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Origin of saline groundwater in parts of the Middle Benue Trough, Nigeria

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ABSTRACT

Determining the origin of saline groundwater is crucial for effective water resource management and protection, and to obtain clues for minerals and petroleum discoveries. Out of groundwater that were sampled and analyzed from part of the Middle Benue Trough, 3 are saline water that are discharged from folded and faulted sandstone of the study areas. Inductively coupled plasma mass spectrophotometer was used to analyze the major cations and trace elements while titration was used to analyze for sulphates (SO₄) and bicarbonates (HCO₃). Chloride (Cl) above 400 mg/l and bromine (Br) were analyzed using the ion chromatographic method. Oxygen isotopes (δ¹⁸O) in water samples were analyzed via CO₂ equilibration, and hydrogen isotopes (δ²H) in water samples were analyzed by thermochemical reduction method. Three different statistical analyses—Piper trilinear diagram and Chadha plot, Cl/Br ratio, and isotopes plot—were used to determine the origin of groundwater in the study area. Using Piper trilinear diagram and Chadha's plot, Cl/Br ratio, and isotope plot, three origins were discovered as meteoric, mixed, and marine. All the saline water in the study area are marine in origin and are associated with sandstone aquifers found in the Asu River Group and Awe Formations which are the oldest formations in the study area. In Nigeria, there is no work done on the use of Chadha's plot and Cl/Br ratios to determine the origin of saline groundwater.

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1. Introduction

The sources of material in total dissolved solids (TDS) and electrical conductivity (EC) that is present in nature, i.e. geological conditions and seawater (Rusydi, 2018). Two principal hydrochemical-type waters were identified within the Amansie and Adansi Districts of the Ashanti Region, Ghana; Ca-Mg-HCO₃ and Na-Cl have been delineated, with Ca-Mg-SO₄, Na-Mg-Ca-HCO₃, and Na-Cl-SO₄-type waters being minor water types. Thus, groundwater within the districts principally evolves from fresh Ca-Mg-HCO₃-type water into Na-HCO₃-type water into Ca-Mg-Cl-type water into Na-Cl-type water along its flow path principally due to ion-exchange

reactions and, therefore, is largely characterized by recharge processes through mixing with waters of geochemically different ionic signatures than processes involving saline-water intrusion (Tay et al., 2018).

Generally, Na-Cl relationships are employed in the origin of salinity in groundwater (Carol et al., 2009; Sami 1992). Salinity may also originate from the dissolution of chloride-rich minerals. If there exists a positive correlation between Na and Cl, then their origin is likely to be from a common source. A high positive correlation between Na and Cl suggests that the salinity of groundwater is due to intermixing of two or more groundwater bodies with different hydrochemical compositions

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(Obiefuna and Orazulike, 2011). The correlation between Na and Cl is normally used to recognize the mechanism of salinity in arid and semiarid regions (Jabal et al., 2014). The unequivocal source for Na and Cl is salts derived from a marine environment. In some other studies, the sources may be from evaporation as well as the dissolution of halite. The dissolution of halite results in the mixing of equal amounts of Na and Cl in groundwater, so the ratio between Na and Cl will be nearly one (Ravikumar and Somashekar, 2017). Seawater intrusion to aquifers can also involve a range of complex hydro-geochemical processes. Seawater intrusion into coastal aquifers has long been recognized as a major concern around the world. The intrusion occurs as a result of the induced flow of seawater into freshwater aquifers originally caused by groundwater development around the coast (Al-Barwani and Helmi, 2006). Basically, freshwater is less dense than saltwater and so it floats on top. Therefore, saline water is found below freshwater discharge from a higher altitude in coastal areas. Also, the boundary between saltwater and freshwater is not distinct; the zone of dispersion, transition zone, or saltwater interface is brackish with saltwater and freshwater mixing. It then means that salinity will increase with depth where both freshwater and saline water occur (Ayolabi et al., 2013). Deeper sandstone layers are often confined and can be artesian (Tijani et al., 2018).

Chloride (Cl) and bromide (Br) ions dissolved in water are tracers close to the ideal behavior (Custodio and Llamas, 1983) due to their hydrophilic character and small ionic size. That means that the physical processes that take place in the terrain (dilution, evaporation, mixtures) affect the absolute concentrations but do not modify the value of chloride to bromide ratio. These ions keep reasonable memory of the soluble original matter. The likely processes that can affect Cl and Br ions, and their ratio, are well-known (Alcalá and Custodio, 2008; Custodio and Herrera, 2000; Davis et al., 1998; Whittemore, 1988). The ratio between chloride and bromine (Cl/Br ratio) can be used as a determinant of groundwater quality, as well as a determinant of groundwater contamination, seawater intrusion, and the origin of seawater intrusion (Naily and Sudaryanto, 2018; Xiaoying et al., 2018).

Isotope fractionation is a geochemical tool used to identify groundwater origin, its age, residence time, and how it is affected by geo-hydrological and meteorological factors. It can also be used to determine the origin and source of contaminants emanating from agricultural activities or other point sources (Pelig-Ba, 2009). Isotopic studies can also be used to monitor groundwater flow in unsaturated porous layers (Rothfuss et al., 2015) and to understand preferential flow pathways (Ma et al., 2017). Environmental isotope

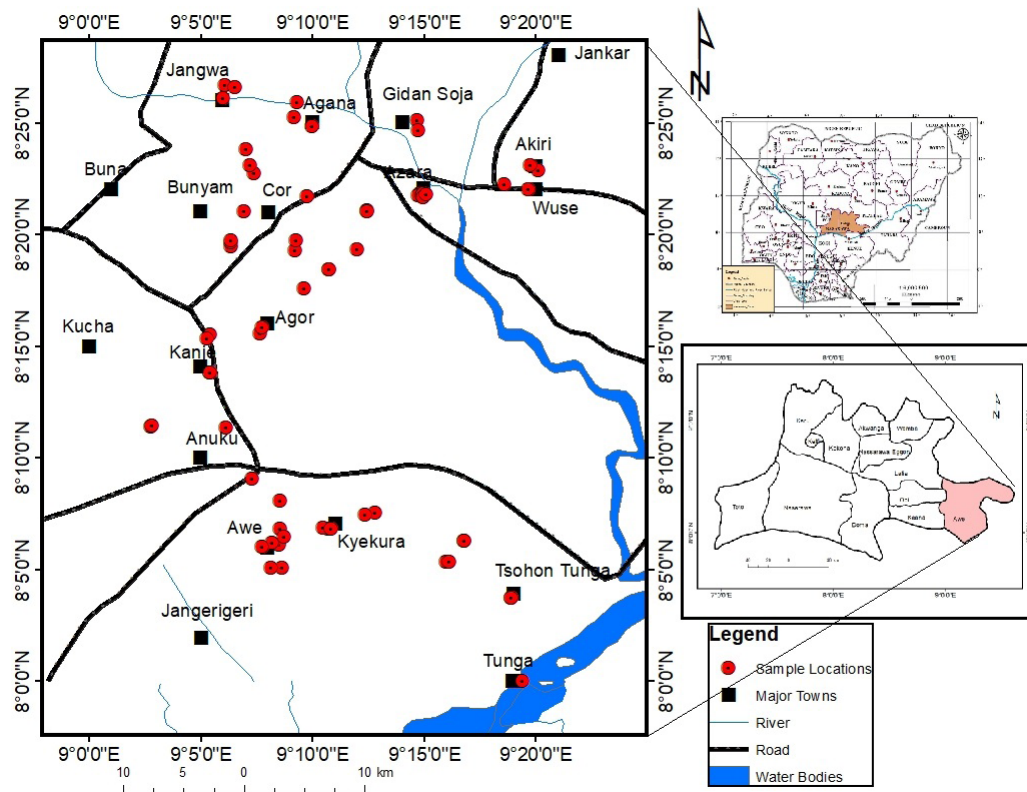


Figure 1. Location map of the study area.

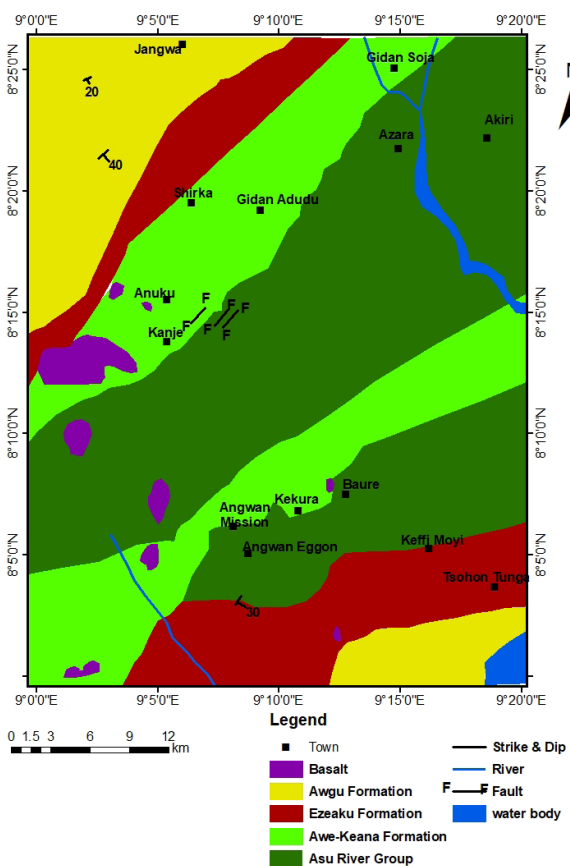


Figure 2. Geological map of the study area.

techniques are pre-eminently suitable for studying the unsaturated and saturated zone, the latter particularly concerning the stable and radioactive natural isotopes. Stable isotope data preferentially yield information on the origin of groundwater (Mebus, 2000). The stable isotopes of ^2H and ^{18}O occur naturally in precipitation and provide a seasonal meteoric signal in temperate, continental systems that are often attenuated in shallow groundwater (Abiye, 2013; Ayolabi et al., 2013; Clarks and Fritz, 1997). Environmental isotopes (stable and radiogenic) as a tool for hydrogeological studies are gaining popularity in recent times and have been used to gain some insights into the subsurface flow and recharge condition (Abiye, 2013, Ayolabi et al., 2013). Naturally occurring stable (^2H , ^{18}O) and radiogenic (^3H and ^{14}C) isotopes of water have been widely used over the past 40 years to solve problems related to groundwater recharge and its residence time (Ayolabi et al., 2013; Clarks and Fritz, 1997; Chen et al., 2006).

2. Geology of the Study Area

The study area is defined by longitudes $9^{\circ}0'0''$ – $9^{\circ}20'0''\text{E}$ and latitudes $8^{\circ}0'0''$ – $8^{\circ}30'0''\text{N}$ and is part of

the Middle Benue Trough (Figure 1). The five formations were encountered in the study area (Figure 4) and these include Asu River Group which is the oldest formation in the study area and was encountered both in the northeastern and southeastern as well as in the southwestern part of the study area. Awe-Keana formations are embedded together in the study area. The Awe formation overlaid the Asu River Group. The Awe-Keana formations were found in the northeastern, northwestern, and southeastern parts of the study area. Ezeaku formation overlaid the Keana formation in the geology of the Middle Benue Trough. This formation was encountered in northwestern and southeastern parts of the study but only in a small portion of the southeastern parts of the study area. Agwu Formation is a young formation found in part of the study area and it was encountered in northwestern and southeastern parts of the study area.

3. Materials and Methods

Fifty-three groundwater samples were sampled using 250 ml plastic bottles that were previously soaked in acidified water, washed, and rinsed with distilled water. At every sampling point, the sample containers were further rinsed with the sampled water before sampling. Two samples were collected at every sampling point, one is acidified with two drops of concentrated hydrochloric acid for homogenization and prevention of absorption/adsorption of elements to the walls of the plastic container while the second sample is not acidified. At each sampling point, the sample containers were rinsed with the sampled water three times before sampling. At every sampling point, coordinate readings were taken using the Global Positioning System instrument. The water EC ($\mu\text{S}/\text{cm}$) and TDS (mg/l) were directly measured using a portable meter in the field, also alkalinity (HCO_3^- - mg/l) was also measured in the field using the titration method. The acidified water samples were transferred into 60 ml plastic bottles and sent to Bureau Veritas Mineral-Laboratories in Canada where an inductive coupled plasma mass spectrophotometer was used for major cations analysis. For the non-acidified water sampled, the titration method was used for SO_4 and Cl in the laboratory of the Geology Department, University of Jos. Oxygen isotopes ($\delta^{18}\text{O}$) in water (brine) samples were analyzed via CO_2 equilibration while hydrogen isotopes ($\delta^2\text{H}$) in water (brine) samples were analyzed by thermo-chemical reduction method both at Queen's Facility for Isotope Research, Department of Geological Sciences in Canada.

4. Results

The results of the analyses are presented in [Table 1](#) below.

Table 1. Concentrations (mg/l) of ions analyzed in groundwater water.

Sample ID	Sources	Longitude	Latitude	pH	TDS	EC	TH	HCO ₃ ⁻	SO ₄ ²⁻	Cl	Ca	K	Mg	Na	Br
A 18	Well	9°14' 4 9.5"	8°21'49.6"	6.97	582	1,164	233	92.92	37.50	100	25.71	12.7	41.35	137.82	0.18
A 19	Well	9°14'4 5.6"	8°21'45.3"	6.81	553	1,106	144	50	42	95	17.89	11.04	24.24	214.85	0.10
A 22a	Well	9°12' 27.6"	8°21' 3.7"	6.71	503	1,011	255	52.52	50.00	70	49.46	27.48	32.40	56.82	<0.50
A 22b	Well	9°12' 27.2"	8°21' 2.8"	6.69	394	770	227	72.72	45.00	70	37.65	27.13	32.74	57.17	<0.50
A 24	Well	9°8'34.3"	8°6'5"	6.96	226	465	87	60.60	66.25	50	28.81	12.02	3.91	69.65	<0.10
A 25	Well	9°8'30.4"	8°6'7.5"	7.27	523	1,044	390	64.64	95.00	50	88.92	5.3	41.96	87.15	0.082
A 26	Well	9°8'38.8"	8°5'3.5"	7.28	360	730	248	62.00	80.50	35	48.14	2.71	31.44	69.14	0.043
A 27	Well	9°8'11.2"	8°6'10.6"	5.9	124	249	89	62.41	81.00	30	29.23	12.40	4.1	29.41	<0.10
A 29	Well	9°19'25.5"	7°59'55.5"	7.77	1,082	2,211	475	72.72	75.00	240	7	67.76	26.79	239.72	0.22
A 30a	Well	9°18'54.5"	8°3'42.9"	7.72	678	1,332	518	40.4	55.00	160	142.38	3.27	40.87	83.22	0.19
A 31a	Well	9°16'49.6"	8°6'17.6"	6.5	285	567	166	32.32	23.50	40	41.65	3.70	15.39	77.52	<0.10
A 32b	Well	9°16'0.3"	8°5'20.9"	7.09	265	518	118	49.00	12.00	15	34.91	12.68	7.96	74.17	0.019
A 33b	Well	9°12'49.5"	8°7'31.7"	5.35	37	76	17	10.00	17.00	20	4.28	1.41	1.45	8.06	<0.010
A 34b	Well	9°10'42.1"	8°6'49.5"	5.16	12	24	10	24.24	16.00	5	3.06	0.48	0.54	2.73	<0.010
A 36a	Well	9°5'24.3"	8°15'30"	6.36	92	184	66	48.60	24.50	15	23.12	2.87	2.36	16.61	<0.010
A 38a	Well	9°5'24.8"	8°13'49.5"	7.10	710	1,414	259	96.96	16.00	220	30.67	5.61	44.70	214.74	0.20
A 46c	Well	9°5'59.9"	8°26'04.0"	6.15	93	186	50	8.08	11.50	30	15.33	10.36	2.92	27.44	<0.01
A 13	Spring	9°20'7.0"	8°22'52.0"	6.24	>10,000	20,000	189	80.80	10.50	3,100	40.2	90.00	22.00	2,813	1.3
A 34a	Spring	9°10'30.1"	8°6'51.5"	5.05	10	21	8	24.00	16.00	10	2.27	0.91	0.58	1.13	<0.010
A 35b	Spring	9°8'8.3"	8°5'3.8"	6.54	>10,000	20,000	322	113.00	14.00	4,600	76	82	33	3,770	1.6
A 36b	Spring	9°5'18.7"	8°15'21.1"	5.56	17	36	19	50.00	29.50	15	5.68	1.59	1.26	13.47	<0.010
A 44	Spring	9°14'41.6"	8°25'05.4"	6.78	19	38	9	8.08	85.00	15	2.76	1.34	0.62	16.57	<0.010
A 5	Borehole	9°6'22.9"	8°19'27.8	6.68	237	475	186	68.68	75.00	5	41.39	5.39	20.47	51.27	<0.010
A 6	Borehole	9°6'21.7"	8°19'37.8	6.32	183	364	183	66.98	72.50	5	35.73	3.10	23.17	44.39	<0.010
A 7	Borehole	9°6'21.4"	8°19'42.6"	6.74	222	447	140	67.43	74.00	5	16.93	3.08	23.85	47.19	0.011
A 9	Borehole	9°9'15.4"	8°19'15.7"	6.58	365	729	167	101.11	17	10	8.81	3.63	35.18	79.74	<0.010
A 10a	Borehole	9°10'44.2"	8°18'24.5"	6.42	355	710	311	105.04	19.00	10	11.95	7.76	68.30	71.79	<0.010
A 10b	Borehole	9°10'46"	8°18'25.9"	6.76	367	737	251	101.00	20.00	10	3.83	7.07	58.69	64.26	<0.010
A 11	Borehole	9°12'00.6"	8°19'18.8"	7.2	302	606	241	100	15	10	6.82	6.65	54.41	57.21	<0.010
A 14	Borehole	9°19'45.7"	8°23'4.4"	6.13	105	223	53	48.48	12.50	25	8.96	5.38	7.61	36.42	0.011
A 15	Borehole	9°18'35.4"	8°22'15.2"	6.82	429	858	162	68.67	18.00	160	17.86	11.53	28.6	228.55	0.017
A 16a	Borehole	9°14' 55.8"	8°21'45.1"	6.32	633	1,266	294	88.81	60.00	80	37.63	4.84	48.91	120.27	0.12
A 16b	Borehole	9°14' 54.4"	8°21'43.6"	6.47	540	1,077	312	80.93	72.10	95	77.76	21.92	29.34	79.45	<0.50
A 17	Borehole	9°14' 58.3"	8°21'48.9"	6.87	1,723	3,420	87	52.63	24	1,000	13.94	25.22	12.73	842.39	0.11
A 20	Borehole	9°14'57.6"	8°21'37.9"	6.6	287	573	167	8.08	50.00	55	13.36	8.68	32.61	98.94	0.55
A 23	Borehole	9°9'46.9"	8°21'41.9"	7	210	422	224	56.43	37.50	15	42.84	4.48	28.90	35.31	0.021
A 28	Borehole	9°19'23.4"	8°0'0.1"	7.04	829	1,665	645	80.87	75.00	180	215.74	11.08	28.14	70.83	0.013
A 30b	Borehole	9°18'54.5"	8°3'42.9"	7.29	329	670	158	56.55	27.50	45	45.68	6.27	11.17	111.14	<0.20
A 31b	Borehole	9°16'49.6"	8°6'17.6"	7.07	270	542	113	31.67	23.50	10	26.08	2.17	11.98	69.68	0.045
A 32a	Borehole	9°16'8.3"	8°5'21.7"	6.6	212	426	186	48.48	11.50	50	54.36	2.48	12.83	41.98	<0.010
A 33a	Borehole	9°12'21.2"	8°7'27.9"	5.2	12	24	7	8.08	17.00	10	2.00	1.79	0.47	1.81	0.047
A 34c	Borehole	9°10'49.7"	8°6'48.6"	5.7	10	20	10	24.48	16.00	10	3.06	0.83	0.64	1.13	<0.010
A 35a	Borehole	9°7'46.1"	8°6'2.2"	6.28	>10,000	20,000	275	113.12	14.00	4,600	58.20	75	32.00	3,460	<0.010
A 37a	Borehole	9°2'47.6"	8°11'23.12"	6.83	412	826	255	65.88	16.00	140	43.04	5.58	36.39	100.5	1.8
A 37b	Borehole	9°2'49.1"	8°11'26.1"	6.7	1,851	3,077	552	38.33	20.00	920	86.05	16.46	82.88	19.35	0.044
A 38b	Borehole	9°5'24.8"	8°13'49.5"	6.83	1,053	2,110	363	100	16.00	400	53.75	8.12	56.15	300.82	0.39
A 39	Borehole	9°6'9"	8°11'22.1"	6.95	288	581	238	64.64	33.00	20	52.55	0.67	26.49	10.97	0.12
A 40	Borehole	9°7'18.8"	8°9'2.7"	7.06	310	624	53	80.81	15.00	15	12.08	1.65	5.58	128.44	0.016
A 41	Borehole	9°8'33.8"	8°6'49.9"	7.24	510	1,018	306	50.37	32.00	35	41.11	4.02	49.82	93.50	<0.010
A 42	Borehole	9°8'45.7"	8°6'27.3"	7.06	310	624	55	73.24	24.00	15	12.97	9.47	5.54	26.34	0.042
A 47	Borehole	9°7'39.1"	8°15'34.3"	7.50	289	576	286	68.68	15.00	25	52.41	2.41	38.16	47.30	0.011
A 48	Borehole	9°7'46.5"	8°15'49.4"	7.56	218	550	293	76.75	12.00	15	50.53	3.10	41.07	53.04	<0.01
A 49	Borehole	9°9'37.6"	8°17'35.2"	7.74	205	412	225	64.65	8.50	10	39.55	2.90	31.09	38.48	0.01
WHO 2011				6.5–8.5	500	1,000	100	0.01	200	250	75	75	50	500	

5. Discussion

5.1. Origin of saline groundwater in the study area

TDS, EC, Cl, K, and Na with the positive correlation in groundwater of the study area mean that they have a common origin, whereas pH and SO₄ with negative correlation specify different sources (Table 2). The correlation between Na and Cl is normally used to recognize the mechanism of salinity in arid and semiarid regions (Jabal et al., 2014). When Na and Cl become the major ions in water, the water develops a salty taste. Generally, Na-Cl relationships are employed in the origin of salinity in groundwater of the study area. The positive correlation between Na and Cl indicates that they have a common origin. A high positive correlation ($r^2 = 0.87$) between Na and Cl suggests that the salinity of groundwater is due to intermixing of two or more groundwater bodies with different hydrochemical compositions (Obiefuna and Orazulike, 2011). The unequivocal source for Na and Cl is salts derived from the marine environment (Ravikumar and Somashekar, 2017).

The PCA of groundwater in the study area generated three PCs together accounting for 80.85% of the variance in the hydrogeochemical dataset. PC1 loaded with EC, TDS, Na, K, and Cl accounted for 46.28% variance. PC2, dominated with a rotated component of Mg, TH, HCO₃, pH accounted 24.333%, and PC3 dominated with the rotated component of Ca and SO₄ which accounted for 10.23% variance (Table 3). Grouping of parameters in the loadings plot suggests their significant mutual positive correlation. The PCs score plots portray the characteristics of the samples and aid to comprehend their spatial distribution (Ravikumar and Somashekar, 2017).

In this study, the ratio between chloride and bromine (Cl/Br) plot (Fig. 5) indicates (70%) seawater intrusion as the origin of most of the groundwater (Naily and Sudaryanto 2018). The Cl/Br ratio in groundwater of the study area is modified by natural processes (climate effect, marine effect, and mixing of halide with recharge water) and anthropogenic processes (halite dissolution and agricultural effects) (Xiaoying et al., 2018). This could be due to the rainfall that had a similar Cl/Br ratio as seawater in the coastal area (Xiaoying, 2018).

The multi-tracer investigation of groundwater chemistry of part of the Middle Benue Trough was carried out using ²H and ¹⁸O isotopes. The groundwater of the trough was found to be stored in three different aquifers (shallow, intermediate, and deeper) based on ²H and ¹⁸O results. The isotopic features suggested that one water sample from the well originated from the shallow aquifer, two water samples from the well, one sample from borehole originated from the intermediate aquifer that resulted from mixing between recent recharge and an older component recharged under climatic conditions cooler than at present. Two water samples (one hot spring and the artesian borehole) originated from the deeper aquifer of the study area (Genet, 2017). The shallow hand-dug wells

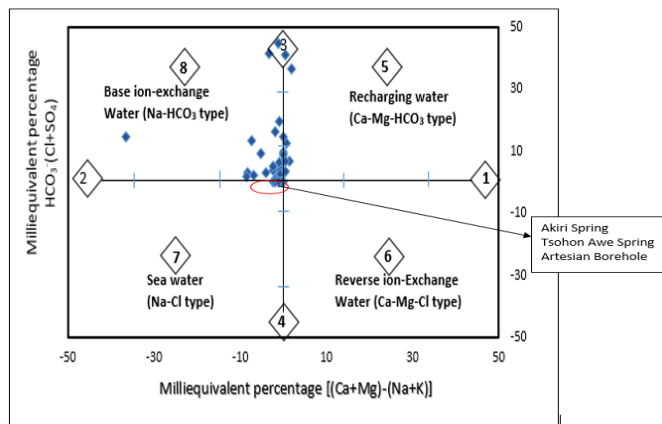


Figure 4. Groundwater samples from parts of the Middle Benue Trough plotted on modified Piper diagram (Chadha, 1999).

PIPER DIAGRAM FOR GROUNDWATER OF THE STUDY AREA

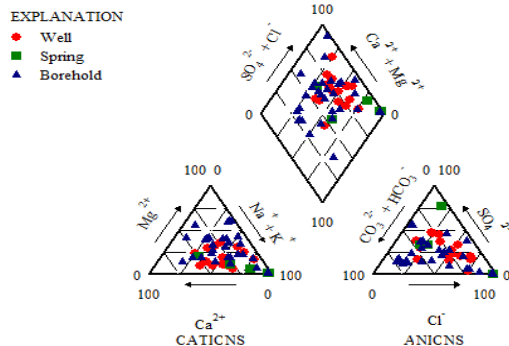


Figure 3. Piper diagram of groundwater in the study area.

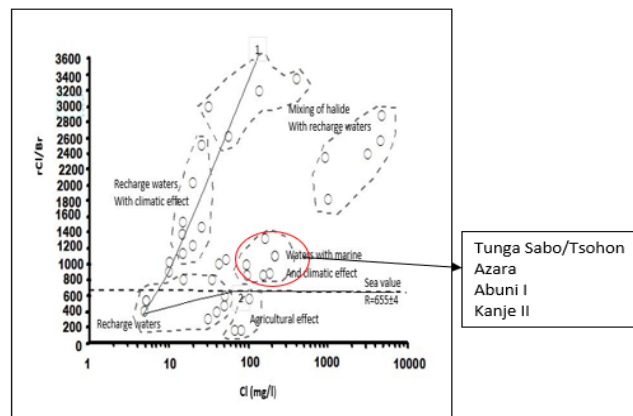


Figure 5. Plot of rCl/Br versus Cl (mg/l) in ground water of the study area. 1: mixing of halides with the recharge waters; 2: contribution of seawater with respect to recharge waters in the study area.

Table 2. Correlation analysis of the groundwater dataset.

Parameter	Temp	Ph	TDS	EC	HCO ₃	SO ₄	Cl	Ca	K	Mg	Na	TH
Temp	1											
pH	-0.268	1										
TDS	0.721 ^a	-0.007	1									
EC	0.722 ^a	-0.006	1.000 ^a	1								
HCO ₃	0.250	0.388 ^a	0.402 ^a	0.405 ^a	1							
SO ₄	-0.293	0.183	-0.201	-0.199	-0.025	1						
Cl	0.662 ^a	-0.053	0.981 ^a	0.980 ^a	0.380 ^a	-0.219	1					
Ca	0.016	0.465 ^a	0.192	0.189	0.225	0.386 ^b	0.173	1				
K	0.548 ^a	0.099	0.884 ^a	0.884 ^a	0.383 ^a	-0.046	0.848 ^a	0.306 ^b	1			
Mg	0.018	0.452 ^a	0.133	0.126	0.561 ^a	-0.003	0.117	0.310 ^b	0.103	1		
Na	0.685 ^a	-0.035	0.984 ^a	0.986 ^a	0.402 ^a	-0.215	0.988 ^a	0.133	0.0860 ^a	0.068	1	
TH	0.021	0.565 ^a	0.204	0.198	0.464 ^a	0.260	0.182	0.849 ^a	0.264	0.0766 ^a	0.128	1

^a Correlation is significant at the 0.01 level (2-tailed).

^b Correlation is significant at the 0.05 level (2-tailed).

(Kanje I, and Agwan Eggon II in Awe) and Akiri borehole samples plotted close to the groundwater meteoric water line [local meteoric water line (LMWL)] while the Jangwa well water sample plotted close to the evaporation line (Table 4). The spring water samples however plotted far away from LMWL and evaporation line. In comparison with the other groundwater samples, samples I13a and I35b are relatively enriched in stable isotopes, they deviate slightly from the LMWL (Fig. 6), they are characterized by comparatively high levels of TDS (>10,000 mg/l) and EC (>20,000 mg/l). The deeper the aquifer, the more depleted the isotopic data are.

Hydrochemical facies graphical representation of groundwater major dissolved constituents (major cations and major anions) helps in understanding its hydrochemical evolution, grouping, and areal

distribution. In the present study, Piper trilinear diagram and Chadha's plot were constructed to evaluate variation in hydrochemical facies. From the groundwater Piper diagram, four hydrochemical facies are identified—NaCl, CaCl, NaHCO₃, and CaHCO₃ (Fig. 3). Among the water types, 11.32% of the groundwater represented Na-Cl-type indicating the influence of seawater mixing with fresh groundwater. The remaining samples plotted in the NaHCO₃ (about 2%), CaHCO₃ (11.32%), and CaCl (20.75%) type field while the remaining samples (about 55%) are in the mixed zone. Water samples found in the mixed zone are water that cannot be identified as neither anion nor cation dominant.

Groundwater principally evolves from fresh Ca-Mg-HCO₃ type water into Na-HCO₃-type water into Ca-Mg-Cl-type water into Na-Cl-type water along its flow path principally due to ion-exchange reactions and therefore, is largely characterized by recharge processes through mixing with waters of geochemically different ionic signatures than processes involving saline-water intrusion (Tay et al., 2018). Chadha's plot identified four hydrochemical facies for the groundwater—CaMgCl, CaMgHCO₃, NaCl, and NaHCO₃ (Fig. 4). The CaMg-Cl-type of water dominates among the four facies with 71.70% and Na-Cl-type is the third prominent with 7.54%. Both CaMg-Cl and Na-Cl water types together represent about 80%. Ca-Mg-HCO₃ water type is the second most prominent with 18.87% and Na-HCO₃ fourth with 1.87% also contributes to the water types. Thus, groundwater within the study area principally evolves from fresh Ca-Mg-HCO₃-type water into Na-HCO₃ type water into Ca-Mg-Cl-type

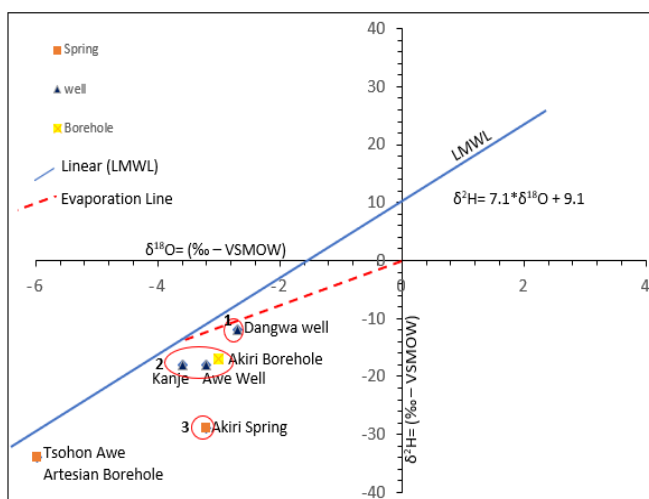


Figure 6. Plot of $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ (‰).

Table 3. Principle component analysis (PCA) of the ground-water dataset.

Parameter	Principal components (PC)		
	PC1	PC2	PC3
EC	0.984	0.127	-
TDS	0.983	0.132	-
Cl	0.983	-	-
Na	0.982	-	-
K	0.853	0.137	0.251
Temp	0.641	-	-0.320
Mg	-	0.899	-
TH	0.157	0.823	0.445
HCO ₃	0.356	0.711	-0.140
pH	-0.120	0.703	0.307
SO ₄	-0.145	-	0.825
Ca	0.195	0.478	0.725
Eigen value	5.554	2.920	1.228
% of variance	46.283	24.333	10.230
Cumulative %	46.283	70.617	80.847

water into Na–Cl-type water along its flow path principally due to ion-exchange reaction. Therefore, it is largely characterized by recharge processes through mixing with waters of geochemically different ionic signatures than processes involving saline-water intrusion (Tay et al., 2018).

Na–Cl facies is the saline water derived from deep groundwater, with high Cl, Na, TDS, and EC. In general, the groundwater is salty and usually derived from aquifers associated with the oldest rocks (Asu River Group and Awe sandstone formations). Deeper sandstone layers are often confined and can be artesian

(Tijani et al., 2018). It can be analyzed that the high content of Cl ion in NaCl water is caused by salt crystal washing process trapped in marine sediments of shallow sea zone due to high evaporation process. Ca–HCO₃ facies is characterized by low EC values (<1,000 µs/cm). This condition provides that the hydrogeochemical is the bicarbonate groundwater with the content of Ca and Mg and high bicarbonate HCO₃, low to moderate Na and K, while the values of TDS and groundwater (pH) are low. The greater EC and TDS values in the two hot springs and artesian boreholes in the study area indicated the higher saltwater intrusion (Valensia et al., 2018). TDS concentration describes the presence of inorganic salts and small amounts of organic matter in the water. The sources of material in TDS and EC come from nature, i.e., geological conditions and seawater, as can be seen in the Chadha's plot, Cl/Br ratio, and isotopic plot (Rusydi, 2018).

6. Conclusion

The use of techniques such as the Piper trilinear diagram and Chadha's plot, Cl/Br ratio, and isotopes gave three origins of water in the study area as meteoric, mixed, and marine. The three saline groundwater in the study area are all marine in origin and are associated with sandstone of the oldest rocks (Asu River Group and Awe Formations) in the study area.

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Table 4. H² and O¹⁸ isotopes analyzed values of groundwater.

ID no	Locations	Sources	Longitudes	Latitudes	Elevation	δ ¹⁸ O (‰) versus VSMOW	δ ² H (‰) versus VSMOW	Remark
I 13a	Akiri salt farm	Spring	9°20'7.0"	8°22'52.0"	116	- 3.2	- 29	Present study
I 13b	Akiri town	Borehole	9°19'45.7"	8°23'4.4"	114	- 3.0	- 17	Present study
I 25	Agwan Eggon II	Well	9°8'30.4"	8°6'7.5"	113	- 2.7	- 12	Present study
I 35b	Tsohongari Awe II	Spring	9°8'8.3"	8°5'3.8"	108	- 5.98	- 34	Nandom and Sallau (2019)
I 38a	Kanje I	Well	9°5'24.8"	8°13'49.5"	173	- 3.2	- 18	Present study
I 46c	Jangwa Town	Well	9°5'59.9"	8°26'04.0"	113	- 3.6	- 18	Present study

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