Environment, Development and Sustainability (2021) 23:11025–11049
https://doi.org/10.1007/s10668-020-01103-3

Assessment of groundwater quality using geoelectrical potential and hydrogeochemical analysis in Eha-Amufu and environs, Enugu state, Nigeria

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Received: 3 April 2019 / Accepted: 17 November 2020 / Published online: 19 January 2021

Abstract

Presently, campaign for potable water supply is on the increase while the need to harness groundwater to alleviate the shortage of potable water is very crucial. This study investigated the groundwater potential of the local geologic formations and to determine the extent and distribution of the saline zones at Eha-Amufu. Integrated approach using geological, geoelectrical and hydrogeochemical investigations was adopted. Twenty-seven (27) vertical electrical sounding (VES) were performed at different locations within the area, using the Schlumberger electrode configuration with a maximum electrode separation of 600 m. Results from the VES revealed that the study area is made up of 3–6 geoelectrical layers, and are predominantly of QH and H curve types. The formations were observed to be characterized by low permeability zones/intervals, suggesting that Eha-Amufu could only possess perched aquifers table which supports the use of hand-dug wells. Hydrochemical analysis of the ten (10) groundwater samples collected from different hand-dug wells indicated that the groundwater is characterized by Calcium (Ca)—Magnesium (Mg)—Chloride (Cl) water type, and could be classified as moderately hard to very hard. Water samples showed evidence of contamination with heavy metal such as Pb^{2+} beyond WHO standard, thereby making it unfit for domestic uses and consumption. Further result probe revealed that the local geology is the major process controlling the fate of groundwater chemistry in the area through weathering and rock–water interaction. Therefore, the present study proposes that other forms of portable water provisions should be explored such as harvesting and treatment of the various river resources in the area using purification plants and development of regional water conduits.

Keywords Vertical electrical sounding · Shale · Weathering · Salinity · Heavy metal · Contamination

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1 Introduction

1.1 Background of study

Water is an indispensable resource and is a primary driver of man's socioeconomic development but its availability in a potable form across places especially in rural areas remains a gigantic problem which needs to be overcome (Bob-Duru 2001). Landmark in Nigeria's legislation is the provision of potable water by government, under the auspices of Government Owned Public Water Utilities (GPWUs), taking its supplies from artificially designed water reservoirs, surface water, viable boreholes and other standing water bodies. In spite of this bold step which aimed at keeping the nation wet with potable water, the GPWUs could not meet the water demand and supply of the masses (Jalali 2007; Okogbue et al. 2012; Aghamelu et al. 2013). This is because regions have witnessed numerical growth and industrial development leading to a global drive towards sustainability (World Commission on Environment and Development 1987).

The populace of Eha-Amufu and environs has decried the acute scarcity of potable water. The situation has been aggravated by lack of institutionalized water supply scheme to support the teeming population of Federal College of Education in Eha-Amufu. Compounding the onerous task of sourcing potable water in Eha-Amufu and its environs is the effect of geology. The low permeable Nkporo and Awgu Shales underlay a vast section of the area, thereby presenting Engineers with a lot of difficulties which are hydro-geologically oriented (Nganje et al. 2015) sequel to the exorbitant cost incurred while drilling boreholes. Unfortunately, in the present study area, land spaces are dotted with numerous perched aquifers which dry up after a short service. Potable water is both a costly and a rare commodity to come by mostly during the dry season when there are limited alternatives such as the rains and streams.

Prominent in most groundwater investigation based researches within the basement and sedimentary complex is the electrical resistivity method via; the vertical electrical sounding (VES) (Olayinka 1992; Vchery and Hobbs 2003; Egwebe et al. 2004; Olaleye 2005; Akaolisa 2006; Alile et al. 2008; Tizro et al. 2010; Arabi et al. 2008; Joshua et al. 2011). VES provides an excellent prediction of the groundwater potential of an area (Olayinka 1992; Selemo et al. 1995; Nwankwoala and Shalokpe 2008; Okogbue and Omonona 2013). Ultimately, VES is very useful in ascertaining and validating the index of resistivity log similar to the induction log of a well without the actual well drilling (Hamill and Bell 1986).

Uma (1998) explained that the natural hydrochemistry of surface and groundwater is principally controlled by the rocks and sediments they are in contact with. Prominent outcrops (which commonly support local salt industries) are found in the Southern and Central Benue Trough which is associated to tectonic elements (intrusive and mineralized vein) together with weathering, precipitation, ion exchange reactions and anthropogenic processes (Nganje et al. 2015). Against this background, the occurrence of saline polluted groundwater in Eha-Amufu is undisputable. Saline groundwater constitutes a serious hydro-geological problem and is the most common of all the pollutants in freshwater (Adeoti et al. 2010) which can be checked through a background evaluation of its hydrochemistry for effective planning, monitoring and protection of water quality (Cocker 1995; Hook 2005; Pazand et al. 2011). To this end, we have placed in high premium unraveling-cum-mapping of the zones of salinity which is considered very essential for the proper management of the groundwater in Eha-Amufu and its environs. Therefore, the trust of this research orient towards undertaking a hydro-geological survey within the town and its environment using advanced geophysical equipment. This will provide a vista for the location of viable aquifers (groundwater source) and sustainable boreholes to forestall problems.

2 Methods of study

2.1 Study area

Eha-Amufu, Southeast Nigeria, is bounded within latitude 6°37′ and 6°45′ and longitudes 7°40′ and 7°50′ (Fig. 1a). The area is accessible by railway and a network of major and minor roads such as Obollo-Nkalagu Express Road connecting Eha-Amufu and Nkalagu.

The climate of the study area falls within wet and dry (Aw) climate of the Koppen classification. The area experiences seven months of effective rainfall, normally from April to October and five months of dry season (November—March). During the rainy season, the intensity of rainfall in the area is about 49 mm per hour at the beginning of the season and the end is often marked by violent thunderstorms (Eze 1998). The total annual rainfall ranges from 2000 to 2500 mm and mean annual temperature range of the study area is 27–28 °C (Monanu 1975a). The area is moderately humid, about 60–80% (Monanu 1975b; Iloeje 1981) and pressure ranges from 1010 to 1012.9 mbar (Monanu and Inyang 1975).

Igbozuruike (1975), Phil-Eze (2001) and Anyadike (2002) associated the vegetation unit in the study area with extensive savanna and rain forest vegetation in varying densities from one area to another occasioned by relief, soil pattern and the prevailing climatic condition.

The study area lies within the Anambra Basin in the western part of the Lower Benue Trough of Nigeria. Anambra Basin originated during the Santonian stage by contemporaneous subsidence of the Anambra platform and the uplift of the Abakiliki–Benue Anticlinorium (Mamah et al. 2014). This basin is peacock headed in its northern limits, where the basin is thought of as a playa lake model within the Benue Trough, but filled with texturally and mineralogical mature sediment of the Cretaceous age. Murat (1972) recorded that the stratigraphic packaging of the Anambra Basin consists of the Nkporo Group, Mamu Formation (Lower Coal Measure) Ajali Formation and Nsukka Formation (Upper Coal Measure). The Npkoro Group consists of Nkporo Shale, Enugu Shale and Owelli Sandstone (Fig. 2).

The vast section of the study area is underlain by Agwu Formation on the southeastern part while the other areas are covered by Nkporo Formation (Fig. 2). Drainage of the area is typically dendritic (Fig. 1b). The Nkporo and Agwu Shale Formations are described as aquicludes due to their low permeability (Offodile 2002). There are no boreholes penetrating these formations in the research area for an independent confirmation of their permeability. Outcrop of the Nkporo Shale is scarce in the study area but cuttings (sample) from hand-dug wells showed that the formation consists of mudstone and black shale with sparse intercalation of sandstones (Fig. 3). Lithological characteristic and faunal content of the Awgu Shale indicate that the sediments were laid in a shallow water environment consisting of gray shale with calcareous sandstone and limestone (Nwachukwu 1972). Shale of Agwu Formation is deposited in a marine setting with closed playa lake model and

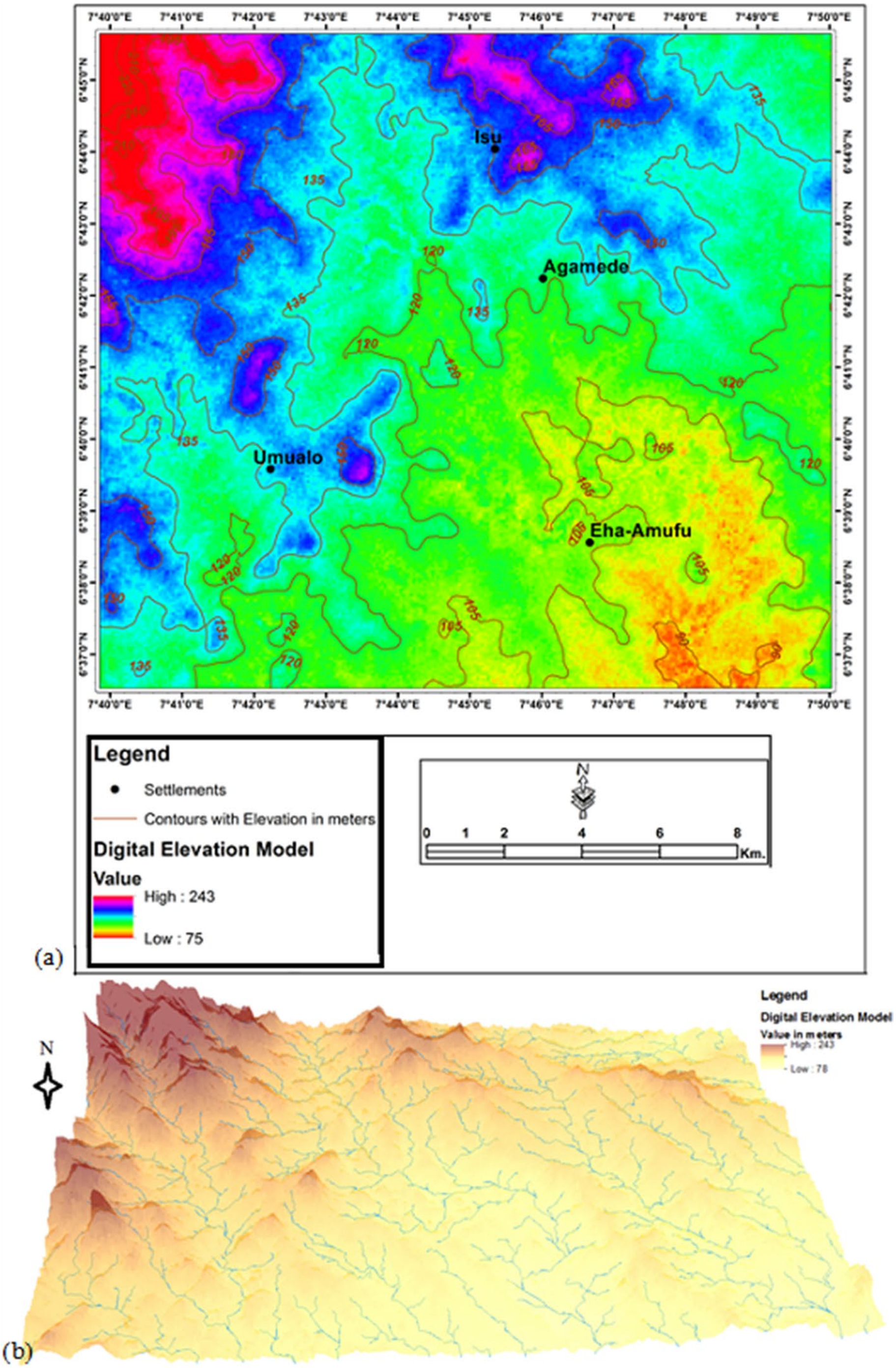


Fig. 1 Elevation map of the study area

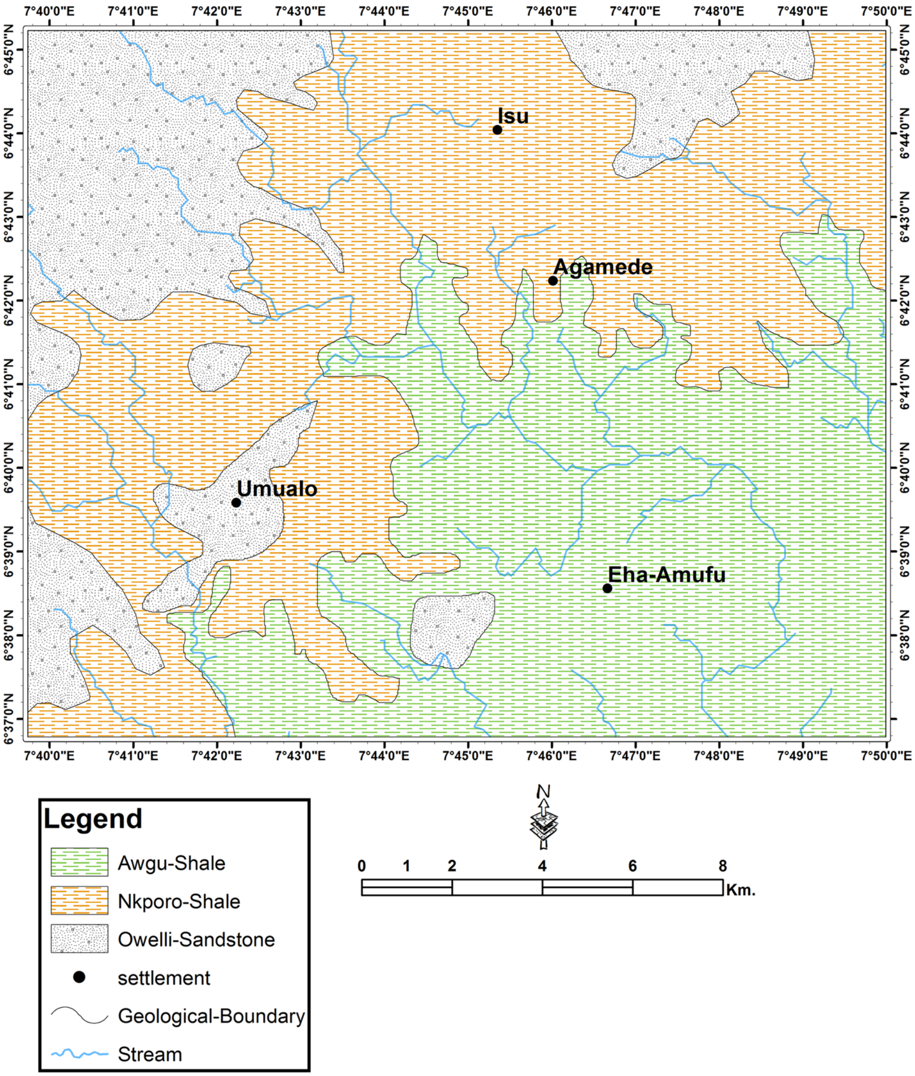
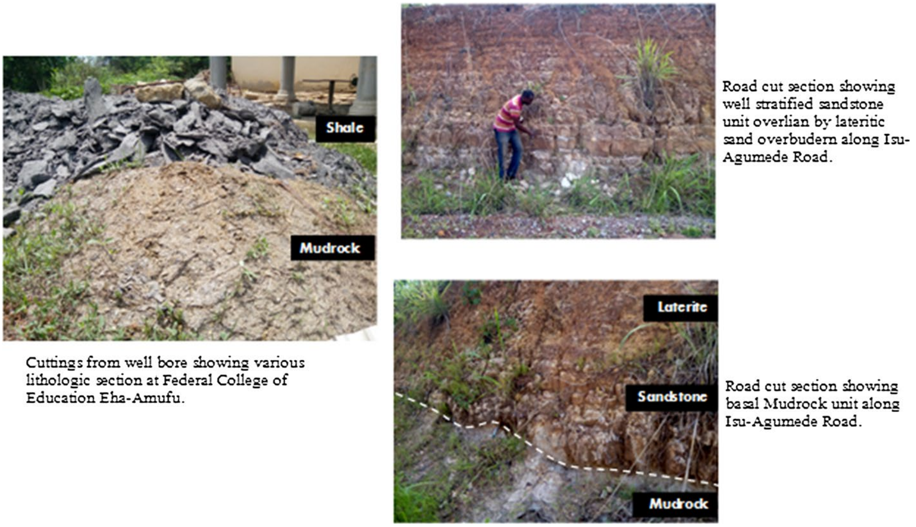


Fig. 2 Geological map of the study area

evaporate depositions, thus explaining the source of salinity/brackish and water hardness in Eha-Amufu (Desborough 1978).

A playa lake Model of deposition implies an increase in magnesium–calcium ratio in the groundwater towards the lake margin. Deposition of dolomitic limestone and brine evolution is dominant at the margins also. Transgressions would mark a reflux of saline water to a playa lake while regressions, especially when evaporation exceeds precipitations and runoff, would lead to settlement and high salinity brines at the deeper portions of the basin. Extreme arid conditions concentrates evaporates and oolites as seen in deepest parts of the basin adjacent to the study area and super salinity may lead to deposition of nachcolite or rock salt (Hite 1972). Due to the salty taste and hardness of the water in Eha-Amufu, the water is not good for domestic purposes. These playa lake



Cuttings from well bore showing various lithologic section at Federal College of Education Eha-Amufu.

Road cut section showing well stratified sandstone unit overlian by lateritic sand overbudern along Isu-Agumede Road.

Road cut section showing basal Mudrock unit along Isu-Agumede Road.

Fig. 3 lithologic section within the study area

concepts underscore the importance of prospecting for groundwater in Eha-Amufu and its environs.

2.2 Geophysical investigation

Vertical electrical sounding survey and hydrogeochemical principles were employed in this work. In line with the custody of practice in geophysical researches, electrical resistivity technique of Vertical Electrical Sounding (VES) was adopted for mapping the saline zones due to its ability to detect increase in conductivity trends or zones within an aquifer that results from increased salinity of pore-water (Loke 1999). It is also useful in determining the tabular nature, geometry and thickness of geological formations in saline zones within formations (Telford et al. 1977). In this research, a total of twenty-seven (27) VES were utilized (Fig. 4), and Schlumberger configuration of a half current electrode spread (AB/2) of 600 m and half potential electrode separation (MN/2) were maintained between 0.5 and 45 m.

The VES curves were quantitatively interpreted by partial curve matching and computer interaction techniques based on linear filter theory using 1P12win computer software. Vertical electrical sounding (VES) was carried out by extending the electrode system (four electrodes) on a straight line, to produce vertical changes in the electrical resistivity of the subsurface; relative to the various strata encountered. Spatial distribution of resistivity within each stratum would delineate conductive zones and would be salinity conduits. Resistivity survey and water analysis complements each other and has been used extensively (Sherif et al. 2006; Srinivas et al. 2013; Akpan et al. 2013).

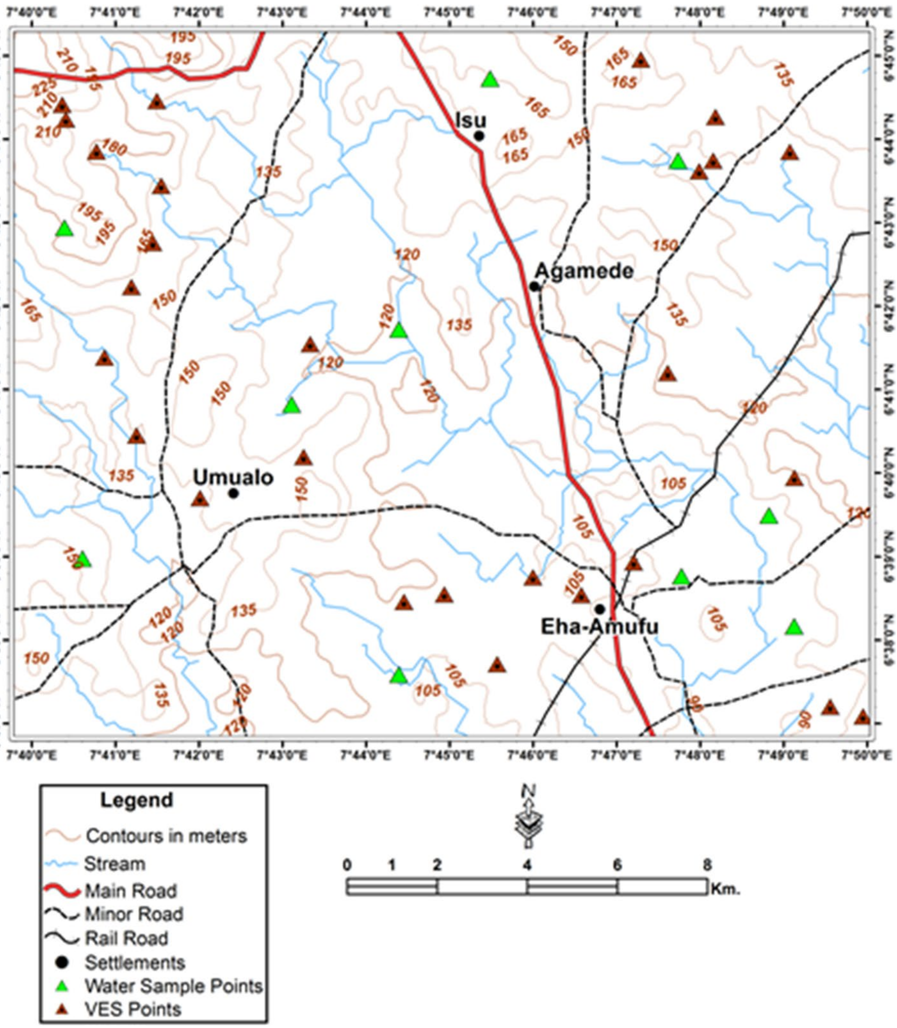


Fig. 4 Drainage and physiographic map of study area

2.3 Hydro-chemical investigation

In addition to the resistivity survey, groundwater sample was collected from (10) hand-dug well during dry season (Fig. 4). The electrical conductivity and temperature of the sample were measured in the field. Total dissolved solid (TDS) where measured using EDTA (Ethylene-Diaminetetra Acetate trimetric method) complex metric method. Cations (Na^+, K^+, Pb^{2+}, Fe^{2+}, Mg^{2+} and Ca^{2+}) and anions (NO_3^-, SO_4^{2-}, Cl^- and HCO_3^-) were analyzed. The pH was determined using a Pye-Unican 290MK PH meter. The reliability of the water quality data was determined using the ionic balance or electric neutrality formula (Hounslow 1995) as shown in Eq. 1.

$$\frac{\sum \text{anion} - \sum \text{cation}}{\sum \text{anion} + \sum \text{cation}} \times 100 \quad (1)$$

From the computation of the ionic balance, the water quality data were found to be 88% reliable.

3 Results

The VES exhibited wide range of variability in curve characteristics at different locations. It recorded curves ranging from AK, QH, Q, KQHK, H, HK, QHA, KHK, KQH, QQH and QQ as shown in Table 1. Resistivity in the area ranges from 0.117 to 2697 Ω while the layer thickness ranges between 0.367 m and infinity (Table 2). Eha-Amufu groundwater recorded pH (5.96–8.04), electrical conductivity (EC) (121.78–1155.36ug/cm), temperature (27.0–28.5 °C), total dissolved solids (TDS) (198–1702 mg/l), total hardness (TH) (44.0–404.0 mg/l), calcium hardness (16.0–320.0 mg/l), Magnesium hardness (10.0–84.0 mg/l). Hydrochemical analysis of the groundwater revealed the presence of Na^{+} (7.0–55.0 mg/l), K^{+} (2.1–11.4 mg/l), Mg^{2+} (2.4–65.5 mg/l), Ca^{2+} (5.4–127.0 mg/l), NO_3^{-} (0.9–16.7 mg/l), HCO_3^{-} (10.0–160.0 mg/l), Cl^{-} (122.1–401.7 mg/l), SO_4^{2-} (11.0–36.1 mg/l), Fe^{2+} (0.03–0.45 mg/l), Pb^{2+} (0.03–0.08 mg/l) as shown in Table 3.

4 Discussion of results

4.1 Geoelectrical delineation of saline zone

Three to six geoelectrical layers were detected within the study area and were predominantly of QH and H curve types (Table 1). According to Telford et al. (1977), electrical resistivity contrast existing between lithological sequences in subsurface are often adequate to enable geo-electric layers delineation and identification of saline and non-saline layers. In this study, all the depth sounding curves interpreted as saline layer are characterized by a steep descent from the non-saline to the saline layer. This decrease could be attributed to

Table 1 Curve types and their frequencies

Curve type	Frequency	Percentage
AK	1	3.7
QH	5	18.5
Q	4	14.8
KQHK	1	3.7
H	6	22.2
HK	2	7.4
QHA	1	3.7
KHK	2	7.4
KQH	2	7.4
QQH	2	7.4
QQ	1	3.7
Total	27	100%

Table 2 Result of vertical electric sounding

	Coordinate	Layer No	Resistivity	Layer Thickness	Inferred Lithology	Remark
1	N6°43′56″	1	2097	3.623	Laterite	
	E7°41′55″	2	22.03	42.38	clayey sand	
		3	53.25	20.73	Sandy clay	Aquifer
		4	9.536	∞	Saline sand	Saline layer
2	N6°43′56″	1	2428	0.735	Laterite	
	E7°40′53″	2	1170	5.737	Sand coarse	
		3	3.448	3.533	Saline sand line	Saline layer
		4	18.94	∞	Sandy clay	
3	N6°43′36″	1	1941	2.37	Laterite	
	E7°40′15″	2	96.1	5.68	Sandy clay	Aquifer
		3	19.1	∞	Saline sand	Saline layer
4	N6°42′29″	1	665	5.5	Sandy soil	
	E7°40″48″	2	55.2	4.1	Sandy clay	Aquifer
		3	6.54	22.4	Saline sand	Saline layer
		4	7.55	∞	Saline clay	
5	N6°39′42″	1	1515	0.589	Laterite	
	E7°44′28″	2	812	4.37	Coarse sand	
		3	22	13.6	Clayey sand	Aquifer
		4	2.53	17.6	Saline clay	Saline layer
		5	130	30	Coarse sand	Aquifer
		6	1.22	∞	Saline clay	
6	N6°39′45″	1	2954	5.82	Laterite	
	E7°43′02′’	2	17.2	157	Clayey sand	Saline layer
		3	360	∞	Coarse sand	
7	N 6	1	1126	2.32	Lateritic soil	
		2	169	6.75	Sandy clay	Aquifer
		3	11.5	152	Saline clay	Saline layer
		4	4.23	∞	Saline clay	
8	N6°38′30″	1	248	3.144	Sandy clay	
	E7°46′1″	2	20.98	10.69	Clayey soil	
		3	2.594	17.11	Saline clay	Saline layer
		4	22.71	39.79	Clay soil	
		5	7.35	∞	Saline clay	
9	N6°38′31″	1	372	1.522	Dry sand	
	E7°46′15″	2	77	6.399	Sandy clay	Aquifer
		3	12.5	41.73	Clay soil	Saline layer
		4	1.871	29.55	Saline clay	
		5	849	∞		
10	N6°41′29″	1	2144	3.974	Laterite	
	E7°40′34″	2	12.88	16.75	Clay soil	
		3	50.8	2.1	Sandy clay	Aquifer
		4	0.9929	∞	Saline clay	Saline layer
11	N6°42′17″	1	2561	5.28	Laterite	
	E7°40′41″	2	32	43.4	Sandy clay	Aquifer

Table 2 (continued)

	Coordinate	Layer No	Resistivity	Layer Thickness	Inferred Lithology	Remark
		3	18.2	∞	Clay soil	
12	N6°42′57″	1	1975	1.751	Lateritic sand	
	E7°40′52″	2	324.3	4.112	Sandy soil	
		3	25.1	10.47	Clay sand	Aquifer
		4	15.35	∞	Clay soil	
13	N6°43′30″	1	1039	3.62	Laterite	
	E7°40′53″	2	197	6.3	Sandy clay	Aquifer
		3	7.49	∞	Saline clay	Saline layer
14	N6°39′43″	1	927	5.79	Lateritic sand	
	E7°43′10″	2	164	111	Coarse sand	Aquifer
		3	0.746	∞	Saline clay	Saline layer
15	N6°43′20″	1	1158	0.367	Lateritic sand	
	E7°40′29″	2	464	4.55	Sandy soil	
		3	30.1	25.7	Sandy clay	
		4	3.61	30.9	Saline clay	Saline layer
		5	98.5	∞	Coarse sand	
16	N6°43′32″	1	1034	2.3	Laterite sand	
	E7°40′15″	2	643	3.38	Coarse sand	
		3	35	19.9	Sandy clay	
		4	3.69	40	Saline clay	Salinelayer
		5	140	∞	Coarse sand	Aquifer
17	N6°44′1″	1	314	3.47	Sandy clay	
	E7°40′00″	2	9.78	184	Clay soil	
		3	0.117	∞	Saline clay	Saline layer
18	N6°43′05″	1	369.9	1.724	Drysandy soil	
	E7°44′49″	2	68.54	7.325	Sandy clay	Aquifer
		3	4.57	3.611	Saline clay	Saline layer
		4	16.54	∞	Clay soil	
19	N6°43′09″	1	2039	3.85	Laterite sand	
	E7°44′56″	2	23.2	30.1	Clayey sand	Aquifer
		3	60.0	∞		
20	N6°43′26″	1	2530	3.17	Lateritic sand	
	E7°44′56″	2	359	7.22	Sandy clay	
		3	2.94	2.43	Saline clay	Saline
		4	23.8	∞	Clay soil	layer
21	N6°40′37″	1	2171	1.1	Dry laterite	
	E7°46′04″	2	1245	2.01	Sandy soil	
		3	29.4	∞	Clay soil	
22	N06°44′28″	1	476.2	0.4826	Sandy soil	
	E7°44′22″	2	136	2.89	Sandy clay	
		3	44.05	8.865	Clayey sand	
		4	5.99	5.254	Saline clay	Saline
		5	11.19	∞		layer
23	N6°39′48″	1	1107	1.55	Laterite sand	

Table 2 (continued)

	Coordinate	Layer No	Resistivity	Layer Thickness	Inferred Lithology	Remark
	E7°44′56″	2	1030	2.46	Sandy soil	
		3	188	83.3	Coarse sand	Aquifer
		4	0.886	∞	Saline clay	Saline layer
24	N06°38′18″	1	2697	5.5	Dry laterite	
	E7°45′26″	2	384.3	0.548	Sandy clay	
		3	24.3	∞	Clay soil	
25	N06°38′36″	1	918	1.88	Lateritic sand	
	E7°45″59″	2				
		3				
			773	3.7	Coarse sand	
			14.3	∞	Clay soil	
26	N06°44′33″	1	341.2	1.458	Sandy soil	
	E07°44′00″	2	317.4	2.705	Sandy clay	
		3	7.9	∞	Saline clay	Saline layer
27	N6°46′29″	1	462.2	2.302	Sandy soil	
	E7°40′55″	2	64.46	7.173	Sandy clay	Aquifer
		3	10.24	∞	Saline clay	Saline layer

increase in porosity, hydraulic conductivity, fluid content, and most possibly a high conductivity arising from saline water. Such steep descents occurred at the study area in VES 4 (55.2–6.54 Ωm), VES 5 (130–1.25 Ωm) and VES 8 (20.98–2.53 Ωm). The thickness of the saline layer/zones and their corresponding resistivity are presented in Table 2.

Figure 5, 6 and 7shows the spatial distribution maps of the element and their accompanying variograms. From the spatial distribution maps, all the elements have similar distribution pattern with the highest concentration found around the northeast while the lowest falls within the North West (Fig. 5a, c, 6a, c, 7a, c). Since the northeast is mostly underlain by shale (Fig. 2), the higher concentration of these element could be attributed to weathering of the shale.

In a variogram, the sill is the net variance where empirical variogram appears to level off. When the variogram point (nugget) plots above the sill it implies a negative spatial correlation but signifies positive spatial correlation when plotted below the sill. However, it is zero when the nuggets are on the sill. From the plotted variograms (Fig. 5b, d, 6b, d, 7b, d), it can be observed that most of the element concentration fall below the sill, indicating a close relationship of element concentration with distance. However some concentration plotted above the sill signifying high concentration with no correlation with other locations.

Integration of hydrogeological and geophysical results with hydrogeochemical data obtained from monitoring wells revealed an empirical relationship between earth resistivity and total dissolved solids (TDS). It was used to delineate the fresh and saline-water zones (Sherif et al. 2006; Srinivas et al. 2013; Akpan et al. 2013). The spatial distributions of the saline and non-saline zones generated using well control in the study area are illustrated in Fig. 8. The figure showed the distribution of saline zone to be on the Northwest (NW) and Southeast (SE) spread. The spatial distribution map of Na and Cl (Fig. 6) agrees with the

Table 3 Hydrochemical analysis of the water sample

Sample code	PH	EC	Temp	TDS	Na^+	K^+	Mg^{2+}	Ca^{2+}	Calcium hardness	Magnesium hardness	Total hardness	NO_3	HCO_3^-	Cl^-	SO_4^{2-}	Fe^{2+}	Pb^{2+}
		(ug/ms)	(°C)	(Concentration of mg/l)													
EHA 1	7.60	283.61	27.0	387	10.1	2.10	5.37	5.38	54.00	22.00	76.00	6.16	10.00	200.30	17.01	0.03	0.08
EHA 2	6.52	589.00	27.1	868	24.0	7.10	2.44	28.80	72.00	10.00	82.00	12.0	35.00	300.80	36.1	0.06	0.04
EHA 3	5.96	292.00	27.5	300	12.01	6.02	4.89	10.00	24.00	20.00	44.00	16.71	20.00	130.00	11.02	0.04	0.07
EHA 4	7.33	1155.36	27.0	1702	12.1	3.50	20.52	127.00	320.00	84.00	404.00	1.75	110.00	500.46	23.00	0.05	0.03
EHA 5	6.12	166.64	28.5	198	7.03	3.00	24.10	11.73	60.00	48.00	108.00	2.00	55.00	122.12	13.00	0.04	0.05
EHA 6	8.04	121.78	28.2	232	16.0	5.00	9.78	48.09	120.00	40.00	160.00	3.00	90.00	139.18	27.00	0.04	0.03
EHA 7	6.00	435.90	27.4	447	24.1	8.02	6.50	5.37	16.00	24.00	40.00	10.60	30.00	250.80	15.00	0.04	0.03
EHA 8	6.88	1041.80	27.5	1531	27.03	11.04	48.00	14.17	120.00	58.00	178.00	0.89	160.00	401.64	19.40	0.05	0.05
EHA 9	7.10	834.04	27.4	1080	55.0	10.00	65.50	9.78	164.00	40.00	204.00	15.30	60.00	308.90	34.00	0.05	0.04
EHA10	7.67	629.04	28.4	879	13.00	7.02	4.45	24.6	60.00	18.00	78.00	1.76	120.00	302.38	24.00	0.04	0.05

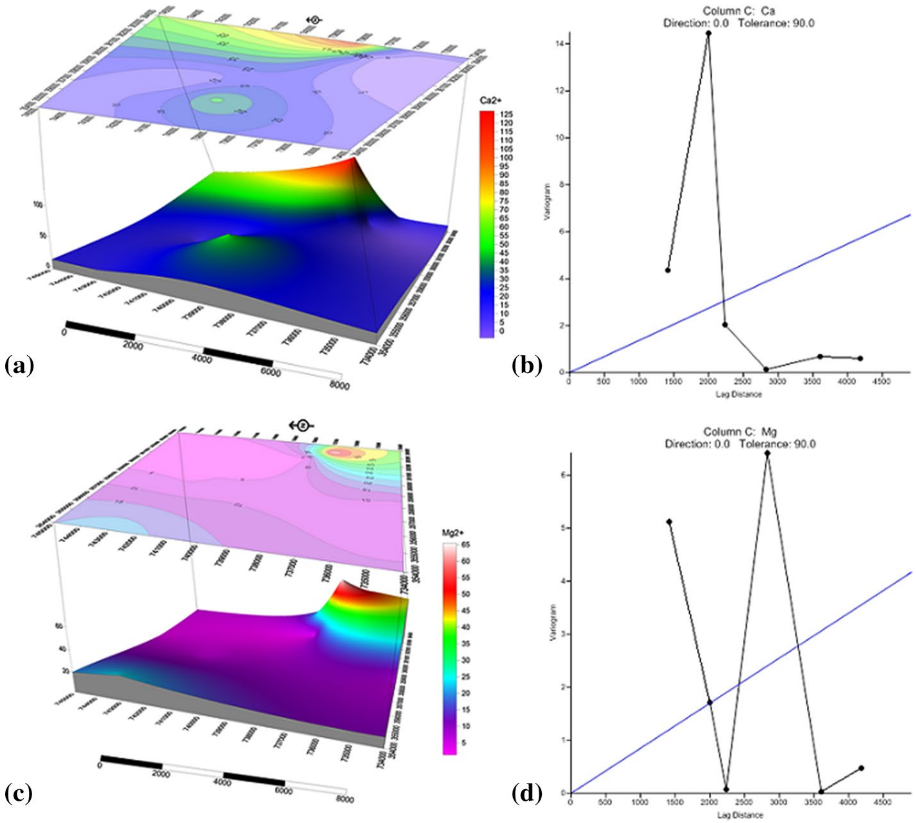


Fig. 5 Spatial distribution map and variogram of Ca and Mg

salinity map (Fig. 8). Both maps were observed to correspond with the VES. Areas of low VES were observed to correspond with high salinity (See Fig. 8; Table 2).

High ratings of conductive zones are southeast and northwest of the study area. The conductive zone on the southeast is a topographic low zone. Thus, the higher the chemical concentration may be mostly attributed to the shale lithology in the area. It also appears to be the discharge area for all streams in the study. The streams define salinity gradients and are trending dominantly northwest–southeast. Geologically, this is the area underlain by the marine and brackish Awgu Shale.

4.2 Hydrogeochemical analysis result and interpretation

The result of hydro-geochemical analysis is presented in Table 3. The sizes of the plots in Fig. 9 show that total dissolved solid (TDS) values do not differ significantly for the entire samples, except for sample Nos. 4, 8, and 9 (Table. 3). Charts and graphs were used to present the hydrogeochemical results for easy assessment of water composition.

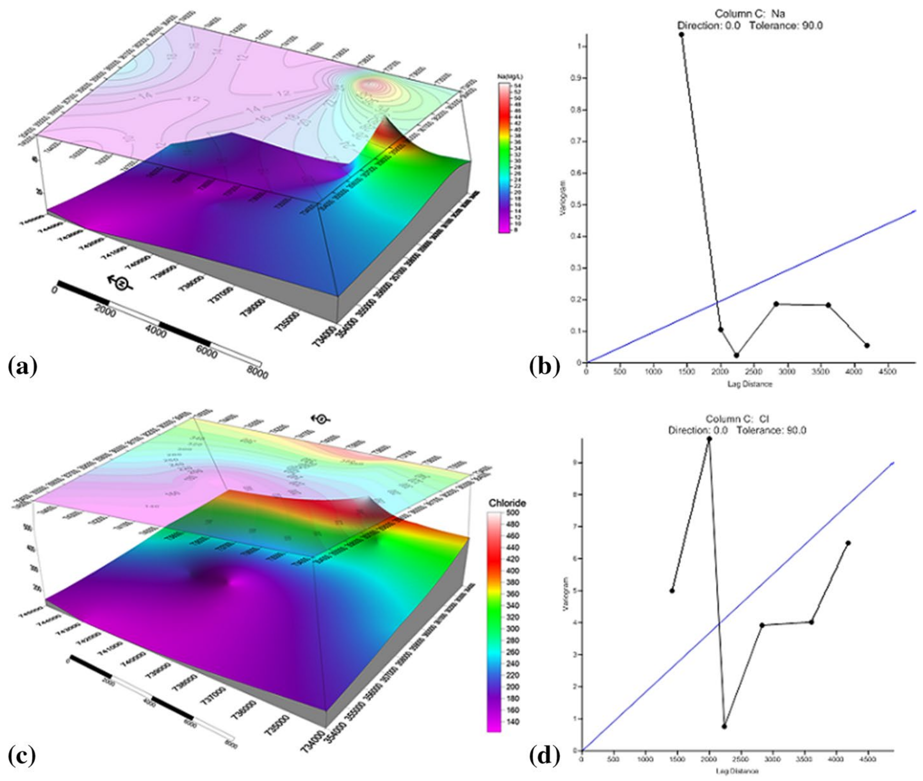


Fig. 6 Spatial distribution map and variogram of Na and Cl

4.2.1 Stiff and piper classification scheme

The Stiff and Piper plots are relatively distinctive methods of showing water composition differences and similarities (Hem 1985; Kumar et al. 2014). Both charts are often used by hydrogeologists and geochemists to display the major ion composition of a water sample. The Stiff patterns are helpful in giving prompt illustrative comparison between water from different sources (Salehi and Zeinivand 2016). The size of the pattern is approximately equal to the total ionic content (Hounslow 1995). On the other hand, Piper diagram is broadly used to understand problems relating to geochemical evolution of groundwater (Kumar et al. 2014). It is applicable in determining water type, hydro-chemical facies and ionic exchange (Freeze and Cherry 1979; Hounslow 1995). Furthermore, piper plot can also reveal the degree of mixing between waters (Sidi et al. 2016).

The shapes of the stiff diagrams (Fig. 10) are varied distinctively suggesting that the water sample is of different sources. The variation in shape pattern can be attributed to fluctuation in the relative concentration of Cl, Ca and Mg in the samples**.** The diamond part of the piper diagram may be used to characterize water of different types (Hounslow 1995). Water plotted at the upper corner of the diamond is primarily composed of Calcium, Magnesium Chloride type (Fig. 11). Therefore, the groundwater in Eha-Amufu area can be classified as Calcium–Magnesium–Chloride (Appelo and Postma 1993; Bahar and Reza

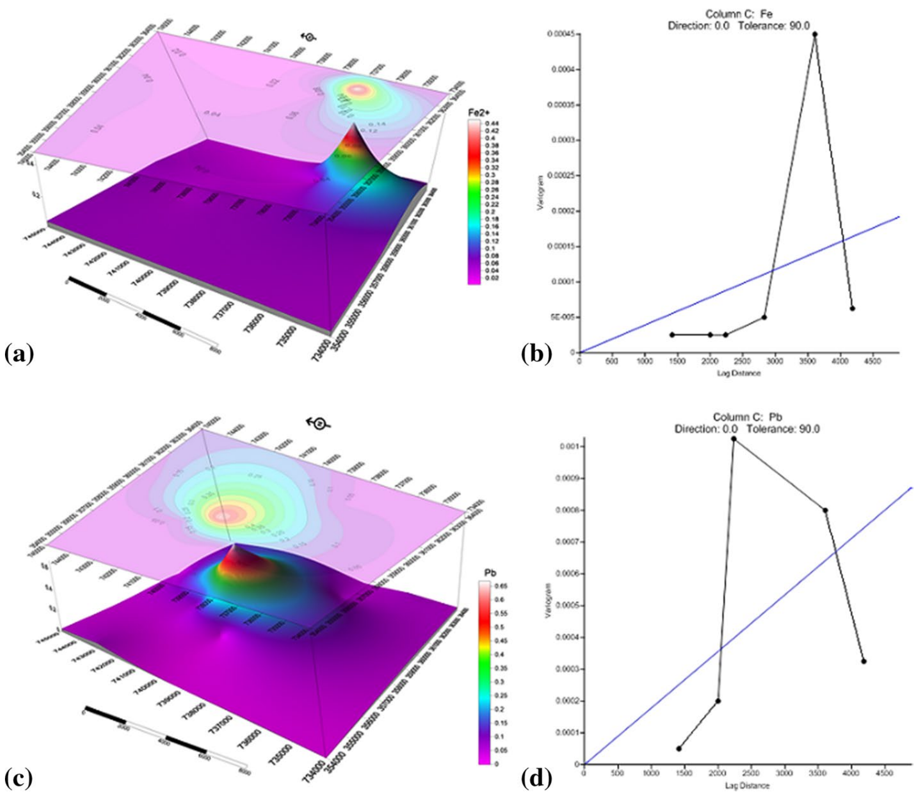


Fig. 7 Spatial distribution map and variogram of Fe and Pb

2010). This water type denotes permanent hardness in water that can only be softened via ion exchange processes.

4.2.2 Gibbs system of classification

Major ion concentrations in groundwater can be explained largely by mixing and water–rock interactions. Basic processes that add to groundwater salinity are controlled by reaction with host rocks, which is influenced by the network of flow paths and the time each path spends in contact with various minerals and mixing with older waters at depth (Marandi and Shand 2018). It has been reported that along extensive flow path with increasing time, groundwater tends to increase salinity, thus changing its type, which often is accompanied by changes in the dominant cation (Chebotarev 1955). Hence, the Gibbs plot could qualitatively be used to determine flow directions and ages of groundwater in wells, and may require isotope geochemistry for improved understanding of hydrogeochemical processes (Marandi and Shand 2018).

The origin of the hydro-chemical ions in the study area is well understood using Gibbs (1970) graphical diagram. Gibbs diagram reveals three groundwater chemical dominances used to establish the relationship of water composition and aquifer lithological characteristics. The chemical dominances are evaporation-crystallization, rock weathering and

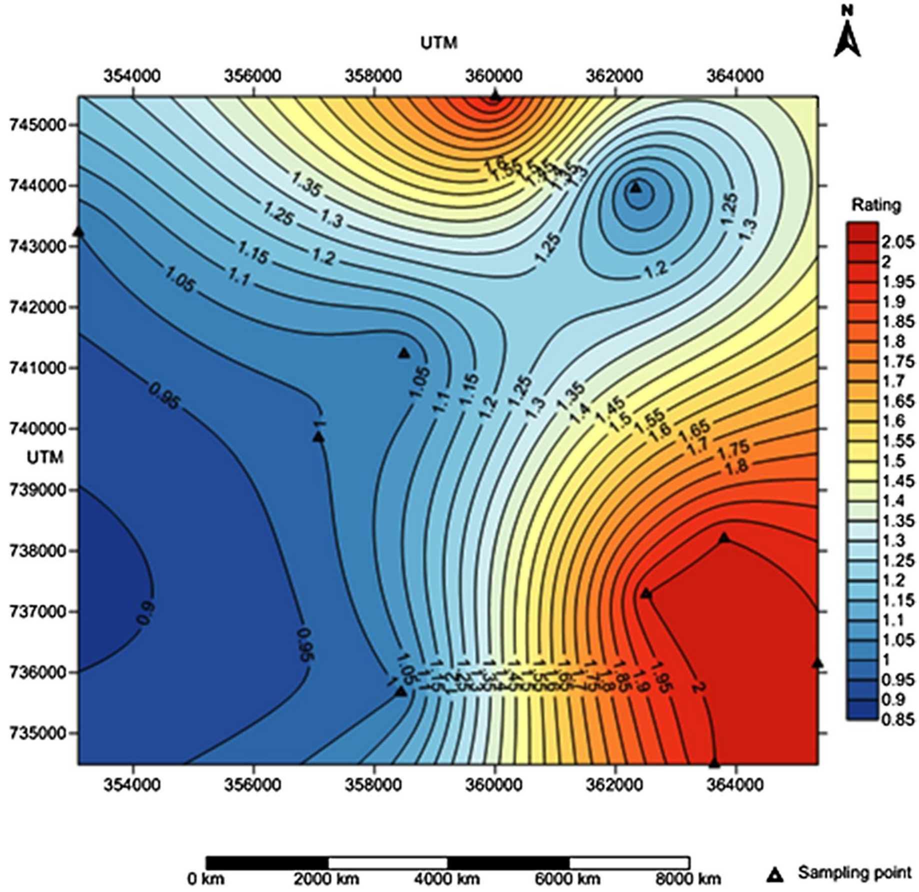


Fig. 8 Distribution of Saline zone

precipitation (Fig. 12). From the graphical plot, it was found that majority of the samples fall in rock weathering dominance, indicating that the major source of dissolved salts in the aquifer is supplied from the host rocks; that is, rock-derived dissolved salts.

4.3 Assessment of groundwater of the study area

Magnesium and Calcium constitute the most prevailing carbonate mineral found in the study area. Enrichment in Mg^{2+}, Cl^{2-} and Ca^{2+} in the groundwater of the study area yields Ca–Mg–Cl as the common water type in the study area. These ions indicate precipitation of halite and dolomite during dry phases in the history of a playa lake.

Magnesium and Calcium are the component of hard water (Neri et al. 1975). Total hardness $CaCO_3$ is an important criterion for ascertaining the suitability of water for domestic, drinking and many industrial uses (Karanth 1994). Hardness of water for domestic uses relates mainly to its reaction with soap, since soap is precipitated principally by Ca^{2+} and

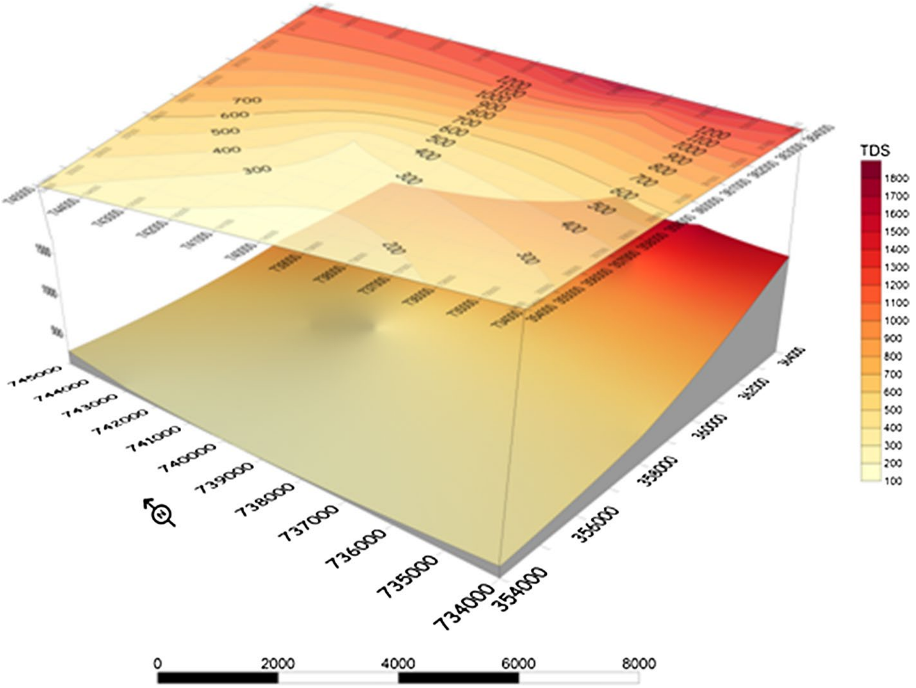


Fig. 9 Total dissolved solute of the area

Mg^{2+}. Hardness of water is defined as the sum of the concentration of these ions expressed as mg/l of $CaCO_3$.Water with hardness ranging from 0 to 60 mg/l, 61 to 120 mg/l, 121to 180 mg/l and > 180 mg/l are regarded as soft, moderately hard, hard and very hard, respectively (Hem 1970).

Groundwater of Eha-Amufu and environs varies in total hardness (Table 3). The wells range between moderately hard to very hard, with total hardness ranging from 76.0 to 404.0 mg/l. The hardness is also evidenced by the mineral saturation of the area—Calcite and Aragonite/dolomite $CaCO_3$. Two hand-dug wells were found to be soft water with total hardness of 40 mg/l and 44 mg/l. This is because the aquifer is highly permeable, and as a result, groundwater flows are active and have less chemical reaction with its surrounding sediment. Variation in hardness in the water is a function of the hydrodynamic dispersion and absorption of the contaminant in the fine grain of the aquifer (Todd 1980). The chemical composition of water in Eha-Amufu environs showed that the water is generally hard. Thus, use of the groundwater for domestic purpose may lead to soap wastage, furring of kettles and boilers together with discoloration and stiffness of textiles. To overcome such occurrences, water should be treated temporally by boiling or permanently by addition of caustic soda or lime, or by filtration through some naturally occurring minerals such as zeolite (Sivasankar and Ramachandramoorthy 2011; Abdolahnejad et al. 2014).

Heavy metals were also analyzed in order to determine their concentration in the groundwater. Iron and lead were detected in the groundwater from the wells, with concentration ranging between 0.03–0.06 and 0.03–0.08 mg/l, respectively (Table 3). The

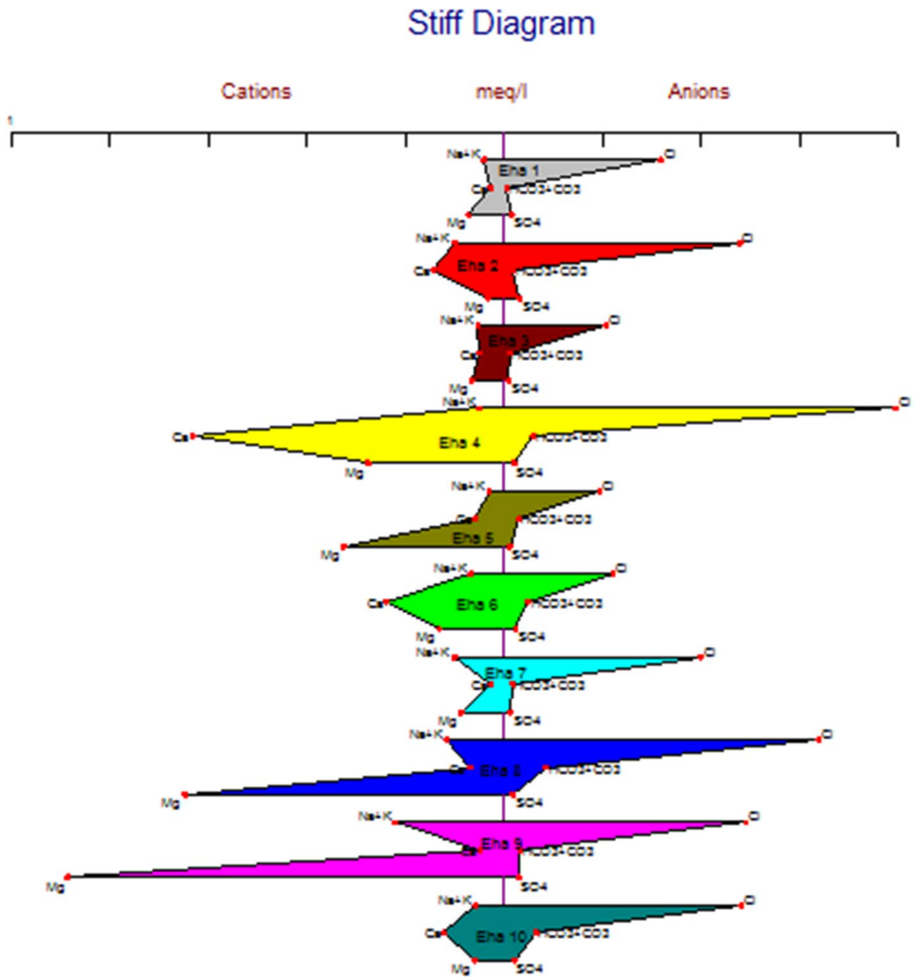


Fig. 10 Stiff diagram of the study area

possible sources of the iron could be the iron minerals (Pyrite, Siderite and Marcasite) which originated from sandstone and shale deposits in the area. Sources of the lead could be from the black Nkporo Shale, reflecting the affinity of Pb for organic matter and clay fractions associated with kaolinite and mica (Heinrichs et al. 1980) or through erosion and leaching of the highly mined limestone deposit abandoned at closely located Nkalagu cement site, which could be mineralized. The high values could also be as a result of anthropogenic factors.

The concentrations were noted to be above the World Health Organization (WHO 2011) standard limits for Iron (0.03 mg/l) and lead (0.01 mg/l) in water. Concentration of lead in the groundwater also failed the Nigerian Standard for Drinking Water Quality (NSDWQ) limit set at 0.01 mg/l while iron was within the NSDWQ limit of 0.3 mg/l. Therefore, the shallow groundwater within Eha-Amufu and its environs is not good for

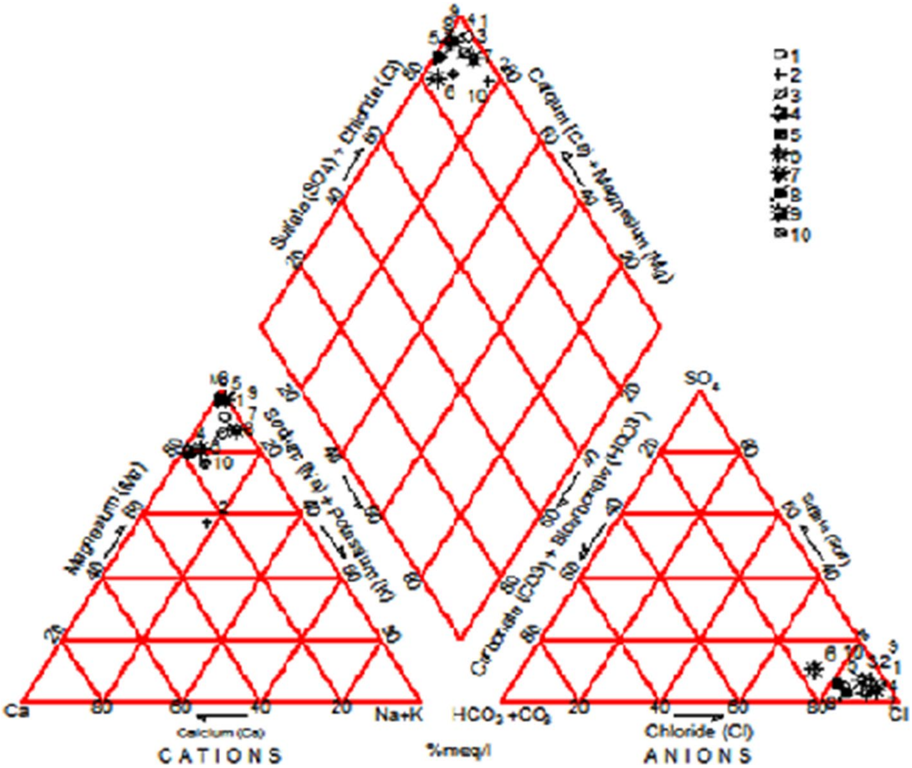


Fig. 11 Piper pattern of the study area

drinking purpose with regard to the WHO stipulated guideline for drinking water. However, a number of techniques have been used to remove heavy metals from contaminated water. They include, chemical precipitation (Fu and Wang 2011); ion exchange (Lai et al. 2016); adsorption (Davarnejad and Panahi 2016); membrane filtration (Rahmanian et al. 2011); reverse osmosis (Yoon et al. 2009); solvent extraction (Lertlapwasin et al. 2010); and electrochemical treatment (Dharnaik and Ghosh 2014). The aforementioned techniques are useful, but has a high-cost implication (Wołowiec et al. 2019). Consequently, treatments may require government and other stakeholders' intervention through the provision of purification plants and regional water conduits.

4.4 Correlation between earth resistivity (ρ_e) and groundwater quality

The integration of electrical resistivity method and geochemical analysis depicts a better representation of groundwater quality in an area (Sherif et al. 2006; Srinivas et al. 2013; Akpan et al. 2013). Hydrogeochemical and geophysical data obtained (Table 4) were statistically evaluated in order to understand the relationship between earth resistivity and hydrochemical properties of the groundwater. Such processes are vital in explaining empirical relationship (Sherif et al. 2006; Srinivas et al. 2013), together with the possibility of identifying a connection between earth resistivity (ρ_e) and the amount of TDS (Ebraheem et al. 1997; Sherif et al.

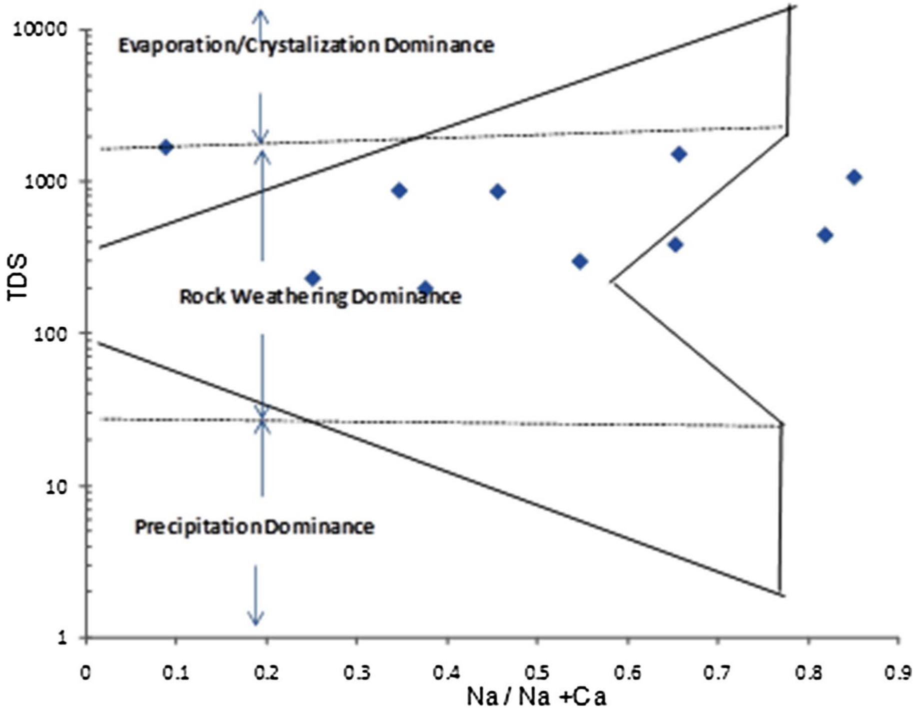


Fig. 12 Gibbs diagram

Table 4 Geophysical and hydrogeological data used for obtaining the empirical relationship

Well no	Water table depth (m)	Electrical conductivity (μg/ms)	Water resistivity (Ω)	Earth resistivity (Ω)	Measured TDS(mg/l)
EHA 1	9.5	283.61	0.0035	64.46	387
EHA 2	30	589.00	0.0017	53.25	868
EHA 3	8.5	292.00	0.0034	68.54	300
EHA 4	10.8	1155.36	0.0009	23.2	1702
EHA 5	10	166.64	0.0060	197	198
EHA 6	15	121.78	0.0082	188	232
EHA 7	13.7	435.90	0.0023	55.2	447
EHA 8	10.6	1041.80	0.0010	25.1	1531
EHA 9	11.3	834.04	0.0012	32	1080
EHA10	24	629.04	0.0016	50.8	879

2006; Srinivas et al. 2013). These ions: Ca^{2+}, Mg^{2+}, total Fe, Na^+, K^+, HCO_3^-, SO_4^{2-}, Cl^-, and NO_3^- constitute 90% of the TDS in natural water (Sherif et al. 2006).

In processing the geophysical and hydrogeological data, the measured EC of groundwater samples were converted into water resistivity (Table 4) using the relation ($\rho_w = {}^1/_{EC}$) as noted by other authors (Vouillamoz et al. 2007; Sherif et al. 2006; Srinivas et al. 2013), where

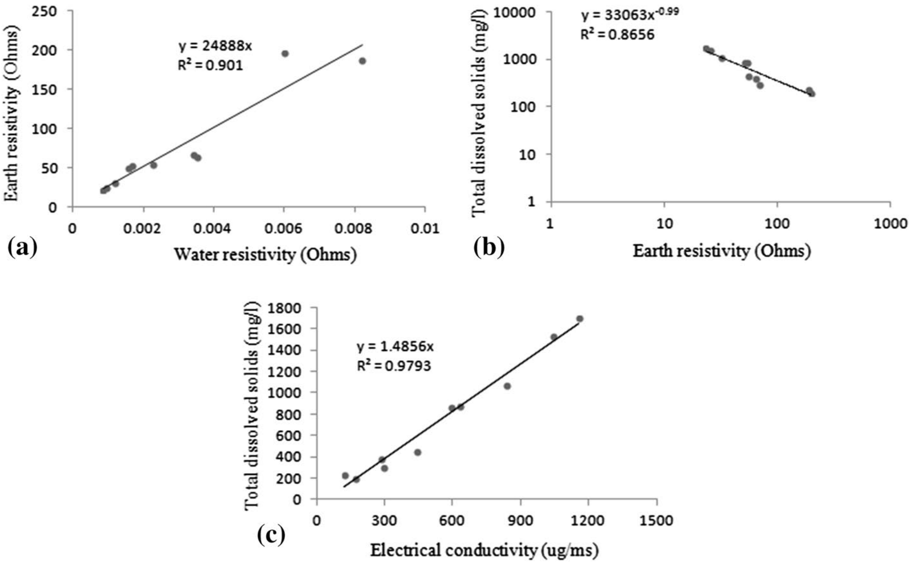


Fig. 13 Relationships between geophysical and geochemical properties

ρ_w is the water resistivity and EC represents the electrical conductivity. In this study, water resistivity (ρ_w) was plotted as a function of earth resistivity (Fig. 13a) and the empirical relationship between them indicated:

$$\rho_e = 24888\rho_w$$

where ρ_e is the earth resistivity and ρ_w is the water resistivity in Ohmmeters.

The attained best of fit line between earth resistivity and water resistivity ($R^2 = 0.901$) shows that the earth resistivity of Eha Amufu which bears the aquifer is mostly of coarse sand and sandy clay with a very shallow water table. This implies that it is strongly affected by groundwater salinity (Sherif et al. 2006). This observation may provide justification for applying resistivity methods in delineating salinity distribution and groundwater contamination zones in recent studies (Sherif et al. 2006; Srinivas et al. 2013; Akpan et al. 2013; Bouderbala and Remini 2014).

From the plot shown in Fig. 13b, regression analysis established a strong positive relationship ($R^2 = 0.9511$) between TDS against $\rho_{e.}$, and the fitted line indicates the following empirical relationship:

$$\text{Log TDS} = 4.519 - 0.99\,\text{Log}\rho e$$

where TDS is the TDS in milligram per liter and ρ_e is the earth resistivity in Ohms. This relation shows that two different groundwater types may be delineated, and these types are fresh ($\rho_e > 22$ Ωm) and saline groundwater ($\rho_e < 22$ Ωm) as shown in Table 2. There is also a possibility of plotting water EC (in µg/ms) against TDS (in mg/l), as shown in Fig. 13c.

5 Conclusion

The result of the VES studies revealed that Eha-Amufu and environs has a shallow groundwater, which explains the abundance of hand–dug wells. The absence of borehole in Eha-Amufu was attributed to low permeability of the shale formations underlying the area. The high salt concentration (low electrical resistivity) found in the study area was localized within the Agwu and Nkporo Shale units interpreted to have been deposited during alternating transgressions and regressions of the Coniacian and Campanian seas, respectively.

Empirical relationship exists between earth resistivity and TDS. It was vital in ascertaining the average TDS along the resistivity profile. Furthermore, it was useful in classifying the groundwater as fresh or saline. Thus, earth resistivity methods are viable and resourceful tools for quantitative and qualitative studies related to groundwater resources.

Based on Piper (1944) plot, result of hydro-chemical analysis revealed one water facie, namely: Ca–Mg–Cl. Also, the groundwater sample for all the locations was observed to have similar ionic content based on Stiff (1951) patterns. This may be an indication that the groundwater of the area came from the same source, with evaporation occurring in the deeper parts of the basin. From Gibbs plot, the groundwater of Eha-Amufu and its environs recharge from precipitation. The origin of ions that favor the accumulation of salts in the groundwater of Eha-Amufu is rock chemical interactions. The hydrochemical analysis also showed that the water is not suitable for drinking due to occurrence of Pb^{2+} in concentrations above the World Health Organization (WHO 2011) and Nigerian Standard for Drinking Water Quality (NSDWQ) limits for drinking water.

Conclusively, the authors suggest that other channels of portable water provision such as harvesting and treatment of river water using purification plants and development of regional water conduits be explored. Furthermore, it is recommended that water from hand-dug well in Eha-Amufu and its environs should be treated to remove heavy metals and reduce salinity before domestic uses in other to prevent outbreak of epidemics in the area.

Acknowledgement The authors acknowledge all the lecturers of the Department of Geology, University of Nigeria, Nsukka, for their advice during the course of this research. The authors will also like to appreciate members of the University of Nigeria Water Resources Management Laboratory Limited for their help in hydro-chemical analyses.

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