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# UPTAKE OF NUTRIENTS AND HEAVY METALS INTO PLANTS AROUND OKPARA MINE: COMPARISON WITH SURFACE WATER CHEMISTRY IN ENUGU, SOUTHEASTERN NIGERIA

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**Abstract**

The aim of this study was to determine the extent of heavy metal in natural waters and the uptake by plants that grow in the AMD zones/non-AMD zones in Okpara coal mine. The study areas were classified into zones A, B and c, Water samples from all the three zones were analyzed in the laboratory,Fifteen [15] water samples and six [6] plant leaves samples were collected from the area.The species of plant leaves collected include Polypodiaceae Pteridium Aquilinum, Anacardiaceae Mangifera Indica and Euphorbiaceae Alchornea Cordifolia. Results revealed that Zone A has low pH value of 3.2 and high $SO_4$ (52.30mg/l – 54.42mg/l), $Na^+$ (105.7mg/l – 108.0mg/l) and $Fe^{3+}$ (7.08mg/l - 13.24mg/l) concentrations, indicating that AMD forming in the zone. In zone B, the pH value ranged from 3.5 to 4.67 and the $SO_4$ (24.02mg/l – 49.55mg/l), $Na^+$ (30.14mg/l – 72.35mg/l) and $Fe^{3+}$ (0.02mg/l – 9.74mg/l) concentrations indicating the influence of AMD from zone A. Meanwhile, in zone C, the pH ranged from 5.4 – 6.8 and the $SO_4$ (0.83mg/l 26.81mg/l), $Na^+$ (12.05mg/l – 171.0mg/l) and $Fe^{3+}$ (0.00mg/l – 0.01mg/l) concentrations indicating AMD-free in the zone. Furthermore, the results revealed that plant leaves within the mine are taking up heavy metals but the level of absorption has no effect on their system.

## 1. INTRODUCTION

Acid mine drainage is one of the problems associated with mining of sulfur-bearing ore deposits. It is characterized by low pH and high $SO_4^{2-}$, $Fe^{3+}$ and heavy metals. Abandoned mines and tailings piles which are flooded can be sources of acid mine drainage and can be a threat to different ecosystems (Moncur et al., 2005). The presence of low pH and high concentrations of $SO_4^{2-}$, $Na^+$, $Fe^{3+}$ and trace metals in surface and ground waters is one of the main problems associated with acid drainage generated in coal mining areas (Veridianap et al., 2013). This is the case in Enugu, Nigeria, where coal was discovered since 1909 by British Geologists which led to the development of five coal fields (Okpara, Onyeama, Iva, Ribadu and Ekulu) in the area (Awoniyi, 1977). One of the coal fields, Okpara mine, was opened in 1952 by Nigerian Coal Corporation but was later closed down in 2004 as a result of economic problems (Nganje et al., 2011). Abandonment of the mine resulted to the flooding of the mine by surface and groundwater. The water draining from the mine has been noted to contain low pH and elevated concentrations of heavy metals that causes significant degradation in the environment. Accumulation of the heavy metals in plants, surface and ground water within the mine has been a great concern due to the

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probability of contamination through the soil root interface, exposure of overburden and mine spoils to oxidation.

Several credible studies (Awoniyi, 1977; Egboka and Uma 1985; Ezeigbo and Ezeanyim, 1993; Ofodile, 2002; Nganje et al., 2010; Utom et al., 2012; Sikakwe et al., 2015; Ozoko, 2015) have been conducted on acid mine drainage within the Enugu coal field and these works have helped to highlight the chemistry of acid mine drainage in Okpara coal mine.

Nagajyoti (2010) reported that various heavy metals are essential for plant growth but plant toxicity resulting from heavy metal uptake varies with plant species, specific metals, concentration, chemical form, soil composition and pH. However, some heavy metals including Pb and Cd are not essential for plant growth. These non-essential heavy metals are readily uptaken and accumulated by plants in toxic forms (Requia et al., 2015). Since areas with suspected AMD formation are susceptible to the production of heavy metals and uptake of heavy metals by plants influences their ability to assimilate pollutants and maintain nutrients in solution, it will be necessary to study plant chemistry especially in areas with suspected AMD formation. Additionally, there is paucity of data on the uptake of heavy metals by plants in Okpara mine. Therefore, this study was designed to evaluate the geochemistry of acid mine drainage in Okpara coal mine and make comparisons with other natural waters with AMD-free zones. Furthermore, plants in the mine area were assessed for heavy metal uptake and the effects of such uptakes will be studied.

## 2. THE STUDY AREA

### 2.1. Location

The study area, Okpara mine is situated at about 5km west of Enugu town, precisely in Akwuke, Enugu South Local Government Area. The area is within latitudes N060231 to N060271 and longitude E070251 to E070301 and covers about 85.5km2. The area can be accessed through Enugu-Port Harcourt expressway and Akwuke junction through Gariki Enugu (Figure 1).

### 2.2. Relief and Drainage

The study area is characterized by two major landforms; highlands and lowlands. The highland areas consist of an asymmetrical ridge that runs northeastward of River Niger to the southern Enugu to Okigwe and is associated with Mamu Formation and Ajali Sandstone. The lowland areas are underlain by Enugu Shale. The study area is drained by the Nyaba River and its tributaries which are dendritic in pattern. The Nyaba River is perennial and heads in the Milikin Hills just above the Okpara mine.

iii. Climate and Vegetation

The study area lies within a tropical rainforest. Two climate seasons exist in the area, rainy and dry season. The rainy season lasts from April to November while the dry season lasts from November to March. The mean annual rainfall in the area is about 1600m (Ofomata, 1965).

## 3. GEOLOGY AND HYDROGEOLOGIC SETTING

Figure 1 shows the three geologic formations that underlain the study area. From the oldest, they include Enugu Shale, Mamu Formation and the Ajali Sandstone. Enugu Shale (Campanian) is composed of marine shales, laminated mudstones and interlaminated very fine-grained sandstones with siltstones. The Mamu Formation (Lower Maastrichtian) is lithologically composed of shales, fine sand and coal seam while the Ajali Sandstone exhibits a characteristic white friable, moderate to poorly sorted, coarse to medium grained, pebbly and cross-bedded sandstones, sometimes occurring with stains of iron. The dip amount ranges from 30 - 100SW. The perennial streams that rise from the base of the escarpment appear to be structurally controlled in their flow pattern, giving rise to a dentritic pattern. The topography of the area also controls the hydrology. The area also consists of two main aquifer systems, unconfined and confined aquifer. The Ajali Sandstone and sand members of Mamu Formation form the unconfined aquifer while the shale members of the Mamu Formation and Enugu Shale form the confined aquifer system that are trapped by hand dug wells with a static water level ranging from 5m to 9m deep.

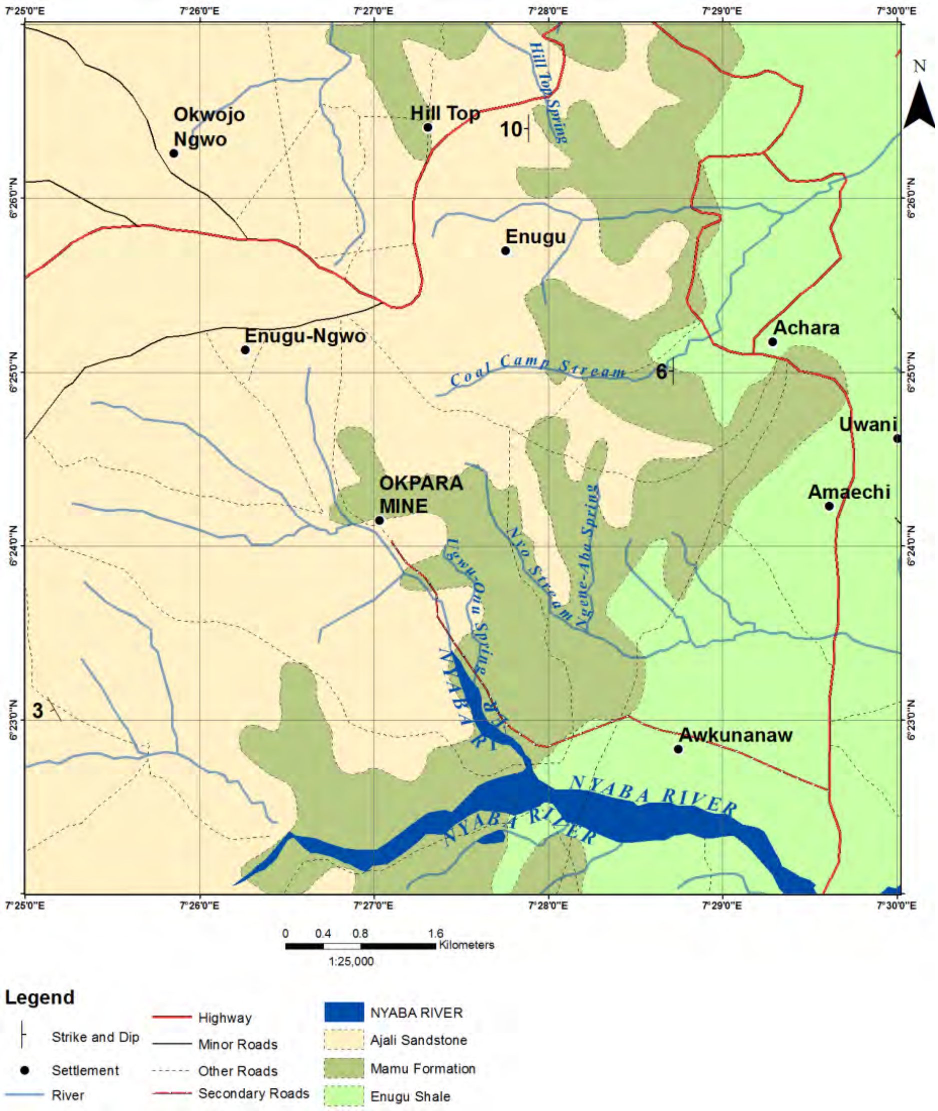


Figure 1: Geologic map of the study area.

## 4. MATERIALS AND METHODS

In order to achieve the objective of this investigation, the entire study area was divided into three zones. Zone A delineates the area where AMD is actively forming, zone B marks the area where AMD mixes with natural waters and zone C is AMD- free. Water samples from all the three zones were analyzed in the laboratory. Plant leaf samples were taken from zones A and C only.

For the purpose of this study, fifteen [15] water samples were collected from the study area. Two [2] samples were collected from zone A. In zone B, four [4] water samples and two [2] soil water samples were collected while seven [7] water samples were collected from zone C. The samples were collected with a 1 litre polyethylene container. The containers were flushed several times with the water to be sampled, filled and tightly closed, leaving only a small air bubble below the stopper. After sampling, each container was carefully labelled and sent to the laboratory for chemical analysis within 24 hours of collection. Selected chemical parameters that characterize AMD, including, pH, $Na^{+}$, $Cl^{-}$, $SO_4^{2-}$, $Fe^{3+}$, $Pb^{+}$, $As^{+}$, $Zn^{+}$, $Mn^{+}$ and $Cd^{+}$ were tested in the laboratory using atomic absorption spectrometer (Buck Model 210/211 GF graphite furnace) for the metals and titrimetric, volumetric and colorimetric methods for the anions. In-situ measurements of pH were determined in field using multiple Ph/conductivity/ TDS/Salinity/ORP meters (EXTECH (341350A).

Additionally, six [6] plant leaves samples were collected from the area. Three [3] samples each from zones A and C, respectively. The collected plant samples were sent to the laboratory for identifications. The plants included, *Polypodiaceae Pteridium Aquilinum, Anacardiaceae Mangifera Indica and Euphorbiaceae Alchornea Cordifolia.* The samples were dried in an oven at $40^{0}$, grinded, digested and diluted to 20ml with distilled water for chemical analysis. The concentrations of various metals including, As, Pb, B, Mn were determined using atomic absorption spectrometer (Buck model 210/211) while that of the anions including, $Cl^{-}$, $SO_4^{2-}$ and $PO_4^{-}$ were determined using standard methods (volumetric, colorimetric and titrimetric methods).

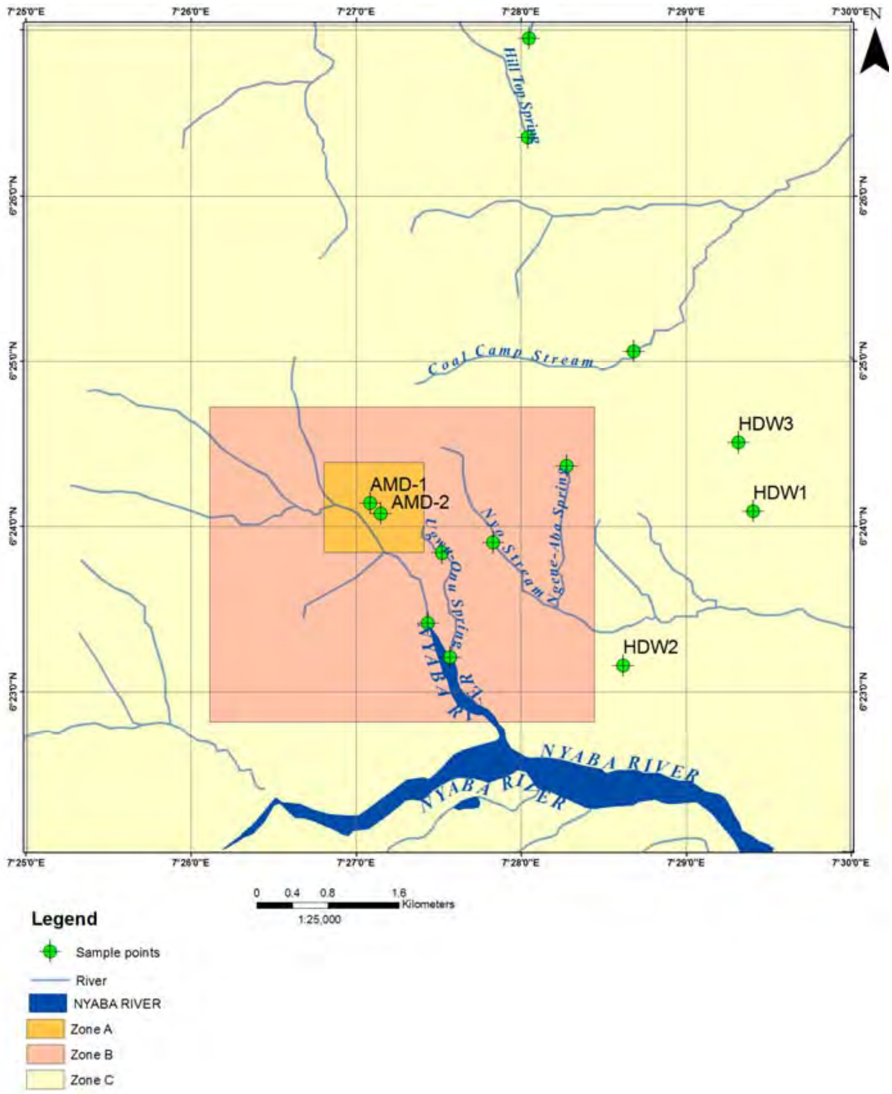


Figure 2: Sampling Map of the Study Area

## 5. RESULTS AND DISCUSSION

The results of physicochemical concentrations of water samples within Zones A, B, and C and plant leave samples are presented in Table 1, 2, 3, 4, and 5.

As shown in Tables 1, 2and 3 above, the water samples from zone A has pH values < 3.3 while zone B has pH values ranging from 3.5 - 4.67, and zone C has pH values within the range of 5.4 - 6.8, generally indicating the acidic nature of the water. The low pH values make the water unsuitable for fish survival. Additionally, acidic waters are susceptible to dissolution of minerals and release of toxic heavy metals in the aquatic environment. Figure 2 shows the spatial distributions of pH in the study area.

In zone A, sodium ($Na^+$) concentration ranged from105.7mg/l to 108mg/l while in zone B, the range was 30.62mg/l to 72.35mg/l. Zone C had sodium ($Na^+$) concentration of 12.05mg/l to 171.0mg/l. The presence of high concentrations of sodium in group A and C were attributed to the processes of weathering and dissolution of clay and feldspathic minerals found in the shale and sandstone within the area (Salufu et al., 2014).

Chloride ($Cl^-$) values ranged from 55.8mg/l to 60.9 in zone A, 18.9mg/l to 45.6mg/l in zone B and 15.5mg/l to 115.0mg/l in zone C. The highest concentrations of chloride were found in zones A and C while the lowest concentration was recorded in zone B.

Table 1: Hydrochemistry of water samples from Zone A (AMD area).

| Parameters | Okpara Mine 1 | Okpara Mine 2 |
|---|---|---|
| pH | 3.2 | 3.2 |
| Na | 105.7 | 108.0 |
| $Cl.^-$ | 60.9 | 55.8 |
| $SO_4^{2-}$ | 52.30 | 54.42 |
| $Fe^{3+}$ | 13.24 | 7.08 |
| Mn | 3.96 | 2.23 |
| Zn | 0.06 | 0.04 |
| Cd | 0.01 | 0.00 |
| Pb | 0.8 | 0.8 |
| As | 1.84 | 1.7 |

Table 2: Hydrochemistry of water samples from Zone B (mixing of AMD with natural waters).

| Parameters | Nyo soil Water | Nyo Stream | Nyaba soil Water | Nyaba River | Ugwu Onu Spring | Ngene-Aba Spring |
|---|---|---|---|---|---|---|
| pH | 3.9 | 3.98 | 3.87 | 3.5 | 3.5 | 4.67 |
| $Na^{2+}$ | 38.24 | 55.01 | 30.62 | 33.80 | 72.35 | 30.14 |
| $Cl.^-$ | 44.7 | 36.8 | 18.9 | 39.1 | 40.8 | 45.6 |
| $SO_4^{2-}$ | 41.41 | 33.52 | 42.05 | 40.10 | 49.55 | 24.02 |
| $Fe^{3+}$ | 0.02 | 0.2 | 0.4 | 0.07 | 9.74 | 0.10 |
| Mn | 0.21 | 0.01 | 0.32 | 0.20 | 0.01 | 0.01 |
| Zn | 0.05 | 0.04 | 0.01 | 0.02 | 0.01 | 0.00 |
| Cd | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Pb | 0.3 | 0.1 | 0.00 | 0.1 | 0.1 | 0.00 |
| As | 0.69 | 0.6 | 0.01 | 0.04 | 0.01 | 0.01 |

Figure 4 shows the spatial distributions of sulfate concentration in the area. Sulfate ($SO_4^{2-}$) values ranged from 52.30mg/l to 54.42mg/l in zone A, 24.02mg/l to 49.55mg/l in zone B and 0.83mg/l to 26.81mg/l in zone C. The high concentration of sulfate found in zone A indicate influence of mining activities in the zone.

Table 3: Hydrochemistry of water samples from Zone C (AMD-free).

| Parameters | Timber Junction HDW | Akwuke HDW | Ayo Stream | Egbo Lane HDW | Coal Camp Stream | Ngwo Hill Top Spring | Milkin Hill Spring |
|---|---|---|---|---|---|---|---|
| pH | 5.8 | 6.8 | 5.6 | 6.2 | 5.4 | 6.7 | 6.4 |
| $Na^{2+}$ | 64.20 | 36.77 | 126.0 | 43.08 | 12.05 | 133.08 | 171.0 |
| $Cl^-$ | 115.5 | 50.3 | 36.8 | 64.7 | 43.7 | 90.00 | 58.1 |
| $SO_4^{2-}$ | 15.25 | 15.25 | 7.20 | 11.41 | 26.81 | 7.20 | 0.83 |
| $Fe^{3+}$ | 0.00 | 0.00 | 0.01 | 0.01 | 0.01 | 0.00 | 0.00 |
| Mn | 0.01 | 0.01 | 0.01 | 0.00 | 0.01 | 0.00 | 0.00 |
| Zn | 0.02 | 0.00 | 0.00 | 0.00 | 0.02 | 0.00 | 0.00 |
| Cd | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Pb | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| As | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |

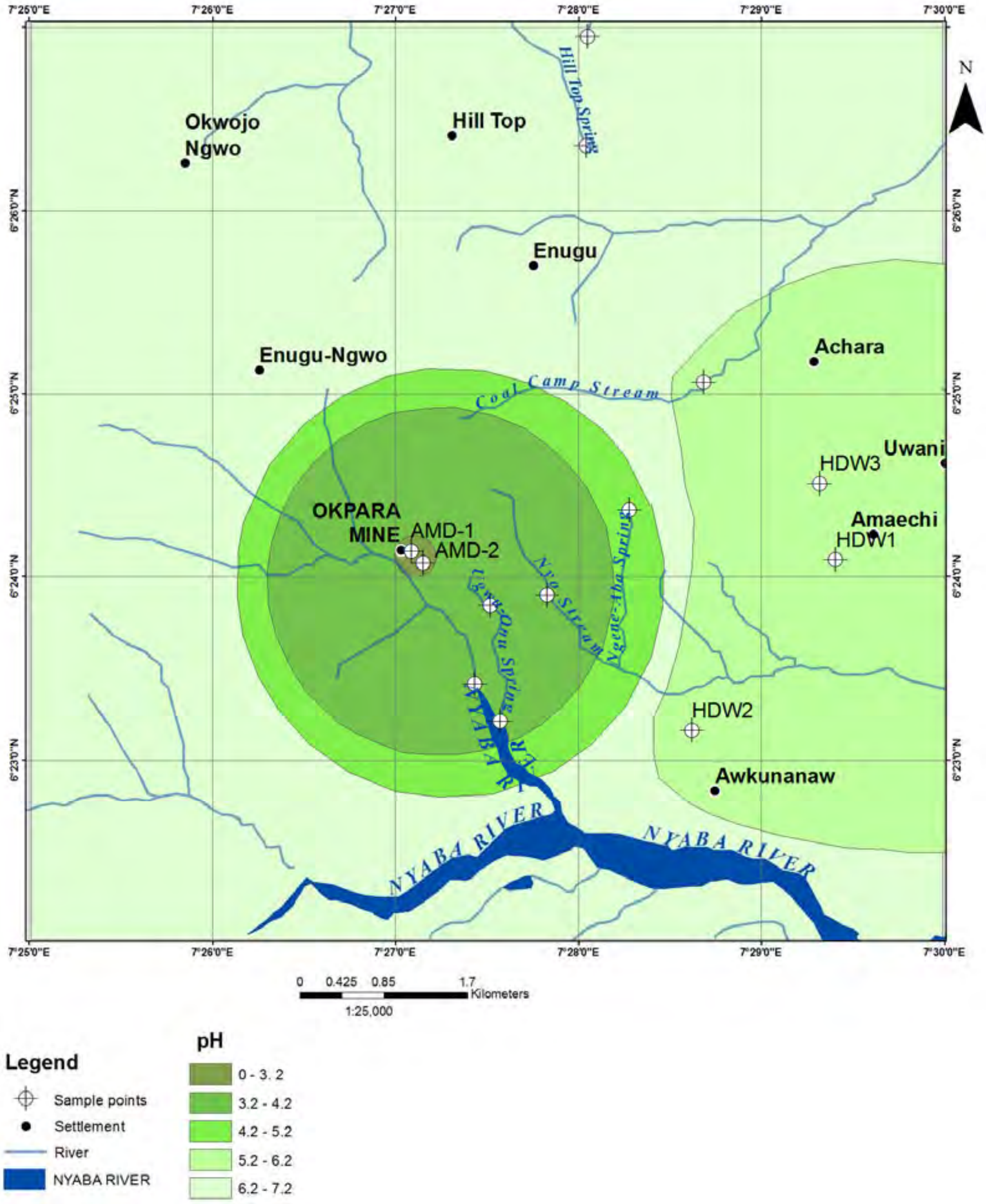


Figure 3: Spatial distributions of pH in the area.

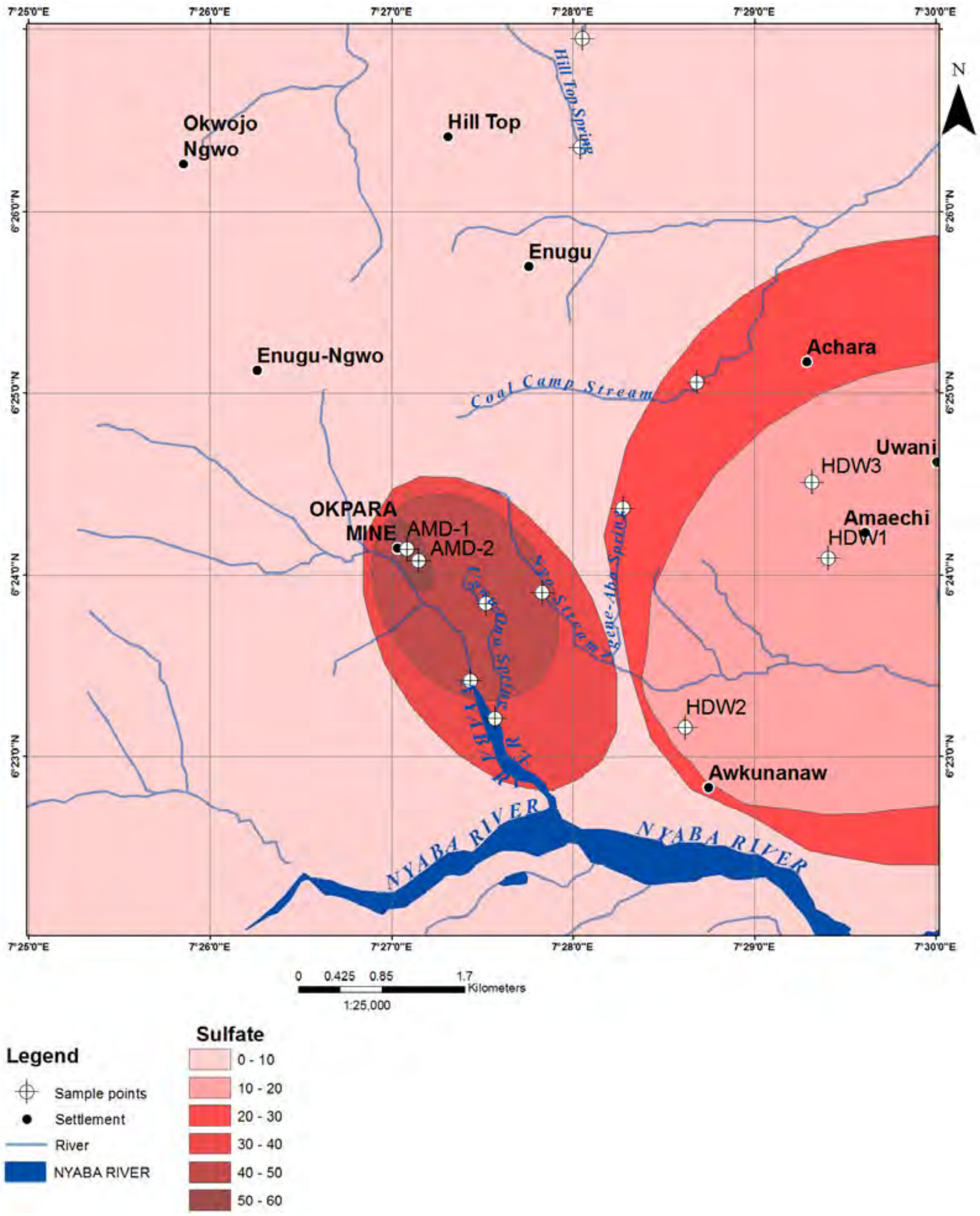


Figure 4: Spatial distributions of Sulfate concentrations in the area.

Iron ($Fe^{3+}$) and Manganese (Mn) are commonly distributed in acid mine drainage. In the study area iron concentration was found to vary from 13.24mg/l to 7.08mg/l in zone A, 0.02mg/l to 9.74mg/l in zone B and 0.00mg/l to 0.01mg/l in zone C. Manganese values varied from 2.23mg/l to 3.96mg/l in zone A, 0.01mg/l to 0.32mg/l in zone B and 0.00mg/l to 0.01mg/l in zone C. The high concentrations of iron and manganese revealed from the results indicate that pyritic mineral is mostly formed in zone A (Figure 5).

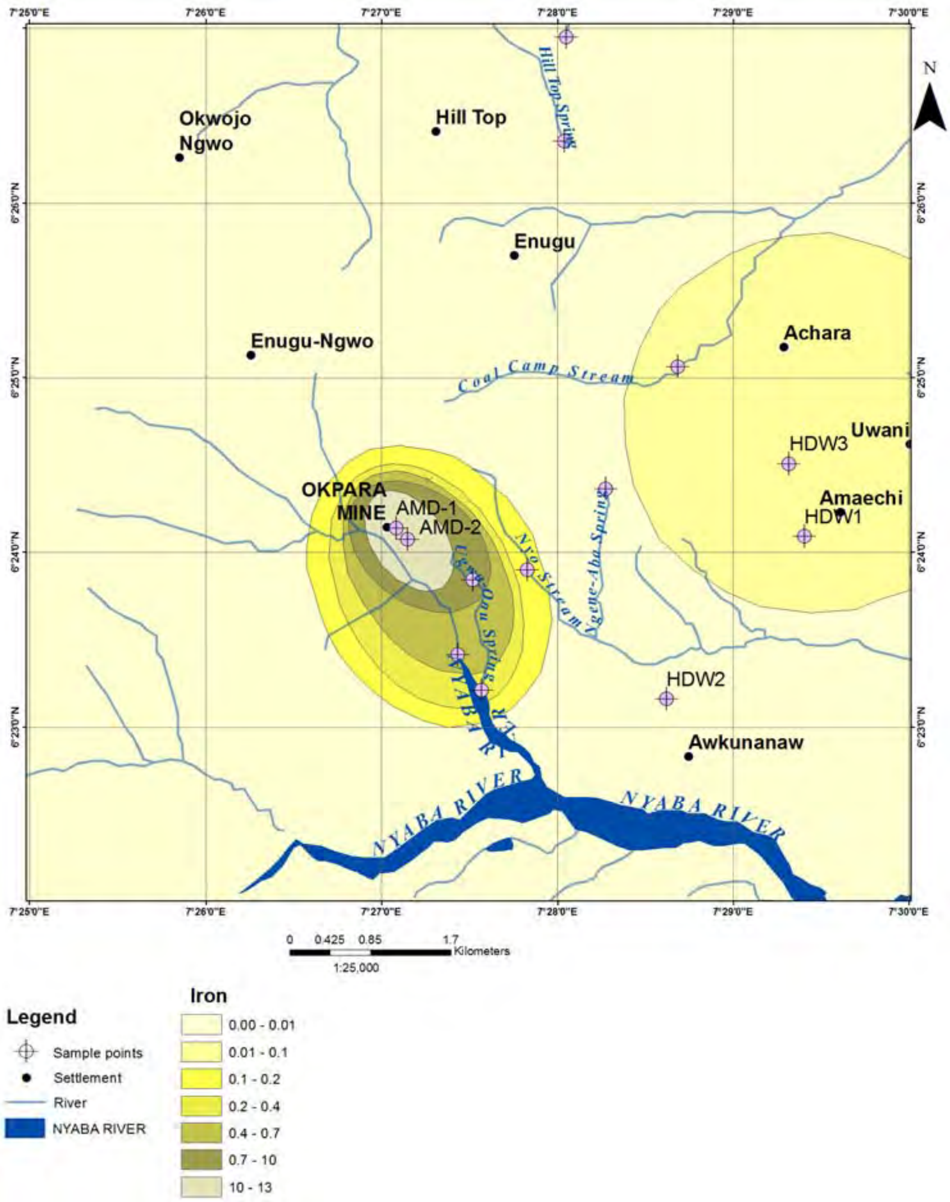


Figure 5: Spatial distribution of iron in the study area.

The concentration of zinc (Zn) ranged from 0.04mg/l to 0.06mg/l in zone A, 0.01mg/l to 0.05mg/l in zone B and 0.00mg/l in zone C. High concentrations of zinc could be an indication of the presence of sphalerite in the area.

Cadmium (Cd) concentration of 0.01mg/l was observed in zone A, while no cadmium was observed in zone B and C. Usually, cadmium is common in organic-rich shale mineral deposits composed mostly of cadmium sulfide (Plant et al., 2000) and it usually occurs at higher concentrations in low-pH conditions.

Lead (Pb) values were within the range of 0.8mg/l in zone A, 0.00mg/l to 0.3mg/l in zone B and 0.00mg/l in zone C. The amount of lead in water depends on pH and standing time of the water (Plant et al., 2000).

Arsenic concentration ranges were between 1.7mg/l to 1.84mg/l in zone A, 0.01mg/l to 0.6mg/l in zone B and 0.00mg/l in zone C. The presence of high concentration of arsenic in zone A may be resultant effects of the disposal of associated mine wastes in the area. These wastes are known sources of natural sulfide minerals such as pyrite and arsenopyrite.

Table 5: Concentration of selected ions in plants of zone A

| Sample No. | Family | Genus | Specie | Mn (µg/l) | Pb (µg/l) | B (µg/l) | As (µg/l) | $SO_4^{2-}$ (mg/l) | $Cl^-$ (mg/l) | $PO_4^-$ (mg/l) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | polypodiaceae | Pteridium | Aquilinum | 1.65 | 1.74 | 0.83 | 0.02 | 97.07 | 78.56 | 20.94 |
| 2 | anacardiaceae | Mangifer a | indica | 1.58 | 1.25 | 1.07 | 0.03 | 59.50 | 78.51 | 15.22 |
| 3 | euphorbiaceae | Alchorne a | cordifolia | 1.37 | 1.25 | 1.34 | 0.01 | 50.24 | 78.51 | 19.00 |

Table 5: Concentration of selected ions in plants of zone C.

| Sample No. | Family | Genus | Specie | Mn (µg/l) | Pb (µg/l) | B (µg/l) | As (µg/l) | $SO_4$ (mg/l) | Cl (mg/l) | $PO_4$ (mg/l) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | euphorbiaceae | Alchornea | cordifolia | 0.82 | 1.05 | 0.65 | 0.01 | 42.42 | 37.61 | 25.65 |
| 2 | anacardiaceae | Mangifera | indica | 0.03 | 0.76 | 1.24 | 0.01 | 40.08 | 27.94 | 29.12 |
| 3 | polypodiaceae | Pteridium | aquilinum | 0.01 | 0.65 | 0.72 | 0.01 | 36.71 | 20.61 | 31.82 |

In the study area, manganese (Mn) value ranged from1.37µg/l to 1.65µg/l in zone A and 0.01µg/l to 0.82µg/l in zone C. Kitao et al., (1987) stated that excess manganese (Mn) concentration in plant leaves causes reduction of photosynthetic rate.

Lead (Pb) is one of the toxic elements in plants. It exerts adverse effect on growth and photosynthetic processes of plants. In the study area, lead varied between 1.25µg/l to 1.75µg/l in zone A and 0.65µg/l to 1.05µg/l in zone C. The result revealed that the leaves of *Polypodiaceae Pteridium Aquilinum, Anacardiaceae Mangifera Indica and Euphorbiaceae Alchornea Cordifolia* within the AMD zone had taken up small amounts of lead but the uptake had no effect on them.

Boron (B) is an essential element for plant growth. The symptoms of boron in plants are dying and stunted growth. The uptake of boron by *Polypodiaceae Pteridium Aquilinum, Anacardiaceae Mangifera Indica and Euphorbiaceae Alchornea Cordifolia* varied from 0.83µg/l to 1.34µg/l within zone A and 0.65µg/l to

1.05μg/l at zone C. It was further revealed that plants in zone A had more boron uptake than plants in zone C. However, no negative impact of boron in plant leaves within zone A was noted.

Arsenic (As) uptake ranged from 0.01μg/l to 0.02μg/l in zone A and 0.01μg/l to 0.03μg/l in zone C. Uptake of arsenic by leaves of *Polypodiaceae Pteridium Aquilinum, Anacardiaceae Mangifera Indica and Euphorbiaceae Alchornea Cordifolia* were evenly distributed in the area and no effect of arsenic was recorded in these zones.

Sulfate ($SO_4^{2-}$) uptake varied from 24.29mg/l to 97.07mg/l in zone A and 4.08mg/l to 42.42mg/l in zone C. The highest sulfate uptake in the leaves of *Polypodiaceae Pteridium Aquilinum, Anacardiaceae Mangifera Indica and Euphorbiaceae Alchornea Cordifolia* was recorded in zone A.

Chloride ($Cl^-$) is another important element for plant growth. The uptake of chloride in the leaves of *Polypodiaceae Pteridium Aquilinum, Anacardiaceae Mangifera Indica and Euphorbiaceae Alchornea Cordifolia* ranged from 22.24mg/l to 78.56mg/l in zone A and 20.61mg/l to 37.61 in zone C. The source of chloride could be from fertilizers and rainwater. The symptomatic effects of excess chloride in plants include scorched, smaller and thicker leaves.

Phosphate ($PO_4^-$) uptake varied from 20.94mg/l to 78.51mg/l in zone A and 15.22mg/l to 21.82mg/l in zone C. High uptake of phosphate was observed in zone A. The source could be attributed to run-offs (such as fertilizers) from agricultural farms around the area.

## 6. CONCLUSION

The study evaluated the geochemistry of acid mine drainage in Okpara coal mine whilst making comparisons with other natural waters with AMD-free zones as well as assessing heavy metal uptake and their effects on plants in the mine area. From the results it was concluded that water samples within the mine had low pH and high $SO_4^{2-}$, $Na^+$, $Cl^-$, $Fe^{3+}$ and heavy metals as compared to the water samples outside the mine which had high pH, $Na^+$ and $CL^-$ and low $SO_4^{2-}$, $Fe^{3+}$ and heavy metals. Thus, there is AMD formation within the mine while outside the mine is AMD-free. Furthermore, plant leaves within the mine has a higher uptake of Mn, Pb, As, $SO_4^{2-}$ and $Cl^-$ relative to plant leaves outside the mine. However, plant leaves outside the mine had higher uptake of B and $PO_4^-$ in comparison to plant leaves within the mine. Thus, heavy metals uptake by the plant leaves within the mine is high although the uptake has no effect on the plant leaves.

Further research is recommended in the area with the major focus on the assessment of the mobility of heavy metals in the waters and plants.

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