

Assessment of Heavy Metal Concentration from a Lead-Zinc Mined Pit at Ebonyi State, Nigeria

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ABSTRACT

This study assessed the concentrations of heavy metals in soil and surface water from a Lead-Zinc mined pit at Enyigba, Ikwo Local Government Area in Ebonyi State, Nigeria. Soil samples were collected and analysed from different soil depths (0 – 15 cm) and (15 – 30 cm) at a tailing down (marked as TD) and refuse dumpsite (marked as RD) and a vegetation site 50 km away which was used as the control site. Surface water samples were collected from the Enyigba River from three (3) points (marked as point A, B, and C) and were analysed using routine laboratory procedures. The following parameters were analysed for soil: particle size distribution, pH, available phosphorus, total nitrogen, organic carbon, organic matter content, calcium, magnesium, potassium, sodium, exchangeable acidity, and effective cation exchange capacity. The results for mean values of soil samples obtained at both depths were 58.86% (sand), 11.73% (silt) and 34.04% (clay). Mean values obtained for heavy metals from the soil for Iron (Fe) ranged from 3.31 to 2.24 mg/kg; Zinc (Zn) 0.70 to 0.62 mg/kg and Lead (Pb) 0.01 to 0.01 mg/kg. Results obtained for surface water around the mined pit showed mean values for Iron (Fe) 0.57 mg/L, Magnesium (Mg) 151.6 mg/L, Calcium (Ca) 76.62 mg/L, Chlorine (Cl₂) 416.6 mg/L and Lead (Pb) 0.01 mg/L. The high concentrations of chlorine make the water unsuitable to be discharged on any agricultural land as plants could accumulate these metals and when consumed could pose serious threat to humans. The discharge from the mining site increased the already slightly high turbidity of the water to a much higher and undesirable level. The mining activity at Enyigba Ikwo LGA, Ebonyi State has negatively impacted the environment through the introduction of heavy metals in soil and surface water, thereby causing an increase in the pollution of the environment. It is recommended that further studies and monitoring should be carried out in the study location for possible remediation.

Keywords: Mining, Heavy metals, Pollution, Ebonyi State, Lead-Zinc mined pits

1.0. Introduction

Heavy metals are persistent, irreversible, and toxic pollutants of great environmental concern and are agreeably one of the major pollutants that are encountered in the soil (Ali and Khan, 2017). The metals that are considered as heavy are those with a density greater than a value of 5 or 6gcm⁻³ (Arantzazu *et al.*, 2000). Heavy metals occur naturally in the environment but may also be introduced into the environment as a result of land use activities and are also released by natural weathering of minerals and human activities (Nagajyoti *et al.*, 2010). Mining industries throughout history has seriously caused immense environmental pollution in industrialized and developing countries and are seen as significant sources of heavy metal contamination of soil and water bodies (Aucamp, 2003). Ahmad *et al.* (2005) reported that increased heavy metal content negatively affects soil microbial population, which may have direct negative effect on soil fertility. Toxic metals are being released into the environment in increasing amounts as exposures to these metals by humans are through the air, food, water and soil. These metals are not subject to chemical degradation and may accumulate in animal and human body tissue to toxic levels (Ali and Khan, 2017). Exposure to heavy metals can become chronic, due to food chain transfer while acute poisoning from heavy metals is rare through ingestion or dermal contact (Giller *et al.*, 1998). This situation is especially critical for fish and other

animals including humans at the top of the food chain. Abakiliki Lead-zinc deposits remain the largest and richest deposits in Ebonyi State, Nigeria and include those at Enyigba and Ameka-Ameri to the south of Abakiliki town, Mkpume-Akwatakwa, Mkpume-Akwaokuoko and Leffin to the north-east of the town. The Enyigba and Ameka-Ameri deposits were first mined in 1925 having constituted an important source of lead-zinc since the 1940's. However, mining ceased at the onset of the civil war and the natives shifted their interest on salt production from the brine pools associated with the lead-zinc deposits. In recent years, mining has continued intermittently, and many firms have renewed interests in operations within the area. This has resulted to abandoned open pit and several heaps of lead-zinc mine waste rocks, which have considerably reshaped the natural topography of the area. The heavy metal load in the soil and plants from the abandoned Enyigba mined pit and its environs have been reported and their prevalence in ground and surface water supplies in Ebonyi state have also been assayed (Afiukwa *et al.*, 2009). However, there is dearth of literature on the impacts of lead-zinc and refuse dumpsite on the fertility indices of the soil and their ecological impacts. The concentration of heavy metals in soil solution plays a critical role in controlling the availability of ions to plant. The solubility and therefore the bioavailability of heavy metal ions vary widely because many factors affect metal availability (Davies *et al.*, 2005). It has been found that soils contaminated by heavy metals tend to exhibit reduced porosity, poor hydraulic conductivity, and high rate of compaction (Udom *et al.*, 2004). Therefore, information available on the level of heavy metals in the surface or near-surface soils of Lead-zinc mine areas as well as surface water from the vicinity of the Eyingba mined pit will be very useful as this research will help to uncover the inherent danger posed to the communities where these disposals of waste from mining activities occur.

2.0. Methodology

2.1. The study area

The Abakiliki mining area lies between 06° 08' N and 06° 24'E and falls within the lower region of the Benue Trough (see Figure 1). It includes Abakiliki town and the highly mineralized rural communities (Enyigba, Amagu, Ameka and Ameri) which are about 14 kilometers south of metropolis (Abakiliki, the capital of Ebonyi State, in the south-eastern part of Nigeria) (Chukwuma, 1993). The routes in the area consist mainly of footpaths and narrow road networks. The area is underlain with poorly bedded shales of the Abakiliki shale age and deposits of galena (PbS) and sphalerite (ZnS) occur as veins and lodes in the oldest exposed sequence of the Abakiliki Basin within which the highly mineralized rural communities are located. The mining areas are inhabited by mostly agrarian people with artisanal lead-zinc mining as secondary operation. The city is in the middle of the south-eastern Nigeria and lies within the mineralized zone of lead-zinc deposits of the River Benue trough which stretches for hundreds of kilometers north-easterly from Zurak. The Benue trough is one of the known major areas with lead-zinc deposit in West Africa. Abakiliki, especially the Enyigba area which is about 14 km south of Abakiliki urban, is overlain with tropical rocks which constitute gneisses, granites shales, sphalerite and crustal rocks (Chukwuma, 1993). The prevailing climate is laden with high rainfall, high temperature, high atmospheric humidity and precipitation usually exceeding evapotranspiration for more than half the year. The Enyigba lead-zinc mine was intermittently mined for lead from 1925. Mining operations ceased due to low economic returns as well as the 1967-1970 Nigerian Civil War that badly affected the industry. This Abakiliki lead-zinc mining area, comprising of Enyigba, Ameka, Ameri and Amagu provide the inhabitants with economic sustenance next to agriculture. With the discovery and exploration of solid minerals in Abakiliki division of old Eastern Nigeria in the 1940s, artisan mining activities have become a significant occupation among the inhabitants, to the extent that all the households within the mining areas are involved in artisanal mining. This has affected the environment of the mining areas negatively, as heaps of mining tails are scattered everywhere and lead-zinc metals are heaped in most households, exposing the inhabitants of mining communities to metal pollution.

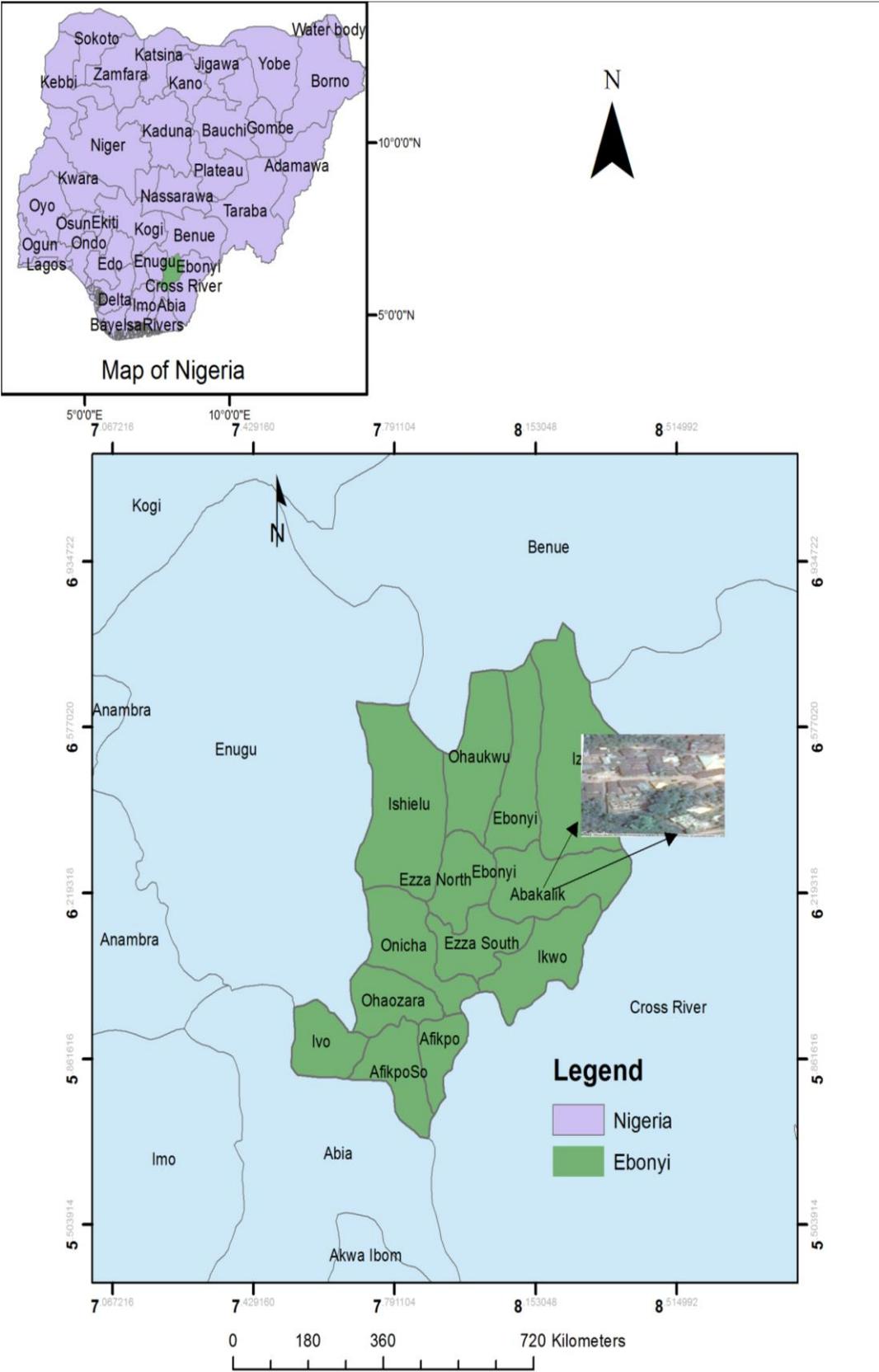


Figure 1: Map of the study area

2.2. Soil sample collection and preparation

The soil samples were collected at a depth 0-15 cm and 15-30 cm from the mine waste dumpsite known as tailing down (TD) and a refuse dumpsite (RDS) within the premises of Royal Salt Company Limited and vegetation site 50 metres away from the company which was used as the control sample using a stainless steel soil auger. The soil samples were transferred into polythene bags and labelled properly and then transported to the laboratory. The soil samples were air dried for three (3) days at room temperature and sieved using a 2mm sieve and kept in a clean and dry place pending analysis.

2.3. Laboratory analysis

Soil samples were analysed in the laboratory using standard laboratory procedures for physical and chemical properties as well as the total heavy metal content of lead and zinc using the method of AOAC (2005). The particle size distribution was determined using the hydrometer method. The textural class of soil samples of tailing down, refuse dump site and control were determined using textural triangle. Soil pH was determined using the glass electrode pH meter. Available Phosphorus in soil was determined using Bray-2 method, Total Nitrogen in the soil sample was determined by Kjeldahl digestion method, Total Exchangeable Bases, Calcium, Magnesium, Potassium and Sodium were determined using 1N NH₄ AOC method, the exchangeable acidity (EA) was determined by 1N KCl Extraction method, Effective cation exchange capacity (ECEC) was determined by the summation of total exchangeable bases (TEB) (Ca, Mg, Na, K) and Exchangeable Acidity (EA). Soil organic carbon was determined by Walkey and Black Wet Oxidation method as modified by Nelson and Sommers (1998), Lead, Iron and Zinc were determined using the digestive method of AOAC. (2005). Water samples were analysed for Temperature, Turbidity, Electrical Conductivity (EC), Total Dissolved Solids (TDS), pH, Alkalinity, Acidity, Hardness, Calcium (Ca), Magnesium (Mg), Lead (Pb), Iron (Fe) and Chlorine (Cl₂) using APHA, 1998 standardized procedures. Data analysis on the physico-chemical properties, heavy metal distribution in the soil and surface water samples were subjected to analysis of variance (ANOVA), while the mean values were separated using the Least Significant Difference (LSD) at $p < 0.05$.

3.0. Results and Discussion

Table 1 below shows the particle size distribution of soil samples from the study site with the mean values of sand, silt and clay at different soil depth (0-15 and 15-30cm).

Table 1: Particle size distribution of the soil

Samples		Sand (%)	Silt (%)	Clay (%)
Tailing down (TD)	0-15 cm	76.10±0.85 ^c	4.45±0.07 ^b	18.50±0.42 ^a
	15-30 cm	70.35±0.49 ^d	2.35±0.21 ^a	26.50±0.42 ^b
Refuse Dumpsite (RDS)	0-15 cm	27.00±0.28 ^a	26.65±0.35 ^d	46.85±0.49 ^f
	15-30 cm	55.90±1.13 ^b	6.40±0.14 ^c	36.65±0.21 ^d
Control	0-15 cm	61.90±1.13 ^c	2.35±0.21 ^a	34.25±0.35 ^c
	15-30 cm	61.90±1.13 ^c	28.20±0.28 ^e	41.50±0.71 ^e

Values with different superscript on the same column are significantly different ($p < 0.05$).

The results in Table 1 indicates that there were variations of significant differences ($p < 0.05$) at the different soil depths with respect to the particle size distribution. The soil was predominantly sandy clay loam at the top (0-15 cm) and sand clay below (15-30 cm). In the topsoil, the sand particles were in the range of 27.00% to 76.10% while the clay particles were in the range of 18.50% to 34.25%. The silt content ranges from 2.35% to 26.65% in the site of influence and 2.35% to 28.20% in the control site. At the lower layer (15-30 cm), the clay particles were in the range of 26.50% to 41.50% while the sand particles occupied the range of 55.90% to 70.35%. Sand ranges from 27.00% to 76.10% at the site of influence (Tailing down and Refuse dump site) and 61.90 % in the control site. The particle size distribution puts the soil in the sandy loamy textural classification.

The results of the physical and chemical properties of soil from the study area are presented in Table 2. The results show that there were variations of significant differences ($p < 0.05$) at the different soil depths.

Table 2: Physical and chemical properties of soil

Parameters/Depths		Tailing Down (TD)	Refuse Dumpsite (RDS)	Control
pH	0 – 15 cm	6.20±0.14 ^b	5.35±0.071 ^a	5.30±0.28 ^a
	15 – 30 cm	5.55±0.21 ^{ab}	5.70±0.41 ^{ab}	5.10±0.14 ^a
Available Phosphorous	0 – 15 cm	15.15±0.21 ^c	10.50±0.28 ^a	17.15±0.21 ^d
	15 – 30 cm	12.80±0.42 ^b	20.10±0.14 ^e	14.50±0.71 ^c
Total Nitrogen	0 – 15 cm	0.13±0.01 ^a	0.09±0.01 ^a	0.11±0.01 ^a
	15 – 30 cm	0.09±0.01 ^a	0.12±0.03 ^a	0.10±0.00 ^a
Organic Carbon	0 – 15 cm	2.49±0.04 ^c	1.03±0.04 ^a	4.22±0.16 ^{ab}
	15 – 30 cm	1.53±0.07 ^b	2.28±0.11 ^c	3.01±0.01 ^a
Organic Matter	0 – 15 cm	4.22±0.02 ^e	1.79±0.06 ^{bc}	5.51±0.13 ^b
	15 – 30 cm	2.07±0.08 ^c	2.59±0.13 ^d	4.02±0.02 ^a
Calcium	0 – 15 cm	3.50±0.14 ^d	1.67±0.05 ^{ab}	2.07±0.09 ^{bc}
	15 – 30 cm	2.15±0.13 ^{bc}	2.70±0.14 ^c	1.22±0.31 ^a
Magnesium	0 – 15 cm	1.62±0.02 ^b	1.07±0.09 ^a	1.16±0.22 ^{ab}
	15 – 30 cm	1.32±0.11 ^{ab}	1.49±0.05 ^{ab}	1.08±0.11 ^a
Potassium	0 – 15 cm	0.12±0.02 ^b	0.05±0.02 ^a	0.08±0.03 ^{ab}
	15 – 30 cm	0.09±0.01 ^{ab}	0.09±0.01 ^{ab}	0.03±0.01 ^a
Sodium	0 – 15 cm	0.21±0.01 ^b	0.09±0.01 ^a	0.11±0.01 ^a
	15 – 30 cm	0.11±0.00 ^a	0.18±0.03 ^{ab}	0.13±0.04 ^{ab}
Exchangeable Acidity	0 – 15 cm	0.56±0.06 ^b	1.38±0.03 ^d	1.13±0.04 ^c
	15 – 30 cm	1.24±0.05 ^{cd}	0.36±0.08 ^a	0.39±0.01 ^{ab}
Effective cation exchange capacity	0 – 15 cm	6.50±0.14 ^d	4.33±0.11 ^b	4.58±0.25 ^{bc}
	15 – 30 cm	4.81±0.14 ^d	5.09±0.16 ^c	3.05±0.07 ^a

Values with different superscript on the same column are significantly different ($p < 0.05$).

The pH values range from 5.10 to 6.20 indicating that the different layers of the soil were acidic. The pH of the soil from the mined pit was higher than that of the soil around the refuse dumpsite and the control sites respectively. Soil pH has been reported as exerting a controlling influence on the availability of micronutrients to plants (Davies *et al.*, 2005). A pH of 6.5-7.5 is reported to be optimal for plant nutrients (Arias *et al.*, 2005). Lee *et al.* (2002) reported that high electrical conductivity in soil and opined that it could be due to excessive concentration of heavy metals. Wan *et al.* (2009) obtained high electrical conductivity in an abandoned mine sites in Malaysia in research on acid mine drainage and heavy metals contamination at abandoned and active mine sites in Pahang. The higher electrical conductivity obtained within the mined pit could be attributed to higher concentration of major cations and anions in the soil. Industrial saline waste and irrigation are the main human activities that add salt to the soil. However, there are no irrigation activities in the study area thus, the high electrical conductivity could be related to the deposits from the mine. The available phosphorous content of the soil at the mined pit was higher than that of the control. The phosphorous concentration decreased with increase in distance away from the mined pit and ranged from 15.15 ppm to 10.50 ppm thus leaving the control soil with the highest value of phosphorous concentration. Similar observation was reported by Edeogu *et al.* (2007) on soil at a quarry site in Ebonyi state. The lower value obtained at the lower depth compared to the upper layer of the soil could be attributed to the effect of leaching. Total nitrogen of the study area ranged from 0.13% to 0.09% as against 0.11% in the control soil. The nitrogen content of the soil could be due to the effect of mineralization as observed by Osakwe and Akpoveta (2012). The cations (Ca, Mg, K, Na, Ea, ECEC and P) were also higher in the point of activities in the soil than in the control area. The cation exchange as shown in the exchangeable acidity result was 0.56 cmolkg⁻¹ in the mined pit soil, 1.38 cmolkg⁻¹ at the refuse dumpsite and 1.13 cmolkg⁻¹ in the control site. The organic carbon (OC) and organic matter (OM) content of the soil also showed variations as both decreased with depth and with distance from the mined pit site to the control site. The mined site had organic matter content of 2.49% in the topsoil (0-15 cm) but decreased to 1.53% in the sub soil (15-30 cm). The organic matter decreased from 4.22% to 2.05% at the mined pit site. However, the organic matter content of the control soil was found to be

higher 4.22%. According to Yun (2003), high organic matter content in the soil contributes significantly to acidity through the contributions from organic acids and biological activities. The higher organic matter content in the control soil may be due to higher vegetation foliage with more leaf falls which necessitated high microbial activity in the decay of the leaves.

The results of Fe, Zn and Pb concentrations in soil samples are presented in Table 3.

Table 3: Heavy metals content in the soil

Samples		Fe	Zn	Pb
A	0-15 cm	3.70±0.14	0.83±0.02	0.02±0.00a
	15-30 cm	2.68±0.05	0.83±0.04	0.01±0.00a
B	0-15 cm	3.67±0.04	0.77±0.04	0.01±0.00a
	15-30 cm	2.95±0.21	0.60±0.02	0.01±0.00a
Control	0-15 cm	2.55±0.49	0.50±0.05	0.01±0.00a
	15-30 cm	1.10±0.14	0.43±0.06	0.01±0.00a

Values with different superscript on the same column are significantly different ($p < 0.05$).

Table 3 shows the heavy metal content of soils from the mined area and the control environment. The result shows that the heavy metals were generally higher at the topsoil than at the sub soil. Also, the heavy metals were considerably higher at site A and B than the control environment. Iron (Fe) ranged from 3.70 mg/kg to 2.55 mg/kg in the topsoil with the mined site having the highest level of Fe. Zinc ranged from 0.83 mg/kg to 0.50 mg/kg in the topsoil with the mined site having the highest level of Zn and the sub-soil ranges from 0.83 mg/kg to 0.43 mg/kg for Zn in all the study sites. All the heavy metals recorded higher values at the mined site as compared to the control soil. This result implies that soils around the lead-zinc mine pit have higher concentration of heavy metal analysed in this study. It was observed that the level of Iron (Fe) on the soil was higher than that of other metals in the soil. It is known that Iron (Fe) pollution of soil cannot be entirely linked to wastes (Eddy *et al.*, 2004) as its presence could be due to lithological or crustal origin (Levy *et al.*, 1992). Zinc concentration at the mined pit (site A) was significantly higher than site B and C respectively. The higher concentration of what obtained in the upper layer at the mine pit could be attributed to recent deposit of splashes from the pit. The higher value obtained around the wastewater area is not surprising since zinc is known to have high mobility in the soil profile (Keller *et al.*, 2002; Krzyztof *et al.*, 2004).

The physical and chemical properties of surface water samples from Enyigba River are presented in Table 4.

Table 4: Physical and chemical characteristics of surface water

Samples	Point A	Point B	Control
Temp °C	26.15±1.06 ^a	26.30±0.71 ^a	26.10±0.14 ^a
Turbidity (NTU)	5.45±0.35 ^a	5.55±0.21 ^{ab}	6.30±0.14 ^b
EC (µs/cm)	503±4.24 ^a	515±7.01 ^a	513±1.41 ^a
TDS (mg/L)	507±3.54 ^a	514±2.12 ^a	528±2.50 ^b
pH	6.20±0.28 ^a	6.35±0.21 ^a	6.35±0.07 ^a
Alkalinity (mg/L)	101.50±2.12 ^a	103.00±1.41 ^a	101.00±1.41 ^a
Acidity (mg/L)	30.75±1.06 ^a	31.00±1.41 ^a	28.75±0.35 ^a
Hardness (mg/L)	197.50±3.54 ^a	207.50±6.36 ^a	214.00±5.66 ^a

Values with different superscript on the same column are significantly different ($p < 0.05$).

Temp = Temperature, EC = Electrical Conductivity, TDS = Total Dissolved Solids

The results ascertain from the direct point of influence Point A varied significantly with the midstream point which is 50m away from the area of activities that received direct discharge and the control which is an area totally void of the pollution. There is no significant variation in the temperature of the water samples in the three sampling locations with values of 26.15 °C, 26.30 °C and 26.10 °C respectively. The turbidity of water samples from the Enyigba River showed variation between the point of influence (Point A) (5.45 NTU) and the control water sample (6.30 NTU). However, the relatively lower turbidity level was attributed to possibly contamination of the water by discharges into the river at the upper locations of the river course. The Enyigba River is open to receive soil debris from the adjoining environment into the water body including animal and human faeces. High turbidity is not desirable in surface water as it leads to restriction of light penetration processes such as flocculation and filtration which increases cost of purification (Uzoukwe *et al.*, 2011). DWAF (1988) reported that high turbidity is associated with microbial contamination.

Muoghala and Omocho (2008) observed that highly turbid water is very unsuitable as a source of water for domestic use in the community. On the whole, the discharge from the mining site increased the already slightly high turbidity of the water to a much higher and undesirable levels, which agrees with the findings of Eze and Chukwu (2003). There was no significant difference in the values of electrical conductivity in surface water sample obtained from the study area. The mean values of EC ranged from 503.00 $\mu\text{s}/\text{cm}$ to 515.00 $\mu\text{s}/\text{cm}$. The recorded values for pH ranges from 6.20 to 6.25 and values for hardness of the water was higher at the control (214.00 mg/L) and for Point B (207.50 mg/L) as against 197.50 mg/L (Point A). Although, recorded values for water hardness were within the permissible limits of 100 mg/L (NESREA, 2009) in water for domestic use. The pH was slightly acidic, however, this value fell within the range of 6.85 recommended for pH in water by Environmental Protection Agency (2009). The slight acidic pH observed may be attributed to the contamination of the water by the high presence of CO_2 and SO_2 due to mining activities. The total dissolved solid (TDS) was high and this could be as a result of high concentration of inorganic salts that are dissolved in the water (WHO, 2007). The TDS obtained in this study was within the FAO standard) of 450 – 2000 mg/L recommended for agricultural use. The chloride content of the water was within acceptable limit of 1000 mg/L (WHO, 2007) and therefore will not pose any harm to agricultural soils. The alkalinity level of the water was in the range of 101.00 mg/L to 103.00 mg/L, while on the acidity levels were relatively higher in the point of influence to the control point with a range of 28.75 mg/L to 31.00 mg/L. The total dissolved solid was in the range of 507.00 mg/L to 528.00 mg/L.

Levels of heavy metals in surface water are presented in Table 5 below.

Table 5: Heavy metal content of surface water

Samples	Point A	Point B	Control
Ca (mg/L)	72.35 \pm 2.33 ^a	78.50 \pm 0.71 ^b	79.00 \pm 1.41 ^b
Mg (mg/L)	148.00 \pm 2.83 ^a	156.00 \pm 1.41 ^b	151.50 \pm 0.71 ^{ab}
Pb (mg/L)	0.01 \pm 0.00 ^a	0.01 \pm 0.00 ^a	0.00 \pm 0.00 ^a
Fe (mg/L)	0.60 \pm 0.14 ^a	0.55 \pm 0.01 ^a	0.56 \pm 0.05 ^a
Cl ₂ (mg/L)	417.00 \pm 7.07 ^a	419.00 \pm 1.41 ^a	414.00 \pm 1.41 ^a

Values with different superscript on the same column are significantly different ($p < 0.05$).

Ca = Calcium, Mg = Magnesium, Pb = Lead, Fe = Iron, Cl₂ = Chlorine

The surface water samples had high chloride (414.00 mg/L to 419.00 mg/L) and calcium content (72.35 mg/L to 79.00 mg/L) respectively from the points. There was no trend applied for all samples as heavy metals varied significantly. The mean concentration for calcium was highest at Control > Point B > Point A, while magnesium (Mg) and Iron (Fe) had Point A > Control > Point B. The mean concentration of chloride was high at Point B > Point A > Control. The concentration of chloride in the water is above allowable safe limits and with this level, accumulation in food samples or through the food chain into human body will lead to low health risks in humans (Chiroma *et al.*, 2014; Kinuthia *et al.*, 2020).

4.0. Conclusions

The mining activity at Enyigba, Ikwo LGA, Ebonyi State showed that heavy metals can negatively impact the environment through mining activities. This study showed that there were significant differences in the parameters analysed for soil at both depths of the study area as well as from the surface water samples from Eyingba River around the mined pit. There is an urgent need to make policies that will guide and regulate mining activities in this area to avoid multiple poisoning effects of these metals. Also, it is important that regular study should be conducted to keep track record on the daily consumption of food items consumed by residents in the Ikwo Local Government Area in order to ascertain the health risk that may arise from the activities from the mining environment.

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