

Hydrochemical characteristics and quality assessment of groundwater from fractured Albian carbonaceous shale aquifers around Enyigba-Ameri, southeastern Nigeria

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Abstract Enyigba-Ameri area is known for its Pb–Zn mining activities and the mine water is usually discharged directly into nearby streams and surface runoff. In order to determine the impacts of mining activities on the quality of water in the area and the general hydrochemical characteristics, field measurements and laboratory tests were carried out on water samples collected from the area. Field measurements and laboratory analyses of physicochemical parameters were determined using standard methods. In addition to the multivariate analyses (principal component analysis and cluster analysis) and ANOVA analysis, ionic cross-plots were used to determine the groundwater physicochemical characteristics and geochemical evolution. From the results, it was observed that Pb^{4+} , Zn^{2+} , Fe^{2+}

& $^{3+}$, Ca^{2+} , Mg^{2+} , and K^{+} had a concentration higher than the stipulated guideline values. Three principal components which explained 87.42% of the total dataset were extracted through the data reduction process. Cluster analysis of the hydrochemical data grouped the water samples into three distinct classes. It was observed that the water chemistry is mainly affected by silicate minerals weathering, carbonate weathering, and base ion exchange processes in descending order. ANOVA analysis showed that Zn^{2+} , Fe^{2+} & $^{3+}$, and Mg^{2+} had mean values that significantly differed from each other based on the sources of the samples. The Wilcox diagram revealed 4 classes of irrigation water types and the irrigation water quality indices showed that the groundwater in the area is not generally suitable for irrigation purposes.

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Introduction

Enyigba-Ameri area is well known for lead–zinc mining and agricultural activities, mainly crop production. Mining has always been carried out using open-cast method. Mine water from the open-cast pit is usually discharged directly into nearby streams without any treatment.

Groundwater constitutes the main source of water supply for drinking, domestic, and agricultural uses while surface water supply is mainly for mining

purposes in the area. The area is fast growing because of the increased mining activities and the presence of a new tertiary institution, thereby increasing the water demand. The Enyigba-Ameri area is underlain by fractured shales of the Asu River Group which constitute the only known aquifer in the area. The quality of water determines its potability and usefulness for other purposes. Environmental factors that determine the quality of a water supply source are related either to geogenic processes or to anthropogenic activities. Hydrochemical data provide powerful tools for determining the hydrochemical characteristics and assessing the quality of water (Aghazadeh and Mogaddam 2010; Okogbue et al. 2012; Onwuka et al. 2013; Omonona et al. 2014, Ravikumar et al. 2015; Towfiqul Islam et al. 2017; Koffi et al. 2017; Omonona and Okogbue 2017; Tiwari et al. 2017). An understanding of the hydrochemical characteristics will give insight into the geochemical evolution of the water sources, water flow regime, and water management practices. Groundwater quality for domestic and agricultural purposes is determined by comparing water indices such as lead (Pb^{4+}), iron (Fe^{2+} & 3^{+}), zinc (Zn^{2+}), chloride (Cl^{-}), nitrate (NO_3^{-}), electrical conductivity (EC), turbidity, pH, sodium adsorption ratio (SAR), and sodium percentage (Na%) with known standards. Previous studies in the area include notable works done by Okogbue and Ukpai (2013a, b) and Obiora et al. (2016). The former assessed the heavy-metal contents in groundwater around Enyigba and Abakaliki areas during the pre-mining era when mining was moribund and the latter evaluated the heavy-metal contamination in soils during the syn-mining period. Presently, no work has been done in the area on the hydrochemical characteristics and water quality assessment since mining began, to assess the impacts of the resumed mining activities. This study is aimed at determining the present hydrochemical characteristics of surface water and groundwater of the area and evaluating the present water quality for various purposes.

Study area setting

Enyigba-Ameri and the surrounding villages of Ameri, Nwakpu, and Echara are all located within the Pb–Zn mining areas of southern Benue Trough. The area is bounded within longitudes $8^{\circ} 06' E$ and $8^{\circ} 12' E$ and latitudes $6^{\circ} 07' N$ and $6^{\circ} 14' N$ (Fig. 1) and is accessible

through a network of major roads, minor roads, and footpaths. Enyigba-Ameri has a moderate relief that ranges from 125 to 250 m above mean sea level (Inyang 1975). The major landforms are the undulating shale outcrops, the valley ridges, and the low lands.

Enyigba-Ameri area is drained by the Ebonyi River. The tributaries of this river which are mostly ephemeral in nature generally flow in N-S direction into the Ebonyi River and exhibit dendritic drainage pattern. The area falls completely within the Guinea Savannah vegetation belt characterized by scattered trees, shrubs, and bushes. The area experiences two distinct seasons: the wet season which lasts from May to October and the dry season that lasts from November to April in each climatic cycle. During the wet season, it experiences a mean precipitation of 2125 mm and 250 mm during the dry season. The average temperature ranges from 27 to 28 °C and the atmospheric pressure varies between 1010 and 1016 millibars.

The Enyigba-Ameri area forms part of the Abakaliki anticlinorium of the southern Benue Trough and is marked by the undulating range of shale outcrops of the Abakaliki shales of the Asu River Group (Albian age) which serve as the host rock for Pb–Zn mineral deposits. The shale underlying the area is predominantly dark gray to black, calcareous, hard, indurated and fractured, fissile, laminated, and interbedded with siltstone and mudstones. The shale outcrops which are highly indurated trend mostly NE-SW with dip direction in NW-SE and dip amounts ranging from 5° to 42° . In addition to the shale rock underlying the area is the alluvium sand exposed mainly along the river and stream channels.

Materials and methods

The geochemical characteristics of the groundwater and surface water of the area were determined through field measurements of physicochemical parameters and laboratory analyses of cations and anions in samples taken from different sources in the area. Garmin e-Trex Global Positioning System (GPS) 76 edition was used to take latitude, longitude, and elevation above sea level of locations for sample collection.

Twenty water samples were collected from different sources (7 from hand-dug well (HDW), 9 from the borehole (BH), 2 from a river (RV), and 2 from mine pit (MPW)) scattered all over the study area. Standard

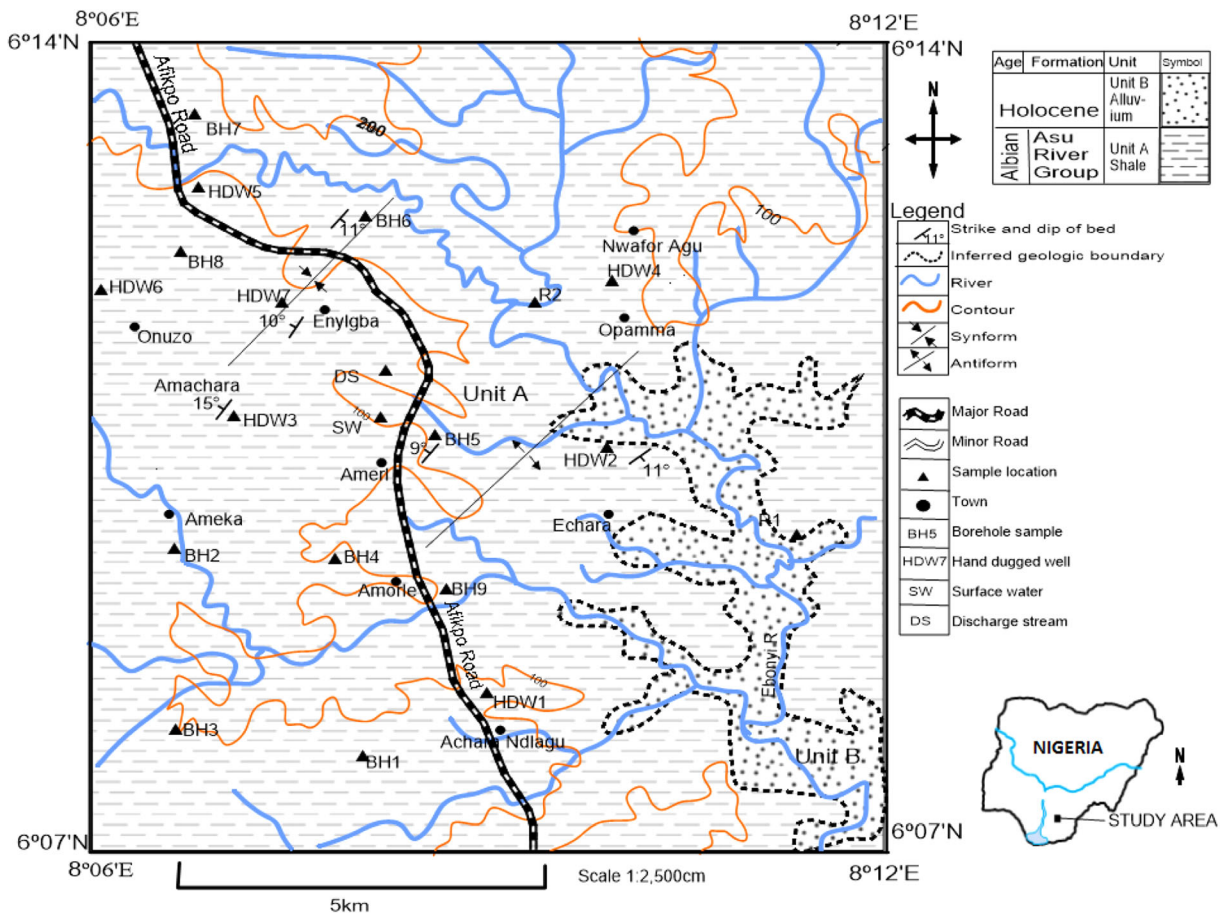


Fig. 1 Location and geologic map of Enyigba-Ameri, southeastern Nigeria

field sampling techniques were followed (Martin 2003). The physicochemical parameters were measured immediately, the samples were collected because of their transient characteristics, while the chemical analyses were carried out at the Chemical Laboratory, United Nation International Children Emergency Fund (UNICEF) Laboratory, Ibadan, Nigeria. The analytical methods used in the determination of the hydrochemical parameters are in accordance with the World Health Organization (WHO 2011) standards.

In each of the samples, 25 parameters were tested for. Total dissolved solids (TDSs), electrical conductivity (EC), and pH were measured with the aid of field probes. The TDS and EC were measured with an already-calibrated Wissenschaftlich Technische Werkstätten Conductivity (WTWC) meter and pH was measured with a pH meter. The WTWC meter was calibrated before use with potassium chloride (KCl) solution (0.01 M) of a conductivity value of 1.413 mS/

cm at 25 °C (APHA, 1995) while the pH meter was calibrated with standard buffer solutions of pH 7.01 and 4.01. Turbidity was determined using the HACH DR/2010 spectrophotometer and measurements were taken at a wavelength of 450 nm. The instrument was zeroed with filtered deionized water (blank) while the turbidity of the sample was measured.

Bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) were determined through titration of the standard solution methods. The concentration of the titrant (H_2SO_4) was set at 0.05 mol/l. Chloride (Cl^-) was determined by titration of the water samples with a standard solution of silver nitrate. The nitrate was determined at a wavelength of 500 nm based on cadmium reduction technique using the HACH DR/2010 spectrophotometer. Sulfate (SO_4^{2-}) was determined using the HACH DR/2010 spectrophotometer (SP). Three main stages are followed in the determination of ionic concentration. The SP setup which, usually

among other things, involved choosing of the wavelength (450 nm for SO_4^{2-}), sample preparation (which includes preparation of blank sample which involves water sample being tested without the reagents), zeroing the SP (the instrument must be zero for each test to establish a zero reference for the measurement), and measuring the prepared samples. A flame photometer (Corning Model 410) was used to determine the concentration of sodium and potassium while an atomic absorption spectrometer (200A Model) was used to determine the concentration of iron, calcium, magnesium, zinc, lead, and cadmium in the water samples. Water samples were processed and standard solutions prepared in line with US EPA (2013), Bureau of Indian Standards (2012), and American Public Health (2005). Five milliliters of concentrated HCO_3^- plus few glass beads were added to 50 ml of well-mixed and acid-preserved water sample in a beaker and the solution was boiled slowly and evaporated on a hot plate up to 10–20 ml. A few milliliters of concentrated HCO_3^- was added until the completion of digestion. The beaker was then washed down with deionized water and then filtered and poured into a 100-ml volumetric flask and made up to 100 ml and mixed thoroughly. In preparing a standard solution, the following processes were followed. Three concentrations of a standard solution of all metal to be analyzed were selected. The blank solution for each metal was prepared by aspirating and adjusting the instrument to zero and after which it was aspirated into flame. A calibration curve was prepared by plotting absorbance against concentration of the standard solution. A prepared sample solution was read directly from the instrument and the appropriate dilution factor for each sample that has a higher concentration of metal ions was made use of (Sharma and Tyagi 2013).

Turbidity and chloride had a detection limit (DL) of 0.01 NTU and 0.01 mg/l respectively during measurements while Na^+ , K^+ , Ca^{2+} , Mg^{2+} , SO_4^{2-} , HCO_3^- , and NO_3^- recorded a DL of 0.05 mg/l. SiO_2 had a DL of 1.0 mg/l. The trace elements, Pb^{4+} and Zn^{2+} , had a DL of 0.10 mg/l while Fe^{2+} & $^{3+}$ and Cd^{2+} 0.01 mg/l.

Data analyses included conversion of the initial unit of measurement, milligram/liter (mg/l) to milliequivalent/liter (meq/l) for the estimation of cation/anion ratios, and milliequivalent percentage (meq/l %) for the

graphical plots of the Piper diagram using Rockworks 16 edition. The data were also standardized before they were statistically analyzed to correct the effects of the varied range of measurements of the various parameters and differences in the units of measurements (Singh et al. 2004; Singh et al. 2009; Mohapatra et al. 2011). All the statistical analyses were carried out using SPSS V.20. Cluster analysis was based on Ward's method and squared Euclidean distance metric mode (Ward 1963; Güler et al. 2002). Principal component analysis, a data reduction technique, was carried out to understand the hydrochemical processes influencing the water chemistry (Okogbue et al. 2012; Srinivasamoorthy et al. 2014; Machiwala and Jhab 2015; Bodrud-Doza et al. 2016; Omonona and Okogbue 2017). The analysis was based on 13 physicochemical parameters as input variables in 20 water samples. Principal components with Eigenvalues ≥ 1.0 were considered significant (Kaiser 1958; Harman 1960). Principal component weight or factor loading ≥ 3.0 were considered significant for the physicochemical parameters, and principal scores loadings ≥ 1.0 were considered significant on the water sampling location (Senthilkumar et al. 2008; Ayuba et al. 2013). Ionic ratios of various ionic pairs used in deciphering the sources of ions and water chemistry were plotted using AquaChem 2011 1.14.

To assess the impact of mining activities on the different sources of the groundwater of the area, analysis of variance (ANOVA) tests were carried out on the data. The data inputted were data collected in 20 different locations in the year 2016 after mining activities had resumed in the area.

Results and discussion

General water chemistry

The results of the water analyses and the World Health Organization (WHO 2011 and Standard Organization of Nigeria (SON 2007) guideline limits are presented in Table 1. pH values ranged from 6.99 to 7.21, with a mean of 7.06; the pH revealed that water from all the types of sample varied between near neutral (weakly acidic) and neutral. Turbidity is a measure of the mudiness of water usually caused by the presence of silty-clay materials, organic matters, and colloidal inorganic particles. It is used to assess the quality of water and filtration effectiveness. Its values in all the types of water

Table 1 Hydrochemical data for the study area

Location	Type of sample	pH [#]	EC (µS/m)	TDS (mg/l)	TH (mg/l)	Turb. (NTU)	Temp (°C)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	Cl (mg/l)	HCO ₃ (mg/l)	SO ₄ (mg/l)
Alike	HDW 1	6.99 ± 0.34	70 ± 2	47 ± 3	82 ± 11	30.1 ± 0.04	28.60	27.20 ± 0.09	6.64 ± 1.23	3.00 ± 0.01	2 ± 1	9.96 ± 0.12	84 ± 1	12 ± 2
Ndufu	HDW 2	7.02 ± 0.42	27 ± 10	18 ± 2	62 ± 9	18.1 ± 0.02	28.90	20.00 ± 0.23	4.88 ± 2.32	3.11 ± 0.02	2 ± 2	6.17 ± 0.02	58 ± 2	10 ± 3
Agu	HDW 3	7.06 ± 0.43	287 ± 11	190 ± 6	170 ± 8	0.08 ± 0.11	28.80	48.00 ± 0.23	11.72 ± 0.28	14.09 ± 0.02	7 ± 2	29.36 ± 0.11	166 ± 2	3 ± 3
Ndebuo	HDW 4	7.00 ± 0.09	28 ± 5	20 ± 4	40 ± 11	3.14 ± 0.11	28.80	14.4 ± 0.91	3.52 ± 1.4	17.0 ± 0.01	9 ± 1	3.92 ± 0.11	38 ± 1	3 ± 3
Health Centre	HDW 5	7.01 ± 0.43	26 ± 8	17 ± 1	182 ± 11	6.24 ± 0.11	30.80	56.00 ± 0.23	13.67 ± 0.21	5.00 ± 0.01	3 ± 2	11.12 ± 0.12	190 ± 2	7 ± 2
Ameka	HDW 6	7.02 ± 0.56	79 ± 10	53 ± 4	100 ± 10	8.20 ± 0.11	29.90	25.60 ± 0.09	6.25 ± 0.21	7.00 ± 0.02	3 ± 2	19.96 ± 0.01	98 ± 12	4 ± 3
Ishiegu	HDW 7	7.03 ± 0.21	85 ± 9	57 ± 4	48 ± 8	50.2 ± 0.02	29.10	16.00 ± 0.32	3.91 ± 0.43	15.00 ± 0.02	8 ± 3	26.81 ± 0.11	52 ± 2	16 ± 3
	Mean	7.01	86.00	57.42	97.71	16.60	29.20	29.60	7.22	9.17	4.80	15.30	98.00	7.800
	Min	6.99	26.00	17.00	40.00	0.08	28.60	14.40	3.52	3.00	2.00	3.92	38.00	3.00
	Max	7.06	287.00	190.00	182.00	50.20	30.80	56.00	13.60	17.00	9.00	29.30	190.00	16.00
FUNAI	BH 1	7.18 ± 0.23	1020 ± 15	680 ± 10	580 ± 11	21.2 ± 0.04	29.30	168.00 ± 0.11	41.02 ± 0.98	98.78 ± 0.01	24 ± 1	103.97 ± 0.11	586.00 ± 11	38 ± 1
Ihotto	BH 2	7.12 ± 0.13	718 ± 10	478 ± 7	320 ± 23	0.01 ± 0.12	29.50	104 ± 1.90	25.39 ± 0.32	14.00 ± 0.02	11 ± 2	41.12 ± 0.11	336.00 ± 2	3 ± 1
Onyekwe	BH 3	7.09 ± 0.34	771 ± 11	514 ± 4	296 ± 11	0.01 ± 0.14	30.40	92 ± 0.44	22.46 ± 0.15	54.25 ± 0.02	13 ± 3	38.29 ± 0.11	320.00 ± 1	64 ± 5
Nwakpu	BH 4	7.02 ± 0.45	95 ± 10	65 ± 4	100 ± 10	21.2 ± 0.03	30.70	32.8 ± 0.11	8.01 ± 0.21	4.00 ± 0.02	1 ± 2	17.68 ± 0.02	100.00 ± 2	8 ± 3
Enyigba	BH 5	7.11 ± 0.43	1360 ± 21	906 ± 5	90 ± 8	0.02 ± 0.01	30.00	32.00 ± 0.11	7.81 ± 0.16	45.25 ± 0.01	30 ± 2	98.99 ± 0.02	94.00 ± 2	12 ± 2
Olua	BH 6	7.08 ± 0.32	107 ± 10	70 ± 2	88 ± 9	39.4 ± 0.01	30.80	28.8 ± 0.23	7.03 ± 1.11	18.00 ± 0.01	7 ± 2	39.45 ± 0.12	90.00 ± 11	22 ± 2
Ndiruruku	BH 7	7.16 ± 0.34	1082 ± 13	721 ± 10	356 ± 9	8.16 ± 0.11	30.00	96.00 ± 0.54	23.44 ± 0.16	26.00 ± 0.01	18 ± 2	91.33 ± 0.01	360.00 ± 2	93 ± 3
Amagu	BH 8	7.1 ± 0.34	741 ± 8	495 ± 5	248 ± 8	0.01 ± 0.14	30.40	59.20 ± 0.11	14.46 ± 0.34	17.00 ± 0.01	9 ± 2	43.38 ± 0.02	254.00 ± 11	32 ± 6
FOLK	BH 9	7.08 ± 0.21	415 ± 8	276 ± 11	198 ± 9	0.01 ± 0.04	30.60	60.00 ± 0.32	14.65 ± 1.77	18.00 ± 0.02	9 ± 1	45.5 ± 0.12	204.00 ± 2	60 ± 2
	Mean	7.10	701.00	467.20	252.80	10.00	30.10	74.70	18.20	32.80	13.50	57.70	260.40	36.80
	Min	7.00	95.00	65.00	88.00	0.01	29.30	28.80	7.03	4.00	1.00	17.68	9.00	3.00
	Max	7.20	1360.00	906.00	580.00	39.40	30.80	168.00	41.00	98.78	30.00	103.97	586.00	93.00
Ebonyi	RIVER	7.03 ± 0.54	66 ± 5	44 ± 3	38 ± 11	73.4 ± 0.03	20.40	12.00 ± 0.21	2.93 ± 1.22	6.10 ± 0.02	4 ± 1	8.24 ± 0.11	44.00 ± 1	18 ± 3
Ebonyi	RIVER	7.01 ± 0.11	48 ± 11	32 ± 3	74 ± 9	82.5 ± 0.12	27.40	21.6 ± 0.21	5.27 ± 0.45	7.00 ± 0.01	2 ± 2	16.15 ± 0.11	80.00 ± 5	18 ± 5
	Mean	7.02	57.00	38.00	56.00	77.99	23.90	16.80	4.10	6.55	3.00	12.19	62.00	18.00
	Min	7.01	48.00	32.00	38.00	73.45	20.40	12.00	2.93	6.10	2.00	8.24	44.00	18.00
	Max	7.03	66.00	44.00	74.00	82.53	27.40	21.60	5.27	7.00	4.00	16.15	80.00	18.00
Eyingba	MPW 1	6.99 ± 0.23	42 ± 5	28 ± 5	68 ± 11	10.0 ± 0.11	29.60	22.40 ± 0.21	5.47 ± 1.22	3.00 ± 0.01	2 ± 2	9.96 ± 0.21	66.00 ± 2	4 ± 1
Ameri	MPW 2	7.21 ± 0.32	1746 ± 12	1165 ± 20	630 ± 6	1.12 ± 0.13	34.00	192.0 ± 0.3	46.8 ± 1.31	76.9 ± 0.02	18 ± 3	121.0 ± 0.11	630.00 ± 11	93 ± 2
	Mean	7.10	894.00	596.50	349.00	5.58	31.80	107.20	26.10	39.99	10.00	65.52	348.00	48.50
	Min	6.99	42.00	28.00	68.00	1.12	29.60	22.40	5.47	3.00	2.00	9.96	66.00	4.00
	Max	7.21	1746.0	1165.00	630.00	10.05	34.00	192.00	46.80	76.98	18.00	121.08	630.00	93.00
WHO			1400	500.00	200.00	1.00	31.00	75.00	30.00	200.00	10.00	250.00		250.00
SON			1000	500.00	150.00	5.00	—	—	0.20	200.00	—	250.00		

Location	NO3 (mg/l)	SiO ₂ (mg/l)	Zn (ppm)	Fe (ppm)	Pb (ppm)	Salinity (0/00)	SAR [#]	Mg hardness	Na %	RSC	Well depth (m)	Aquifer type
Alike	0.24 ± 0.01	19.3 ± 2.13	0.00 ± 0.01	2.12 ± 0.02	5.98 ± 0.21	0.02 ± 0.01	0.13	64.10	8.71	-0.52	8.40	Unconfined
Ndufu	1.10 ± 0.01	1.11 ± 0.18	0.00 ± 0.01	2.02 ± 0.01	0.62 ± 0.02	0.02 ± 0.02	0.16	72.33	11.75	-0.45	6.70	Unconfined
Agu	0.21 ± 0.01	0.00 ± 0.12	0.11 ± 0.02	0.00 ± 0.11	0.00 ± 0.02	0.03 ± 0.01	0.47	56.95	19.07	-0.63	10.20	Unconfined

Table 1 (continued)

Location	NO3 (mg/l)	SiO ₂ (mg/l)	Zn (ppm)	Fe (ppm)	Pb (ppm)	Salinity (0/00)	SAR [#]	Mg hardness	Na%	RSC	Well depth (m)	Aquifer type
Ndebuo	0.18±0.02	0.00±0.12	0.01±0.01	0.23±0.10	0.07±0.01	0.01±0.01	1.04	87.49	49.03	-0.38	8.60	Unconfined
Health Centre	0.19±0.02	1.21±0.1	0.00±0.01	0.94±0.01	0.17±0.01	0.02±0.01	0.15	47.91	6.983	-0.80	5.80	Unconfined
Ameka	0.40±0.02	3.10±0.11	0.02±0.01	1.82±0.11	2.53±0.11	0.08±0.01	0.32	74.99	17.54	-0.19	7.20	Unconfined
Ishingu	1.01±0.02	6.01±0.11	0.03±0.01	4.35±0.02	1.82±0.11	0.04±0.02	0.87	88.91	43.35	-0.27	6.30	Unconfined
	0.47	4.39	1.33	0.02	0.74	0.03	0.45	70.38	22.35	-0.46	5.80	
	0.18	0.00	0.00	0.00	0.00	0.00	0.13	47.91	6.98	-0.80	7.60	
	1.10	19.32	4.35	0.11	2.53	0.08	1.04	88.91	49.03	-0.18	10.20	
FUNAI	0.49±0.01	5.12±3.11	0.00±0.11	0.10±0.10	0.26±0.11	0.18±0.01	1.77	28.69	29.46	-2.15	27.50	Unconfined
Ihotto	0.41±0.02	0.00±1.20	0.00±0.11	0.33±0.11	0.11±0.01	0.07±0.01	0.31	38.19	10.90	-1.77	32.80	Unconfined
Onyekwe	2.61±0.01	0.00±0.11	0.00±0.01	0.00±0.01	0.09±0.02	0.07±0.02	1.31	53.84	29.48	-1.19	37.90	Unconfined
Nwakpu	0.19±0.01	2.00±0.11	0.06±0.01	7.36±0.01	0.80±0.12	0.03±0.02	0.16	58.89	7.99	-0.66	35.80	Unconfined
Enyigba	0.33±0.02	0.00±0.01	0.00±0.01	0.00±0.02	0.00±0.02	0.20±0.03	1.86	77.23	54.98	-0.69	38.10	Unconfined
Olua	0.92±0.03	5.09±0.01	0.04±0.11	4.53±0.02	1.47±0.011	0.08±0.02	0.77	71.37	32.31	-0.54	24.70	Unconfined
Ndiuruku	3.36±0.02	2.90±0.02	0.00±0.10	0.21±0.03	0.12±0.11	0.20±0.02	0.61	45.35	19.15	-0.82	26.70	Unconfined
Amagu	1.35±0.02	0.00±0.02	0.00±0.01	0.00±0.03	0.08±0.02	0.08±0.02	0.51	57.61	18.96	0.02	36.50	Unconfined
FOLK	2.44±0.02	1.21±0.02	0.01±0.11	0.42±0.02	0.05±0.11	0.09±0.02	0.54	52.79	19.43	-0.85	28.40	Unconfined
	1.34	1.81	1.43	0.01	0.33	0.11	0.87	53.77	24.74	-0.96	24.70	
	0.19	0.00	0.00	0.00	0.00	0.03	0.16	28.69	7.99	-2.15	32.04	
	3.36	5.12	7.36	0.06	1.47	0.20	1.86	77.23	54.98	0.01	38.10	
Ebonyi	1.03±0.02	4.32±0.11	0.02±0.01	8.81±0.01	0.45±0.11	0.02±0.03	0.41	100.85	30.45	-0.11	n.a	Surface
Ebonyi	1.03±0.02	23.0±0.02	0.12±0.01	25.6±0.11	1.34±0.02	0.03±0.01	0.35	79.81	19.04	-0.20	n.a	Surface
	1.03	13.66	17.22	0.07	0.89	0.02	0.37	90.33	24.75	-0.15	n.a	
	1.03	4.32	8.81	0.02	0.45	0.02	0.35	79.81	19.04	-0.20	n.a	
	1.03	23	25.63	0.12	1.34	0.03	0.41	100.85	30.45	-0.11	n.a	
Eyingba	0.51±0.01	3.09±0.03	0.04±0.11	5.46±0.11	0.53±0.02	0.02±0.02	0.15	68.93	10.38	-0.48		Surface
Ameri	2.41±0.01	1.09±0.12	0.92±0.01	0.00±0.02	0.00±0.11	0.21±0.20	1.29	39.46	22.08	-3.11		Surface
	1.46	2.09	3.79	0.48	3.25	0.12	0.72	54.20	16.23	-1.79	51.50	
	0.51	1.09	2.12	0.04	0.53	0.02	0.15	39.46	10.38	-3.11	48.00	
	2.41	3.09	5.46	0.92	5.98	0.21	1.29	68.93	22.08	-0.48	55.00	
	50.00	-	3.00	0.30	0.01	-	2.0*	50*	35*	-	n.a	
	50.00	-	3.00	0.30	0.01	-	-	-	-	-	n.a	

FUNAI, Federal University Ndufu Alike Ikwo campus; HDW, hand-dug well; BH, borehole; MPW, mine pit water; TH, total hardness; Temp, temperature; Turb., turbidity; Min, minimum; Max, maximum; WHO, World Health Organization; SON, Standard Organization of Nigeria; # no unit; *Ayuba et al. (2013)

sample of the area ranged from 0.01 to 82.53 NTU with a mean of 18.67 NTU. River water has the highest turbidity among the types of sample and this could be a result of higher clay, silt, finely divided inorganic and organic matter, algae, soluble colored organic compounds, and plankton and other microscopic organisms in river water than the other types of sample. Although turbidity is not necessarily a scourge to human health, it is an essential physicochemical marker of the possible presence of pollutants that would be of concern for health.

TDS values in all the types of water sample ranged from 17 to 1165 mg/l with a mean of 293.80 mg/l. TDS

value was observed to increase with depth and this might be attributed to more interaction and dissolution of minerals of the host rock at greater depths. The spatial distribution of TDS across the study area is presented in Fig. 2. EC is a measure of the total ionic components in water; the more solutes present in water, the more the EC. EC ranged from 26 to 1746 $\mu\text{S}/\text{m}$ with a mean of 440.65 $\mu\text{S}/\text{m}$. This wide range in EC values revealed the high diversity in the geochemical processes that shape the chemistry of the water of the area. As TDS, EC was also observed to increase with well depth. The contribution to the water EC characteristics could be attributed to dissolution of minerals in the shale rock matrix.

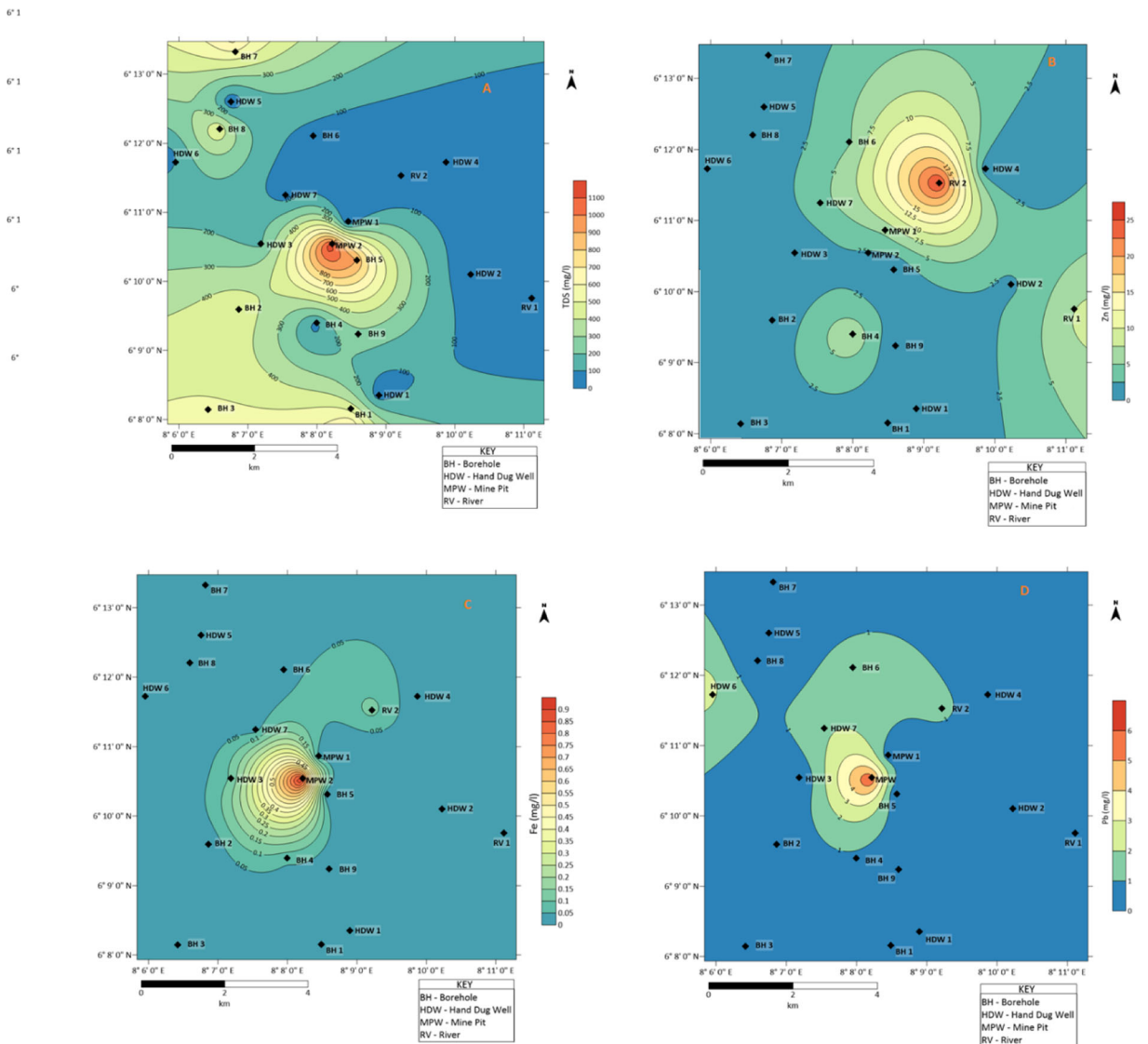


Fig. 2 Spatial distribution of **a** total dissolved solids (TDS), **b** zinc (Zn), **c** iron (Fe), and **d** lead (Pb) across the study area

The hardness of water limits its use for domestic and agricultural activities. Water hardness can give rise to the formation of scum (whitish scale) in pots, boiler rings, and irrigation equipment; it may also cause health problems to humans such as kidney failure (WHO 2011). The values of total hardness ranged from 40 to 182 mg/l with a mean of 97.71 mg/l. The water of the area classified into soft water, moderately hard water, hard water, and very hard water.

The calculated charge ratio between the sum of cations and sum of anions was 2.03% which is within the acceptable limits of < 10% which confirms the reliability of the analytical results (Datta and Subramanian 1998; Singh and Hassin 2002). The abundance of the major ions in the water samples in decreasing order is $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ and $\text{Mg}^{2+} > \text{Na}^+ > \text{Ca}^{2+}$. HCO_3^- is the most dominant ion and the average HCO_3^- concentration accounts for about 29.80% of the total major ions while NO_3^- accounts for only 0.33% of the total major ions expressed in the equivalent units.

The concentration of heavy metals in water varied across the different water sample types. The concentration of Zn^{2+} is ranged from below detection limit (BDL) to 25.63 ppm with a mean of 4.09 ppm. The results showed that the rivers are more contaminated with Zn^{2+} than any other water source type (Fig. 2). The concentration of $\text{Fe}^{2+} \& \text{3}^+$ ranged from BDL to 0.92 ppm with a mean of 0.10 ppm. The spatial distribution of $\text{Fe}^{2+} \& \text{3}^+$ is presented in Fig. 2 which showed the region around the mine pit is the most contaminated. Pb^{4+} concentration ranged from BDL to 5.98 ppm with a mean of 1.02 ppm, the metal ion concentration is most elevated in the region around the mine pit (Fig. 2), and this may be attributed to the metal extraction activities in that region. The concentrations of Cd^{2+} in water of the study area are generally low, lower than the detection limit (0.01 ppm) in most of the sampled points.

Hydrochemical facies

The Piper (1994) diagram for the hydrochemical data of the study area revealed three hydrochemical facies, namely, $\text{Ca}^{2+}-\text{Mg}^{2+}-\text{HCO}_3^-$ facies, $\text{Na}^+-\text{K}^+-\text{Cl}^- - \text{SO}_4^{2-}$ facies, and $\text{Ca}^{2+}-\text{Mg}^{2+}-\text{Cl}^- - \text{SO}_4^{2-}$ facies (Fig. 3). Seventeen water samples belonging to different sources (HDW, BH, MPW, and RV) were plotted within the $\text{Ca}^{2+}-\text{Mg}^{2+}-\text{HCO}_3^-$ facies field. This hydrochemical facies demonstrates the dominance of

alkaline earth metals over the alkali metals ($\text{Ca}^{2+} + \text{Mg}^{2+} > \text{Na}^+ + \text{K}^+$) and weak acidic anions over strong acidic anions ($\text{HCO}_3^- > \text{Cl}^- + \text{SO}_4^{2-}$). This water type is generally formed from precipitation; thus, it shows zones of fresh water recharge. The primary water hardness (carbonate hardness exceeds 50%) associated with this water type can be removed by mere boiling. One groundwater sample from a borehole was plotted within the $\text{Na}^+-\text{K}^+-\text{Cl}^- - \text{SO}_4^{2-}$ facies field. This facies indicates the dominance of alkali metals over alkaline earth metals ($\text{Na}^+ + \text{K}^+ > \text{Ca}^{2+} + \text{Mg}^{2+}$) and strong acidic anions over weak anions ($\text{Cl}^- + \text{SO}_4^{2-} > \text{HCO}_3^-$). Two groundwater samples (one from a hand-dug well and the other from a borehole) belong to the $\text{Ca}^{2+}-\text{Mg}^{2+}-\text{Cl}^- - \text{SO}_4^{2-}$ facies and this facies denotes the dominance of alkaline earth over alkalis $\text{Ca}^{2+} + \text{Mg}^{2+} > \text{Na}^+ + \text{K}^+$ and strong acidic anions over weak acidic anions ($\text{Cl}^- + \text{SO}_4^{2-} > \text{HCO}_3^-$). The predominance of the $\text{Ca}^{2+}-\text{Mg}^{2+}-\text{HCO}_3^-$ facies over the other two facies and the absence of the other facies type ($\text{Na}^+ + \text{K}^+ + \text{HCO}_3^-$) indicate a relatively short residence time of the groundwater in the fractured shale aquifer of the area.

The predominance of the carbonate water type over the other water types also revealed that the groundwater is freshwater in nature and the variation in chemistry may be a result of base rock-groundwater interactions and anthropogenic factors.

Statistical analyses

Correlation matrix

Pearson product moment correlation matrix (Table 2) showed the various ionic pairs that are significantly related. Parameters with correlation coefficient values that are significantly related at 0.01 and 0.05 levels are written with asterisks (Table 2). The ionic pairs that are statistically related at 0.01 and 0.05 levels are thought to be released from the same sources and/or through same geochemical processes. For example, Ca^{2+} , K^+ , Mg^{2+} , Cl^- , SO_4^{2-} , HCO_3^- , and $\text{Fe}^{2+} \& \text{3}^+$ are released from the same sources and through the same geochemical processes. Correlation matrix reveals also the contributing ions of composite parameters like TDS, TH, and turbidity. TDS, a direct measure of the conductivity of water, is found to be very strongly dependent on

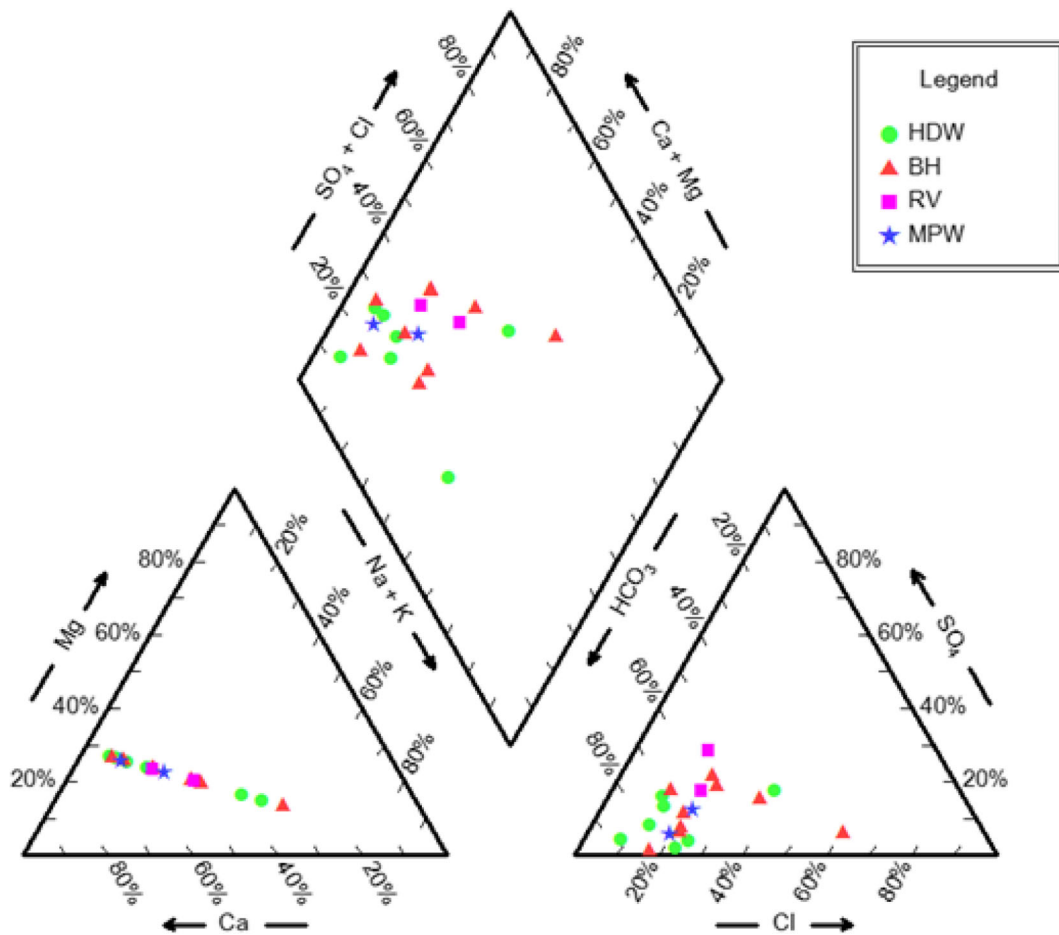


Fig. 3 Piper diagram of the 20 water samples labeled according to the water sample type (HDW, hand-dug well; BH, borehole; RV, river; MPW, mine pit)

the concentration of Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , and HCO_3^- , and strongly dependent on the concentration of NO_3^- , Cd^{2+} , and $\text{Fe}^{2+} \& \text{3}^+$. Cd^{2+} has a negative correlation coefficient with TDS and this indicates an inverse relationship; an increase in Cd^{2+} concentration results in a decrease in TDS. Likewise, TH, a combined measure of Ca hardness and Mg hardness, is very strongly dependent on Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , and HCO_3^- , and strongly dependent on NO_3^- and $\text{Fe}^{2+} \& \text{3}^+$ in addition to temperature. Turbidity is very strongly positively correlated with SiO_2 and Zn^{2+} and very strongly negatively correlated with temperature. This thus shows that an increase in the concentration of Zn^{2+} and SiO_2 in groundwater of the area increases the turbid nature of the water, while an increase in temperature brings about a decrease in

turbidity of the water. Pb^{4+} has a very strong correlation coefficient with $\text{Fe}^{2+} \& \text{3}^+$ but low correlation coefficient with Zn^{2+} ; likewise, Zn^{2+} has a very strong correlation coefficient with Fe but low with Pb^{4+} . Cd^{2+} has low correlation coefficients with the other trace elements (Pb^{4+} , Zn^{2+} , and $\text{Fe}^{2+} \& \text{3}^+$).

Cluster analysis-groundwater classes

Different water groups were defined by the dendrogram generated by cluster analysis. Three broad classes or groups of water were identified based on the inspection of the cluster analysis dendrogram (Fig. 4). The linkage distance between group 1 and the other two groups (group 2 and group 3) is quite high (190), and this indicates that the geochemical

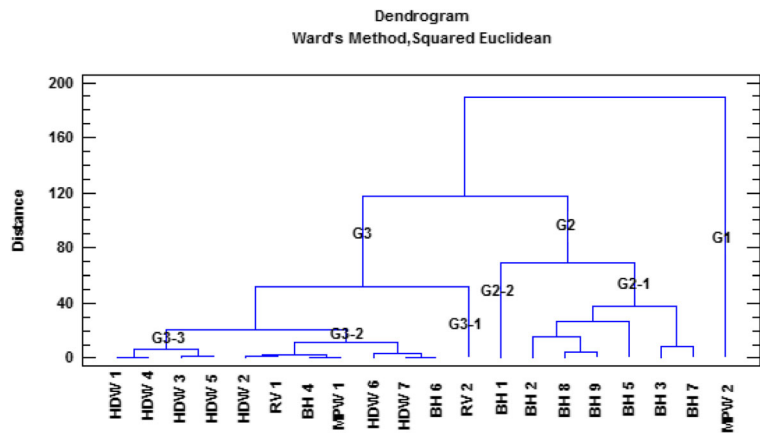
Table 2 Pearson product moment correlations

	pH#	EC	TDS	TH	Turb.	Tem	Ca	Mg	Na	K	Cl	SO ₄	HCO ₃	NO ₃	SiO ₂	Zn	Fe	Cd	Pb	
pH#	1																			
EC	0.916**	1																		
TDS	0.915**	1.000**	1																	
TH	0.883**	0.797**	0.797**	1																
Turb.	-0.351	-0.441	-0.441	-0.383	1															
Tem	0.399	0.439	0.439	0.462*	0.655**	1														
Ca	0.875**	0.798**	0.798**	0.995**	-0.383	0.471*	1													
Mg	0.875**	0.798**	0.798**	0.995**	-0.383	0.471*	1.000**	1												
Na	0.810**	0.793**	0.793**	0.823**	-0.254	0.343	0.830**	0.830**	1											
K	0.802**	0.870**	0.870**	0.599**	-0.364	0.279	0.601**	0.601**	0.809**	1										
Cl	0.934**	0.943**	0.943**	0.796**	-0.326	0.446*	0.791**	0.791**	0.835**	0.892**	1									
SO ₄	0.729**	0.691**	0.691**	0.699**	-0.199	0.357	0.681**	0.681**	0.580**	0.481*	0.687**	1								
HCO ₃	0.883**	0.798**	0.798**	0.999**	-0.380	0.455*	0.995**	0.995**	0.824**	0.601**	0.791**	0.702**	1							
NO ₃	0.536*	0.488*	0.488*	0.452*	-0.115	0.215	0.429	0.429	0.315	0.289	0.450*	0.921**	0.459*	1						
SiO ₂	-0.334	-0.314	-0.314	-0.230	0.712**	-0.276	-0.232	-0.232	-0.198	-0.318	-0.230	-0.121	-0.229	-0.126	1					
Zn	-0.335	-0.342	-0.342	-0.312	0.800**	-0.369	-0.309	-0.309	-0.275	-0.388	-0.289	-0.160	-0.310	-0.068	0.670**	1				
Fe	0.466*	0.523*	0.524*	0.549*	-0.087	0.404	0.575**	0.575**	0.434	0.194	0.485*	0.494*	0.535*	0.302	-0.036	0.078	1			
Cd	-0.408	-0.503*	-0.503*	-0.247	0.162	-0.135	-0.262	-0.262	-0.352	-0.536*	-0.464*	-0.311	-0.242	-0.252	0.010	0.384	-0.243	1		
Pb	0.316	0.324	0.325	0.374	0.081	0.374	0.394	0.394	0.309	0.050	0.352	0.363	0.359	0.229	0.040	0.174	0.878**	-0.152	1	

**Correlation is significant at the 0.01 level (2-tailed)

*Correlation is significant at the 0.05 level (2-tailed)

Fig. 4 Dendrogram resulting from the cluster analysis for the 20 water samples, showing the distribution of the water samples into 3 clusters



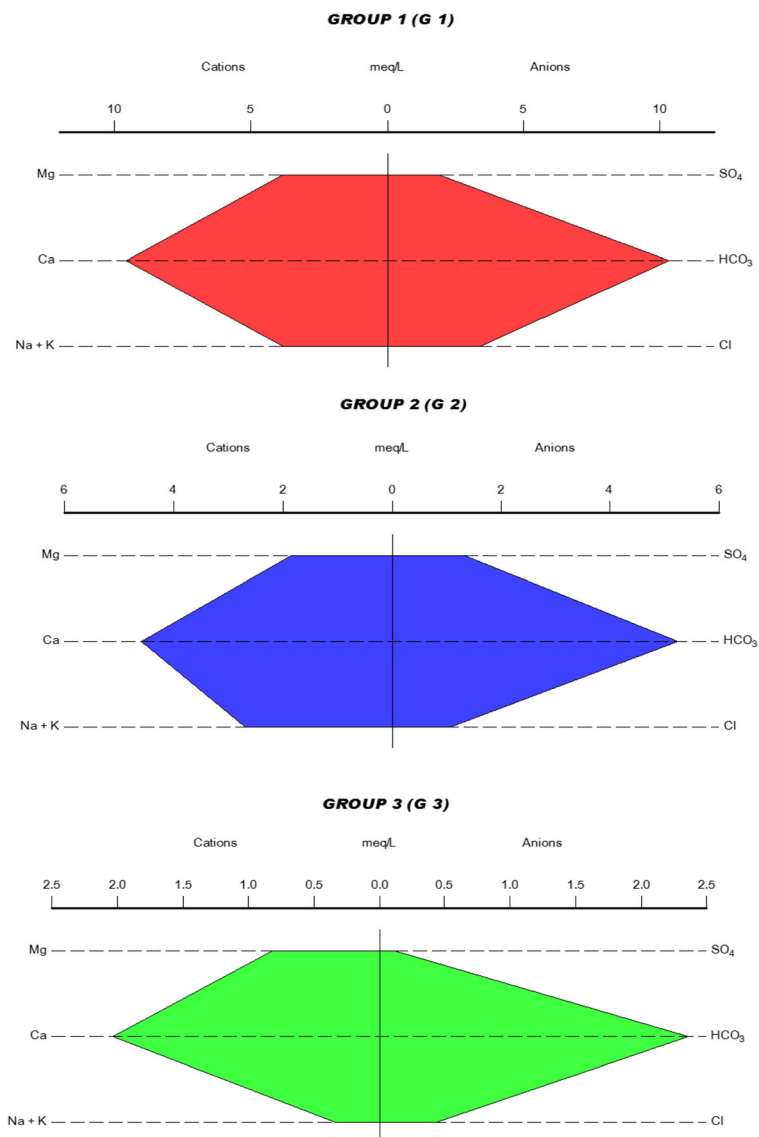
characteristics of the group 1 water samples are clearly different from those of the other groups. While group 3 has a linkage distance of 70, group 2 has the least linkage distance of 50. It was observed that the measured values of EC, TDS, and TH and the concentrations of the ions Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , HCO_3^- , and NO_3^- decreased from water group 1 to water group 3. The group 1 cluster ($n = 1$) is composed of a surface water sample with an excessively high TDS value (>1000 mg/l), high NO_3^- , and high trace metal concentrations. The group 2 ($n = 7$) water is composed all of deep borehole groundwater samples with elevated TDS (median concentration, 514 mg/l) and low trace metal concentrations. The group may be subdivided into two subgroups, G2-1 ($n = 1$) and G2-2 ($n = 6$). G2-1 is characterized by lower values of the physicochemical parameters (EC, TDS, TH, turbidity), major ions (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , HCO_3^-), and trace metals (Pb^{4+} , Fe^{2+} & $^{3+}$) except Zn^{2+} and Cd^{2+} than those of G2-2. Also, the G2-1 boreholes are deeper than the G2-2 borehole. Group 3 ($n = 12$) is composed of water from all the different water sample types (HDW, BH, MPW, and RV) and is characterized by low TDS values (median concentration, 53 mg/l) and very high trace metal concentration. This group can be divided into 3 subgroups, namely, G3-1 ($n = 1$), which consists of a surface water sample (RV), G3-2 ($n = 7$), which consists of different water sample types and G3-3 ($n = 4$), which consists of shallow hand-dug wells. The G3-1 has similar physicochemical and major ions characteristics with the G3-2 and G3-3 but very distinct trace metal

concentrations characteristics from the other subgroups. The G3-1 water sample has extremely high trace metal concentration than G3-2 and G3-3 water samples. G3-2 water samples have slightly higher trace metal concentrations than those of G3-3 water samples. The stiff pattern of the three groups of water samples is presented in Fig. 5, which shows that the three water groups are essential for the hydrochemical facies with very little variation in shapes.

Principal component analysis—sources of ions in water and their controlling processes

Three principal components, PC 1, PC 2, and PC 3 which explained 87.42% of the total dataset, were extracted through the data reduction processes (Table 3). Ca^{2+} , Cl^- , HCO_3^- , SO_4^{2-} , Mg^{2+} , and Na^+ have high positive loading factors on principal component (PC) 1, explaining 60.41% of the variation in the total dataset. PC 2 has high positive loadings on Fe^{2+} & $^{3+}$, Zn^{2+} , and Pb^{4+} which explained 15.7% of the total dataset while PC 3 has high negative loadings on SO_4^{2-} and NO_3^- which explained 11.3% of the total dataset. Because of the high associations and correlations between $\text{Ca}^{2+} + \text{Mg}^{2+}$ and HCO_3^- , and Na^+ and Cl^- , PC 1 which explains the highest variance in the dataset may be defined as “hardness and salinity” factor. PC 2, because of its high loadings on only the trace metals which are thought to be released from the mining activities in the area, may be defined as “mining activities” factor. PC 3 that explained the least variance of the dataset has high loadings on just SO_4^{2-} and NO_3^- . The

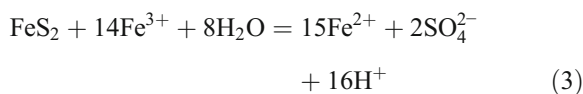
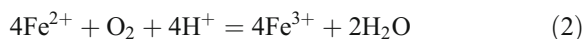
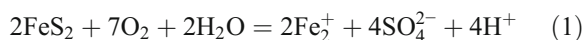
Fig. 5 Stiff diagram of the 20 water samples constructed based on the median concentrations of the different water groups (G1, G2, and G3)



occurrence of high loadings of SO_4^{2-} in PC 1 and PC 3 suggests multiple sources for the ion. In PC 1, SO_4^{2-} has loading alongside with the major ions (Ca^{2+} , Na^+ , Mg^{2+} , Cl^- , and HCO_3^-). These ions are assumed to be released via various geogenic geochemical processes. One may suggest that SO_4^{2-} in PC 1 may have been released from geogenic processes also. The geogenic source of SO_4^{2-} may be derived from pyrite oxidation.

Pyrite (FeS_2) occurs as a secondary mineral in the Enyigba-Ameri Pb^{4+} and Zn^{2+} minerals and associated sediments. The observed high values of SO_4^{2-} in waters in the area may be attributed to the oxidative weathering of pyrites as shown in the reactions

equations (Lowson et al. 1993):



The association of NO_3^- with SO_4^{2-} in PC 3 suggests anthropogenic sources of SO_4^{2-} in addition to its non-

Table 3 Component weights

Parameters	PC 1	PC 2	PC 3
Ca	<i>0.386615</i>	-0.105416	0.152847
Cl	<i>0.354644</i>	-0.113236	0.0452834
HCO ₃	<i>0.385337</i>	-0.129157	0.10952
SO ₄	<i>0.336768</i>	0.0318058	-0.511923
Mg	<i>0.386619</i>	-0.105423	0.152848
Na	<i>0.345982</i>	-0.160086	0.201278
NO ₃	0.243489	0.0509743	-0.740977
Zn	-0.112627	<i>0.555438</i>	-0.126887
Fe	0.276024	<i>0.501489</i>	0.187662
Pb	0.213355	<i>0.599191</i>	0.190493
Eigenvalue	6.04084	1.56986	1.13127
% variation	60.408	15.699	11.313
Cumulative % variation	60.408	76.107	87.420

Significant factor loading is written in italics

anthropogenic (geogenic) source. NO₃⁻ is usually derived from anthropogenic sources and the association of this ion with SO₄²⁻ in PC 3 suggests an anthropogenic source for SO₄²⁻, in addition to those derived from oxidation of pyrite and related minerals. NO₃⁻ may be released from domestic wastes and from agricultural activities, and likewise, SO₄²⁻ may be released from domestic wastes as well as sulfate-rich fertilizers. PC 3, therefore, may be defined as domestic wastes and agricultural activities factor.

Figure 6 shows the consistencies between PCA results and CA results. The principal component scores (Table 4) represent the influence of the

principal components (hardness and salinity factor, mining activities factor, and domestic wastes and agricultural activities factor) on the various water samples (Onwuka et al. 2013). It is clear from the figure that a plot of PC 2 against PC 1 showed the distinction that exists between the groups of water samples (Fig. 6a). Group 1 water sample was plotted at the top right corner, a zone of high hardness and salinity factor, and high mining activities factor. Group 2 groundwater samples were plotted at the middle of the left side, and group 3 water samples were plotted almost at the lower central portion. Figure 6a showed that the G2-2 is more influenced

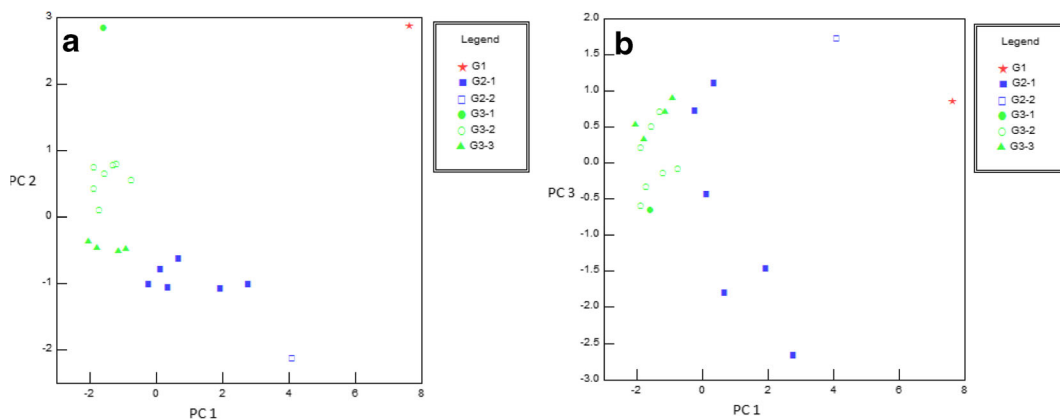


Fig. 6 Plot of the component scores for PC 1 (hardness and salinity factor) and PC 2 (mining activities factor) (a); PC 3 (domestic wastes and agricultural activities factor) and PC 1

(hardness and salinity factor) (b), with the water samples labeled according to their respective water groups

Table 4 Principal component scores and water group

S/N	Location	Type of water sample	Component 1	Component 2	Component 3	Group
1	Alike	HDW 1	<i>- 1.75075</i>	- 0.468287	0.318195	G3-3
2	Ndufu	HDW 2	<i>- 1.70148</i>	0.0903064	- 0.339142	G3-2
3	Agu	HDW 3	- 0.878638	- 0.484353	0.888521	G3-3
4	Ndebu	HDW 4	<i>- 2.02326</i>	- 0.384186	0.531477	G3-3
5	Health Centre	HDW 5	<i>- 1.10258</i>	- 0.529755	0.705538	G3-3
6	Ameka	HDW 6	<i>- 1.26863</i>	0.771533	0.700019	G3-2
7	Ishiagu	HDW 7	<i>- 1.19063</i>	0.780648	- 0.145782	G3-2
8	FUNAI	BH 1	<i>4.09568</i>	<i>- 2.14167</i>	<i>1.71162</i>	G2-2
9	Ihotto	BH 2	0.378222	<i>- 1.06213</i>	<i>1.09771</i>	G3-2
10	Onyinkwe	BH 3	<i>1.93772</i>	<i>- 1.09088</i>	<i>- 1.46923</i>	G2-1
11	Nwapku	BH 4	<i>- 1.53739</i>	0.639712	0.495039	G3-2
12	Enyigba	BH 5	- 0.200602	<i>- 1.02766</i>	0.718353	G2-1
13	Olua	BH 6	- 0.743866	0.535355	- 0.0841703	G3-2
14	Ndiuruku	BH 7	<i>2.76817</i>	<i>- 1.02744</i>	<i>- 2.66723</i>	G2-1
15	Amagu	BH 8	0.155501	- 0.801995	- 0.440516	G2-1
16	FOLK	BH 9	0.697083	- 0.640485	<i>- 1.80525</i>	G2-1
17	Ebonyi	RV 1	<i>- 1.84746</i>	0.728942	- 0.608101	G3-2
18	Ebonyi	RV 2	<i>- 1.58142</i>	2.83834	- 0.658843	G3-1
19	Enyigba Mine	MPW 1	<i>- 1.85699</i>	0.408287	0.200899	G3-2
20	Ameri Mine	MPW 2	<i>7.65132</i>	2.86572	0.850901	G1

Significant factor score is written in italics

by hardness and salinity factor than the mining activities factor, while G2-1 is influenced by both hardness and salinity factor and mining activities factor. The figure also revealed a decreasing effect of the influence of the mining activity factor on the water of G3-1 through G3-2 to G3-3. The plot of PC 3 against PC 1 further iterates the distinction between group 2 and group 3 (Fig. 6b). The chemistry of group 3-3 water samples which are all shallow hand-dug wells, group 1 water sample, and some group 2 water samples are strongly influenced by domestic wastes and agricultural activities factors.

Gibbs diagrams (Gibbs 1970) of the hydrochemical data of the groundwater are presented in Fig. 7, with the water samples labeled according to the different water groups. The figure revealed that all the water groups were plotted within the rock dominance zone, which indicates that the chemistry of all the water samples is influenced by geology: rock-water interaction processes. The group 1 water sample is discernable from the other groups by high TDS. High TDS in this surface water sample may be attributed to the effect of

evaporation processes. TDS was observed to decrease from group 1 through group 2 to group 3. The water of other groups were observed to plot far away from the right side of the rock dominance section, which indicates that there is no effect of freshening on the water samples (Fig. 7). Elevated concentrations of the trace elements in groups 1 and 3 water sample are unexplained through the TDS and ionic ratios plots.

Figure 8 shows that G3 water samples have the lowest enrichment of Ca^{2+} , Mg^{2+} , and HCO_3^- concentrations, while group 1 sample showed the highest concentrations of these ions and group 2 water samples in between group 1 and group 3. The three water groups were plotted above the theoretical line of calcite and plagioclase dissolution (Subramani et al. 2009; Srinivasamoorthy et al. 2014). Ca-rich and Mg-rich minerals can be proposed for the sources of Ca^{2+} , Mg^{2+} , and HCO_3^- in the water of the area. The equations representing weathering of Ca-rich silicates and the dissolution of calcite presented in Eqs. 4 and 5 respectively may be regarded as the enrichment of Ca^{2+} , Mg^{2+} , and HCO_3^- in all the water samples.

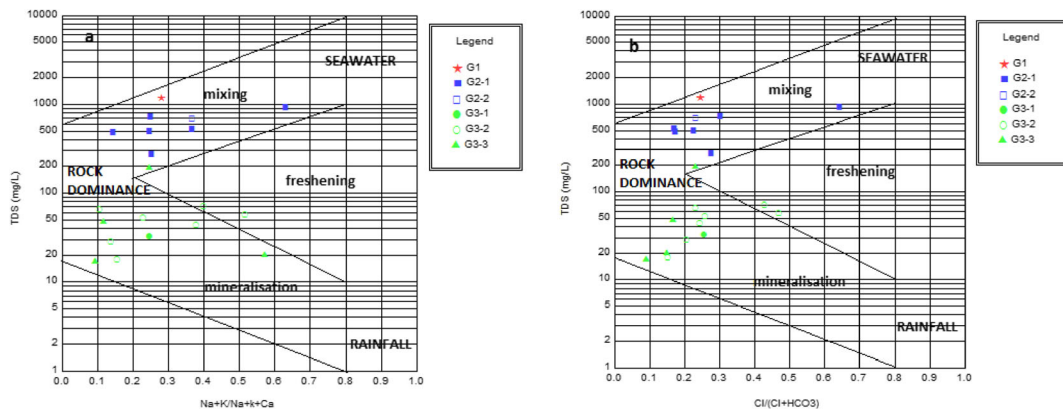
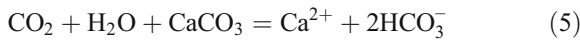
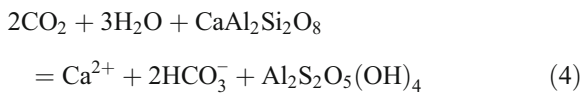
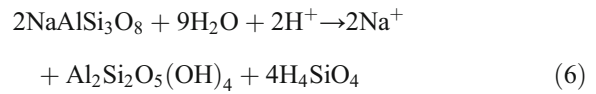


Fig. 7 Gibbs diagram plotting the TDS concentration as a function of the ratio between Na + K and Na + K + Ca (a), Cl and Cl + HCO₃ (b), with the samples labeled according to their respective water groups



The plagioclase (pure anorthite-CaAl₂Si₂O₈) in Eq. 4 is a component of shale which underlies the entire area, and it is easily weathered (Subramani et al. 2009). This may account for the enrichment of Ca²⁺, Mg²⁺, and HCO₃⁻. Calcite (limestone) is also found within the shale lithology. The reactions above are also consistent with the water groups defined by cluster analysis. The three water groups were plotted within the rock dominance of the Gibbs diagrams. A plot of Ca²⁺ against Mg²⁺ (Fig. 8) showed that all the groups were plotted above the [Ca²⁺]:2[Mg²⁺] line, revealing the dominance of silicate weathering over calcite dissolution. Fig. 8 revealed the possibility of another form of geochemical processes affecting the water chemistry aside from silicate weathering and carbonate dissolution. The plot revealed one group 2 water sample with high Na⁺ concentration associated with a lower Ca²⁺ concentration than the other samples. The chemistry of this water sample might be influenced by ion exchange processes. Ion exchange process is characterized by a deficit in Ca²⁺ concentration versus Na⁺ concentration in water (Appelo and Postma 2005). A plot of Na⁺ against Cl⁻ (Fig. 8) revealed the source of salinity in the area. A molar ratio of Na/Cl greater than 1 reflects the effect of silicate weathering for the release of Na⁺ (Srinivasamoorthy et al. 2014), as seen in Eq. 6.



The figure also revealed that excess of Cl⁻ over Na⁺ exists, as NaCl in solution (groundwater). The excess Cl⁻ may be the result of base ion exchange processes and/or may be due to contamination emanating from anthropogenic activities (Jones et al. 1999; Vengosh et al. 2002).

Assessing the water physicochemical characteristics from different water sample types

Water samples were collected from various sources including boreholes (BH), hand-dug well (HDW), river (RV), and mine pit (MPW). The difference in the mean of the physicochemical characteristics across different water sample types was tested using the one-way analysis of variance (ANOVA), and the result is presented in Table 5. The mean pH of MPW (7.21) was significantly higher than that of RV (7.01, *p* value < 0.05). Similarly, the concentration of Ca²⁺ was higher in MPW (192.0) than in RV source (18.67), HDW (29.57) or BH (74.78). This relationship was statistically significant (*p* < 0.05). However, samples collected from rivers had a higher significant mean value (83.20, *p* < 0.05) of the percentage of Mg hardness than samples collected from MPW (39.47), HDW (70.39), or BH (53.78). Similarly, samples collected from rivers had higher significant Fe²⁺ & ³⁺ concentration (13.30, *p* < 0.05) than samples collected from HDW (1.64) or BH (1.44). Other characteristics with differing significant mean values include EC, TDS, TH, turbidity, temperature, Na⁺, Zn²⁺, salinity, and

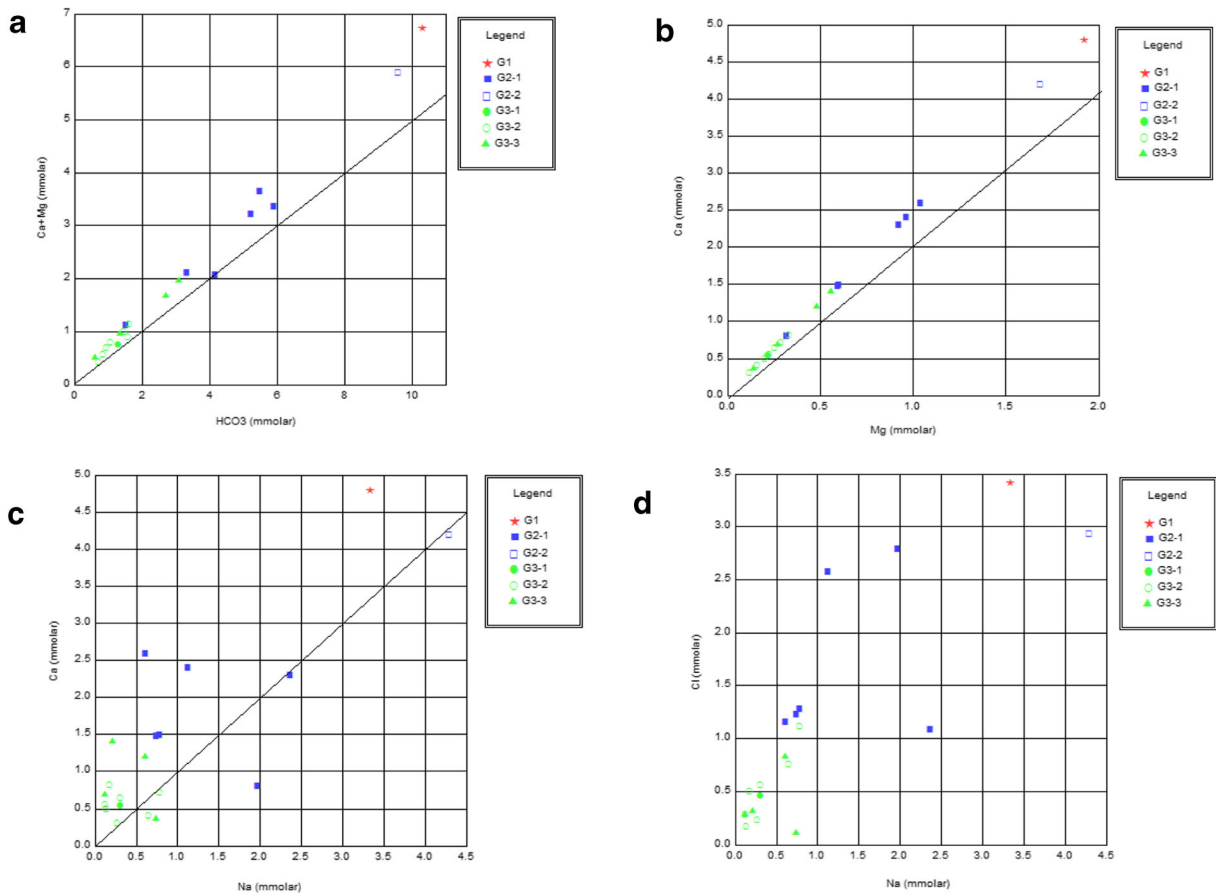


Fig. 8 Plot of HCO₃⁻ concentration versus Ca²⁺ concentration (theoretical line; anorthite or calcite dissolution: [Ca²⁺]:0.5[HCO₃⁻]) (a), Ca²⁺ concentration versus Mg²⁺ concentration (theoretical line; silicate weathering: [Ca²⁺]:2[Mg²⁺]) (b), Ca²⁺

concentration versus Na⁺ concentration (c), and Cl⁻ concentration versus Na⁺ concentration (d) with the groundwater samples labeled according to their respective water groups

Mg²⁺. For instance, the highest concentration of Zn²⁺ was found in MPW (0.92) and the lowest in BH water (0.01). This difference was statistically significant ($p < 0.05$). In contrast, the lowest concentration of Pb⁴⁺ was found in MPW (BDL) and the highest in HDW 1.60. This relationship was however not significant ($p > 0.05$). The processes that control the release of the various ions were found to be independent of the water sample type (see Table 4 and Figs. 8 and 9) as no single geochemical process was observed to affect the water chemistry of any particular water sample type.

Water quality for drinking

For drinking and domestic purposes, the quality of the water was assessed by comparing the ionic concentration with the WHO (2011) and SON

(2007) guideline values. The pH values of the water fall within the limits of the WHO (2011) and SON (2007). All the water samples except samples from BH 2, BH 3, BH 5, HDW 3, HDW 4, HDW 5, BH 9, and HDW 6 have high to very extremely high turbidities that are above the 1NTU and 5NTU stipulated by the WHO (2011) and SON (2007) respectively. Water from sampling locations at FUNAI, Onyekwe, Enyigba, Ndiuruku, and Ameri have TDS values above the stipulated guideline values (500 mg/l) by WHO (2011) and SON (2007). Only Ca²⁺ (4 water samples), Mg²⁺ (2 water samples), and K⁺ (1 water sample) among the major ions have concentrations above guidelines values stipulated by WHO (2011) and SON (2007). The remaining major and minor ions were found to be below or within the guideline's limits. Among the

Table 5 ANOVA table testing difference in mean concentration of physiochemical properties between different sources

		N	Mean	Std. deviation	95% confidence interval for mean		Minimum	Maximum	F	Sig.
					Lower bound	Upper bound				
pH	BH	9	7.10	0.05	7.07	7.14	7.02	7.18	14.677	<0.001*
	HDW	7	7.02	0.02	7.00	7.04	6.99	7.06		
	River	3	7.01	0.02	6.96	7.06	6.99	7.03		
	MPW	1	7.21				7.21	7.21		
EC	BH	9	701.00	431.55	369.28	1032.72	95.00	1360.00	12.621	<0.001*
	HDW	7	86.00	92.33	0.61	171.39	26.00	287.00		
	River	3	52.00	12.49	20.97	83.03	42.00	66.00		
	MPW	1	1746.00				1746.00	1746.00		
TDS	BH	9	467.22	287.54	246.20	688.24	65.00	906.00	12.652	<0.001*
	HDW	7	57.43	60.96	1.05	113.80	17.00	190.00		
	River	3	34.67	8.33	13.98	55.35	28.00	44.00		
	MPW	1	1165.00				1165.00	1165.00		
TH	BH	9	252.89	159.74	130.10	375.67	88.00	580.00	8.063	0.0010*
	HDW	7	97.71	57.24	44.77	150.65	40.00	182.00		
	River	3	60.00	19.29	12.09	107.91	38.00	74.00		
	MPW	1	630.00				630.00	630.00		
Turb.	BH	9	9.89	14.08	-0.94	20.71	0.00	39.00	4.061	0.0300*
	HDW	7	16.43	18.00	-0.22	33.07	0.00	50.00		
	River	3	55.33	39.58	-42.98	153.65	10.00	83.00		
	MPW	1	1.00				1.00	1.00		
Tem	BH	9	30.22	0.67	29.71	30.73	29.00	31.00	6.141	0.0060*
	HDW	7	29.43	0.79	28.70	30.16	29.00	31.00		
	River	3	25.67	5.13	12.92	38.41	20.00	30.00		
	MPW	1	34.00				34.00	34.00		
Ca	BH	9	74.78	45.32	39.94	109.61	29.00	168.00	9.071	<0.001*
	HDW	7	29.57	16.21	14.58	44.56	14.00	56.00		
	River	3	18.67	5.77	4.32	33.01	12.00	22.00		
	MPW	1	192.00				192.00	192.00		
Mg	BH	9	18.11	10.98	9.67	26.55	7.00	41.00	9.142	<0.001*
	HDW	7	7.43	3.99	3.73	11.12	4.00	14.00		
	River	3	4.33	1.15	1.46	7.20	3.00	5.00		
	MPW	1	47.00				47.00	47.00		
Na	BH	9	32.78	29.36	10.21	55.35	4.00	99.00	4.533	0.02*
	HDW	7	9.14	6.01	3.58	14.70	3.00	17.00		
	River	3	5.33	2.08	0.16	10.50	3.00	7.00		
	MPW	1	77.00				77.00	77.00		
NO ₃	BH	9	1.34	1.17	0.44	2.25	0.19	3.36	2.206	0.130
	HDW	7	0.48	0.40	0.10	0.85	0.18	1.10		
	River	3	0.86	0.30	0.11	1.60	0.51	1.03		
	MPW	1	2.41				2.41	2.41		
SiO ₂	BH	9	1.81	2.13	0.17	3.45	0.00	5.12	1.543	0.2420
	HDW	7	4.39	6.91	-2.00	10.78	0.00	19.32		
	River	3	10.14	11.16	-17.58	37.85	3.09	23.00		

Table 5 (continued)

		N	Mean	Std. deviation	95% confidence interval for mean		Minimum	Maximum	F	Sig.
					Lower bound	Upper bound				
Zn	MPW	1	1.09				1.09	1.09		
	BH	9	1.44	2.66	-0.60	3.48	0.00	7.36	6.359	0.0050*
	HDW	7	1.64	1.47	0.28	3.00	0.00	4.35		
	River	3	13.30	10.81	-13.55	40.15	5.46	25.63		
Fe	MPW	1	0.00				0.00	0.00		
	BH	9	0.01	0.02	0.00	0.03	0.00	0.06	216.256	< 0.001*
	HDW	7	0.02	0.04	-0.01	0.06	0.00	0.11		
	River	3	0.06	0.05	-0.07	0.19	0.02	0.12		
Cd	MPW	1	0.92				0.92	0.92		
	BH	9	0.00	0.00	0.00	0.01	0.00	0.01	1.585	0.2300
	HDW	7	0.00	0.00	0.00	0.01	0.00	0.01		
	River	3	0.01	0.00	0.01	0.01	0.01	0.01		
Pb	MPW	1	0.00				0.00	0.00		
	BH	9	0.33	0.49	-0.05	0.71	0.00	1.47	1.240	0.3300
	HDW	7	1.60	2.16	-0.40	3.60	0.00	5.98		
	River	3	0.77	0.49	-0.45	2.00	0.45	1.34		
Salinity	MPW	1	0.00				0.00	0.00		
	BH	9	0.11	0.06	0.06	0.16	0.03	0.20	7.566	0.0020*
	HDW	7	0.03	0.03	0.01	0.05	0.00	0.08		
	River	3	0.02	0.01	0.01	0.04	0.02	0.03		
Mg hardness (%)	MPW	1	0.21				0.21	0.21		
	BH	9	53.78	15.18	42.11	65.45	28.70	77.24	4.151	0.0200*
	HDW	7	70.39	15.20	56.33	84.44	47.92	88.91		
	River	3	83.20	16.22	42.90	123.50	68.93	100.85		
	MPW	1	39.47				39.47	39.47		

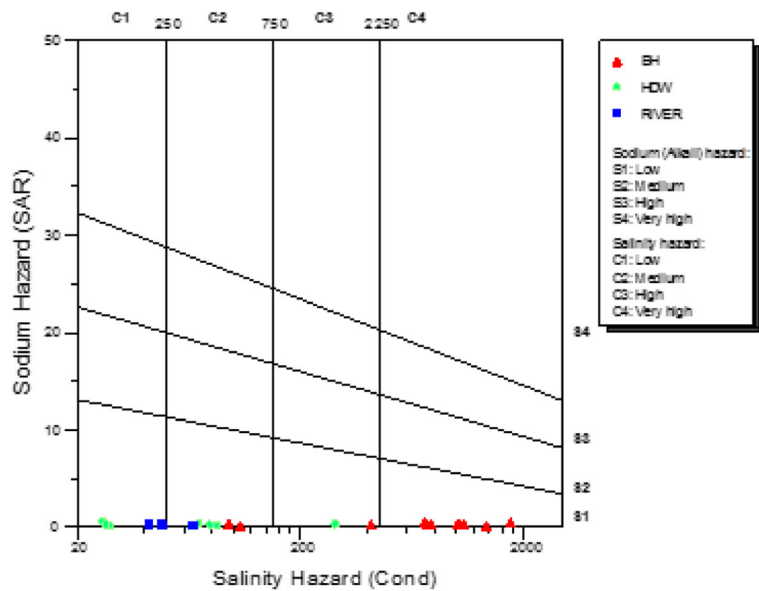
MPW, mine pipe water; BH, borehole; HDW, hand-dug well. * $P < 0.05$ (statistically significant)

trace ions analyzed in the water samples, only Cd^{2+} was observed to be below the stipulated guideline values in the entire water samples. Pb^{4+} , Zn^{2+} , and Fe^{2+} & $3+$ concentrations in HDW 7, BH 6, and BH 1 samples respectively were observed to be above the stipulated guideline values. These contaminations stem from the mines, mining activities, and interplay of oxidized iron minerals at low pH in aquifers of the area. The low degree of contamination from the major and minor ions could be attributed to the fact that the unfractured host rock (shale) is an aquifuge. The higher degree of contamination from Pb^{4+} and Zn^{2+} , in spite of the aquifuge nature of the host rock (shale), could be attributed to the very high release or discharge of Pb^{4+} and Zn^{2+} from the mining activities.

Water suitability for irrigation purposes

The irrigation water quality was accessed based on certain irrigation water quality indexes (electrical conductivity (EC), sodium percentage (Na %), residual sodium carbonate (RSC), and sodium adsorption ratio (SAR)). The water of the area is not generally suitable for irrigation purposes with respect to EC as 25% each of the surface water samples and groundwater samples fall within the “permissible class”; however, 75% of the surface water belongs to the “excellent class” and 50% of the groundwater samples belongs to the “excellent class” and 25% belongs to the “good class” (Table 6). Water belonging to the “permissible class” must be used with caution for irrigation purposes. The amount of sodium concentration in water for irrigation purposes

Fig. 9 Wilcox diagram from different water samples



is evaluated based on Na%. The Na% is evaluated using the relationship (Wilcox 1955):

$$Na\% = \frac{(Na^+ + K^+)}{(Ca^{2+}Mg^{2+} + Na^+ + K^+)} \times 100 \quad (7)$$

In this present study, 50% each of the surface water samples belong to “excellent class” and “good class” 62.5% of the groundwater samples fall within the “excellent class” and 18.75% each fall within “good class” and “permissible class” (Table 6). High Na⁺ content at “permissible class” affects soil structure and soil texture. High Na⁺ reduces soil porosity and permeability; thus, it reduces soil porosity and permeability for air and water passage during the wet season and makes soil to be hardened and crack during dry season.

RSC used calculated using the relationship developed by Eaton (1950):

$$RSC = (HCO_3^- + CO_3^{2-}) - (Ca^{2+} + Mg^{2+}) \quad (8)$$

The RSC values in the area ranged from -3.11 to 0.197 with a mean of -0.792. RSC in the study area is generally lower than 1.25; hence, all the surface water and groundwater samples fall within the “good class.” This shows that there are no excess precipitates of the carbonates in solution in relation to the alkaline earth elements and this renders the water samples suitable for irrigation purposes in respect to RSC.

SAR is a composite index and it denotes alkali and sodium risk to soil and crops and is estimated from:

$$SAR = \frac{Na^+}{\sqrt{\left[\frac{Ca^{2+} + Mg^{2+}}{2} \right]}} \quad (9)$$

The SAR of surface water and groundwater of the area ranged from 0.133 to 1.86 with a mean of 0.66. All the water samples belong to the “excellent class.” The SAR and the RSC of water of the study area are generally very low and this could be explained in terms of the aquifuge nature of the host rock when not fractured. Although the area is an agrarian region where more agricultural contamination is anticipated because the host rock, shale is not permeable to transmit contaminants quickly down the subsurface when contaminants are released from the surface. The surface contaminants are lost to surface runoff than seepage and percolation down to the subsurface.

The Wilcox diagram (Fig. 9) revealed that the water of the area belongs to water of “low sodium (and alkali) hazard” and water of “low salinity,” “medium salinity,” “high salinity” and “very high salinity.” The river water used mainly for irrigation purposes falls within the “low sodium (and alkali)”/“low salinity” and “low sodium (and alkali)”/“medium salinity” fields and thus satisfies the requirements for irrigation purposes for rice, yam, and cassava grown in the area.

Table 6 Suitability of water for irrigation based on EC, Na%, RSC, and SAR

Quality parameter	Range	Classification	Number of samples ($n = 20$)		% of samples	
			Surface ($n = 4$)	Groundwater ($n = 16$)	Surface water	Groundwater
EC (Wilcox 1995)	< 250	Excellent	3 (RV 1, RV 2, MPW 1)	8 (HDW 1, HDW 2, HDW 4, HDW 5, HDW 6, HDW 7, BH 4, BH 6,)	75	50
	250–750	Good	Nil	4 (HDW 3, BH 2, BH 8, BH 9)	Nil	25
	750–2000	Permissible	1 (MPW 2)	4 (BH 1, BH 3, BH 5, BH 7)	25	25
	2000–3000	Doubtful	Nil	Nil	Nil	Nil
	> 3000	Unsuitable	Nil	Nil	Nil	Nil
Na % (Wilcox 1995)	< 20	Excellent	2 (RV 2, MPW 1)	10 (HDW 1, HDW 2, HDW 3, HDW 5, HDW 6, BH 2, BH 4, BH 7, BH 8, BH 9)	50	62.50
	20–40	Good	2 (RV 1, MPW 2)	3 (BH 1, BH 3, BH 6)	50	18.75
	40–60	Permissible	Nil	3 (HDW 4, HDW 7, BH 5)	Nil	18.75
	60–80	Doubtful	Nil	Nil	Nil	Nil
	> 80	Unsuitable	Nil	Nil	Nil	Nil
RSC (Richards 1954)	< 1.25	Good	4 (RV1, RV 2, MPW1, MPW 2)	16 (HDW 1, HDW 2, HDW 3, HDW 4, HDW 5, HDW 6, HDW 7, BH 1, BH 2, BH 3, BH 4, BH 5, BH 6, BH 7, BH 8, BH 9)	100	100
	1.25–2.50	Doubtful	Nil	Nil	Nil	Nil
	> 2.50	Unsuitable	Nil	Nil	Nil	Nil
SAR (Richards 1954)	< 10	Excellent	4 (RV1, RV 2, MPW1, MPW 2)	16 (HDW 1, HDW 2, HDW 3, HDW 4, HDW 5, HDW 6, HDW 7, BH 1, BH 2, BH 3, BH 4, BH 5, BH 6, BH 7, BH 8, BH 9)	100	100
	10–18	Good	Nil	Nil	Nil	Nil
	18–26	Doubtful	Nil	Nil	Nil	Nil
	> 26	Unsuitable	Nil	Nil	Nil	Nil

Conclusions

Contamination scenario and hydrochemical characteristics of surface water and groundwater of the Enyigba-Ameri area have been studied. The water of the area ranged from neutral to slightly alkaline, classified into soft (30%), moderately hard (25%), hard (25%), and very hard (20%) categories based on TDS and three hydrochemical facies namely, $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-$ facies, $\text{Na}^+\text{-K}^+\text{-Cl}^-\text{-SO}_4^{2-}$ facies, and $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-Cl}^-\text{-SO}_4^{2-}$ facies based on the major ions concentration.

The principal component analysis and ionic cross plots revealed that the water chemistry of both

surface water and groundwater is being shaped by anthropogenic activities, weathering of Pb–Zn and Fe-rich minerals, the dissolution of silicate and carbonate minerals, and base ion exchange processes.

The study has revealed the potential contaminants of water in the Enyigba-Ameri area to include Pb^{4+} , Zn^{2+} , and Fe^{2+} & $^{3+}$ emanating from the mining activities. In spite of the generally high aquifer protective capacity of shale that underlies the entire area (where it is not fractured), the groundwater has been seriously polluted by Pb^{4+} , Zn^{2+} , and Fe^{2+} & $^{3+}$ compared to other potential contaminant parameters such as NO_3^- and Cd^{2+} because of the large volume of Pb^{4+} and Zn^{2+} laid waste water discharged from

the mines indiscriminately. The assessment of water of the area revealed that the water of the area is not generally suitable for agriculture and irrigation purposes.

Evaluation of the four water sources (BH, HDW, MPW, and RV) characteristics sampled showed that there was a significant difference in mean of (EC), TDS, TH, turbidity, pH, temperature, and salinity, and concentration of Na^+ , Zn^{2+} , Fe^{2+} & $^{3+}$, Ca^{2+} , and Mg^{2+} across the water sources. This increase is however not dependent on the varying (or diverse) locations of sample collection.

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