

# Geochemistry of Surface Waters, In Ishiagu, Ebonyi State, Nigeria.

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## Abstract

Ishiagu is one of the important lead-zinc mining districts in Nigeria. It is underlain by two sedimentary formations, Abakaliki and Ezeaku Formations. The Abakaliki Formation experienced intense tectonic and intrusive activities during Santonian times that helped establish its geochemical signature. Samples of water were taken from surface waters (comprising rivers, wetlands and pit lakes) in the area and analysed chemically in order to check if the surface mining activities were impacting the water quality in any way. The results showed moderately acidic waters with pH ranging from 4.8 – 6.8, and relatively low solute concentrations. Calcium ( $\text{Ca}^{2+}$ ) and Sodium ( $\text{Na}^+$ ) account for more than 80% of the cation chemistry while the dominant anions are bicarbonates ( $\text{HCO}_3^-$ ) and sulphates ( $\text{SO}_4^{2-}$ ). Analysis for heavy metals indicate that all the surface water bodies are polluted with respect to nickel and lead. Only two samples were polluted with respect to manganese. The wetland sample showed promise in the positive modification of polluted water.

**Key words:** *Ishiagu; surface waters; nickel; lead; wetlands*

## INTRODUCTION

Ishiagu is one of the economically important towns in Ebonyi State, southeastern Nigeria. Its economic relevance is basically due to agricultural and mining activities in the area.

Lead/Zinc deposits were discovered in the area in the 1950s according to Bogue (1952) and this has attracted a lot of attention from government establishments and mining companies to the area.

Ishiagu belongs to Ivo local government area of Ebonyi state. It has a population of about 10,000. As a rural community, the primary occupation of the people is farming but a few people work with quarrying companies.

## RELIEF AND DRAINAGE

The study area (Ishiagu) has an undulating terrain characteristic of the Cross River Plains geomorphological province. The highest elevation is about 110m above sea level and formed by erosion-resistant igneous intrusives while the lower areas are underlain by soft rocks. Ishiagu is drained by a number of rivers such as Ikwo River, Ivo River, Odu River and Ihetutu streams (Figure 1). The main river Ivo takes its source from the Udi-Okigwe cuesta and then splits into smaller streams such as Ikwo, Ngado, Ihetutu and Eku rivers that create dendritic drainage pattern in the study area.

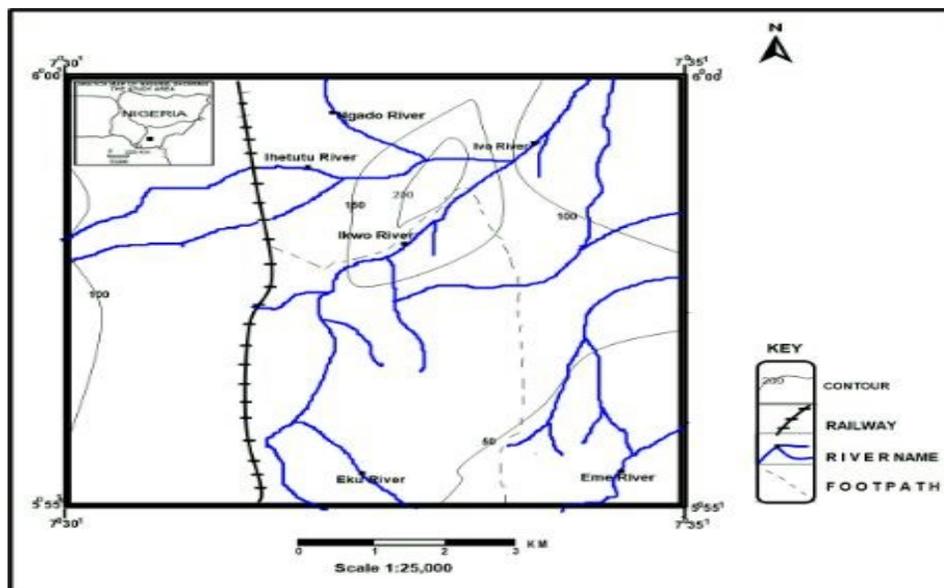


Figure1: Topographic map of Ishiagu

**CLIMATE AND VEGETATION**

Ishiagu has two main seasons – a dry season that run from November to March and a rainy season from April to October. According to Ofomata (2002), Ishiagu has annual precipitation of about 1925mm which is relatively high. He also estimates the average temperature to be about 27°C. As part of the sub-savannah, the common vegetation are tall grasses and small trees. Crops commonly cultivated at Ishiagu include rice, cassava, yams and vegetables like pumpkin and spinach.

**GEOLOGIC SETTING**

The study area is underlain by two rock formations as indicated in the geologic map of the study area (Fig. 2). The oldest is Abakaliki Formation which comprises two

mappable units of shales and sandstones. The shale unit was referred to as Ivo Shale by Ezepue (1984) and consists of clay, siltstones and dark grey calcareous shales while the sandstone unit consists of fine to medium grained calcareous sandstone. The two units dip between 15° to 22° to the northwest, and 20°-30° to the southeast. The Abakaliki Formation is unconformably overlain by a sandstone member of the Ezeaku Formation. This sandstone member of Ezeaku Formation was dated Turonian by McConnell (1949). It grades from siltstone to fine-medium grained sandstone with dips ranging from 18° to 38° to the southeast direction. Ezepue (1984) described a set of fractures running NW to SW in the area. According to him, these fractures run transversely to the fold axis and may have been due to the tectonic activities that folded the rocks

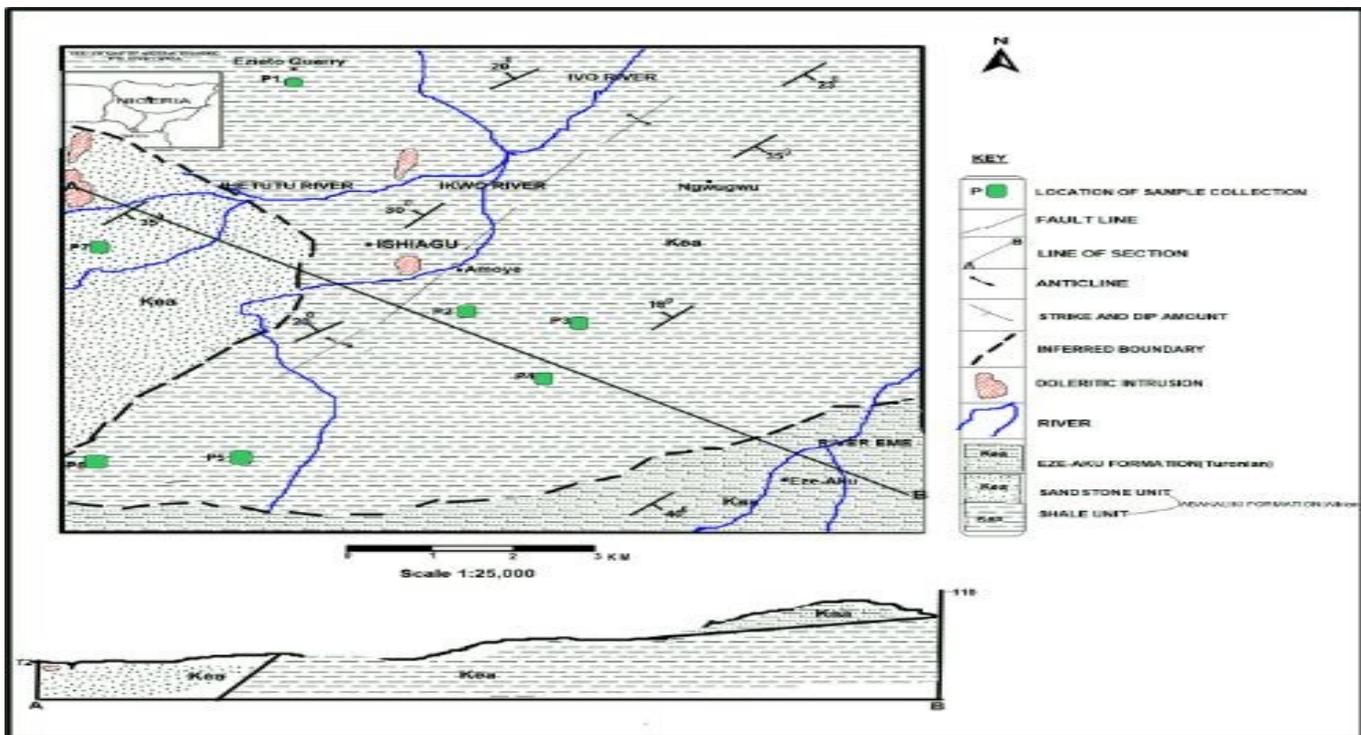


Figure 3 shows that rocks at Ishiagu are not only mineralized of leaching of metals from sediments that were heated by but folded. Infact, there is an anticlinal axis running from circulating connate waters which occurred between Albian and Ishiagu towards the north. The mineral deposits at Ishiagu have Cenomanian times. Ezepue (1984) identified siderite, galena been studied by Mckay (1946); Reymont (1965); Orajaka and sphalerite in the area. Mamah et al (2000) discovered that (1965) and Olade (1975, 1976). According to Olade and some secondary minerals in the area were formed as a result of Morton (1980), the lead-zinc deposits were formed as a result of metasomatic alteration.

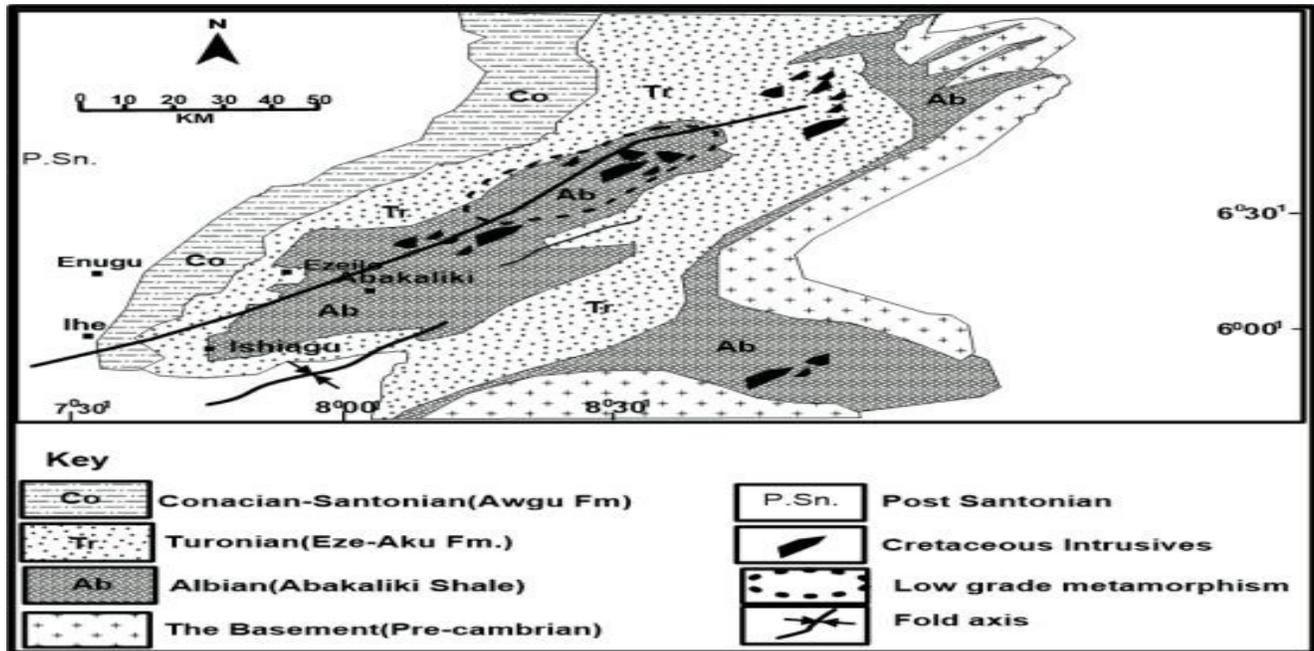


Figure 3 Geological setting of Ishiagu and Abakaliki pb-zn vein alignment (after Akande and Erdtmann, 1998)

They identified these secondary minerals as anglesite ( $PbSO_4$ ), cerussite ( $PbCO_3$ ) and smithsonite ( $ZnCO_3$ ). The composition of the igneous rocks at Ishiagu range from intermediate to basic according to Ofoegbu (1985). They occur as dolerite sills and dykes within the Abakaliki Formation. The mineral suite in the sills and dyke include biotite, plagioclase, hornblende, augite, quartz and calcite and has been confirmed by Chukwu (1981) to be of Santonian age. Since the predominant rock formations in Ishiagu are shales, boreholes (i.e. groundwater) are not an important source of water. The people of the area depend primarily on surface water bodies. Surface water bodies include the various streams in the areas, wetlands and pit lakes. The pit lakes were formed by the activities of mining companies. The aim of this paper is to determine geochemical characteristics of surface water bodies in the area. This preliminary assessment will help to indicate whether these surface water bodies are being impacted by the mining activities in the study area or not.

### MATERIALS AND METHODS

Water samples were taken from Ikwo river, five pit lakes and one wet land. The sample bottles were flushed with the water to be sampled before collection. Parameters such as EC, TDS, temperature and pH were measured in the field before samples were taken with the aid of a multiparameter water quality meter (Hanna93103). All the temperature measurements were taken at 10am in the morning. In order to stabilize certain chemical species, the samples were acidified to a pH of 2 before samples

were taken to the laboratory. Cations were analysed with the aid of Atomic Absorption Spectrometer (AAS) at FAT LAB, Ibadan, Oyo State Nigeria while the anions were analysed using the methods of American Public Health Association as described by Clesceri et al., (1998).

### RESULTS

Results of the chemical analysis of the water samples are given by table 1. This shows the major element chemistry. The pH values of the water ranges from 4.8 at the Obeagu pit lake to 6.8 at the Ihetutu wet lands. Total dissolved solid (TDS) levels indicate waters that range from very dilute to mildly brackish. The range is from 107.2mg/l at Eziato pit lake to 804.0mg/l at the Ihetutu pit lake. This was also confirmed by the values of electrical conductivity which range from 70.9ms/cm to 202.2ms/cm. Cations concentrations in the areas are dominated by calcium and sodium ions.  $Ca^{2+}$  and  $Na^+$  make up over 80% of the major cations.  $Ca^{2+}$  ion ranges from 0.40mg/l at Obeagu pit lake to 36.04mg/l at Eziato pit lake while  $Na^+$  goes from 4.21mg/l at Obeagu pit lake to 51.52mg/l at the Ikwo river.  $Mg^{2+}$  varies from 0.20mg/l at Obeagu pit lake to 10.65mg/l at Eziato. Potassium ( $K^+$ ) ranges from 0.42mg/l at Obeagu pit lake to 8.31mg/l at the Ikwo river. The dominant anions are bicarbonates and sulphates. Chlorides are somewhat subordinate. Bicarbonates ( $HCO_3^-$ ) range from 30.5mg/l in many of the samples to 61.00mg/l at Eziato pit lake and Ihetutu wetland while sulphates ( $SO_4^{2-}$ ) vary from 12.46mg/l at the Ikwo River to 35.15mg/l at the Eziato

pit lake. Chlorides (Cl<sup>-</sup>) range from 10.80mg/l at Ihetutu pit lake to 19.80mg/l in Eziato, Ndiuzie and Ikwo river.

Table 1: Chemistry of the major elements of the water samples

Chemical Parameters mg/L	Location						
	Eziato Pit lake(P1)	Ndiuzie Pit lake(P2)	Ikwo River (P3)	Obeagu Pit lake (P4)	Ihetutu Pit lake(P5)	Ihetutu wetland(P6)	Setraco Lake(P7)
Temp(°C)	30.7	34.0	15.4	18.0	28.8	20.0	15.5
EC µs/cm	160	202.2	80.0	90.4	120.0	100.2	70.9
TDS	107.2	135.3	536.0	630.0	804.0	683.0	529.0
pH	5.1	6.0	5.9	4.8	5.2	6.8	6.2
Calcium (Ca <sup>2+</sup> )	36.04	3.11	2.01	0.40	4.16	5.84	18.65
Potassium (K <sup>+</sup> )	0.96	1.94	8.31	0.42	0.61	3.32	4.36
Magnesium (Mg <sup>2+</sup> )	10.65	2.08	2.14	0.20	1.72	1.52	4.78
Chloride(Cl <sup>-</sup> )	19.80	19.80	19.80	14.40	10.80	12.60	14.40
Sulphate(SO <sub>4</sub> <sup>2-</sup> )	35.15	22.41	12.46	26.52	19.07	15.40	18.75
Bicarbonate(HCO <sub>3</sub> <sup>-</sup> )	61.00	30.50	30.50	30.50	30.50	61.00	30.50

Table 2 shows the heavy metal concentration of the water samples in micrograms per litre. The heavy metals chosen for analysis were manganese (Mn); nickel (Ni); iron (Fe), copper (Cu); Zinc (Zn) and lead (Pb) because of a prior knowledge of the mineral suite at Ishiagu. Manganese (Mn) values range from 0.00µg/l in several samples to 210µg/l at Ikwo River. Nickel (Ni) varies from 330µg/l at Ihetutu wet land to 2200µg/l at Ndiuzie

pit Lake. Total Iron (Fe) goes from zero in the Setraco lake to 4560µg/l at Ndiuzie pit lake. Values of Copper (Cu) varies from 400µg/l at Setraco to 1200µg/l at Ndiuzie pit lake. Zinc (Zn) values go from 30µg/l at Ikwo River to 820µg/l at Ihetutu pit lake. Lead (Pb) varies from 100µg/l at Ihetutu wetland and Setraco lake to 2990µg/l at Ikwo River.

Chemical parameters in µg/ l	Location							Average Values
	Eziato Pit lake(P1)	Ndiuzie Pit lake(P2)	Ikwo River (P3)	Pit lake (P4)	Ihetutu Pit lake(P5)	Ihetutu wet land(P6)	Setraco Lake( P7)	
Manganese (Mn)	110	0.00	210	0.00	0.00	0.00	0.00	45µg/l
Nickel (Ni)	510	2200	800	1500	1200	330	620	1022.86
Iron (Fe)	100	4560	310	100	400	200	0.00	810/945
Copper (Cu)	600	1200	900	1100	1110	400	400	815.71
Zinc (Zn)	70	260	30	40	820	400	50	238.57

Lead (Pb)	1100	1100	2990	1100	600	100	100	1012.86
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**DISCUSSION**

The pH range of the surface water samples indicate a geochemical environment that range from acidic, mildly acidic to neutral. The low pH of 4.8 maybe an indication of acid mine drainage at the Obeagu pit lake. The almost neutral condition at the Ihetutu wetland (i.e. pH = 6.8) could be a reflection of buffering processes generated by the wet land. It is interesting to note that at the Ihetutu pit lake, the pH is acidic (i.e. 5.2) but changes to neutral in the wet land.

The fact that Ca<sup>2+</sup> values are consistently greater than the Mg<sup>2+</sup> ions in the waters show that the origin of the waters is primarily meteoric. There is little or no contribution from connate waters that may have contributed magnesium.

Table 3 shows the maximum contaminant levels (MCL) allowed for manganese, nickel, iron copper, zinc and lead. In some of the parameters, the U.S.E.P.A. guidelines appear to be more stringent. If the guidelines are applied to the heavy metal concentrations in table 2, it will be seen that most of the concentration levels of heavy metals in Ishiagu actually exceed the permitted limits. For manganese, the range in Ishiagu goes from 0.0 µg/l in several samples to 110 µg/l at Eziato pit lake and 210 µg/l at the Ikwo River. The MCL for the WHO/USEPA ranges from 50 – 100 µg/l (table 3). The implication is that Eziato pit lake and Ikwo River waters are polluted with respect to manganese. For nickel, the MCL is 70 µg/l but the range for the study area is 330 – 2200 µg/l with an average value of 1022.86 µg/l which is about 14.6 times greater than the MCL. Iron (Fe) ranges from 0.00 – 4560 µg/l. Its average of 810 µg/l is 2.7 times greater than the MCL permitted by WHO AND U.S.E.P.A. Copper values go from 400 – 1200 µg/l with an average of 815.71 µg/l which is less than the 1300 µg/l MCL prescribed by USEPA. The average value for zinc is 238.57 µg/l which is far less than the 5000 µg/l provided by USEPA. Values for lead range from 100 – 2990 µg/l with an average of 1012.86 µg/l which is 67 times greater than MCL given by USEPA and 101 times greater than that of WHO. The general implication therefore is that many waters in the area are polluted with respect to manganese, nickel and lead. This is certainly connected with anthropogenic activities related to the mining of Lead-Zinc in Ishiagu.

Table 3: MCL (maximum contaminant levels) values for heavy metals according to U.S.E.P.A (2010) and W.H.O. (2006)

Heavy Metals(µg/L)	USEPA	WHO
Manganese(Mn)	50	100

Nickel (Ni)	70	70
Iron (Fe)	300	300
Copper (Cu)	1300	2000
Zinc (Zn) – µg/L	5000	-
Lead (Pb) – µg/L	15	10

It is interesting to note that the Ihetutu Wetland seems to have low concentration values or most of the heavy metals especially manganese, nickel, iron, copper and lead. It was noted earlier that its pH was a bit higher than other samples. These lower values are due to the geochemical contribution of the wetland processes to the modification of the polluted waters. The studies of Reddy and Delaune (2008) and Kadlec and Wallace (2009) indicate that wetlands can modify the chemistry of polluted waters.

**CONCLUSION**

This preliminary assessment of the chemical quality status of the surface waters in Ishiagu suggests the surface-mining of lead-zinc in the area is negatively impacting surface water bodies. Further studies will have to be conducted to also assess impacts on groundwater and plants. Eventually it will also be necessary to examine the extent to which the human population has been affected.

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