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Physicochemical Studies for Risk Identification, Assessment, and Characterization of Artisanal Barite Mining in Nigeria

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Citation: Afolayan, D.O.; Eggleston, C.M.; Onwualu, A.P.; Adetunji, A.R.; Tao, M.; Amankwah, R.K. Physicochemical Studies for Risk Identification, Assessment, and Characterization of Artisanal Barite Mining in Nigeria. *Sustainability* **2021**, *13*, 12982. https://doi.org/10.3390/su132312982

Academic Editor: Franco Ajmone Marsan

Received: 16 September 2021
Accepted: 25 October 2021
Published: 24 November 2021

Abstract: Over 90% of barite mining activities in Nigeria are carried out by artisanal and small-scale miners (ASMs), and up to 75% of these miners operate informally, without mining license and rights. Such mining activities endanger human lives through the uncontrolled release of toxic heavy metals and other pollutants which are major causes and consequences of severe health hazards in children and adults living close to the mining sites. This paper is in two parts. The first section assesses the extent of heavy metal contamination of Cd, Cu, Fe, Pb, Ba, and Zn in drinking water by the mine water and tailing effluents. The second section estimates heavy metals' toxicity and exposure level and analyzes and characterizes other human health risks in tailing effluents selected from three barite mining sites in Nigeria. Inductively coupled plasma mass spectroscopy (ICP-MS) results show that the concentrations of Ba and Pb among other heavy metals are above the allowable limits for drinking water. Index of geo-accumulation (Igeo) and contamination factor (CF) for Ba, Fe, and Pb were classified as moderately to extremely polluted (based on the Igeo) and highly contaminated (based on the CF). The calculated non-carcinogenic risk for Ba is 0.87 and 0.99 for Pb. HQ/HI (health quotient/health index) for Zn, Cu, and Fe is $\leq$0.005. The results indicate that some precautionary measures should be taken to avert the non-carcinogenic risk of Ba and Pb. It is important that barite mining is carried out in a responsible manner, respecting local and national mining laws and global environmental standards.

Keywords: contamination factor; hazard index; maximally exposed individual; artisanal barite mining; barite dosage

1. Introduction

Mining and processing of minerals have a significant impact on economic well-being in several ways [1–3]. The abundant supply of cheap labor, limited availability of capital, lack of advanced methods and technologies for mineral exploitation, and poor existing transportation networks, together with an urgent demand for minerals both within the continent and abroad, have led to the rapid establishment of mining activities, without due consideration of many types of consequences [4,5]. Nigeria and most countries in Africa have not attained their full potential in hazard and fatality response management in mining due to the lack of capital and technological means to identify mining hazards and to assess and characterize potential risks to human health as is necessary to improve the safety of the miners [4,6,7].

Recently, the Nigerian government has identified seven strategic minerals for attention and has proposed a ban on their importation to help stimulate the local mining industry and improve the nation's economic prosperity [8]. These include coal, Fe ore, bitumen, gold (Au), limestones, lead-zinc (Pb-Zn), and barite [8]. However, an enabling environment for mining these strategic minerals remains a major concern. Barite ore, among others, contains non-barite minerals with associated metals such as Pb, Zn, Sn, Cu, Cd, Fe, and others [9,10]. These elements and compounds constitute a threat to mining communities' health and well-being during mining and mineral processing [4,11]. Huge barite deposits are formed along river beds, and the mined pits are usually submerged with water. Overflow from these pits finds its way into major streams within the mining communities which are flooded to cover a wider area around the river bank during the wet season, as shown in Figure 1 [5,12]. The barite pits serve as ponds for fishing, and their water is used for bathing, drinking, washing clothes, and harvesting crops during the dry season.

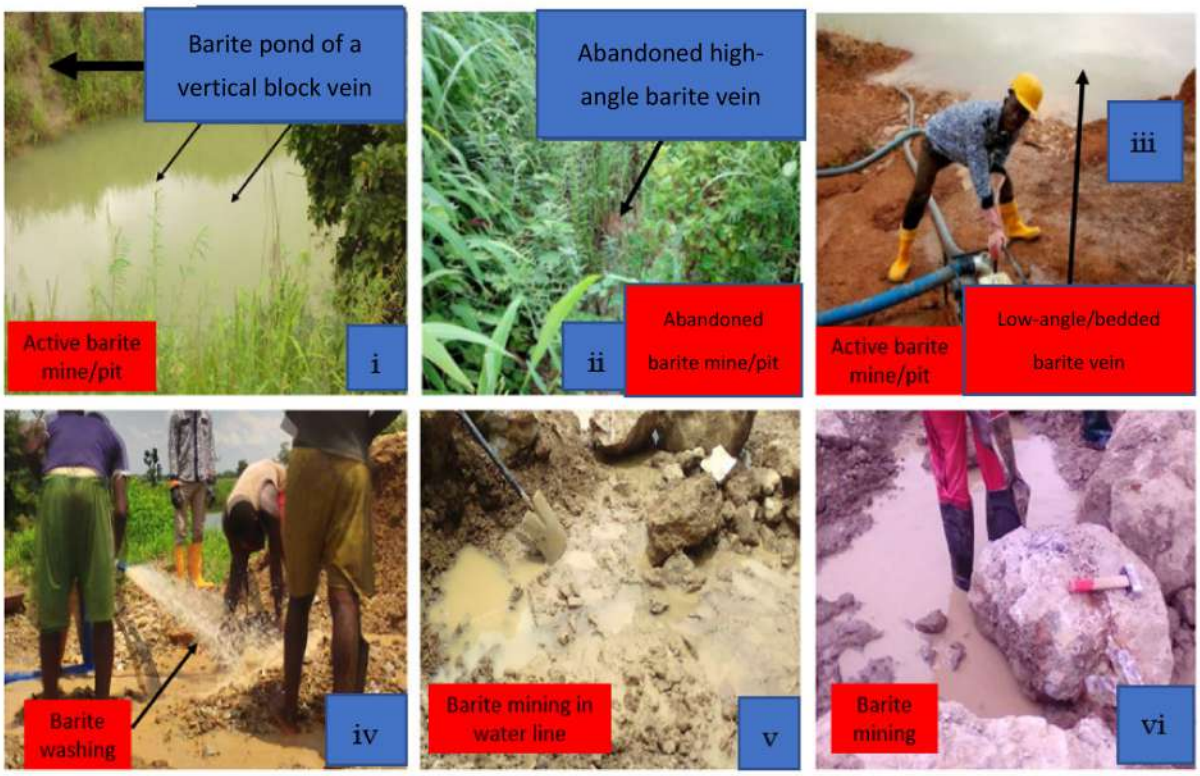


Figure 1. Barite mines and mining activities at barite fields under study ((**i**–**iii**): active and abandoned barite pits in Nigerian barite fields, (**iv**–**vi**): washing and pre-processing of barite ores).

Several works have examined and analyzed heavy metal contamination of water and the environment due to geologic and anthropogenic activities such as artisanal mining and mineral extraction activities [9–17] and other sources [18,19]. Such research focused on the determination of ecotoxicity levels in soils, arable crops, vegetables, aquatic lives, and the environment and assessed health hazards due to mining at gold, Pb-Zn-F, coal, granite, silica/sand, Pb, Fe ore, and barite mines [14–16,20–33]. However, scientific information about heavy metal contamination and the danger imposed on human lives and the environment due to barite mining is still often unknown and reliable data relatively scarce [4].

Research articles in the literature on heavy metal contamination due to barite mining primarily have emphasized the toxicity of heavy metals other than barium [11,16,17,20,34,35]. Studies on the heavy metal contamination due to barite mining focused on commonly known heavy metals such as Pb, As, Mn, Cr, and Cd. Research works similar to the present study focused on the hydrochemical analysis of water samples from ponds and rivers close to barite mines and human health risk assessment [36,37]. These few pieces of work also presented valid safety assessments of barite mining based on local and national health and environmental standards [26,38,39]. This work may be sufficient if barite mining in Nigeria and Africa is to be carried out by local-investor-backed companies following environmental best practices. However, barite, like any other minerals of interest, is mined by artisans and operated informally [5,38,40]. Barium dosage above 4 g/day can cause acute diseases and is dangerous to the entire ecosystem's well-being over a long time [37–40]. Barite mineral, although non-carcinogenic, may be associated with lead sulfide (PbS) and encrusted with FeS_2 or Fe-FeS_2 microcrystals. Sulfuric acid mine runoff is unavoidable when barite tailings containing sulfide minerals are exposed to water and oxygen [37,41,42]. Thus, it is necessary to assess the poisonous level of barium as a heavy metal that forms part of the total toxic index to ensure the safety of miners, mining communities, mammals, and the entire ecosystem. The knowledge generated will be useful for modifying ASMs in Nigeria.

This work identified heavy metal contaminants in mine water samples and effluents of barite tailings randomly selected from three barite mining sites in Northeastern and Northcentral Nigeria. It examined the contribution of ASMs in barite mining and extraction to water contamination/pollution with and without the interference of any geologic processes (erosion, landforms, depositions, and weathering processes). The extent of pollution caused by artisanal mining activities and its consequences for the ecosystem and human health were assessed.

2. Materials and Methods

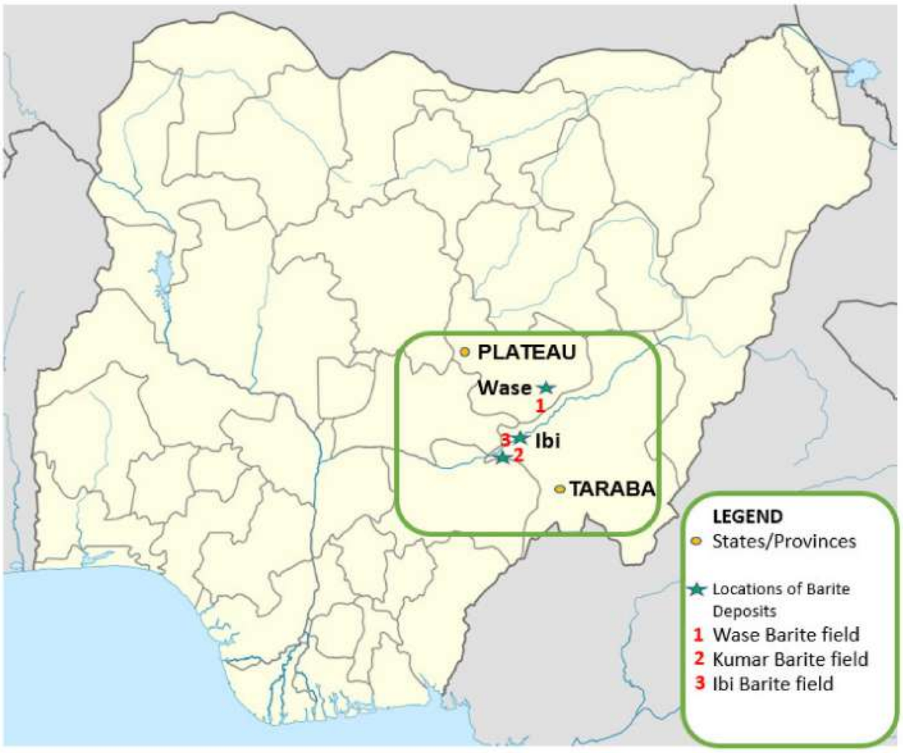
2.1. Sample Collection, Chemical Digestion, and Analytical Methods

Barite rocks were randomly sampled from Ibi, Wase, and Kumar barite sites (not less than 15 barite rock samples were taken from each site between July and September 2019). These were pulverized and digested using 2 mL of hydrochloric acid (98%), 10 mL of sulfuric acid (97%), and 5 mL of nitric acid (68%) (Lab Alley, Spicewood, TX, USA; Palmer Eldritch, USA; Alliance Chemicals, Taylor, TX, USA). These samples were filtered to remove non-soluble particles and labeled as KB1, IB1, WB1, KB2, IB2, and WB2. Digestates (filtrates of the digested samples) of barite tailings (tailing effluents) and powder samples were analyzed using ICP-MS. Chemical absorption and digestion of samples were performed at the Environmental and Water Research Laboratories, Civil and Environmental Engineering Department, Worcester Polytechnic Institute, USA. Similarly, tailing effluents and water samples were analyzed at the Wole Soboyejo Biomaterial Laboratories, Worcester Polytechnic Institute, USA.

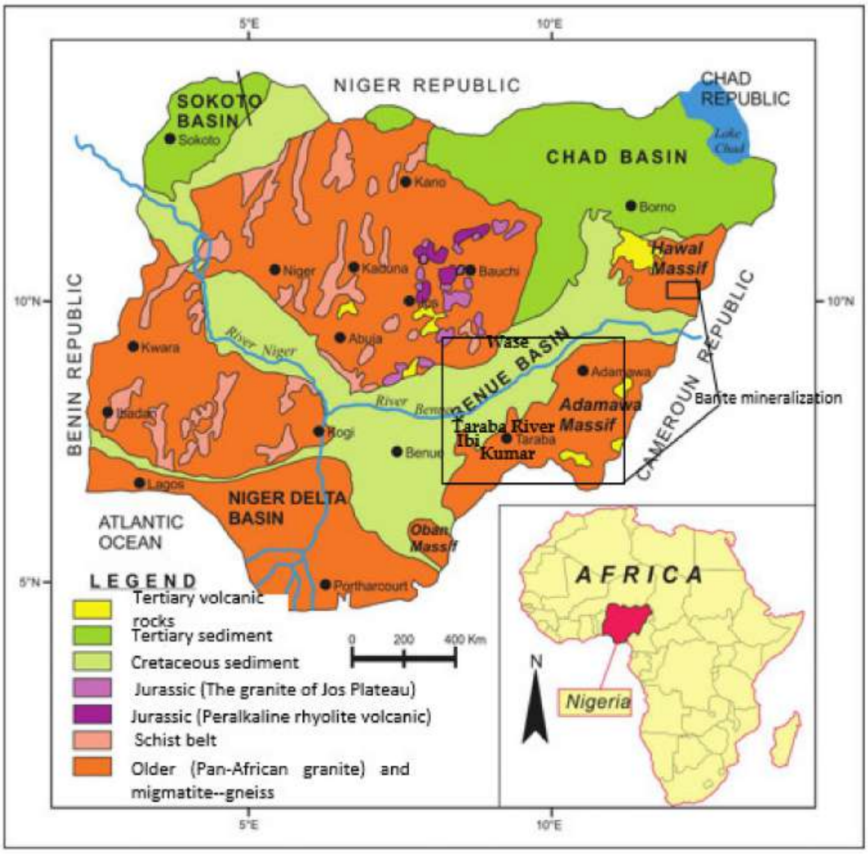
The safety of barite mining was assessed by comparing the heavy metal concentration in mine water and tailing effluents with environmental and health standards (World Health Organization (WHO), European Union (EU), Nigerian Standard for Drinking Water Quality (NSDWQ), Nigerian Industrial Standard (NIS), United States Environmental Protection Agency (US EPA), and China Ministry of Health National Standards (CMHNS)) [43–49]. This study was limited to analyzing mine water samples and digestates of mine tailings from the abandoned and active mining sites. Thus, no medical examination was performed as part of this study.

2.2. Site Description

The mineralized zone of the Nigerian Benue Trough consists of the upper, middle, and lower divisions. The central geological structure forms part of the broader West and Central African Rift System within the Trough. During a series of Cretaceous stages, these activities led to the formation of mineral deposits overlaid with Tertiary and more recent sediments. The Trough was formed by rifting the central West African basement, beginning in the Cretaceous period, and accumulated sediments deposited by rivers and lakes as shown in Figures 1 and 2 [7,41,42,44–52]. The basin subsided and was covered by seafloor sediments accumulated under oxygen-deficient bottom conditions during the late early to middle Cretaceous. As the southern Atlantic Ocean started to open up in the Cretaceous, sedimentary rocks formed in the rift valleys, and volcanic rocks such as basalt occurred along the edges of the rift. These igneous–metamorphic rock mixes are hosts to minerals such as barite, calcite, galena, hematite, magnetite, and a host of others [12,51,53,54].



(**a**)



(**b**)

Figure 2. (**a**) Map of Nigeria showing the study areas. (**b**) Simplified geological map of Nigeria showing the igneous and metamorphic outcrops of the Precambrian Basement Complex, other rocks as major aquifers, water reserves, and some spotlights of barite mineralization within the study areas and other extended mineral ore concentrations (modified/adapted from [55]).

The middle section of the Trough contains several barite veins formed at the late early to middle Cretaceous and toward the end of the Cretaceous. The veins formed in the first phase of deformation vary in quality due to the presence of non-barite minerals [12,54]. The current study characterized sources of health hazards traceable to heavy metal contamination caused by barium and other non-barium metals in barite tailings and ponds at Ibi, Wase, Kumar, and other selected barite fields, as shown in Figure 2a,b.

The barite mining sites are characterized by an equatorial climate with dry and wet seasons and with an average daily temperature that ranges between 25 °C and 35 °C across the year [56,57]. The wet season usually covers April to October, with the mean annual rainfall between 1000 mm and 1350 mm. Moreover, with the presence of the Benue and Taraba Rivers as the major basin, the area is heavily subjected to gullies and massive flooding due to natural events (hazards) and anthropogenic activities (barite mining). There are ferruginous tropical soils and alluvial soils (classified as Ferric Luvisol and Fluvisols), which are derived from the crystalline acid rocks of the basement complex [56]. Wase site is characterized by quaternary sedimentary deposits and weathered and tectonically fractured zones of crystalline rocks. Groundwater circulation occurs partly through fractured crystalline and volcanic rocks and partly within alluvial, eluvial, colluvial, and chemically degraded deposits. These aquifers host and distribute soil water and are disturbed by mining activities. Mining excavations, drilling, and open and blasted wells create direct access to groundwater. They are contaminated by the oxidation of abandoned mine tailings, leaching of heavy metals, and drainage of materials from active and abandoned mines [36,58–60]. Thus, the groundwater, which is a major source of freshwater within the mining areas, is distributed based on the volume of rainfall, streamflow, weathering and mining activities, and the texture and structure of the rocks.

2.3. Characterization of Mine Water Sample

2.3.1. Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) Analysis of Water Samples

The elemental composition of the samples was measured using PerkinElmer ICP mass spectrometer, NexION^{TM} 350X Model (PerkinElmer Company, Waltham, MA, USA). The equipment can identify and measure concentration of metal ions, with a wide dynamic range and high-level sensibility. The digestates of barite tailings or extracts were diluted to 1% (100 times). With an ultra-purity level of 99.9%, argon was used as carrier gas and produced partially ionizing plasma that excites the ions in the water samples injected into the mass spectrometer. ICP-MS calibration was performed using standard solutions (0.1 ppm, 0.4 ppm, 0.6 ppm, and 1 ppm) (as recommended by the National Institute of Standards and Technology). The R^2 values obtained by the calibration curves (>0.996) justified the accuracy of the calibration procedures. The concentration of various elements was compared using values obtained during the calibration, and the concentration of each element is presented in parts per million (ppm) or mg/L. The differences were less than 15%. In case of higher concentration, the solution was diluted and re-analyzed to ensure accurate heavy metal quantification of the digestates (analyzed water samples). The limit of detection (LOD) and limit of quantification (LOQ) for each metal are presented in Table A5 (Appendix A).

2.3.2. Heavy Metal Toxic Unit (TU) of Mine Water

The toxic unit (TU) is the ratio of metals' calculated concentration in a liquid medium to the severe-effect level (SEL) value. TU presents potential acute toxicity limits for the contaminants in the media. The sum of low-effect levels (LELs) for metals under consideration for this study is 4. Potential acute toxicity of the media occurs whenever the sum of the toxic units is greater than 4 (that means the toxicity of one or more metals in the media exceeds the recommended LEL). Thus, the sum of toxicity values of metals in a medium cannot sufficiently pose/cause acute toxicity in humans if the value is less than 4 and each toxic unit is far below the lowest LEL [35,61,62].

$$TU = \frac{\text{Concentration of metal in media}}{\text{SEL}} \quad (1)$$

Under a given condition, the SEL values for Zn, Cu, Fe, Pb, and Cd are shown in Table 1 [53,63–69].

Table 1. SEL and TU of heavy metals in the environment.

Heavy Metals	Severe-Effect Level (SEL)	TU (mg/L)	Standards
Zn	820	3.0–5.0	EU, NIS, US EPA [45,62,70]
Cd	10	0.001–0.005	EU, NIS, US EPA [53,64–66,69]
Cu	110	1.3–3.0	EU, NIS, US EPA [45,71]
Ba	Not yet reported	0.7–4.0	EU, NIS, US EPA [46]
Fe	4	0.3	EU, NIS, US EPA [46,62,71]
Pb	250	0.005–0.01	EU, NIS, US EPA [62,71,72]

EU: European Union, NIS: Nigerian Industrial Standard, US EPA: United States Environmental Protection Agency.

The SEL value for Ba was not available in the literature, as shown in Table 1. However, the TU for Ba compounds, soluble and insoluble, is reported and found to be between TUs for Cu and Fe. Thus, TUs and SELs for Cu and Fe were used to obtain an approximate SEL value for Ba by applying the linear interpolation formula. The SEL value of 64.6 was calculated using Equation (2) and used in this study based on the SEL values of Cu and Fe.

Equation (2) is obtained by substituting the dependent variables and variables at different points, where Ba (independent variable), Fe (1), and Cu (2), respectively.

$$SEL_{Ba} = \frac{(MAL_{Ba} - MAL_{Fe})(SEL_{Cu} - SEL_{Fe})}{(MAL_{Cu} - MAL_{Fe})} + SEL_{Fe} \quad (2)$$

where:

SEL_{Ba} : SEL for barium
SEL_{Cu} : SEL for copper
SEL_{Fe} : SEL for iron
MAL_{Ba} : maximum allowable limit for barium
MAL_{Cu} : maximum allowable limit for copper
MAL_{Fe} : maximum allowable limit for iron

2.4. Quantitative Risk Analysis and Calculation

2.4.1. Contamination Assessment

This describes the extent to which Ba, Fe, Zn, Pb, Cu, and Cd contaminate water in the ponds, rivers, and other water used for different activities by the artisanal miners and mining communities.

Geo-Accumulation Index (Igeo)

Muller (1969) calculated and classified the geo-accumulation index (Igeo) using Equation (3) [73].

$$Igeo = log_2 \frac{C_n}{1.5 \times B_n} \quad (3)$$

C_n is the concentration of metal in water samples (mg/L or ppm), and B_n is the metal concentration in water before the introduction of metals due to mining activities (mg/L or ppm). The constant value of 1.5 is a correction factor introduced into the equation to minimize the degree of deviation in the background values due to the lithologic variations in the water. Thus, the sample is unpolluted when Igeo < 0; unpolluted to moderately polluted (0 ≤ Igeo < 1); moderately polluted (1 ≤ Igeo < 2); moderately to severely polluted (2 ≤ Igeo < 3); severely polluted (3 ≤ Igeo <4); severely to enormously polluted (4 ≤ Igeo < 5); and enormously polluted (Igeo ≥ 5).

Contamination Factor (CF)

The contamination factor (CF) is a single-element index and classifies water contamination according to the work of Hakanson (1980). The contamination is low for CF < 1; moderately contaminated for 1≤ CF < 3; significantly contaminated for 3 ≤ CF < 6; and very high contamination for CF ≥ 6. The expression for CF is given in Equation (4). In this study, the CF for all elements in the tailing effluents is defined as the CF of the mining environment. This is limited to water samples from barite ponds and tailings within the three artisanal barite mining sites under study [74].

$$\mathrm{CF} = \frac{\mathrm{CM}}{\mathrm{CB}} \quad (4)$$

CF is the contamination factor (dimensionless/unitless), CM is the mean metal concentration (mg/L), and CB is the concentration of elements in the background sample (mg/L).

2.4.2. Health Risk Assessment and Chronic Daily Intake (CDI)

Metals transported by water or dispersed as sediments in the water get into the human body through the oral and dermal pathways. Muhammad et al. (2011) defined oral ingestion through drinking water as the chronic daily intake (CDI), which is given in Equation (5) [75,76]. The CDI expresses the degree of toxicity of heavy metals and presents the risk level. In risk assessment, CDIs are compared to the maximum tolerable daily intake (MTDI). The daily intake is described as chronic when the daily dose exceeds MTDI (CDI > MTDI). CDI varies as a function of mean heavy metal concentration in water, dose intake, and body weight:

$$CDI\left(\frac{\mu\mathrm{g}}{\mathrm{kg\ day}}\right) = \frac{C_{MW} \times IR}{BW} \quad (5)$$

C_{MW} is the concentration of heavy metals in water (mg/L), and BW and IR are the body weight (kg) and daily water ingestion rate (mg/day), respectively. These values are taken from Tables A1–A3 in Appendix A [23,43,44,46,47,49,72,77].

2.4.3. Exposure Assessment

US EPA (2016) and Adewumi and Laniyan (2020) calculated the average annual exposure to heavy metals in water samples due to oral ingestion (EXP_{ing}) and dermal (skin) exposure (EXP_{dem}) using Equations (6) and (7), respectively.

$$EXP_{ing} = \frac{CM_0 \times I_R \times E_F \times E_D}{B_W \times AT} \quad (6)$$

$$EXP_{derm} = \frac{CM_0 \times I_R \times E_F \times E_D \times S_A \times P_C \times CF}{B_W \times AT} \quad (7)$$

EXP_{ing} and EXP_{derm} are the exposure dose rate through ingestion (mg kg^{-1}d^{-1}) and diffusion through the skin (dermal pathway) (mg kg^{-1}d^{-1}); CM_0: concentration of heavy metals in the sample (mg/L); I_R: ingestion rate (mg/day); E_F: exposure frequency (days/year); E_D: exposure duration (years); B_W: body weight (kg); AT: average time (days); S_A: skin surface area (cm^2); P_C: dermal permeability coefficient; CF: conversion factor (kg/mg). Exposure dose rate via ingestion and diffusion along the skin can vary with the concentration of the heavy metals, their solubility in tissue fluids, amount of blood circulation, the toxicity of the metals, exposure duration, and time. A small concentration of toxic chemicals such as Pb can cause severe damage to the body over a long time. These exposure indices are computed using values presented in Tables A1–A3 [16,47].

2.5. Risk Characterization

2.5.1. Hazard Quotient (HQ)

HQ is defined as a single-element hazard quotient and quantifies a single-element risk. In the case of two or more heavy metals, the multi-elemental risk assessment is performed using the hazard index, as presented in Equation (8) [54,55,69].

$$HQ = \frac{CDI_{non\ carcinogenic}}{RfD} \quad (8)$$

For non-carcinogenic elements, the risk is defined as the hazard quotient (HQ). HQ is the hazard quotient and measures the amount or percentage propensity to hazard caused by the ingestion of metals or exposure through the dermal pathway for non-carcinogenic substances. $CDI_{non\ carcinogenic}$: chronic daily intake for non-carcinogenic heavy metals such as Ba, Zn, Cu, and Fe. In addition, RfD is the reference dose factor and the no-observable-adverse-effect level (NOAEL) over the uncertainty factor (UF). The reference dose (RfD) and uncertainty factor (UF) for each heavy metal are used to estimate the intake rate of toxic metals via oral and dermal pathways for the non-carcinogenic effect. Based on RfD and UF, the risk threshold and associated damages are identified as chronic doses accumulated. Exposure to heavy metals above an acceptable threshold of 10^{-6} (1 part per million) (LOAEL) results in a lifetime risk called individual excess lifetime cancer risk (IELCR). However, there is certainly no threshold for carcinogenic risk because the effect of the episodic doses accumulates whenever the exposure is sure. Thus, NOAEL and LOAEL hold that an individual excess lifetime or very low cancer risk (IELCR) exist for carcinogenic effect (risk level 1) while risk levels for the non-carcinogenic effect are defined using scale 1–4 (no risk to high risk) [72,77–80].

Nazaroff and Alvarez-Cohen (2001) and US EPA (2016) established that water is probably safe and no longer harmful to human health when HQ is far below the lowest-observable-adverse-effect level (LOAEL) or <1 (where LOAEL is unity). However, it is regarded as toxic, unsafe, and may initiate chronic disease when HQ is above the LOAEL or HQ > 1. Similarly, RAIS (2020) and Rapant et al. (2010) classified non-carcinogenic risks as "negligible chronic risk (HQ < 0.1), low risk (0.1 < HQ < 1), medium risk (1 < HQ < 4), and high risk (HQ > 4)" [79,80].

RAIS (2020) and EPA (1989) calculated the non-carcinogenic risk as to the ratio of the hazard quotient to the hazard index (HQ/HI). There is an adverse non-carcinogenic risk to human health when (HQ/HI) = 1 while the 0.1 < (HQ/HI) < 1 indicates that some precautionary measures should be taken to avert potential danger or mining hazards. When (HQ/HI) < 0.1, safety is guaranteed or an adverse health effect is not likely [81–83].

2.5.2. Maximally Exposed Individual (MEI)

Maximally exposed individual (MEI) assesses the risk to health and well-being of the mining community (residents) and miners. The harm caused by non-carcinogenic substances such as Ba, Cu, Zn, and Fe was examined and compared to values at the threshold below which the human body can manage the risk or recover before subsequent exposure [77,81]. MEI was computed using Equation (9).

$$MEI = C\frac{CR \times EF \times ED}{BW \times AT} \quad (9)$$

MEI is maximally exposed individual (mg $kg^{-1}d^{-1}$); C is the average concentration of contaminant at exposure (mg/L in water samples); CR: contact rate (L/day); EF: exposure frequency (days/year); ED: exposure duration (years); BW: body weight (kg); and AT: period over (days) which exposure is typical.

3. Results

3.1. Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) Analysis

The ICP-MS analysis in Figure 3 identifies Zn, Cu, Ba, Cd, Fe, and Pb metal ions in the mine tailings in different quantities. In this study, the metal concentrations in mine tailings decrease in the order of Ba > Fe > Pb > Zn > Cu > Cd. The concentration of each metal ion in all the samples was compared with the global ecological, environmental, and health standards. Zn, Cu, and Cd are below the maximum allowable limit set by WHO, EU, NIS, US EPA, and CMHNS for ecological and health safety. However, the content of Ba in KB1 and IB1 and Fe in KB1, IB1, and WB1 is relatively higher than the maximum allowable limits set by the governing standards, as shown in Table A4. Similarly, Pb in WB2 is above the health and environmental risk levels recommended by the local and international agencies. This outcome indicates that the water used in the ore washing will result in water pollution and heavy metal ingestion if returned to rivers and streams used by people.

Medical research reports on the human intake of Fe by the NIS (2015) and DNR (2017) show that Fe in water has no identifiable damage or adverse effect on human health when the concentration is below 45 mg/day in men (tolerable upper intake level in an adult only). The maximum concentration of Fe obtained in WB1 mine tailing was 3.1245 mg/L. This was followed by KB2 (0.7895 mg/L) and IB1 (0.389 mg/L). The concentration of Fe in KB2, IB2, and WB2 was found to be between 0.003 and 0.2829 mg/L. However, the day-to-day consumption of iron in the water contaminated by barite mine tailings could be greater than the value reported in this study. Research has also shown that Fe in surface water at an artisanal gold mine in Nigeria during the wet season can be higher than the value reported in this study [12,13,15–17]. Water with high Fe can have a sense of taste, subject to microbial attack by Fe utilization, and be colored. Thus, water quality is compromised, becomes prone to biocides, and makes the water treatment process unrealizable [45]. The taste of the mine water was not examined during the survey. However, the water samples are brownish-red.

Ba is considered non-carcinogenic in humans and animals (animal trials on mice) [43,44,84]. However, an acute oral dose is between 3 and 4 g/day in humans. In the current study, the concentration of Ba in mine tailing digestate IB1 is 12.40 mg/L, followed by 11.06 mg/L in digestate KB1, as shown in Figure 3. The lower concentration of Ba observed was between 0.66 and 1.75 mg/L in KB2, IB2, WB1, and WB2 digestates. These values are higher than the maximum allowable limit values (as shown in Figure 3). Several research studies have shown that Ba in drinking water may be responsible for dental caries in children, cardiovascular and heart diseases, nephropathy in laboratory animals, and a potential cause of high blood pressure in humans, as reported by WHO (2004) [50,85,86].

Pb is toxic for humans, plants, and animals. It is also the major cause of kidney malfunction and serious hematologic and brain damage in mammals [87,88]. Pb levels are found to be above the maximum permissible values indicated by WHO, EU, and NIS in WB2 (0.69 mg/L) and KB1 (0.03 mg/L), as shown in Table A4. The lowest Pb levels were between 0.0005 mg/L and 0.007 mg/L in WB1, IB1, KB2, and IB2. The allowable limit for Pb is 0.01 mg/L (EU, NIS, Nigerian Standard for Drinking Water Quality, and CHMNS standards) and 0.005 (US EPA standard). Pb concentration in tailing digestates WB2 and KB1 exceeds the limit of drinking water.

Zn, Cu, and Cd concentrations in the digestate of the mine tailings are in all cases below the maximum allowable limits; in particular, Cd has an undetectable concentration. The highest concentration for copper is 0.019 mg/L in KB1. Digestates of KB1, IB1, WB1, KB2, IB2, and WB2 have Zn concentrations in the range of 0.003 mg/L and 0.04 mg/L. Similarly, the average Cu concentration in the digestates was $\leq$ 0.01 mg/L. The concentrations of zinc and copper in all the digestates were lower than the allowable limits recommended by the standards. This implies that zinc and copper toxicities of the tailings' digestates cannot be responsible for irritability and muscular stiffness in humans [89]. Zn and Cu concentrations may be low and high in soil and water around barite mining sites and gold mining sites, as reported in the literature [20,26,90,91]. Thus, the zinc and copper concentrations vary across barite mining sites but are lower than those in gold and Pb-Zn mining sites.

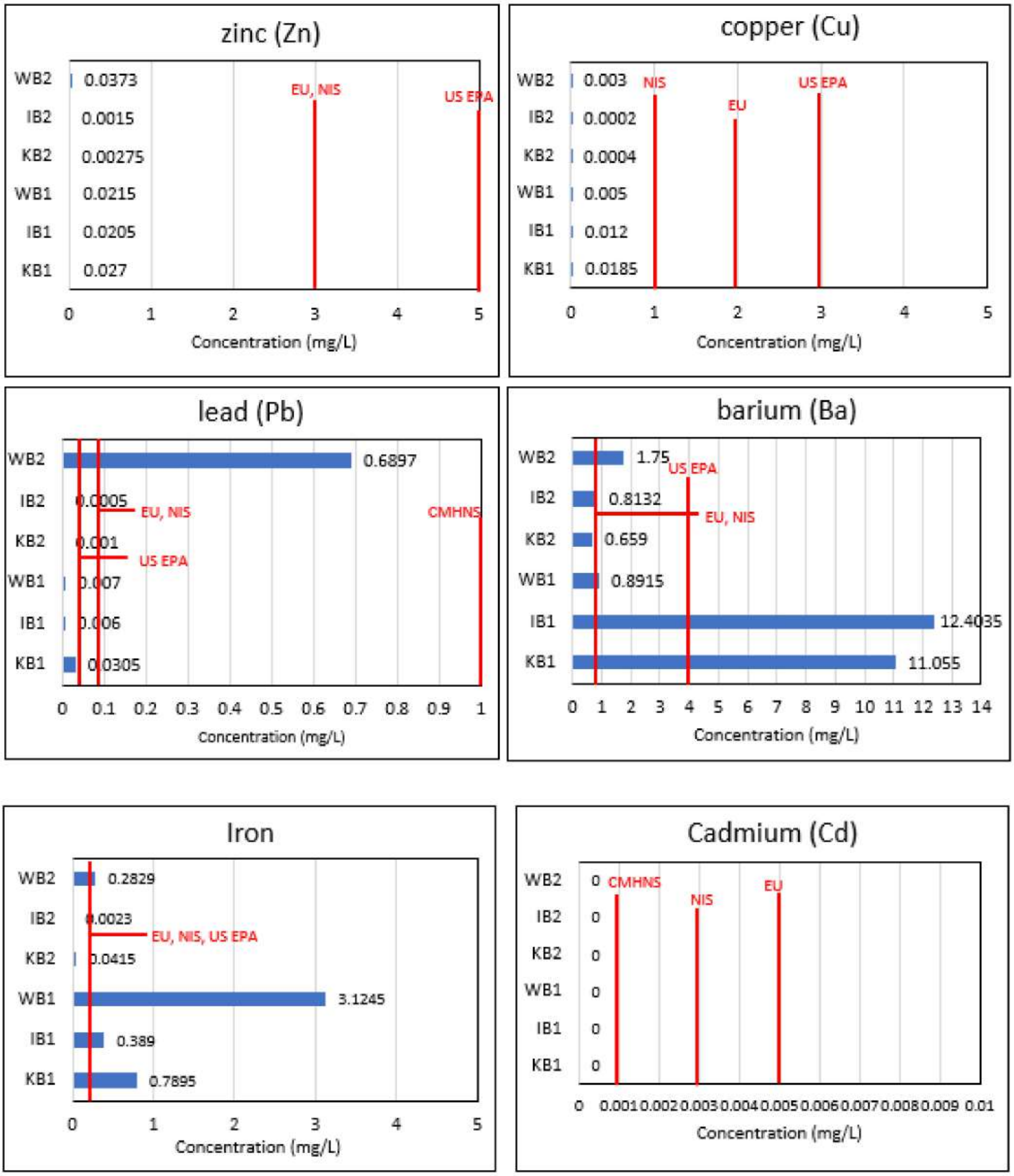


Figure 3. Concentration of heavy metals associated with artisanal barite mining (ABM) at some mining sites within the Middle Benue Trough, Nigeria. WHO: World Health Organization; EU: European Union; NIS: Nigerian Industrial Standard; USEPA: United States Environmental Protection Agency; CMHNS: China Ministry of Health National Standards.

3.2. Heavy Metal Toxic Unit (TU) Results

Table 2 shows that the heavy metal toxicity is of the order Cd < Zn < Cu < Pb < Ba < Fe. The contributions of Fe (79.75%) and Ba (19.60%) dominate the toxicity index. Zn, Cu, and Pb contributed 0.010%, 0.017%, and 0.62%, respectively, to the total toxic unit (TTU) of pollutants associated with barite mining. There is a clear indication that the activities of barite mining are free of cadmium toxicity. Moreover, the total TU in the media is 0.9797, which is far less than 4 (toxicity of each element is less than the SEL), indicating low toxicity or low chronic risk level. The sum of low-effect levels (LELs) for metals under consideration for this study is 4, which agrees with the scale used to characterize the chronic risk level as stipulated by the United States Environmental Protection Agency (US EPA). Scales 1–4 are standardized scales used to characterize chronic risk levels. Scale 4 is defined as a high chronic risk level. Potential acute toxicity of the media occurs whenever the sum of the toxic units is greater than 4 (that means the toxicity of one or more metals in the media exceeds the recommended low-effect level (LEL)) [11,61,62]. The toxic level (TU) of the media increases in the order of IB2 < KB2 < WB2 < IB1 < KB1 < WB1. However, it was reported that the toxic level of heavy metals in sediments and soil is higher than in mine water or water contaminated by heavy metals from the field sites. The continuous release and subsequent accumulation of these toxic metals into the ecosystem may increase the TUs and result in numerous ecological and health risks if the exploitation process remains unchecked.

Table 2. Toxic units and contamination factor (CF) of identified heavy metals associated with some barite mines in Nigeria.

Heavy Metals	Maximum Metallic Conc in Media (ppm)	SEL	Toxic Unit (TU)	% TU
Zinc	0.0805	820	0.0000975	0.010
Copper	0.0185	110	0.000168	0.017
Iron	3.1245	4	0.78135	79.750
Lead	1.516	250	0.0061	0.62
Cadmium	0.000	10	0.000	0.00
Barium	12.4035	64.6	0.192	19.6

$\sum = 0.9797$.

3.3. Hazard/Risk Assessment of Water Contaminated by Tailing Effluents and Barite Ponds

3.3.1. Geo-accumulation Index (Igeo)

Figure 4 shows that in all cases analyzed, Zn and Cu concentrations at abandoned barite mining sites do not pollute water resources (Igeo < 0). Pb, Fe, and Ba concentrations at some sites have Igeo values greater than zero, indicating that the barite tailings and ponds are moderately-severely polluted (Pb and Ba in KB1, Ba in IB1, and Fe in WB1—Igeo = 2–3) to enormously polluted (Pb in WB2—Igeo > 5). Cu has Igeo < 0, and thus its concentration does not pollute the water.

3.3.2. Contamination Factor (CF)

Table 3 shows that Zn and Cu have a very low CF (<0.02) in all analyzed sites. Site KB2 was low in contamination as it had a CF < 1 for all metals analyzed. Pb, Fe, and Ba have CF values greater than zero, indicating that the barite ponds and water resources are moderately contaminated (Pb in IB1 and WB1 and Fe in KB1 and IB1) to highly contaminated (Pb in KB1, Ba in KB1 and IB1, and Fe in WB1). The contamination assessment studies based on Igeo and CF showed that some of the mine water is moderately to severely polluted by Ba and Fe, extremely polluted by Pb, and very highly contaminated by Ba, Pb, and Fe.

Table 3. Contamination factor (CF) of heavy metals in mine water and tailing effluents.

Elements	Ba	Pb	Zn	Cu	Fe
(CF) (dimensionless)					
KB1	5.528	6.100	5.4×10^{-3}	1.4×10^{-2}	2.630
IB1	6.202	1.200	4.1×10^{-3}	3.8×10^{-3}	1.297
WB1	0.446	1.400	4.3×10^{-3}	3.0×10^{-4}	10.415
KB2	0.330	0.200	5.5×10^{-4}	7.7×10^{-4}	0.138
IB2	0.407	0.100	3.0×10^{-4}	——-	0.008
WB2	0.875	137.940	7.46×10^{-3}	2.3×10^{-3}	0.943

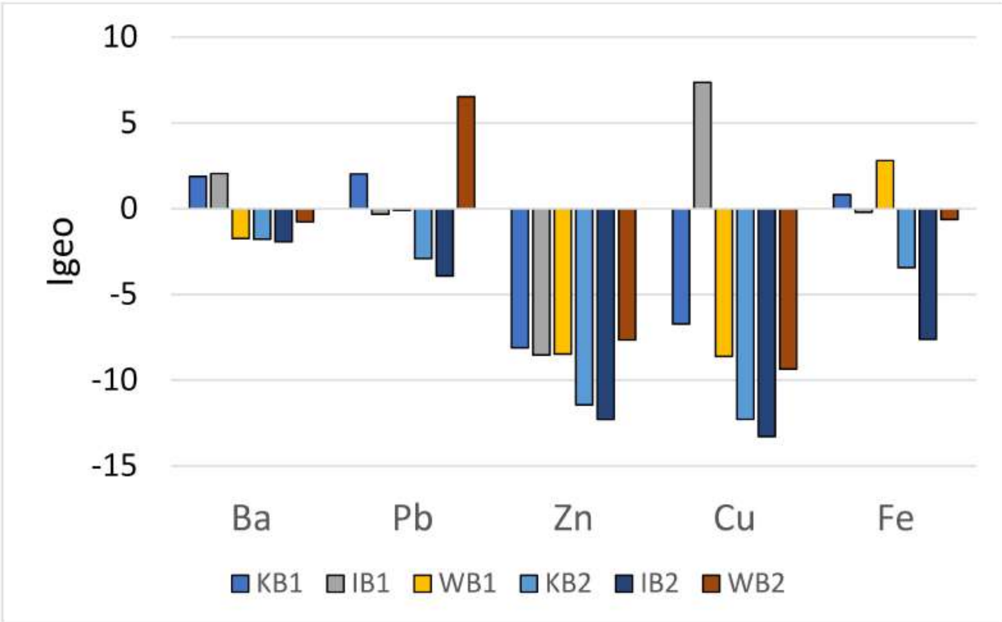


Figure 4. Geo-accumulation index (Igeo) for the water samples.

3.4. Health Risk Assessment

3.4.1. Chronic Daily Intake (CDI)

Table 4 shows that the CDI for Ba, Pb, Zn, Fe, and Cu in barite ponds or mine water and tailing effluents is between 2.35×10^{-6} mg/kg day (for Cu in IB2) and 1.46×10^{-1} mg/kg day (for Ba in IB1) for an adult and between 2.19×10^{-6} mg/kg day (for Cu in IB2) and 1.36×10^{-1} mg/kg day (for Ba in IB1) for children. These concentrations indicate the lifetime average daily dose. The result presents the possible consequence of long-term exposure to heavy metals—accumulation through ingestion and dermal pathway that can initiate chronic diseases in humans over a long period. The heavy metals' concentration at barite mining sites for Pb was higher than those reported for cosmetics (Pb at 0.02885 mg kg^{-1} d^{-1}) [18] and is within the range reported for Pb, Zn, Cu, and Fe on artisanal gold mining sites [18,35].

3.4.2. Maximally Exposed Individual (MEI)

In Table 4, Ba shows the highest values (for residents and workers) in KB1, IB1, and WB1. Pb, Fe, and Zn show higher values for residents than workers for KB1, IB1, KB1, and WB2. Exposure levels for Zn, Cu, and Fe are low for residents and workers at the mining sites and may not pose any health risk. Miners who reside outside the mining community consume 5.20×10^{-1} mg kg^{-1} d^{-1} of Ba, 1.48×10^{-2} mg kg^{-1} d^{-1} of Pb, 6.75×10^{-3} mg kg^{-1} d^{-1} of Zn, 1.18×10^{-4} mg kg^{-1} d^{-1} of Cu, and 3.06×10^{-2} mg kg^{-1} d^{-1} of Fe.

Table 4. Chronic daily intake (CDI) and maximally exposed individual (MEI) to heavy metals in mine water and tailing effluents.

Samples	Ba	Pb	Zn	Cu	Fe
(CDI) Adult (mg kg^{-1} d^{-1})					
KB1	1.29×10^{-1}	3.58×10^{-4}	3.17×10^{-4}	2.17×10^{-4}	9.27×10^{-3}
IB1	1.46×10^{-1}	7.05×10^{-5}	2.41×10^{-4}	1.41×10^{-4}	4.56×10^{-3}
WB1	1.05×10^{-2}	8.21×10^{-5}	2.52×10^{-4}	5.87×10^{-5}	3.67×10^{-2}
KB2	7.70×10^{-3}	1.17×10^{-5}	3.22×10^{-5}	4.70×10^{-6}	4.87×10^{-4}
IB2	9.50×10^{-3}	5.87×10^{-6}	1.76×10^{-5}	2.35×10^{-6}	2.70×10^{-5}
WB2	2.05×10^{-2}	8.09×10^{-3}	4.38×10^{-4}	3.52×10^{-5}	3.32×10^{-3}
(CDI) Child (mg kg^{-1} d^{-1})					
KB1	1.21×10^{-1}	3.34×10^{-4}	2.95×10^{-4}	2.03×10^{-4}	8.65×10^{-3}
IB1	1.36×10^{-1}	6.57×10^{-5}	224×10^{-4}	1.32×10^{-4}	4.26×10^{-3}
WB1	9.70×10^{-3}	6.67×10^{-5}	2.35×10^{-4}	5.48×10^{-5}	3.42×10^{-2}
KB2	7.20×10^{-3}	1.10×10^{-5}	3.01×10^{-5}	4.38×10^{-6}	4.54×10^{-4}
IB2	8.90×10^{-3}	5.47×10^{-6}	1.64×10^{-5}	2.19×10^{-6}	2.52×10^{-5}
WB2	1.92×10^{-2}	7.56×10^{-3}	4.09×10^{-4}	3.29×10^{-5}	3.10×10^{-3}
(MEI) Resident (mg kg^{-1} d^{-1})					
KB1	3.03×10^{-1}	8.36×10^{-4}	7.40×10^{-4}	5.07×10^{-4}	2.16×10^{-2}
IB1	3.40×10^{-1}	1.64×10^{-4}	5.61×10^{-4}	3.29×10^{-4}	1.07×10^{-2}
WB1	5.20×10^{-1}	1.92×10^{-4}	5.89×10^{-4}	1.37×10^{-4}	8.56×10^{-2}
KB2	1.81×10^{-3}	2.74×10^{-5}	7.53×10^{-5}	1.10×10^{-5}	1.13×10^{-3}
IB2	2.22×10^{-2}	1.37×10^{-5}	4.11×10^{-5}	5.48×10^{-6}	6.30×10^{-5}
WB2	4.79×10^{-2}	1.89×10^{-2}	1.89×10^{-2}	8.22×10^{-5}	7.75×10^{-3}
(MEI) Worker (mg kg^{-1} d^{-1})					
KB1	1.08×10^{-1}	2.99×10^{-4}	2.64×10^{-4}	1.81×10^{-4}	7.71×10^{-3}
IB1	1.21×10^{-1}	1.64×10^{-4}	2.00×10^{-4}	1.18×10^{-4}	3.82×10^{-3}
WB1	1.86×10^{-1}	5.86×10^{-5}	2.10×10^{-4}	4.89×10^{-5}	3.06×10^{-2}
KB2	7.43×10^{-3}	9.79×10^{-6}	2.69×10^{-5}	3.92×10^{-6}	4.04×10^{-4}
IB2	7.93×10^{-3}	4.89×10^{-6}	1.47×10^{-5}	1.96×10^{-6}	2.25×10^{-5}
WB2	1.71×10^{-2}	6.75×10^{-3}	6.75×10^{-3}	2.94×10^{-5}	2.77×10^{-3}

3.5. Hazard Exposure Assessment

Risks due to heavy metal contamination are difficult to quantify, but it is important to identify the sources of hazard and the exposure level to humans.

The results (Table 5) show that oral ingestion (EXP_{ing}) is between 1.03×10^{-1} and 1.399×10^{1} mg kg^{-1}d^{-1} for Ba, 5.48×10^{-4} and 1.78 mg kg^{-1} d^{-1} for Pb, 8.80×10^{-4} and 8.82×10^{-2} mg kg^{-1} d^{-1} for Zn, 1.17×10^{-4} and 2.02×10^{-2} mg kg^{-1} d^{-1} for Cu, and 1.35×10^{-3} and 3.42 mg^2 L^{-1} kg^{-1} d^{-1} for Fe, respectively. Similarly, the values of EXP_{derm} are between 4.55×10^{-5} and 1.27×10^{-3} mg kg^{-1} d^{-1} for Ba, 4.60×10^{-9} and 2.06×10^{-5} mg kg^{-1} d^{-1} for Pb, 2.07×10^{-8} and 1.64×10^{-6} mg kg^{-1} d^{-1} for Zn, 4.60×10^{-9} and 4.26×10^{-7} mg kg^{-1} d^{-1} for Cu, and 5.29×10^{-8} and 1.06×10^{-4} mg kg^{-1} d^{-1} for Fe, respectively. Ba, Pb, and Fe show the highest values for EXP_{ing}, while Cu has the lowest value for EXP_{ing}. Similarly, Ba also shows the highest value for EXP_{derm}. The miners and people living within the mining sites are more exposed to associated health hazards through ingestion than a dermal pathway. Similarly, results also show that the estimated health risks of heavy metals per kilogram of children's body weight are higher than adults.

3.6. Hazard Characterization

Hazard Quotient

HQ (Table 6) for Ba in adults and children ranges between 1.03×10^{-1} and 1.94 in children and 1.11×10^{-1} and 2.08 in adults; 3.90×10^{-3} and 1.19×10^{1} in children and 4.20×10^{-3} and 1.27×10^{1} in adults for Pb; 5.48×10^{-4} and 1.36×10^{-2} in children and 1.08×10^{-3} and 1.46×10^{-2} in adults for Zn; 5.48×10^{-5} and 5.07×10^{-3} in children and 5.87×10^{-5} and 5.40×10^{-3} in adults for Cu; and 1.76×10^{-5} and 6.06×10^{-3} in children and 3.86 × 10^{-5} and 5.24 × 10^{-2} in adults for Fe. Ba and Pb show high values for HQ (in children and adults), while Cu and Fe show the lowest values for HQ. Similarly, the HQs of tailing effluents KB1 and IB1 for Ba and WB2 for Pb are between 1 and 6. In addition, based on the non-carcinogenic risk classifications by [79]. HQs of Zn, Cu, and Fe for all water samples are less than 0.1 for the water samples WB1, KB2, and IB2. Such HQ is classified as negligible chronic risk (HQ < 0.1) [79,80] and cannot lead to adverse health implications. This indicates that an adverse effect is quite low.

Table 5. Exposure assessment (EXP) of heavy metals in mine water and tailing effluents through ingestion (EXP_{ing}) and skin (dermal pathways (EXP_{derm})).

Elements	Ba	Pb	Zn	Cu	Fe
EXP_{ing} (mg kg^{-1} d^{-1}) Adult					
KB1	6.49 × 10^{0}	1.79 × 10^{-2}	1.59 × 10^{-2}	1.09 × 10^{-2}	4.60 × 10^{-1}
IB1	7.28 × 10^{0}	3.52 × 10^{-3}	1.20 × 10^{-2}	7.05 × 10^{-3}	2.23 × 10^{-1}
WB1	5.20 × 10^{-1}	4.11 × 10^{-3}	1.26 × 10^{-2}	2.94 × 10^{-3}	1.83 × 10^{0}
KB2	3.86 × 10^{-1}	5.87 × 10^{-4}	1.61 × 10^{-3}	2.34 × 10^{-4}	2.43 × 10^{-2}
IB2	4.77 × 10^{-1}	2.94 × 10^{-4}	8.80 × 10^{-4}	1.17 × 10^{-4}	1.35 × 10^{-3}
WB2	1.03 × 10^{-1}	4.05 × 10^{-1}	2.19 × 10^{-2}	1.76 × 10^{-3}	1.66 × 10^{-1}
EXP_{ing} (mg L^{-1} kg^{-1} d^{-1}) Child					
KB1	12.11 × 10^{0}	3.58 × 10^{-2}	2.96 × 10^{-2}	2.02 × 10^{-2}	8.65 × 10^{-1}
IB1	13.99 × 10^{0}	7.04 × 10^{-3}	2.24 × 10^{-2}	1.31 × 10^{-2}	4.26 × 10^{-1}
WB1	9.76 × 10^{-1}	8.22 × 10^{-3}	2.36 × 10^{-2}	5.48 × 10^{-3}	3.42 × 10^{0}
KB2	7.22 × 10^{-1}	1.17 × 10^{-3}	3.02 × 10^{-3}	4.38 × 10^{-4}	4.54 × 10^{-2}
IB2	8.92 × 10^{-1}	5.48 × 10^{-4}	1.64 × 10^{-3}	2.20 × 10^{-4}	2.52 × 10^{-3}
WB2	1.92 × 10^{0}	7.56 × 10^{-1}	4.08 × 10^{-2}	3.28 × 10^{-4}	3.10 × 10^{-1}
EXP_{derm} (mg kg^{-1} d^{-1}) Adult					
KB1	1.12 × 10^{-3}	4.15 × 10^{-7}	5.52 × 10^{-7}	2.30 × 10^{-7}	2.69 × 10^{-5}
IB1	1.27 × 10^{-3}	8.17 × 10^{-8}	4.18 × 10^{-7}	4.09 × 10^{-7}	1.32 × 10^{-5}
WB1	9.11 × 10^{-5}	9.53 × 10^{-8}	4.39 × 10^{-7}	1.70 × 10^{-7}	1.06 × 10^{-4}
KB2	6.73 × 10^{-5}	1.36 × 10^{-8}	5.62 × 10^{-8}	1.36 × 10^{-8}	1.41 × 10^{-6}
IB2	8.31 × 10^{-5}	6.81 × 10^{-9}	3.06 × 10^{-8}	6.81 × 10^{-9}	7.83 × 10^{-8}
WB2	1.79 × 10^{-4}	9.39 × 10^{-6}	7.62 × 10^{-7}	1.02 × 10^{-7}	9.63 × 10^{-6}
EXP_{derm} (mg kg^{-1} d^{-1}) Child					
KB1	7.63 × 10^{-4}	2.81 × 10^{-7}	3.73 × 10^{-7}	4.26 × 10^{-7}	1.82 × 10^{-5}
IB1	8.56 × 10^{-4}	5.52 × 10^{-8}	2.83 × 10^{-7}	2.76 × 10^{-7}	8.95 × 10^{-6}
WB1	6.16 × 10^{-5}	6.44 × 10^{-8}	3.00 × 10^{-7}	1.15 × 10^{-7}	7.19 × 10^{-5}
KB2	4.55 × 10^{-5}	9.21 × 10^{-9}	3.08 × 10^{-8}	9.21 × 10^{-9}	9.55 × 10^{-7}
IB2	5.61 × 10^{-5}	4.60 × 10^{-9}	2.07 × 10^{-8}	4.60 × 10^{-9}	5.29 × 10^{-8}
WB2	1.21 × 10^{-4}	6.35 × 10^{-6}	5.15 × 10^{-7}	6.90 × 10^{-8}	6.51 × 10^{-6}

HI (Table 6) shows high values for WB2, KB1, and IB1 in adults and KB1, IB1, and WB2 in children. HI of 5.81 × 10^{1} (WB2 in adults), 2.14 × 10^{0} (KB1 in adults), 2.15 × 10^{0} (IB1 in adults), 1.98 × 10^{0} (KB1 in children), 2.00 x 10^{0} (IB1 in children), and 5.69 × 10^{0} (WB2 in children) indicate elevated non-carcinogenic risks. Similar research on water sources contaminated by ores also reported HQ and HI > 1 and may be higher than values obtained in this study [11,80,92,93]. For Ba, HQ/HI is 0.97 (considering IB1 for adults), 0.92 (considering KB2 for adults), 0.86 (considering KB1 for adults), 0.55 (considering WB1 for adults), and 0.005 (considering WB2 for adults). Similarly, Ba in children accounts for HQ/HI of 0.97 (considering IB1) and 0.87 (considering KB1). HQ/HI shows the highest values for Pb, having 0.99 (considering WB2 for adults) and 0.95 (considering WB2 for children). Non-carcinogenic risk is sure for Ba (considering IB1 and KB2) and Pb (considering WB2). Adults and children living near the mining sites may suffer the adverse effects of heavy metal contamination due to barite mining. HQ/HI for Zn, Cu, and Fe is $\leq$0.005. The results indicate that some precautionary measures should be taken to avert the potential danger or non-carcinogenic risk of Ba and Pb. In the case of Zn, Cu, and Fe, an adverse health effect is not likely.

Table 6. Risk characteristics (hazard quotient (dimensionless) (HQ) and hazard index (HI) (dimensionless)) of heavy metals in mine water and tailing effluents.

Samples	Hazard Quotient (HQ)					Hazard Index
	Ba	**Pb**	**Zn**	**Cu**	**Fe**	**(HI)**
(HQ) Adult						
KB1	1.85×10^{0}	2.56×10^{-1}	1.06×10^{-2}	5.40×10^{-3}	1.32×10^{-2}	2.14×10^{0}
IB1	2.08×10^{0}	5.03×10^{-2}	8.02×10^{-3}	3.52×10^{-3}	6.52×10^{-3}	2.15×10^{0}
WB1	1.50×10^{-1}	5.87×10^{-2}	8.41×10^{-3}	1.47×10^{-3}	5.24×10^{-2}	2.71×10^{-1}
KB2	1.11×10^{-1}	8.41×10^{-3}	1.08×10^{-3}	1.17×10^{-4}	6.96×10^{-4}	1.21×10^{-1}
IB2	1.36×10^{-1}	4.20×10^{-3}	5.87×10^{-3}	5.87×10^{-5}	3.86×10^{-5}	1.46×10^{-1}
WB2	2.94×10^{-1}	5.78×10^{1}	1.46×10^{-2}	8.80×10^{-4}	4.70×10^{-3}	5.81×10^{1}
(HQ) Child						
KB1	1.73×10^{0}	2.39×10^{-1}	9.86×10^{-3}	5.07×10^{-3}	6.06×10^{-3}	1.98×10^{0}
IB1	1.94×10^{0}	4.70×10^{-2}	7.49×10^{-3}	3.29×10^{-3}	2.98×10^{-3}	2.00×10^{0}
WB1	1.40×10^{-1}	5.47×10^{-2}	7.85×10^{-3}	1.37×10^{-3}	2.39×10^{-2}	2.28×10^{-1}
KB2	1.03×10^{-1}	7.80×10^{-3}	1.00×10^{-3}	1.10×10^{-4}	3.18×10^{-4}	1.12×10^{-1}
IB2	1.27×10^{-1}	3.90×10^{-3}	5.48×10^{-4}	5.48×10^{-5}	1.76×10^{-5}	1.32×10^{-1}
WB2	2.74×10^{-1}	5.40×10^{0}	1.36×10^{-2}	8.22×10^{-4}	2.17×10^{-3}	5.69×10^{0}

4. Discussion

The barite mines are moderately to severely polluted by Ba and Fe and extremely polluted by Pb whose samples' Igeo showed high values (i.e., WB2, WB1, KB1, and IB1). Similar studies have shown that surface water and soil in a gold mining site may be moderately to heavily polluted by Pb and severely polluted by Cu and Zn [15,20]. High Igeo values might be attributed to artisanal and small-scale mining activities and anthropogenic removal of the heavy metals within the mining sites. Pb and Ba concentration in tailing digestates exceeds the limit of drinking water. Research has shown that Pb concentration in artisan gold mining sites (Pb > 131 mg/L) is higher than the highest values (i.e., 0.6897 mg/L in WB2) reported in this study [11,23,89]. Although Pb concentration reported in this study is minimal, Pb accumulation in humans over a long time may increase blood lead level (BLL) and result in fatigue. High BLL has been reported to cause muscular weakness, damage to body organs, and death of children [89,94,95]. Similarly, a high concentration of barium in water causes vasoconstriction, alters nerve reflexes, results in muscle weakness, and damages the myelin sheath when Ba binds with sulfate and lead (Pb) [43,44].

The contamination assessment studies on mine water and tailing effluents collected in August 2017 and August 2019 (rainy season) showed that the total toxic unit (TU) for the heavy metals was below the allowable limit (TU < 4). However, the chronic risk level characterization based on the HQ revealed a low chronic risk level (considering short-term risk assessment). The estimated health risks of heavy metals per kilogram of body weight of children are higher than adults. HQs and HIs uncovered that Ba and Pb, in some instances, pose a relatively low health risk and can contribute medium to high health risk in other artisanal barite mining sites.

The presence of Ba and Pb in KB2 and IB2 poses a relatively low risk to health which shows that some precautionary measures should be taken to avert disaster. However, Ba in KB1 and IB1 and Pb in WB1 will contribute medium to high risk (for 1 < HQ < 4, and HQ > 4). Thus, an adverse effect due to the non-carcinogenic risk is expected. It is estimated that residents of the mining sites may consume more heavy metals in water than miners who reside within the neighboring communities. The maximally exposed individuals (MEIs) are the children, miners, and residents of the mining sites and are more at risk of toxic heavy metals. It is vital that barite mining is carried out responsibly, respecting local and national mining laws and global environmental standards.

5. Conclusions

This study identified Cd, Zn, Ba, Cu, Pb, and Fe as major contaminants that cause water pollution due to artisanal barite mining. The chemical parameter Cd was not detected (concentration lower than the LOD). In this study, it appears that the heavy metals with concentrations above the limits were Fe, Ba, and Pb. Cu and Zn in this study showed low concentrations, always below the permissible values (Zn and Cu) or even close to zero (Cd). Ba, Pb, and Fe tailing effluents and mine water samples will probably contaminate rivers used by miners and surrounding mining communities. ICP-MS results show that the concentrations of Ba and Pb, among other heavy metals, are above the allowable limits stated by WHO, EU, US EPA, CMHNS, NIS, and NSDWQ. The chronic daily intake (CDI) assessment revealed that the accumulation of heavy metals through ingestion and the dermal pathway is possible and can initiate chronic diseases in humans over a long time.

Aside from environmental influences, artisanal mining also contributes additional risks that jeopardize miners' well-being and the entire mining environment. The study recommends that some precautionary measures should be taken by miners, environmental and health specialists, owners of mining sites, and mine inspectors to avert disaster and, in some situations, signals that an adverse effect due to the non-carcinogenic risk is expected. Therefore, it is concluded that barite mining should be carried out responsibly, respecting local and national mining laws and global environmental standards. Affordable water filters or carbon filters specifically designed to remove lead and Ba will help reduce the quantity of heavy metals consumed in drinking water. Other water treatment methods such as reverse osmosis and distillation can also serve as alternatives recommended by the center for disease control.

Author Contributions: Conceptualization, D.O.A.; Data curation, D.O.A.; Formal analysis, D.O.A.; Investigation, D.O.A., C.M.E. and A.P.O.; Methodology, D.O.A.; Resources, D.O.A.; Supervision, C.M.E., A.P.O., M.T. and R.K.A.; Validation, D.O.A. and A.P.O.; Visualization, D.O.A. and A.R.A.; Writing—original draft, D.O.A.; Writing—review and editing, D.O.A., C.M.E., A.P.O., A.R.A. and M.T. All authors have read and agreed to the published version of the manuscript.

Funding: The study (Ph.D. program for the first author) was funded by the Regional Scholarship Innovation Fund (RSIF).

Institutional Review Board Statement: Institutional approval was obtained from the African University of Science and Technology prior to the study.

Informed Consent Statement: Informed consent was obtained from all subjects involved in the study (The study did not involve humans).

Data Availability Statement: Raw data is available on request.

Acknowledgments: Authors acknowledge the support of Worcester Polytechnic Institute (WPI), USA, African University of Science and Technology (AUST), Nigeria, and Pan African Material Institute (PAMI), Nigeria. Authors are also grateful to Harold Webb Walker and Wenwen Yao, both of the Civil and Environmental Engineering Department, WPI, USA. They took the time to read the manuscript in its earlier version, and their recommendations are worthwhile.

Conflicts of Interest: Authors declare that they have no competing financial interests or personal relationships that could have appeared to influence any part of this work as reported in the paper.

Appendix A

Table A1. Risk contribution of heavy metals in mine water samples and tailing effluents.

Elements	Kp or Pc ($cm\ h^{-1}$)	RfD_{ing} ($mg\ kg^{-1}\ d^{-1}$)	RfD_{derm} ($mg\ kg^{-1}\ d^{-1}$)	References
Pb	0.0004	0.0014	0.00042	[46]
Ba	0.003	0.07	0.000062	[46,49]
Fe	0.001	0.7	0.14	[46]

Table A1. *Cont.*

Elements	Kp or Pc (cm h^{-1})	RfD_{ing} $\left(mg\ kg^{-1}\ d^{-1}\right)$	RfD_{derm} $\left(mg\ kg^{-1}\ d^{-1}\right)$	References
Cd	0.001	0.0005	0.000025	[23,46]
Cu	0.001	0.04	0.008	[46]
Zn	0.0006	0.03	0.06	[46,72]

Kp or Pc is the partition/permeability coefficient; RD is the same as RfD: reference dose.

Table A2. Risk contribution of heavy metals in mine water samples and tailing effluents.

Elements	Inhalation RfD	Oral CSF	Dermal CSF	Inhalation CSF	References
Pb	NA	0.0085	NA	420	[47,49,72]
Ba	0.0076	ID	ID	ID	[23,46]
Fe	NA	NA	NA	NA	[46,47]
Cd	0.000057	NA	NA	6.3	[23,49]
Cu	NA	NA	NA	NA	[23,49]
Zn	NA	NA	NA	NA	[49,72]

ID: inadequate data, NA: not available, CSF: carcinogenic slope factors.

Table A3. Exposure factors for the health risk assessment of heavy metals in mine water samples and tailing effluents.

Parameters	Unit	Child	Adult/Resident	Worker	References
Body weight (BW)	kg	15	70	70	[23,49]
Contact rate (CR)	L/day	1.0	2.0	1.0	[77]
Exposure factor (EF)	days/year	350	350	250	[49]
Exposure duration (ED)	years	6	30	25	[43,49]
Exposure time (ET)	days	2190	10950		[44,49]
Exposure frequency (ER)	Days/year	365	365	365	[23,49]
Ingestion rate (IR or I_R)	mg/day	200	100		[49]
Inhalation rate (IRih)	m^3/day	10	20		[49]
Skin surface area (SA/EA)	cm^2	2100	5800		[49]
Soil adherence factor (AF)	mg/cm^2	0.2	0.07		[43,49]
Dermal adsorption factor (ABS)	none	0.1	0.1		[23,49]
Dermal exposure (FE)	none	0.61	0.61		[49]
Particulate emission factor	m^3/mg	1.3×10^9	1.3×10^9		[49]
(PEF)					
Conversion factor (CF)	kg/mg	10^{-6}	10^{-6}		[23,49]
Average time (AT)					
For carcinogens	days	365 × 70	365 × 70		[49,77]
For non-carcinogens		365 × ED	365 × ED		[49,77]

Table A4. Mean metal concentration in analyzed samples and the maximum tolerable daily intake in drinking water [11,35,43,45,47,49].

Samples/Standards	Zn (mg/L)	Cu (mg/L)	Fe (mg/L)	Ba (mg/L)	Pb (mg/L)
KB1	0.027	0.0185	0.7895	11.055	0.0305
IB1	0.0205	0.012	0.389	12.4035	0.006
WB1	0.0215	0.005	3.1245	0.8915	0.007
KB2	0.00275	0.0004	0.0415	0.659	0.001
IB2	0.0015	0.0002	0.0023	0.8132	0.0005

Table A4. *Cont.*

Samples/Standards	Zn (mg/L)	Cu (mg/L)	Fe (mg/L)	Ba (mg/L)	Pb (mg/L)
WB2	0.0373	0.003	0.2829	1.7500	0.6897
WHO	3.000	2.000	0.300	4.000	0.010
EU	3.000	2.000	0.300	0.700	0.010
NIS	3.000	2.000	0.300	0.700	0.010
US EPA	5.000	1.300–3.000	0.300	2.000–4.000	0.005
CMHNS	NA	NA	0.050	NA	0.010–1.000

NA: not available.

Table A5. List of the LODs of the inspection method, relevant information about the validation, and analysis condition parameters.

Elements Examined	Limit of Detection (LOD) (ppm)	Limit of Quantification (LOQ) (ppm)
Ba	0.000693	0.29907
Cu	0.000693	0.30207
Fe	0.0001287	0.29312
Pb	0.000429	0.29804
Zn	0.000858	0.29508

$$\mathrm{LOD} = \frac{3.3\,RSD}{S}$$

$$\mathrm{LOQ} = \mathrm{LOD} + R$$

where LOD is the limit of detection, LOQ is the limit of quantification, RSD is the standard deviation (obtained from ICP-MS), and R is the validated lowest spike recovery (obtained from ICP-MS). The equations are used in line with standards and published articles [96–98]. Condition parameter: collision–reaction interface (CRI), $R^2 > 99.6\%$ accuracy as shown on the calibration curve.

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