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Analysis of Heavy Metals Contamination and Quality Parameters of Groundwater in Ihetutu, Ishiagu

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ABSTRACT

The levels of some quality parameters and heavy metals in groundwater in Ihetutu minefield of Ishiagu were analyzed in four seasons (rainy, late rainy, dry, and late dry), in order to evaluate the deterioration of the groundwater qualities in the area. Pb-Zn mining and several other related activities have been going on for several decades in Ihetutu, and thus render the groundwater resources in the area less available for consumption, through toxic chemical substances expected to be constantly discharged to the groundwater bodies from the mines and other domestic wastes. The aim of this study was thus to determine the levels of heavy metals and other physico-chemical properties in the groundwater, to assess its suitability for drinking and other domestic purposes in Ihetutu. Samples were collected from dug-wells and underground water platforms, and analyzed using standard procedures, for their physico-chemical properties and heavy metals levels. Results obtained for the various seasons ranged as pH = 6.80-8.72, EC = 190.00-1120.00 μ S/cm, alkalinity = 4.20-30.60 mg/L, TDS = 105.00-567.00 mg/L, TH = 8.00-44.00 mg/L, Cl⁻ = 26.00-126.00 mg/L, Cu = 0.00-0.30 mg/L, Zn = 0.00-0.42 mg/L, Fe = 0.00-3.93 mg/L, Mn = 0.00-0.59 mg/L, and Pb = 0.00-0.43 mg/L. Average levels of analyzed parameters in study area were: pH = 7.56, EC = 424.06 μ S/cm, alkalinity = 17.88 mg/L, TDS = 218.69 mg/L, TH = 21.88 mg/L, Cl⁻ = 54.31 mg/L, Cu = 0.20 mg/L, Zn = 0.51 mg/L, Fe = 2.55 mg/L, Mn = 0.32 mg/L, Pb = 0.38 mg/L. Mean levels of most parameters were found to be within standard guidelines/limits but were above control levels, giving an indication of deterioration of the groundwater qualities in the area. Also, seasonal concentrations of most parameters, including the heavy metals were in the order of LDS>DRS>LRS>RNS. Heavy metals mean concentrations also trended in the order of Fe>Zn>Pb>Mn>Cu. Correlations among heavy metals were all positive, with the strongest between Cu and Pb ($r = 0.921$) while the least was between Cu and Mn ($r = 0.176$). ANOVA showed no statistically significant differences among sampling stations in study area, as p -values (0.757) was higher than the significance level ($\alpha = 0.05$). Comparison of the results with control values, indicated cases of deterioration of the groundwater quality in the study area. This confirmed that the groundwater resources in the area were adversely affected by wastes and discharges from the mining activities and several other sources including domestic wastes.

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1. Introduction

Mining has become an indispensable component of economic resource at Ihetutu, Ishiagu, in Ivo River Local Government Area of Ebonyi State of Nigeria. Ihetutu mine in Ishiagu is the oldest mine in his study on lead (Pb) mining carried out at four mining sites in Ebonyi State ^[1]. It is thus expected that various toxic chemical substances including heavy metals, etc must have accumulated to very high levels in the area, considering the very long time of existence and operation of the mines.

Mining operations constitute the most important sources of pollutants such as heavy metals and many other toxic chemical substances in the environment. It is a business that seriously damages the environment ^[2]. Its operations and associated industries generate large volumes of wastewater, drainage wastes and tailings, which plunders the landscape and contaminate the surrounding environment with inorganic pollutants, particularly heavy metals. Most mining operations have serious adverse effect on air, water, soil and vegetation ^[3]. On a global scale, it was estimated that about 3000 billion tons of mine overburden is dumped annually, and that about 386,000 hectares of land is disturbed by mining activities ^[4].

Activities of mining are well known for their dangerous impact on the environment due to deposition of large volume of waste on the soil and water. Adverse environmental consequences of open pit mining include sediment and water qualities degradation due to destruction of vegetation, exposure of the soil to surface run-offs, as well as dumps that have been confirmed to accommodate harmful minerals and chemicals that contaminate the soil, plant, water and air quality ^[5].

Various chemicals used during ore processing cause high degree of pollution of groundwater bodies. Through wrong application, faulty disposal system, poor storage system and several other conditions prevalent at the time of operations, these chemicals used at mine sites could also cause intense pollution of the environment ^[6]. Water pollution increases due to human population, industrialization, the use of fertilizers in agriculture and man-made activity^[7], which include mining operations, artisan activities; and natural sources such as weathering of rocks.

The objective of this research was to evaluate the quality of groundwater available for drinking and other domestic purposes in Ihetutu where several mining activities have been ongoing for several decades now. Groundwater resources were only some few kilometers away from the numerous Pb-Zn mining sites, and were thus expected to be seriously polluted by wastes leachates and discharges

from the mines and its wastes dumps and tailings; and other point and non-point sources including domestic wastes and run-offs from farms. This suspicion made it imperative to carry out this study. Huge amount of toxic chemical substances constantly discharged into groundwater bodies have become sources of contamination and threat to human health, thus making assessment of their levels and impacts a necessary one.

2. Materials and Methods

2.1 The Study Area

The Ihetutu Hill is located in Ishiagu, Ebonyi State of Nigeria, and is within the Lower Benue trough. Lead-zinc and hard rock (aggregate) mining has been ongoing in the area since the 1950s. The Ishiagu area covers an expanse of about 450 km² and supports an estimated population of over two hundred and fifty thousand persons ^[8,9]. The study area falls within latitudes 5° 51' N and 5° 59' N and longitudes 7° 24' E and 7° 40' E covering an area of over 450 km². The area is accessible through the Enugu - Port Harcourt Railway line, the Enugu-Port Harcourt oil pipeline, the Enugu - Port Harcourt Express Road, the Lekwesi-Obiagu Road which, and the Okigwe - Afikpo Road ^[10] (Figures 1).

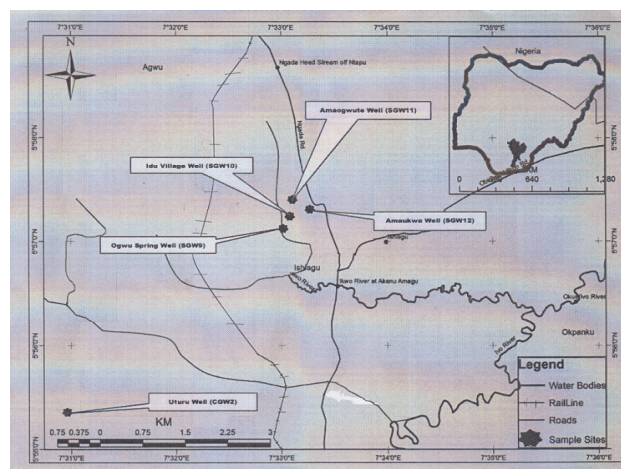


Figure 1. Map showing sampling stations in study and control areas

2.2 Sample Collection and Analysis

Samples were collected in four seasons including rainy season (May), late rainy season (September), dry season (December), and late dry season (April) from both study and control areas (which is about 12 km away from the study area). Four groundwater samples were collected from the study area, each season, directly from dug-wells and underground spring water platforms and labeled as SGW9,

SGW10, SGW11, SGW12, while one sample was collected from the control area and labeled as CGW2 each season also. Collected samples were digested and analyzed to determine the physico-chemical parameters and heavy metal concentrations, using standard methods and procedures^[11]. pH and Electrical Conductivity were determined in-situ (on site).

Table 1. Sampling Field Data Summary

| Sampling Stations | Sampling Dates | Sampling Seasons | Station Locations | Latitude | Longitude |
|-------------------|---|-----------------------------|-----------------------------|------------|------------|
| CGW2 (Control) | 13/05/2018; 29/09/2018; 29/11/2018; 12/04/2019 | RNS; LRS; DRS; LDS | Ukwu Okwe Well, Uturu. | N 5°50'54" | E 7°29'32" |
| SGW9 | 13/05/2018; 01/10/2018; 01/12/2018; 14/04/2019 | RNS; LRS; DRS; LDS | Ogwu spring well, Ihetutu. | N 5°57'3" | E 7°33'4" |
| SGW10 | 13/05/2018; 01/10/2018; 01/12/2018; 14/04/2019 | RNS; LRS; DRS; LDS | Idu Compound Well, Ihetutu. | N 5°57'7" | E 7°33'6" |
| SGW11 | 13/05/2018; 01/10/2018; 01/12/2018; 14/04/2019 | RNS; LRS; DRS; LDS | Amaogwute Well, Ihetutu. | N 5°57'11" | E 7°33'8" |
| SGW12 | 13/05/2018; 01/10/2018; 01/12/2018; 14/04/2019 | RNS; LRS; DRS; LDS | Amaukwa Well, Ihetutu. | N 5°57'12" | E 7°33'15" |

Note: RNS = Rainy Season, LRS = Late Rainy Season, DRS = Dry Season, LDS = Late Dry Season

3. Results and Discussion

3.1 Physico-chemical Properties of Groundwater in Ihetutu

3.1.1 pH

pH peaked during the dry season (DRS) at CGW10, CGW11, CGW12 but during the late dry season (LDS) at CGW9 and the control station (CGW2); while the lowest values at all sampling stations were recorded during the rainy season (RNS) (Figure 2). Mean pH values range was 7.46-7.67, with SGW10 having the highest and SGW12 the lowest. However, the control groundwater (CGW2) with a mean value of 7.32 is lower than the mean pH values of all the samples from the study area (Table 2). Average pH value in study area was 7.56 (Table 3). This value was within the standard guidelines of USEPA, SON, NESREA and WHO (Table 4). The increased pH values in the groundwater samples could be due to the increasing buffering capacity of alkaline minerals leaching from surrounding underground and surface rocks/soil, to the groundwater. The increase in pH could also be due to the reduction in the rate of photosynthetic activities in

the well, and absorption of carbon dioxide and bicarbonates^[12]. Discharge of domestic waste and other organic pollutants into the water bodies that run through the farms and located along the paths of the villagers could also be responsible for the increase in pH^[13].

Table 2. Mean values of physico-chemical parameters and Heavy Metals in groundwater

| Parameter | (CGW2) | SGW9 | SGW10 | SGW11 | SGW12 |
|------------------------|--------|--------|--------|--------|--------|
| pH | 7.32 | 7.53 | 7.67 | 7.58 | 7.46 |
| EC (µS/cm) | 184.75 | 251.25 | 475.50 | 662.00 | 307.50 |
| TDS (mg/L) | 128.50 | 136.50 | 245.00 | 333.50 | 159.75 |
| TH (mg/L) | 22.00 | 13.90 | 25.15 | 23.53 | 24.95 |
| Alkalinity (mg/L) | 19.03 | 11.88 | 26.28 | 19.95 | 13.40 |
| Cl ⁻ (mg/L) | 70.75 | 42.25 | 56.25 | 79.00 | 39.75 |
| Cu (mg/L) | 0.25 | 0.14 | 0.27 | 0.18 | 0.27 |
| Fe (mg/L) | 3.39 | 1.86 | 3.52 | 3.47 | 2.23 |
| Zn (mg/L) | 2.40 | 0.00 | 0.41 | 0.38 | 0.74 |
| Mn (mg/L) | 0.07 | 0.10 | 0.37 | 0.54 | 0.22 |
| Pb (mg/L) | 0.33 | 0.00 | 0.42 | 0.30 | 0.41 |

3.1.2 Electrical Conductivity

Mean EC ranged from 251.25 to 662.00 µS/cm with SGW11 having the highest value while SGW9 had the lowest. All study area values were higher than that of control (CGW2) (Table 2). Seasonal conductivity values for groundwater samples from the study area also increased in the order of RNS<LRS<DRS<LDS (Figure 3), exception of SGW12 which peaked during the dry season (DRS). Average conductivity value in study area was 424.06 µS/cm (Table 3). This was above EU standard value of 250 µS/cm but below SON standard value of 1000 µS/cm (Table 4). High concentration of dissolved salts due to poor irrigation management, minerals from rain water runoffs, or discharges (leachates) from mines could lead to increase in conductivity^[14].

3.1.3 Total Dissolved Solids (TDS)

Mean TDS values ranged from 136.50 to 333.50 mg/L, and were all higher than the mean value of the control sample (CGW2) which was 128.50 mg/L (Table 2). Seasonal TDS values for the samples also increased in the order of RNS<LRS<DRS<LDS, exception of SGW12 which rather peaked during the dry season (DRS) (Figure 4). Average TDS value in study area was 218.69 mg/L (Table 3), and was below USEPA, SON and NESREA guidelines (Table 4). The groundwater samples mean values were all below standard reference values indicating a rating of no overall pollution. Decrease in mean TDS concentration in ground-

water samples could also result from high dilution effect from the rain water during the rainy seasons. The low concentration of TDS especially in the groundwater, and some surface water samples could also be due to the presence of granitic materials which resists dissolution in that area^[15].

3.1.4 Alkalinity

Alkalinity increased from rainy to dry season in the samples, though there was a decrease in the late dry season (LDS) at SGW10, SGW11 and SGW12 (Figure 5). Mean values also ranged from 11.88 to 26.28 mg/L, with SGW9 having the lowest value and SGW10 the highest. Compared with control (CGW2) value of 19.03 mg/L, SGW9 and SGW12 values were lower while those of SGW10 and SGW11 were higher (Table 2). Increase in alkalinity could be due to the discharge of carbonate and bicarbonate salts from surrounding rocks/soils to the water bodies. Average alkalinity value in study area was 17.88 mg/L (Table 3). It has been reported that, in the Ishiagu mining area, there is significant volume of mine waste and large scale presence of carbonate minerals, especially dolomite and siderite, which makes the acid mine drain (AMD) in the area to tend towards a neutral or alkaline state^[16].

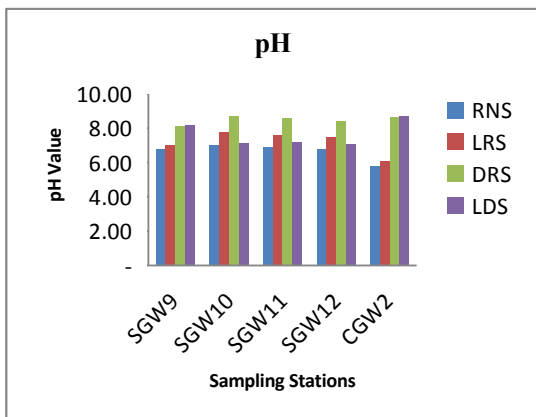


Figure 2. Seasonal levels of pH

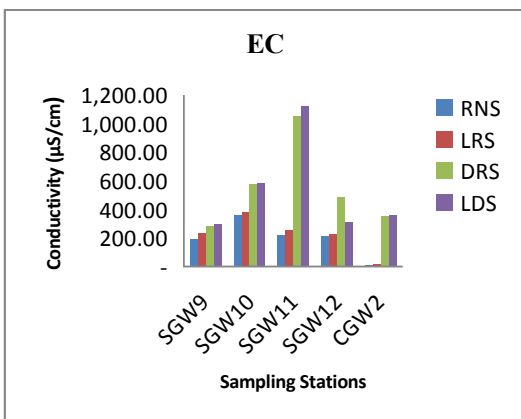


Figure 3. Seasonal concentrations of EC

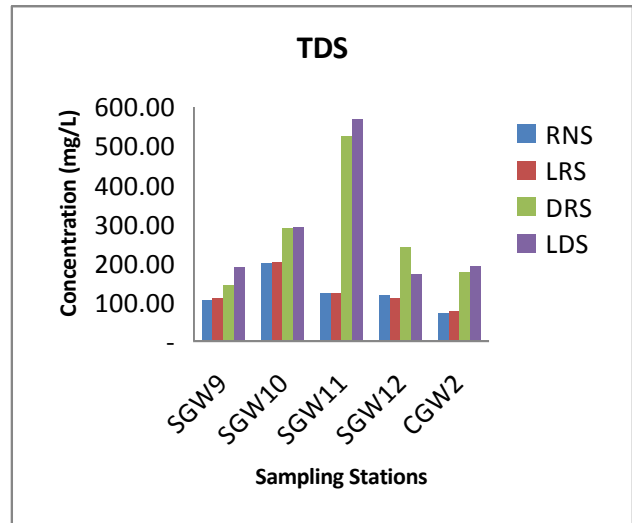


Figure 4. Seasonal concentrations of TDS

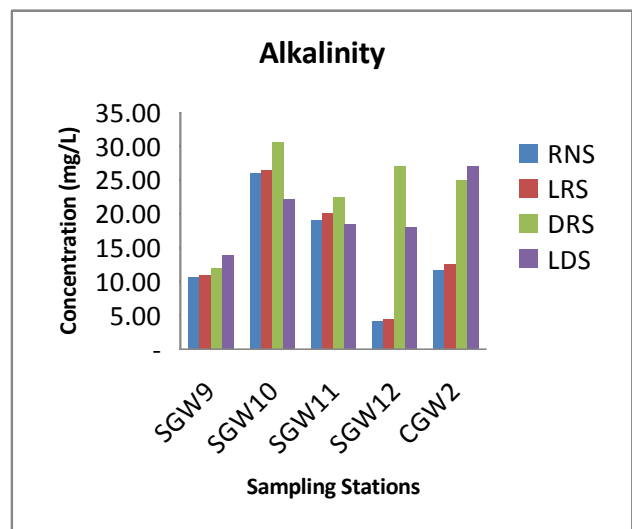


Figure 5. Seasonal concentrations of alkalinity

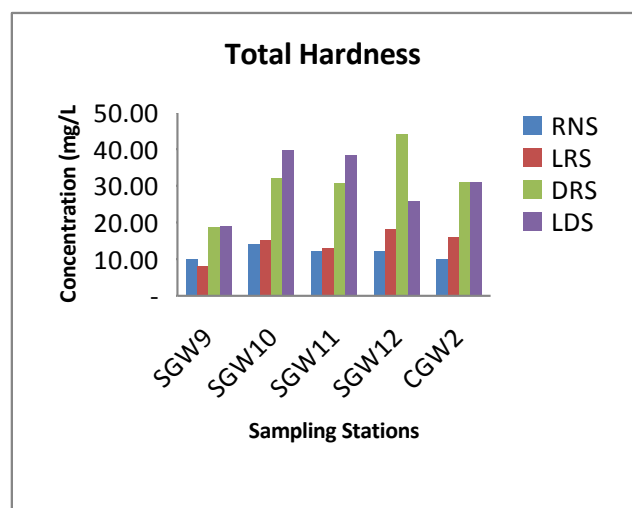


Figure 6. Seasonal concentrations of Total Hardness

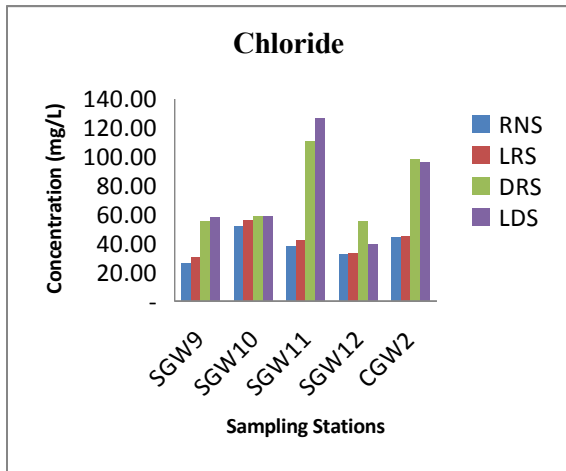


Figure 7. Seasonal concentrations of Chloride

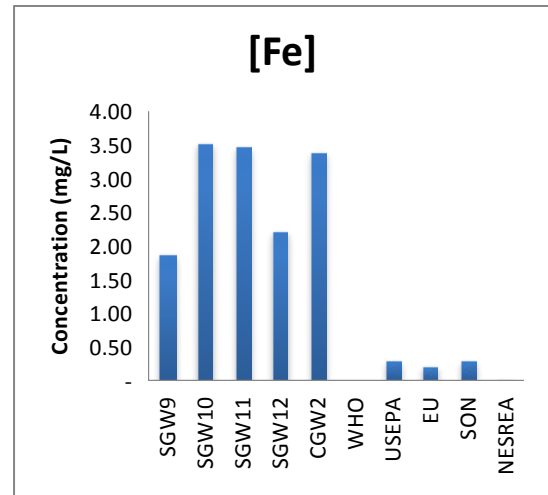


Figure 10. Mean Conc. of Fe in Groundwater, with Control and Standard guidelines

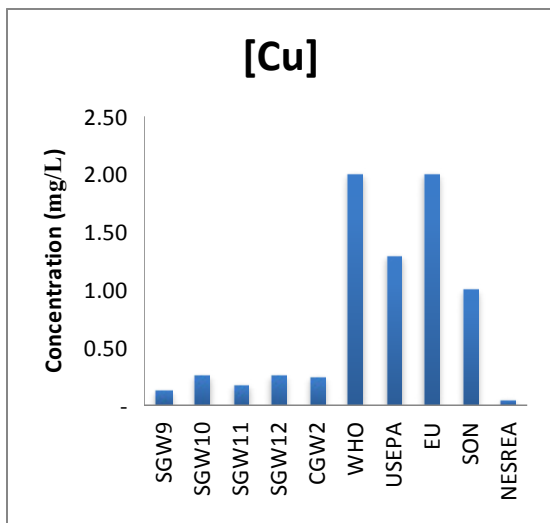


Figure 8. Mean Conc. of Cu in Groundwater, with Control and Standard guidelines

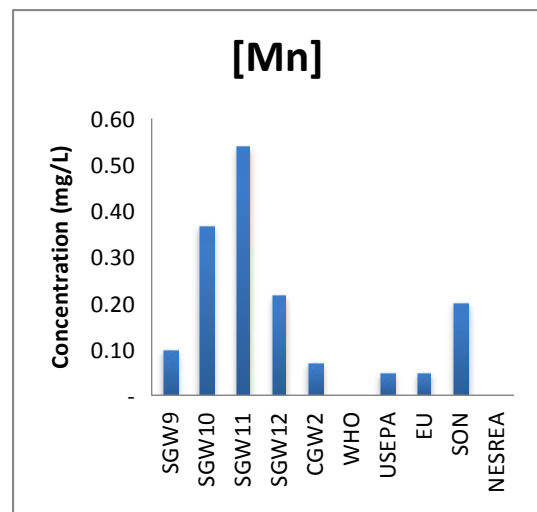


Figure 11. Mean Conc. of Mn in Groundwater, with Control and Standard guidelines

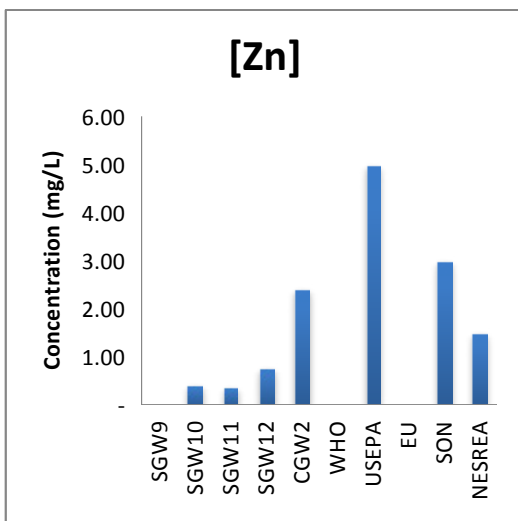


Figure 9. Mean Conc. of Zn in Groundwater, with Control and Standard guidelines

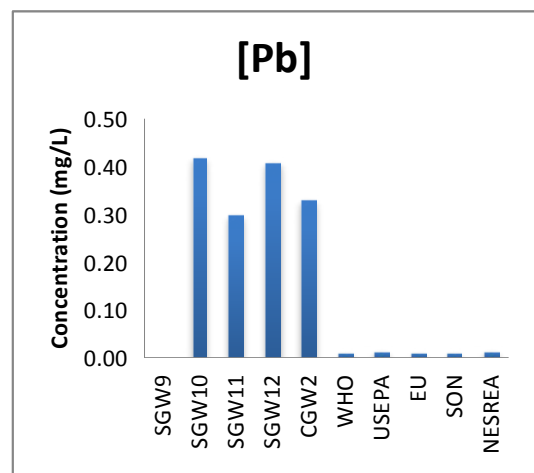


Figure 12. Mean Conc. of Pb in Groundwater, with Control and Standard guidelines

3.1.5 Total Hardness

Hardness is a measure of the capacity of water to form precipitates or foam with soap and scales with certain ions present in the water^[17]. It is defined as the sum of the concentrations of calcium (Ca²⁺) and magnesium (Mg²⁺) ions expressed as mg/L of CaCO₃, since soap is precipitated mostly by these ions^[18]. Mean levels in groundwater ranged from 13.90 mg/L at SGW9 to 25.15 mg/L at SGW10 (Table 1). Seasonal concentrations were highest during late dry seasons (LDS) at SGW9, SGW10, SGW11 and SGW2 (control station) but during dry season (DRS) at SGW12 (Figure 6). Average total hardness value in study area was 21.88 mg/L (Table 3), and was

below SON, NESREA and WHO guidelines (Table 4). Total hardness values of all samples were within standard limits/guidelines and thus satisfactory. Also according to some standard classifications^[19], the water samples were classified to be soft, as their concentrations were all within the range of 0 - 60 mg/L.

3.1.6 Chloride

Mean concentration ranged from 39.75-79.00 mg/L. Exception of SGW11, all study area samples had concentrations lower than control (CSW2) value (Table 2). Chloride levels in samples also increased from rainy to dry season, exception of SGW10 and SGW12 whose concentrations,

Table 3. Seasonal levels of physico-chemical parameters and Heavy Metals in groundwater

| Sample Station | Sample Season | pH | EC (µS/cm) | TDS (mg/L) | TH (mg/L) | Alk (mg/L) | Cl ⁻ (mg/L) | Cu (mg/L) | Fe (mg/L) | Zn (mg/L) | Mn (mg/L) | Pb (mg/L) |
|-------------------|----------------|-------------|---------------|---------------|--------------|--------------|------------------------|-------------|-------------|-------------|-------------|-------------|
| | RNS | 6.80 | 190.00 | 105.00 | 10.00 | 10.60 | 26.00 | 0.08 | 0.44 | <0.001 | 0.09 | <0.001 |
| SGW9 | LRS | 7.00 | 232.00 | 109.00 | 8.00 | 11.00 | 30.00 | 0.09 | 0.45 | <0.001 | 0.10 | <0.001 |
| | DRS | 8.15 | 285.00 | 143.00 | 18.70 | 12.00 | 55.00 | 0.18 | 3.11 | <0.001 | 0.10 | <0.001 |
| | LDS | 8.17 | 298.00 | 189.00 | 18.90 | 13.92 | 58.00 | 0.20 | 3.43 | <0.001 | 0.11 | <0.001 |
| SGW10 | RNS | 7.00 | 360.00 | 198.00 | 14.00 | 26.00 | 52.00 | <0.001 | <0.001 | <0.001 | 0.17 | <0.001 |
| | LRS | 7.80 | 382.00 | 201.00 | 15.00 | 26.40 | 56.00 | <0.001 | <0.001 | <0.001 | 0.21 | <0.001 |
| | DRS | 8.72 | 578.00 | 289.00 | 31.90 | 30.60 | 58.60 | 0.30 | 3.11 | 0.41 | 0.59 | 0.42 |
| | LDS | 7.16 | 582.00 | 292.00 | 39.70 | 22.10 | 58.40 | 0.24 | 3.92 | 0.41 | 0.51 | 0.43 |
| SGW11 | RNS | 6.90 | 220.00 | 121.00 | 12.00 | 19.00 | 38.00 | 0.06 | <0.001 | <0.001 | 0.49 | <0.001 |
| | LRS | 7.60 | 258.00 | 121.00 | 13.00 | 20.00 | 42.00 | 0.11 | <0.001 | <0.001 | 0.53 | <0.001 |
| | DRS | 8.60 | 1 050.00 | 525.00 | 30.80 | 22.40 | 110.00 | 0.24 | 3.01 | 0.34 | 0.59 | 0.29 |
| | LDS | 7.20 | 1 120.00 | 567.00 | 38.30 | 18.40 | 126.00 | 0.30 | 3.93 | 0.42 | 0.54 | 0.30 |
| SGW12 | RNS | 6.80 | 210.00 | 116.00 | 12.00 | 4.20 | 32.00 | <0.001 | 0.29 | <0.001 | <0.001 | <0.001 |
| | LRS | 7.50 | 225.00 | 110.00 | 18.00 | 4.40 | 33.00 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
| | DRS | 8.43 | 483.00 | 241.00 | 44.00 | 27.00 | 55.00 | 0.27 | 2.75 | 0.42 | 0.23 | 0.42 |
| | LDS | 7.09 | 312.00 | 172.00 | 25.80 | 18.00 | 39.00 | 0.27 | 3.66 | 1.06 | 0.21 | 0.41 |
| | AVERAGE | 7.56 | 424.06 | 218.69 | 21.88 | 17.88 | 54.31 | 0.20 | 2.55 | 0.51 | 0.32 | 0.38 |
| CGW2 (control) | RNS | 5.80 | 13.00 | 72.00 | 10.00 | 11.60 | 44.00 | <0.001 | 3.60 | <0.001 | 0.07 | <0.001 |
| | LRS | 6.10 | 15.00 | 75.00 | 16.00 | 12.50 | 45.00 | <0.001 | 3.96 | <0.001 | 0.06 | <0.001 |
| (control) | DRS | 8.67 | 352.00 | 176.00 | 31.00 | 25.00 | 98.00 | 0.25 | 2.87 | 0.40 | 0.06 | 0.32 |
| | LDS | 8.70 | 359.00 | 191.00 | 31.00 | 27.00 | 96.00 | 0.24 | 3.12 | 4.40 | 0.08 | 0.33 |

Note: RNS = Rainy Season; LRS = Late Rainy Season; DRS = Dry Season; LDS = Late Dry Season.

Table 4. Standard Guidelines for Drinking Water

| Parameter | USEPA ^[20] | SON ^[21] | NESREA ^[22] | WHO ^[23] | EU ^[24] |
|-------------------|-----------------------|---------------------|------------------------|---------------------|--------------------|
| pH | 6.5 - 9.5 | 6.5 - 8.5 | 6.5 - 9.2 | 6.5 - 9.5 | NM |
| EC (µS/cm) | NM | 1,000.00 | NG | NG | 250.00 |
| TDS (mg/L) | 500.00 | 500.00 | 1,500.00 | NG | NM |
| Chloride (mg/L) | 250.00 | 250.00 | 600.00 | 250.00 | 250.00 |
| TH (mg/L) | NM | 150.00 | 500.00 | 200 | NM |
| Alkalinity (mg/L) | NG | NG | NG | NG | NG |
| Cu (mg/L) | 1.30 | 1.00 | 0.075 | 2.00 | 2.00 |
| Zn (mg/L) | 5.00 | 3.00 | 0.80 | NG | NM |
| Fe (mg/L) | 0.30 | 0.30 | 1.00 | NG | 0.20 |
| Mn (mg/L) | 0.05 | 0.20 | 0.50 | NG | 0.05 |
| Pb (mg/L) | 0.015 | 0.01 | 0.075 | 0.01 | 0.010 |

Note: NG = No guidelines; NM = Not mentioned

like that of the control sample (CGW2), decreased during the late dry season (LDS) (Figure 7). Average chloride level of 54.31 mg/L obtained in the study area (Table 3) was below referenced standard guidelines (Table 4). High presence of chloride in water could be due to pesticides from farms, continuous discharge of mine wastes, and effluents containing chloride salts from chloride rich rocks in the area. However, the lower chloride concentrations observed during the rainy season could be due to dilution of the water by rain water^[7]. High chloride content in water causes eye and nose irritation, stomach discomfort, increase in corrosive character of the water^[12].

3.2 Heavy Metals in Groundwater

3.2.1 Copper

Mean copper concentrations in groundwater ranged from 0.14 mg/L at SGW9 (Ogwu spring well) to 0.27 mg/L at both SGW10 and SGW12 (Table 2). SGW9 and SGW11 were lower in mean concentrations than that of control (CGW2). Average level of Cu in study area was 0.20 mg/L while seasonal concentrations were also higher in the dry seasons than in the rainy seasons, and in the order of RNS<LRS<DRS<LDS (Table 3). All samples were within the standard guidelines of USEPA, SON, WHO, and EU^[20-24] but higher than that of NESREA^[22] (Figure 8).

3.2.2 Zinc

Mean concentrations of Zn ranged from 0.00 mg/L at SGW9 (seasonal concentrations <0.001 mg/L) to 0.74 mg/L at SGW12 (Table 2). All stations had lower mean concentrations than the control groundwater (CGW2) in Uturu. Average Zn concentration in study area was 0.51 mg/L, and seasonal concentrations were higher in the dry seasons than in the rainy seasons (Table 3). Zn concentrations were below USEPA, SON, and NESREA limits^[20-22] (Figure 9). The percentage of zinc in the earth crust is approximately 0.05 g/kg, and its major common mineral is sphalerite (ZnS), which usually unites with other sulfides^[19], and could infiltrate underground water resources.

3.2.3 Iron

Mean Fe concentration ranged from 1.86 mg/L at SGW9 to 3.52 mg/L at SGW10. SGW9 and SGW12 had lower mean concentrations than the control sample (CGW2) at Uturu (Table 2). Groundwater samples in the study area were observed to be polluted with iron, as they all had mean concentrations well above USEPA, SON, and NES-

REA limits^[20-22] (Figure 10). Average Fe concentration in study area was 2.55 mg/L, while seasonal levels were also higher in the dry seasons than in the rainy seasons, in the order of RNS<LRS<DRS<LDS (Table 3). Iron in groundwater could result from natural sources such as minerals from sediments and rocks; or from mining, industrial wastes, and corroding metals in the surrounding soil^[25]

3.2.4 Manganese

Groundwater samples in the study area had mean manganese concentrations ranged of 0.10 mg/L at SGW9 to 0.54 mg/L at SGW11. All samples from the study area had higher mean manganese concentrations than the control (CGW2) sample (Table 2). Only SGW11 has higher Mn concentration than NESREA recommended value of 0.50 mg/L (Figure 11). Average level of Mn in the study area was 0.32 mg/L, while seasonal concentrations were also higher in the dry seasons than in the rainy seasons (Table 3).

3.2.5 Lead

Lead mean concentrations ranged from 0.00 mg/L at SGW11 (<0.001 mg/L seasonal concentrations) to 0.42 mg/L at SGW10. However, control (CGW2) value was higher than that of SGW9 and SGW11 (Table 2). Average Pb concentration in study area was 0.38 mg/L and seasonal levels higher in the dry seasons than in the rainy seasons (Table 3). All samples also had higher mean values than referenced standard limits of USEPA, SON, NESREA, WHO, and EU^{[20][21][22][23][24]} (Figure 12), exception of SGW9 (Ogwu Spring well). This indicated a situation of lead pollution of the underground water bodies at the affected stations in the study area, which could be due to high concentrations of lead ore deposits in the area^[26]. Water-soluble zinc in soils can contaminate groundwater^[27] through leaching from the soil to the water body.

3.3 Correlations of Heavy Metals in Groundwater

There were positive correlations among the heavy metals. However, strongest positive correlation was between Cu and Pb ($r = 0.921$) while the least was between Cu and Mn ($r = 0.176$) (Table 5). The positive correlations could be an indication of the same source of heavy metals pollution^[28], which could be natural sources including weathering of rocks, the Pb-Zn mining activities in several parts of the Ihetutu area, and other sundry point and non-point sources such as leachates from domestic wastes dumps.

Table 5. Correlation of heavy metals in groundwater samples from Ihetutu hills

| | <i>Cu</i> | <i>Zn</i> | <i>Fe</i> | <i>Mn</i> | <i>Pb</i> |
|-----------|-------------|-------------|-------------|-------------|-----------|
| <i>Cu</i> | 1 | | | | |
| <i>Zn</i> | 0.829069551 | 1 | | | |
| <i>Fe</i> | 0.347291232 | 0.223578813 | 1 | | |
| <i>Mn</i> | 0.175777928 | 0.287296924 | 0.917268323 | 1 | |
| <i>Pb</i> | 0.921198549 | 0.883311653 | 0.597831537 | 0.525299475 | 1 |

3.4 Analysis of Variance (ANOVA)

ANOVA was carried out on the means of the different stations, using Microsoft Office Excel (2007), at a significance level, $\alpha = 0.05$. The results showed no statistically significant differences in means of the parameters among sampling stations in study area, as *p-values* was higher than the significance level ($p = 0.757$).

4. Conclusion

This research was undertaken to analyze heavy metals contamination and quality of groundwater within Ihetutu mining areas in Ishiagu. The study has revealed that the quality of groundwater available in the area was poor, though most of the results obtained were within standard guidelines/limits of USEPA, SON, NESREA, WHO, and the EU. Also, exception of SGW9 (Ogwu spring well), mean levels of Pb, Cu, Fe, Zn and Mn in the study area were higher than the control (pre-mining/background) level; and were in the order of Fe>Zn>Pb>Mn>Cu. This indicated a case of quality deterioration of the groundwater available at these stations/locations when compared to the control values obtained; and also confirmed that groundwater resources in the study area have been adversely impacted upon by leachates/discharges from the mine wastes, tailings, surrounding rocks, and several other point and non-point anthropogenic sources including domestic wastes and run-offs from farms. Seasonal levels of most of the parameters analyzed including TDS, EC, pH, total hardness, chloride, and the heavy metals were also higher in the dry seasons than in the rainy seasons, and in the order of RNS<LRS<DRS<LDS. However, it is recommended that adequate measures must be urgently taken by the mining companies operating in the area to ensure that wastes and other toxic substances generated from their operations are not discharged into the groundwater bodies which serve as the main sources of drinking water to the people. The government must through its regulatory agencies including NESREA urgently ensure proper monitoring of the activities of mining companies and other waste disposal processes in the area; and also

enforce compliance with laid down standards/regulations. This will safeguard the groundwater resources in the area, and consequently human lives that depend on it.

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