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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  $05^{\circ}30'-06^{\circ}10'$  North and longitudes  $08^{\circ}00'-08^{\circ}50'$  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  $30^{\circ}$ 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 1 and Ibogo are located in the Preccambrian 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 15,000m2 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 Okurumetet. 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- $\mu$ m memebrane. 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

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