Hg, and Zn) are higher in pond water samples from GP 2 relative to GP 1 across the two seasons. However, the average concentrations of Mn, Ni and Pb were higher in pond water samples from GP 1 relative to GP 2. It is also noted that concentration of Fe was similar for pond water in both sedimentary (GP 1) and basement (GP 2) areas.

On the other hand, in respect of stream water, the concentrations of TDS/EC, As, Mn, Ni and Pb were higher in GP 1 relative to GP 2, while the reverse was the case in respect of Ba, Fe, Hg and Zn. Considering the different mine sites, for pond water, no defined patterns of metal distribution in terms of highest and lowest concentration was observed for GP 1. However, for GP 2, highest concentrations for some metals (Ba, Fe, Hg, Mn and Zn) were recorded at Ibogo, a basement site. The stream water followed the same pattern of distribution (Table 8). The reason for these differences is that minerals are easily weathered from sedimentary rocks of Mamfe Embayment (GP1). The spatio-temporal variations of the heavy metals were related to variations in flow regimes, seasons and magnitude of mine waste generated (Adamu et al., 2003; Nganje et al., 2010).

4.4. Association between elements and sources of elements

Pearson correlation analysis showed significant correlation (P < 0.05) of pH with Zn; EC/TDS with Ni, Mn, Pb; Ba with Fe, Hg; Fe with Hg; Mn with Ni, Pb and Pb with Zn (Table 9). Generally, the correlations between other variables were weak (r ≤ ±0.30) and not significant (P > 0.05). Poor correlation was attributed to differences in sources of materials and geochemical behaviour of parameters

Table 7
Statistical summary of physical parameters^a and trace elements of pond and stream water for abandoned barite mines in sedimentary and basement areas.^b

Source	Units	Pond								Stream							
		Sedimentary				Basement				Sedimentary				Basement			
Lithology		GP 1	GP 2							GP 1	GP 2						
Statistics		Mean	Min	Max	SD	Mean	Min	Max	SD	Mean	Min	Max	SD	Mean	Min	Max	SD
Temp	°C	29.250	28.700	30.000	0.421	29.120	28.600	30.000	0.522	29.231	28.000	30.000	0.510	29.271	28.800	30.000	0.434
Colour	Pt Co	53.625	15.000	200.000	62.443	314.800	40.000	470.000	165.091	177.325	3.400	600.000	138.257	138.143	50.000	360.000	110.789
pH		5.668	5.000	6.000	0.403	5.236	5.000	5.640	0.325	5.911	5.000	7.000	0.510	5.759	4.800	6.500	0.457
TDS	mg/l	202.000	40.000	430.000	115.856	83.000	30.000	130.000	47.645	174.625	44.000	410.000	101.605	98.000	40.000	181.000	43.839
EC	μS/cm	286.750	70.000	600.000	164.869	136.600	52.000	210.000	75.874	243.781	66.000	520.000	135.501	154.143	56.000	270.000	63.694
TSS	mg/l	24.750	8.000	40.000	11.399	208.800	10.000	900.000	387.124	238.375	6.000	706.000	207.780	307.071	23.000	870.000	343.492
DO	mg/l	3.013	2.400	4.400	0.768	3.260	2.000	4.600	1.130	3.100	1.200	5.000	0.981	3.164	1.800	4.500	0.971
HT	mg/l	17.541	2.300	57.480	17.465	9.824	5.000	15.100	4.167	23.264	0.500	112.750	32.850	10.055	2.060	20.160	5.974
As	mg/l	0.002	0.000	0.006	0.002	0.005	0.000	0.010	0.005	0.003	0.000	0.018	0.005	0.001	0.000	0.004	0.001
Ba	mg/l	0.214	0.010	0.900	0.286	0.871	0.364	2.000	0.760	0.220	0.050	1.200	0.267	0.382	0.000	1.200	0.353
Fe	mg/l	0.991	0.030	3.120	0.988	1.138	0.070	3.600	1.651	0.907	0.020	4.700	0.962	2.677	0.000	13.800	4.273
Hg	mg/l	0.019	0.001	0.100	0.033	0.020	0.001	0.040	0.016	0.010	0.000	0.200	0.035	0.040	0.000	0.500	0.123
Mn	mg/l	0.389	0.130	1.110	0.308	0.158	0.000	0.300	0.126	0.142	0.000	0.530	0.167	0.109	0.000	0.600	0.173
Ni	mg/l	0.016	0.002	0.042	0.017	0.004	0.002	0.006	0.002	0.002	0.000	0.013	0.003	0.001	0.000	0.003	0.001
Pb	mg/l	0.669	0.030	3.030	1.037	0.028	0.010	0.060	0.022	0.068	0.000	1.030	0.194	0.007	0.000	0.030	0.009
Zn	mg/l	0.335	0.020	1.700	0.559	0.498	0.170	0.880	0.347	0.083	0.010	0.700	0.135	0.032	0.010	0.070	0.019

^a Adapted from Baldi et al. (1996).^b See Table 5 for explanation on abbreviations.
GP 1 – Sedimentary, GP 2 – Basement.**Table 8**
Mean values of physical parameters^a and trace elements of pond and stream water for different barite mines sites in basement and sedimentary areas.^b

Location	Lithology	Group	No of samples Wet & dry seasons	Temp °C	Colour Pt Co	pH	TDS mg/l	EC μS/cm	TSS mg/l	DO mg/l	HT mg/l	As mg/l	Ba mg/l	Fe mg/l	Hg mg/l	Mn mg/l	Ni mg/l	Pb mg/l	Zn mg/l
Nde	Sedimentary	GP 1	2	28.850	33.500	5.100	220.000	270.000	29.500	3.400	8.300	0.001	0.060	0.860	0.011	0.380	0.017	1.975	1.000
Alese			2	29.300	24.500	5.750	159.500	232.000	27.000	2.500	7.115	0.004	0.101	1.025	0.006	0.315	0.019	0.030	0.200
Okumeritet			2	29.100	139.000	6.000	88.500	155.000	19.000	3.700	15.010	0.003	0.195	1.575	0.006	0.235	0.003	0.125	0.095
Iyametet	Basement	GP 2	2	29.750	17.500	5.820	340.000	490.000	23.500	2.450	39.740	0.001	0.500	0.505	0.055	0.625	0.025	0.545	0.045
Akpet 1			2	28.800	332.000	5.320	85.000	135.000	23.000	4.450	10.050	0.006	0.560	2.015	0.021	0.150	0.004	0.015	0.470
Ibogo			2	29.000	40.000	5.000	30.000	52.000	24.000	2.800	6.500	0.004	1.182	0.260	0.020	0.165	0.004	0.040	0.525
Nde	Sedimentary	GP 1	8	29.438	128.375	5.638	178.875	274.750	169.750	2.488	7.483	0.007	0.223	1.200	0.034	0.345	0.002	0.020	0.190
Alese			8	29.213	328.425	5.650	169.375	223.625	209.375	3.375	3.278	0.001	0.380	0.763	0.002	0.048	0.002	0.079	0.075
Okumeritet			8	29.313	140.750	6.100	119.750	147.250	264.375	3.113	39.279	0.002	0.093	0.718	0.002	0.098	0.003	0.145	0.043
Iyametet	Basement	GP 2	8	28.963	111.750	6.255	230.500	329.500	310.000	3.425	43.019	0.002	0.186	0.948	0.002	0.076	0.002	0.030	0.025
Akpet 1			8	29.450	282.000	5.658	113.250	173.625	322.875	2.663	7.660	0.001	0.298	0.608	0.004	0.035	0.001	0.007	0.026
Ibogo			8	29.150	68.500	5.738	85.125	141.250	336.250	3.450	12.751	0.001	0.466	4.746	0.076	0.183	0.001	0.007	0.038

^a Adapted from Baldi et al. (1996).^b See Table 5 for explanation on abbreviations.

Table 9
Correlation matrix for physical parameters and heavy metals.

	Temp	Colour	pH	TDS	EC	TSS	DO	HT	As	Ba	Fe	Hg	Mn	Ni	Pb	Zn
Temp	1.00															
Colour	0.02	1.00														
pH	0.04	0.00	1.00													
TDS	0.07	-0.26	-0.01	1.00												
EC	0.01	-0.26	-0.07	0.92	1.00											
TSS	-0.35	0.19	0.01	-0.19	-0.18	1.00										
DO	-0.74	0.13	-0.03	-0.16	-0.15	0.25	1.00									
HT	0.05	-0.30	0.28	0.48	0.45	-0.18	-0.06	1.00								
As	-0.13	-0.05	-0.21	-0.07	-0.02	-0.05	0.03	-0.11	1.00							
Ba	0.15	0.19	-0.20	-0.02	0.06	-0.16	-0.10	-0.10	-0.03	1.00						
Fe	0.06	-0.17	-0.16	-0.04	0.01	-0.21	-0.01	0.00	-0.11	0.46	1.00					
Hg	-0.13	-0.13	-0.05	-0.03	0.03	-0.07	0.09	-0.03	0.18	0.31	0.61	1.00				
Mn	0.07	-0.32	-0.09	0.28	0.37	-0.28	-0.19	-0.02	0.34	0.23	0.14	0.29	1.00			
Ni	0.10	-0.25	-0.17	0.33	0.30	-0.24	-0.11	0.07	-0.08	0.06	-0.02	0.06	0.54	1.00		
Pb	-0.09	-0.19	-0.20	0.31	0.28	-0.18	0.03	0.11	-0.11	-0.04	-0.06	0.00	0.30	0.30	1.00	
Zn	-0.19	-0.09	-0.32	0.14	0.17	-0.18	0.18	-0.11	0.04	-0.07	-0.02	-0.05	0.22	0.07	0.73	1.00

Bold correlations are significant at $p < 0.05000$.

(Cox, 1995; Edet et al., 2003; Florea et al., 2005; Bhattacharya et al., 2006).

R-mode factor analysis highlighted five factors with eigenvalues >1 and explained 66.22% of total variance in water quality parameters (Table 10). Factor 1 account for 20.95% of data variance with positive loadings on TDS/EC and HT. This was related to natural geochemical processes (mineral dissolution) that released these elements into the hydrological system with attendant increase in ionic concentration and TDS. Factor 2 accounts for 13.67% of data variance with strong positive loadings on Ba, Fe and Hg due to anthropogenic process of barite mining activities (Akpeke, 2008). High loading for Fe in factor 2 is attributed to geogenic processes. Factor 3 accounts for 13.45% of data variance with strong negative loadings on temperature and positive dissolved oxygen. The factor was interpreted to be related to biological process. Factor 4 showed significant positive loadings on Pb and Zn explained 10.02% of total data variance. It is interpreted as reflective of hydrochemical processes (weathering, hydrolysis, leaching, dilution and evaporation) controlling metal distribution of elements in the water. Factor 5 with negative loading for As and Mn explained 8.13%. This is due to natural geochemical processes (weathering and mineral dissolution)

Table 10
Varimax factor loading for physical parameters and heavy metals.

Parameter	Factor				
	1	2	3	4	5
Temp	-0.01	0.01	-0.91	-0.09	0.09
Colour	-0.51	-0.07	-0.02	-0.01	0.34
pH	0.25	-0.18	0.01	-0.54	0.24
TDS	0.85	-0.04	-0.10	0.20	-0.03
EC	0.83	0.04	-0.07	0.21	-0.10
TSS	-0.23	-0.22	0.48	-0.22	0.13
DO	-0.11	0.05	0.86	0.11	0.09
HT	0.77	-0.03	0.01	-0.20	0.19
As	-0.17	-0.08	0.13	-0.10	-0.81
Ba	-0.12	0.71	-0.24	0.08	0.05
Fe	0.02	0.89	-0.02	-0.02	0.07
Hg	0.05	0.77	0.21	-0.11	-0.28
Mn	0.28	0.24	-0.20	0.27	-0.71
Ni	0.34	0.06	-0.24	0.32	-0.36
Pb	0.28	-0.05	0.04	0.83	0.02
Zn	0.03	-0.05	0.17	0.87	-0.03
Eigenval	3.35	2.19	2.15	1.60	1.30
% Total variance	20.95	13.67	13.45	10.02	8.13
Cumul. eigenval	3.35	5.54	7.69	9.29	10.60
% cumul total variance	20.95	34.62	48.07	58.09	66.22

Bold correlations are significant at $p > 0.70000$.

4.5. Contamination assessment

The average levels of parameters in comparison with maximum admissible levels (MAL) for drinking water by SON (2007) and WHO (2008) are presented in Table 5. The Table 1 shows that average concentrations of pH, DO, Fe, Mn, Hg and Pb in pond-and stream water are not within the prescribed MAL standards. Elevated concentration of elements as a result of contamination can be measured in a number of ways. Nishida et al. (1982) and Sundaray et al. (2011) produced pollution index and enrichment ratio respectively (called contamination index, CI in this study).

The contamination class for each site is presented in Table 11. Comparatively, high average values of CI (>5) indicating high contamination are obtained from Nde, Iyametet (PW) and Ibogo (SW). These are related to anthropogenic activities and probably responsible for relatively high enrichment of Mn, Ni, Pb and Zn. This is supported by the fact that the pond water are highly contaminated relative to the stream water.

The Nemerow single-factor pollution indices (P_i) are summarized in Table 12. The averaged P_i values ranked as follows $Fe > Pb > Ba > Zn > Mn > Hg > Ni > As$ for pond water and $Fe > Ba > Mn > Pb > Zn > Hg > Ni > As$ for stream water. The P_i further

Table 11
Contamination indices (CI) and classification for of ponds and streams near abandoned barite mine sites.

Source	Location/values	Nde	Alese	Okumeritet	Iyametet	Akpet 1	Ibogo
Pond	CI values	26.31	1.36	2.50	14.13	3.10	1.87
	Remarks	C	SC	SC	C	SC	SC
Stream	CI values	4.88	1.39	2.20	0.76	0.67	10.00
	Remarks	SC	SC	SC	NC	NC	C

CI – contamination index, NC – not contaminated (CI < 1); SC – slightly contaminated, (CI 1–5); C – contaminated (CI > 5).

Table 12
Nemerow single-factor pollution indices (P).

Source	Metal	Nde	Alese	Okumeritet	P Iyametet	Akpet 1	Ibogo	Mean	Min	Max	SD
Pond	As	0.002	0.005	0.004	0.001	0.008	0.006	0.004	0.001	0.008	0.003
	Ba	0.089	0.106	0.236	0.728	0.591	1.643	0.566	0.089	1.643	0.589
	Fe	1.044	1.314	2.471	0.616	2.917	0.367	1.455	0.367	2.917	1.024
	Hg	0.016	0.008	0.008	0.081	0.032	0.020	0.028	0.008	0.081	0.028
	Mn	0.390	0.323	0.292	0.901	0.237	0.183	0.388	0.183	0.901	0.261
	Ni	0.024	0.029	0.003	0.034	0.005	0.005	0.017	0.003	0.034	0.014
	Pb	2.557	0.030	0.179	0.812	0.018	0.051	0.608	0.018	2.557	1.002
	Zn	1.395	0.221	0.114	0.059	0.596	0.725	0.518	0.059	1.395	0.506
Stream	As	0.008	0.002	0.003	0.003	0.002	0.002	0.003	0.002	0.008	0.002
	Ba	0.279	0.520	0.099	0.317	0.382	0.594	0.365	0.099	0.594	0.178
	Fe	1.477	0.918	0.958	1.924	0.889	6.487	2.109	0.889	6.487	2.183
	Hg	0.076	0.005	0.005	0.005	0.008	0.192	0.048	0.005	0.192	0.076
	Mn	0.407	0.063	0.107	0.155	0.046	0.251	0.171	0.046	0.407	0.137
	Ni	0.003	0.003	0.007	0.005	0.002	0.002	0.004	0.002	0.007	0.002
	Pb	0.022	0.185	0.378	0.047	0.012	0.010	0.109	0.010	0.378	0.148
	Zn	0.345	0.094	0.044	0.030	0.043	0.041	0.100	0.030	0.345	0.122

Table 13
Exposure duration, ADD (mg/kg-day) for pond and stream water.

Source	Location	ADD				
		As	Hg	Ni	Pb	Zn
Pond	Nde	3.23E–05	0.000339	0.000549	0.063735	0.032271
	Alese	0.000113	0.000177	0.000613	0.000968	0.006454
	Okumeritet	9.68E–05	0.000177	8.07E–05	0.004034	0.003066
	Iyametet	1.61E–05	0.001775	0.000791	0.017588	0.001452
	Akpet 1	0.000194	0.000662	0.000129	0.000484	0.015167
	Ibogo	0	0.000323	8.07E–05	0.000968	0.014199
Stream	Nde	0.00023	0.001109	7.26E–05	0.000645	0.006131
	Alese	4.03E–05	6.86E–05	6.86E–05	0.002541	0.00242
	Okumeritet	5.65E–05	6.86E–05	0.000101	0.004679	0.001372
	Iyametet	5.24E–05	6.45E–05	6.86E–05	0.000968	0.000807
	Akpet 1	2.82E–05	0.000121	4.44E–05	0.000234	0.000847
	Ibogo	4.03E–05	0.002461	4.44E–05	0.00023	0.00121

Table 14
Non-carcinogenic risk (hazard quotient, HQ), overall toxic risk (hazard index, HI) and carcinogenic risk (ADD_{life} × SF).

Source	Location	HQ					∑HQ = HI	ADD _{life} × SF
		As	Hg	Ni	Pb	Zn		
Pond	Nde	0.108	1.129	0.027	18.210	0.108	19.582	0.072
	Alese	0.376	0.592	0.031	0.277	0.022	1.297	0.251
	Okumeritet	0.323	0.592	0.004	1.153	0.010	2.081	0.215
	Iyametet	0.054	5.916	0.040	5.025	0.005	11.039	0.036
	Akpet 1	0.645	2.205	0.006	0.138	0.051	3.046	0.430
	Ibogo	0.000	1.076	0.004	0.277	0.047	1.404	0.000
Stream	Nde	0.766	3.698	0.004	0.184	0.020	4.673	0.511
	Alese	0.134	0.229	0.003	0.726	0.008	1.101	0.090
	Okumeritet	0.188	0.229	0.005	1.337	0.005	1.763	0.125
	Iyametet	0.175	0.215	0.003	0.277	0.003	0.673	0.117
	Akpet 1	0.094	0.403	0.002	0.067	0.003	0.569	0.063
	Ibogo	0.134	8.202	0.002	0.066	0.004	8.409	0.090

indicated that the ponds and stream waters were strongly contaminated with Fe, Hg and Pb.

Table 13 summarizes the outcomes of the ADD estimates for As, Hg, Ni, Pb and Zn with pond and stream ways. The HQ values for As, Hg, Ni, Pb and Zn were all <1. The human risk assessment of As, Hg, Ni, Pb, and Zn showed HQ values suggesting an acceptable level of non-carcinogenic adverse health risk (Table 14) in majority of the cases. However, HQ values show unacceptable risk for Hg (at Nde, Iyametet, Akpet I and Ibogo) and Hg, Pb (at Nde, Okumeritet and Iyametet) in pond water. Hg and Pb also showed unacceptable risk for in stream water at Okumeritet. This is consistent with the absence of any reported significant non carcinogenic risk from these PTEs by oral exposure. The HI values of all the PTEs (As, Hg, Ni, Pb, Zn) ranged from 0.515 to 11.128 for pond water and from 0.293 to 4.851 for stream water. The HI values for pond water at Nde, Alese, Okumeritet, Iyametet, Akpet I and Ibogo were >1. Also, the stream water at Nde, Alese, Okumeritet and Ibogo showed HI values >1, indicating unacceptable risk for non-carcinogenic adverse health effect.

For the study area, only As is a carcinogen. The mean cancer risks of being exposed to As by the drinking water ranges from 0 to 5.53×10^{-6} (PW) and from 0 to 7.60×10^{-5} (SW) (Table 14). The As cancer risk through drinking water does not exceed the acceptable risk of 1 in 10,000 (0.0001) for regulatory purposes.

5. Summary and conclusion

The present investigation was to appraise the degree of contamination and human risk assessment due to abandoned barite mine sites. The study has shown varying trends of contamination by different elements based on two methods, Contamination index and Nemerow pollution index, while human health risk assessment indicated the health risk through drinking water from the ponds and streams in the area. The study is summarized as follows:

1. The average concentration of Fe, Hg, and Pb were above the required standards and despite the fact that the average concentration of As, Ba, Mn, Ni and Zn were below required standards, the mining activities at all sites impacted the sediments quality.
2. The mean concentrations of Ba, Fe, Hg, Mn, Ni, Pb and Zn were higher in pond water compared to stream water in wet season.
3. Fe, Hg, Mn, Ni, Pb, and Zn were higher in pond water samples from sedimentary relative to basement across different seasons. However, the mean concentrations of As, Ba, Pb and Fe were higher in pond water samples from basement area compared to sedimentary area. On the other hand, in respect of stream water, Hg, Mn, Ni and Pb are higher in sedimentary area relative to basement area, while the reverse is the case for As, Ba, Fe and Zn.
4. Factor analysis indicated four factors have been interpreted to be related to natural input from parent material (weathering and mineral dissolution), anthropogenic activities, biological process and geogenic (hydrochemical) processes controlling metal distribution (weathering, hydrolysis, leaching, dilution and evaporation).
5. Contamination index showed contaminated pond water at Nde and Iyametet, while Nemerow pollution index, P_i indicated that the ponds and stream waters are strongly contaminated with Fe, Hg and Pb
6. The human risk assessment of some heavy metals (As, Hg, Ni, Pb, and Zn) showed hazard quotient (HQ) and Hazard index (HI) values suggesting an acceptable level of non-carcinogenic adverse health risk with values <1. However, Hg and Pb for some locations showed HQ values >1, indicating an unacceptable non carcinogenic health risk in these locations. These locations are

Nde, Iyametet, Akpet I and Ibogo) for Hg and Nde, Okumeritet and Iyametet for Pb

7. The cancer risk of As through drinking water is within acceptable risk.

It can therefore be concluded that barite mining has caused pollution by Fe, Hg and Pb of ponds and streams in abandoned mine areas of the study area. The pollution due to barite mining has not been attention compared to ore minerals, especially in low income country. This study is expected to led to the formulation of clear policies in Nigeria in particular and the world at large on environmental management and sustainable development due to barite mining.

Conflict of interest

There is no conflict of interest in this MS.

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