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Influence of Hydrogeochemical Factors on the Natural Water Systems of Uburu-Okposi area, Lower Benue Trough, Southeastern Nigeria, using Geochemical and Multivariate Statistical Methods

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Abstract

The influence of hydrogeological processes on water systems of the Uburu-Okposi area, Lower Benue Trough was investigated to understand the interplay between aquifer materials and the water system resulting in its chemical composition modification. Forty (40) water samples (ground and surface sources) were randomly collected and analyzed for their physicochemical properties.

Results from in-situ measured physicochemical parameters are pH: 5.29–8.98, EC: 206–6970 us/cm, and TDS: 112–4690 mg/l. Laboratory results shows Na⁺ as the dominant cation (4.4–4900 mg/l) with Cl⁻ as the dominant anion (14.4–6300 mg/l). The values were indicative of salinization. Factors influencing water chemistry were determined using Saturation Index (SI), Ionic Ratio, and Bivariate plots. 65% of samples had positive Chloro Alkali Index (CAI) ratio suggesting direct base-exchange reaction as a dominant factor governing water chemistry. CAI 1 & 2 large absolute values show cation exchange as a principal influence on groundwater chemistry. Estimated SI showed Dolomite, Calcite, Aragonite, and Magnesite were supersaturated therefore, they influenced water chemistry. Bivariate plots identified Ion Exchange (carbonate and silicate weathering) as another principal influence on water chemistry. Gibbs plot showed 92.5% samples plotted in the rock–water interaction field with 7.5% plotting within the evaporation-precipitation field. Principal Component Analyses (PCA) extracted six components factors, the first three factors accounted for above 50% of the total variation collectively responsible for the hydrochemical processes in the area via water-rock interactions, carbonate dissolution, and ion exchanges.

Conclusively, geogenic factors are the major influence on water chemistry in the study area.

1. Introduction

Uburu and Okposi area are among the localities characterized by seepages of saline groundwaters within the lower (southern) extension of the Benue Trough, Nigeria (BTN). These seepages occur mostly in form of concentrated discharge (springs) with the localized occurrence of thermal brines with an upward rising hydrostatic pressure probably associated with the confined nature of the aquifer at depth.

Groundwater constituents are an important source of hydrogeochemical information about earth surface weathering processes (Garrels *et al.* 1967). Therefore, in-depth knowledge of the solute composition could assist in constraining the major chemical reactions contributing to groundwater mineralization (White et al. 1963; Polzer and Hem 1965; Bricker et al. 1968; Teddy 1971; Hem 1977; Freeze and Cherry 1979; Drever 1988; and Diop and Tijani 2014). According to Batabyal (2017), hydrogeochemical studies give a clear comprehension of the subsurface geologic environments and the processes involved in the chemical evolution of groundwater. These processes are largely controlled by the physical and chemical interactions between groundwater and the aquifer materials (Nyende et al. 2014) resulting in its seasonal, temporal, and spatial variations in chemistry and consequently quality (Rajmohan and Elango 2004). Furthermore, the complex interactions of multiple factors such as geology, mineral composition of an aquifer, weathering, water-rock interactions, topography, tidal effects, climate, and anthropogenic activities are important determinants of groundwater chemistry (Mohapatra et al. 2011; Sigh *et al.* 2011; and Belkhiria et al. 2012). This implies both geogenic and anthropogenic sources contribute to the water chemistry and quality. For instance, Kumar (2013), studied groundwater chemistry and identified natural processes as controlling factors of the hydrochemistry, while Ishaku et al. (2012) identified anthropogenic contaminations, natural mineralization, and cation exchange as factors controlling the hydrochemistry.

Different studies (Orajaka 1972; Offodile 1976; Egboka and Uma 1986; Uma et al. 1990; Uma and Loehnert 1992; Loehnert and Uma 1992; Tijani et al. 1996; Loehnert *et al.* 1996; Tijani 1997; Tijani and Uma 1998; Tijani 2004; and Umar and Igwe 2019) have been carried out on the chemistry of groundwater resources within the Benue Trough using different geochemical approach (isotopes, chemical and geophysical data) to decipher its salinity origin. However, Batabyal (2017) recognized that human factors such as groundwater over-abstraction and excessive application of chemical fertilizers can result in some degree of groundwater salinization. Locally, in the study area, specific information on the hydrogeochemical interaction of the groundwater and the aquifer materials is lacking or rather have been discussed "in-passing".

It is upon this backdrop that this work is aimed at evaluating the influence of hydrogeochemical processes on the water systems at the Uburu-Okposi area. The multivariate statistics, Principal Component Analysis (PCA), Piper diagram, and PHREEQC modeling of speciation index for mineral phase were deployed to analyze the hydrochemical characteristic of groundwater. This was achieved with the following specific objectives as; (1) to characterize aquifer waters via piper diagram, and (2) to identify the hydrochemical controls on the groundwater chemistry via saturation index, ionic ratios, and scatter plots to also understand discernible patterns.

1.1 Geology and Hydrogeology of the Study area

Abakaliki and its environs are underlain by the Southern Benue Trough (Reyment 1965). The origin of the Benue rift is closely associated with the breakup of Gondwanaland during the separation of the African and South American Plates, and the opening of the South Atlantic Ocean, in the Early Cretaceous (Wright 1976). Benkhelil *et al.* (1989), described the Benue Trough as an intracratonic rift system or an intercontinental Cretaceous Basin trending in a NE-SW direction.

The southern section of the trough (Fig. 1), which underlies most parts of Southeastern Nigeria, has a stratigraphic record of deposits represented by sediments of three main marine depositional cycles: Albian-Cenomanian, Turonian-Santonian, and Campano-Maastrichtian (Reyment 1965). The first marine transgression in the trough is generally believed to have started in the mid-Albian period with the deposition of the Asu River Group made up of predominantly shales and localized occurrences of sandstone, siltstone, and limestone facies (Hoque and Nwajide 1988). According to Simpsons (1954), the Asu River Group is the oldest sedimentary rock in southeastern Nigeria. It is well exposed around the Abakaliki axis where they are locally referred to as "Abakaliki Shale". They are overlain by the Eze-Aku Formation, with no defined evidence to suggest the break between the Asu River Group and the Eze-Aku Shale, although the junction has not been seen. Locally, the Uburu-Okposi area is underlain by two principal geologic units comprising the Asu-River Shale and Eze-Aku Shale Formations (Fig. 2). To the NW axis of the study area lies the Awgu Formation made up of predominantly Shales.

Hydrogeologically, the saline groundwaters in the study area are primarily confined to the predominantly shaly marine deposits (Asu-River Group) just like other parts of the Benue Trough where similar saline groundwaters abound. The occurrences of saline groundwaters in these areas are usually in the form of springs and ponds (Tijani 2004), with a typical uprising thermal spring spot at Uburu saline lake. However, the variation in the local lithology at the outcrop sites from predominantly shale in the lower region to sandstones (with intercalation of shale/limestone units) in the middle region suggests that the saline groundwaters are not lithologically controlled (Uma and Loehnert 1992). Rather, the occurrences and movements are controlled by the fracture systems in the trough.

2. Materials And Methods

Sampling and In-situ Measurements

The chemical characteristics of groundwater resources in Uburu-Okposi were determined via the collection of forty (40) samples into colorless polyethylene bottles (60cl for anions and 100ml for cations) from different sources. The sample bottles for the cation analyses in the laboratory were acidified immediately with three drops of Nitric acid (HNO_3^-) to; (i) ensure the stability of samples (ii) avoid absorption on the wall of the container. Before sampling, the sample bottles were pre-rinsed with distilled water while on-site, each bottle was rinsed thrice with the water to be sampled before samples were collected. However, the samples were filtered in-situ using 0.45 Im membranes.

At each sampling location, pH (precision \pm 0.01), Electrical Conductivity; EC (precision \pm 1 µS/cm), and Total Dissolved Solids; TDS (precision \pm 2 mg/l) were measured in-situ using a portable hand-held multi-parameter meter according to Haritash et al. (2017). Furthermore, geographical coordinates of each sample location were noted with a global positioning system (GPS) to mark them on the map (Fig. 2) and site-specific conditions noted. All the samples were stored in an icebag and transported within 48 hours (two days) of collection to the laboratory for chemical analysis.

Laboratory Analysis

In the laboratory, cations such as Calcium (Ca²⁺), Magnesium (Mg²⁺), Sodium (Na⁺), Potassium (K⁺), and Iron (Fe²⁺) were determined using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) while anions like Bicarbonate (HCO_3^-), Chloride (Cl⁻), Carbonate ($CO_3^{2^-}$), Sulphate (SO₄²⁻), Phosphate (PO₄³⁻) and Nitrate (NO₃⁻) were analyzed for using Ion Chromatography (IC). However, for quality control/ assurance to ensure reliability and accuracy of results, blank samples were sent for chemical analyses and charge balance errors (CBE) were estimated for major ions in the water samples (Appelo and Postma 2005). All the samples had CBE within limits of ± 5% according to Freeze and Cherry (1979). Consequently, laboratory data were subjected to further evaluation.

Statistical Analysis

Physicochemical parameters of the forty (40) groundwater samples were subjected to statistical evaluation through multivariate statistical analysis. This was achieved utilizing principal component analysis (PCA) in a bid to evaluate factors influencing the groundwater chemistry and sources of pollution in the aquifers (Kura *et al.* 2013). Among the families of multivariate statistical analysis, PCA is the most widely used technique (Ranjan et al. 2012; and Kura *et al.* 2013). It is a technique that identifies patterns in data and then presents them based on their similarities and differences. Delineating patterns in data with a complex relationship is not an easy task, thus utilizing PCA in such a case would provide a reliable result (Smith 2012; and Kura *et al.* 2013). The main objective of PCA is to summarize a multivariate dataset by reducing the statistical noise in the data, exposing the outlier, and then arranging the components in descending order (from the largest contributor to the least) as accurately as possible with as few principal components as possible (Panteleit et al. 2001). Variables are normalized individually to unit variance and, as such, contribute equally when the correlation matrix is used (Farnhana et al. 2004).

3. Results

Ion Distribution

Table 1 presents the statistical summary of the physicochemical parameters of groundwater resources of the Uburu-Okposi area. The pH value of the water samples ranges from 5.3 to 8.9, averaging 6.7 short of seawater value (8.22 mg/l) with Cv < 15% (Table 1). The samples' pH values were

slightly acidic reflecting the dominance of acidic species such as Chlorine (Cl⁻) and alkaline species like Na⁺ over the lower concentrations of the alkaline earth such as Ca²⁺ and Mg²⁺ (Haritash et al. 2017). TDS range from 112 to 4670 mg/l varying considerably among samples (Cv > 100%) with an average 657 mg/l concentration falling behind its equivalent seawater concentration. Thus, the samples are classified as fresh water in line with Freeze and Cherry (1979) pointing to diluted saline water in pore spaces of the underlying geology. EC is the indirect inference of TDS present in groundwater. Here, EC range from 206 to 6970µS/cm, with an average value of 987 µS/cm, corresponding with the range in the measured TDS value, thereby reflecting low mineralized groundwater due to infiltration in the area.

Furthermore, the trend in abundance of cations and anions concentrations follows; $Na^+ > Ca^{2+} > K^+ > Mg^{2+}$ and $Cl^- > HCO_3^- > NO_3^- > SO_4^{2-} > PO_4^{3-} > CO_3^-$ orders, respectively. Na^+ and Cl^- constitute more than 75% separately in most cases (Table 1, Fig. 3a and b), reflecting Na-Cl dominated water type in the area. Na^+ ranges from 4.4 to 4900 mg/l averaging 209.76 mg/l, which is lower than a standard seawater value (Table 1). Likewise, K^+ ranges from 0.5 to 1550 mg/l averaging 53.7 mg/l, still far behind a standard seawater value according to Sandford and Wood (1991). High Na^+ and K^+ concentrations compared to Ca^{2+} and Mg^{2+} in the southern part of the study area are attributed to the salinization process or effects of silicate weathering. The high Ca^{2+} concentrations observed in the northern extension of the study area (Fig. 3) can be linked with carbonate dissolution of the underlying calcareous shale and associated lenses of carbonate layers. The high concentration of Ca^{2+} and Mg^{2+} in samples 2, 15, and 31 is an indicator of possible water hardness. This was corroborated by the values of their estimated total hardness which were generally > 180 mg/l and thus; categorized as very hard water.

However, Cl⁻ concentrations range between 14.4 to 6300 mg/l (average: 277.42 mg/l). Though Cl⁻ was short of a standard seawater value (Table 1), high Cl⁻ concentrations were recorded by the two saline lakes and a borehole sample (about 50-100m to the saline lake) depicting possible hydraulic connection with these lakes resulting in its increased salinization. HCO_3^- concentration was found to be in sync with the hydrogen ion concentration (pH) of the samples as it varies from 6.1 to 244 mg/l with an average of 58.5 mg/l expected (usually low) of a typical seawater concentration. The observed HCO_3^- range is probably attributed to a low concentration of the divalent cations of Ca^{2+} and Mg^{2+} in the study area causing mild hardness. NO_3^- concentration in the study area ranges from 20.9 to 69.8 mg/l with an average of 42.5 mg/l. The recorded high values are likely connected to anthropogenic sources vis-à-vis irrigation return flow and domestic wastewater discharge from septic tanks.

Physico-chemical parameters were graphically displayed to discern the analogous relationship existing among the variables (outlier values from samples 15 and 31 were not inclusive). Figure 4 depicted the parameters are moderately-weakly correlated with each other. Na-Mg, K-Mg, Cl-Mg, K-Na, and Cl-Na are positively and moderately correlated with correlation coefficients (R): 0.41, 0.46, 0.49, 0.33, and 0.65 respectively. No correlation was observed for HCO₃-Na, Cl-HCO₃, SO₄-HCO₃, SO₄-Mg, and SO₄-Na with correlation coefficients (R): 0.01, 0.01, 0.03, 0.03, and 0.05 respectively. It can be inferred from Fig. 4 that the samples have undergone diverse hydrogeochemical processes such as ion exchange, recharge, water-rock interaction, and weathering of carbonate minerals and mixing of fresh and saline water, etc.

Table 1	
Statistical Summary of the Physico-Chemical Parameters (Se	awater value
after Sandford and Wood 1991)	

S/N	Parameters	Min.	Max.	Ave.	CV.	Seawater
1	рН	5.29	8.89	6.69	10	8.22
2	EC (µS/cm)	206	6,970	987	142	-
3	TDS (mg/l)	112	4,670	649	144	35,145
4	TH (mg/l)	1.66	1,1256	402	440	-
5	Ca ²⁺ (mg/l)	0.39	414.02	45.34	186	412
6	Mg^{2+} (mg/l)	0.16	512	20.43	397	1,292
7	Na ⁺ (mg/l)	4.40	4900	209.76	382	10,768
8	K ⁺ (mg/l)	0.51	1,550	53.72	462	380
9	Fe ²⁺ (mg/l)	0	1.50	0.16	245	-
10	Cl⁻ (mg/l)	14.40	6300	277.42	363.88	19,353
11	HCO ₃ ⁻ (mg/l)	6.10	244	58.50	103	142
12	CO ₃ ²⁻ (mg/l)	0	0	0	625	-
13	SO ₄ ²⁻ (mg/l)	0	7.49	0.71	229	2,712
14	P04 ³⁻ (mg/l)	0.03	3.10	0.35	147	-
15	NO ₃ ⁻ (mg/l)	20.89	69.83	42.54	24.62	-

4. Discussion

Geochemical Modelling

Chemical composition in different areas is principally influenced by the presence of different solutes derived from rocks and soils weathering and erosion or the atmosphere (Saleh et al. 1999). As groundwater flows through diverse aquiferous materials, rock-water interaction influences the dominance of ionic species. Saturation/Speciation index (SI) is the deviation of water from equilibrium to dissolved minerals, quantitatively, it is useful in distinguishing different stages of hydrochemical evolution and gives an insight into the processes controlling groundwater and surface water chemistry by predicting the possible reactivity of the subsurface mineralogy (Disli 2017).

Geochemical modeling was performed using the default value of 25°C using the PHREEQC.v.2 software (Parkhurst and Appelo, 1999). The PHREEQC.v.2 software allows the calculation of solute thermodynamic and saturation conditions relative to selected mineral phases (Halite, NaCl; Mirabilite, Na₂SO₄; Rhodochrosite, MnSO₄; Siderite; FeSO₄; Dolomite, CaMg(CO₃)₂; Calcite, CaCO₃; Aragonite, CaCO₃; Magnesite, MgCO₃; Nahcolite, NaHCO₃, and Anhydrite; CaSO₄) in accordance to the locality's lithology (Hallouche et al. 2017). Mineral dissolution or precipitation is limited by the saturation indices for each mineral (Deutsch 1997). The SI of any mineral can be calculated using the formulae;

SI = log IAP/ kt;(1)

Where; kt: Equilibrium solubility product of chemical specie involved, and IAP: Ion Activity Product of dissociated chemical specie in solution.

A saturation index less than zero (SI < 0) implies undersaturation with a particle mineral species and thus, the mineral tends to dissolve in the water present. Saturation index equal to zero (SI = zero), an equilibrium condition exists between the water and the mineral which may control the constituent concentration present in that mineral while saturation index greater than zero (SI > 0) indicates supersaturation of a mineral species in the solution and thus the mineral would precipitate or crystallize out of solution (Truesdell and Jones 1974; Subyani 2005; and Cidu et al. 2009).

Table 2 presents the SI results while it is graphically represented by Fig. 5. The water samples in the study area were generally supersaturated with $CaMg(CO_3)_2$, $CaCO_3$, $MgCO_3$ with saturation indexes 5.58–11.05, 1.77–5.68, 1.91–5.81, and 0.96–4.75 respectively. The sample SI concentration for Na_2SO_4 , $NaHCO_3$ and NaCl, $FeSO_4$, $MnSO_4$, and $CaSO_4$ varied from undersaturated-supersaturated. Supersaturation of carbonate phases may influence the groundwater composition and could result in the precipitation of calcium (Ca^{2+}) and/or Ca-Mg carbonate under suitable

physicochemical conditions. In Fig. 5, 40% of the groundwater samples were undersaturated with $CaSO_4$, which implies that sulphate $(SO_4^{2^-})$ presence is not a major influence on the groundwater chemistry in the study area.

Dissolution of evaporites such as NaCl, $CaSO_4.2H_2O$, Na_2SO_4 will result in salts accumulation during water-rock interaction (Horst et al. 2011; and Mongelli et al. 2013). This probably explains the salinity in the saline lake samples 15 and 31 where NaCl supersaturated was recorded (Fig. 5). However, gypsum is more soluble in water with an important chloride component and high ionic strength, compared to fresher water, due to the lower activity coefficient (Sacks and Tihansky 1996). Thus, though samples 1, 3, 4, 5, 6, 8, 27, and 30 had higher sulphate concentrations, they were more under-saturated with anhydrite than sample 15 which is sulphate rich. This is confirmed by the characteristic foul smell possibly associated with H_2S formation in samples 10, 13, 14, 18, 32, 33, 34, 36, and 37.

The saturation or supersaturation of carbonate minerals in saline samples could be due to an increase of HCO_3^- concentration resulting from SO_4^{2-} reduction, Ca^{2+} release from cation exchange, as well as Mg^{2+} increase due to the incongruent dissolution of dolomite (Appelo and Postma 2005; and De Montety et al. 2008). The precipitation phenomenon is illustrated by Eqs. 2 and 3;

Table O

S/N	CaCO ₃	CaCO ₃	CaSO ₄	CaMg(CO ₃) ₂	CaHCO ₃	MgCl	MgSO ₄	MgCO ₃	NaCl	Na ₂ SO ₄	NaHCO ₃	FeSO ₄	MnSO ₄
1	4.44	4.58	-4.58	8.72	-3.62	-2.35	-5.06	3.65	-2.93	-7.04	-5.71	-4.08	-11.50
2	4.76	4.90	-4.71	9.71	-1.70	-1.99	-4.85	4.32	-3.08	-7.34	-3.95	-4.20	-11.84
3	3.38	3.52	-5.78	7.09	-4.68	-3.62	-5.76	3.09	-4.90	-8.45	-6.98	-5.15	-14.52
4	4.59	4.73	-4.65	9.30	-3.47	-2.40	-4.86	4.08	-3.66	-7.52	-5.96	-4.15	-11.69
5	5.15	5.29	-4.19	10.34	-1.76	-0.90	-4.49	4.55	-1.74	-6.73	-3.93	-3.74	-10.53
6	3.95	4.09	-5.23	8.33	-4.11	-2.82	-5.11	3.75	-4.33	-8.02	-6.53	-4.66	-13.14
7	3.93	4.07	0.09	8.47	-4.13	-2.27	0.38	3.91	-3.38	-2.13	-5.98	0.08	0.22
8	4.31	4.45	-6.62	8.76	-3.45	-2.75	-6.79	3.83	-4.09	-9.53	-5.99	-5.89	-16.62
9	4.69	4.83	0.85	9.38	-2.67	-2.72	0.53	4.06	-4.30	-2.45	-5.60	0.76	2.13
10	4.65	4.79	0.81	9.10	-2.71	-2.03	0.28	3.81	-2.75	-1.83	-4.99	0.73	2.05
11	4.07	4.21	0.23	8.57	-4.00	-2.82	0.35	3.88	-4.36	-2.59	-6.44	0.20	0.57
12	4.08	4.22	0.24	8.60	-3.98	-2.81	0.36	3.89	-4.35	-2.58	-6.43	0.21	0.61
13	4.53	4.67	0.69	8.85	-2.53	-3.01	0.16	3.69	-4.48	-2.71	-5.56	0.61	1.73
14	4.63	4.77	0.79	8.76	-2.66	-2.80	-0.03	3.50	-3.63	-2.25	-5.33	0.70	1.97
15	1.77	1.91	-2.21	8.20	-0.75	2.26	-2.72	0.96	2.29	-4.09	-2.25	-1.97	-5.55
16	3.30	3.44	-0.54	6.62	-4.76	-3.64	-0.84	2.69	-3.79	-2.39	-6.24	-0.48	-1.36
17	3.90	4.04	0.06	8.25	-3.46	-3.06	0.19	3.72	-4.47	-2.62	-5.77	0.05	0.14
18	3.60	3.74	-0.24	7.54	-4.46	-3.48	-0.23	3.30	-4.34	-2.49	-6.34	-0.21	-0.59
19	4.42	4.56	0.58	9.23	-3.64	-1.79	0.65	4.18	-3.33	-2.29	-6.14	0.52	1.46
20	3.58	3.72	-0.26	7.51	-4.48	-3.70	-0.23	3.30	-5.22	-3.15	-7.00	-0.23	-0.66
21	4.42	4.56	0.58	9.10	-2.69	-2.65	0.52	4.05	-3.79	-2.01	-4.91	0.51	1.4
22	4.65	4.79	0.81	9.46	-2.33	-2.60	0.65	4.18	-4.02	-2.17	-4.94	0.72	2.02
23	3.83	3.97	-0.01	7.91	-2.65	-3.12	-0.08	3.45	-3.11	-1.47	-3.74	-0.01	-0.03
24	4.60	4.74	0.76	8.91	-2.46	-3.19	0.16	3.69	-4.85	-2.90	-5.75	0.67	1.90

25	3.55	3.69	-0.29	7.49	-3.61	-3.69	-0.22	3.31	-4.14	-2.06	-5.01	-0.26	-0.73
26	4.71	4.85	0.87	9.20	-2.27	-3.31	0.33	3.86	-5.11	-2.86	-5.63	0.77	2.18
27	2.64	2.78	-7.71	5.58	-5.42	-4.70	-7.74	2.30	-3.87	-8.32	-5.65	-6.87	-19.38
28	3.47	3.61	-0.37	7.40	-3.59	-3.58	-0.23	3.30	-4.55	-2.61	-5.46	-0.33	-0.93
29	4.65	4.79	0.81	9.26	-2.20	-2.85	0.44	3.97	-4.21	-2.31	-4.96	0.72	2.04
30	4.39	4.53	-5.09	8.92	-3.67	-2.54	-5.26	3.90	-3.77	-7.90	-6.11	-4.53	-12.78
31	5.67	5.81	1.83	11.05	-0.97	0.42	1.22	4.75	0.94	0.34	-2.10	1.63	4.60
32	4.67	4.81	0.83	9.35	-2.25	-2.35	0.52	4.05	-3.72	-2.25	-4.96	0.74	2.08
33	4.48	4.62	0.64	9.28	-2.28	-2.31	0.64	4.17	-3.40	-1.85	-4.40	0.57	1.60
34	4.46	4.60	0.62	9.07	-2.46	-2.59	0.46	3.99	-4.04	-2.39	-5.09	0.55	1.55
35	4.70	4.84	0.86	8.99	-2.22	-2.97	0.14	3.67	-3.96	-2.25	-4.96	0.76	2.15
36	4.77	4.91	0.93	8.82	-1.99	-3.37	-0.12	3.41	-4.39	-2.54	-5.09	0.83	2.35
37	4.67	4.81	0.83	9.20	-2.18	-2.98	0.36	3.89	-4.76	-2.81	-5.46	0.74	2.09
38	4.36	4.50	0.52	8.77	-2.92	-3.10	0.25	3.78	-4.75	-2.80	-5.87	0.46	1.31
39	4.65	4.79	0.81	9.39	-2.03	-1.76	0.57	4.10	-2.57	-1.63	-4.10	0.72	2.04
40	4.65	4.79	0.81	9.38	-2.03	-1.76	0.57	4.10	-2.57	-1.63	-4.10	0.72	2.04

Table 2

Ionic Ratios

The variation in the major cation/anion chemical concentrations in groundwater and observed water types indicates an integration of processes controlling its geochemistry in the aquifer. HCO_3^- dominance in groundwater suggests organic matter decomposition, carbonate dissolution, and probably an atmospheric influence on CO_2 (g) dissolution as some of the processes responsible for observed hydrochemical distribution.

Figure 6 suggests the mechanisms controlling the hydrochemistry of the studied groundwater while the saturation indices (Fig. 5) support the discussion (Mapoma et al. 2017). The likelihood of carbonate dissolution, silicate weathering, and evaporite dissolution was investigated using a bivariate plot of HCO₃⁻/Na⁺ vs Ca²⁺/Na⁺ (meq/I) and Mg²⁺/Na⁺ vs Ca²⁺/Na⁺ (meq/I) (Mukherjee and Fryar 2008; Halim et al. 2010; and Mapoma et al. 2017).

Bivariate plots of HCO_3^{-}/Na^+ vs Ca^{2+}/Na^+ and Mg^{2+}/Na^+ vs Ca^{2+}/Na^+ revealed three data clusters points. These are cluster 1: carbonate dissolution, cluster 2: silicate weathering and Cluster 3: evaporite dissolution (Fig. 6a and b). Furthermore, these plots (Fig. 6a and b) revealed that silicate weathering influnces groundwater geochemistry compared to carbonate weathering and evaporite dissolution. Mg^{2+} versus Ca^{2+} normalized plot shows that Mg^{2+} is mostly influenced by both carbonate dissolution and silicate weathering as the plots scatter in the region of silicate weathering-carbonate dissolution. Therefore, aluminosilicates, silicates, and carbonates (dolomite) are responsible minerals for the presence of Mg^{2+} (Mapoma et al. 2017). This is supported by the SI (Fig. 5), which revealed that carbonate end members vis-a-vis magnesite and dolomite are supersaturated in the water, hence confirming that the dissolution of $MgCO_3$ and $CaMg(CO_3)_2$ are responsible for the observed Mg^{2+} levels.

The plot of $Ca^{2+} + Mg^{2+}$ versus HCO_3^- reveals most samples scatter along a 1:1 line (Fig. 7a), indicating that these solutes are primarily contributed by carbonate (calcite and dolomite) dissolution except samples 15 and 31 (Hallouch *et al.* 2017). Figure 6b further reveals the presence of carbonate dissolution and silicate weathering processes occurring in the study area causing excess Ca^{2+} concentration probably linked with anhydrite dissolution.

Furthermore, the Ca^{2+}/Mg^{2+} ratio indicates calcite dissolution in groundwater (Mayo and Loucks, 1995). Generally, the Ca^{2+}/Mg^{2+} ratio of groundwater in sedimentary rocks is > 1; this is due to Ca^{2+} predominance in this type of rock, including water movement in gypsiferous formations

(Schoeller 1964). Ca^{2+}/Mg^{2+} values < 1 indicate Mg^{2+} contribution from dolomite and dolomitic limestone. In this study, Ca^{2+}/Mg^{2+} range from 0.68-15.00 and were generally greater than 1 (Table 3). This implies the occurrence of calcite and silicate dissolution.

The Ca^{2+} vs SO_4^{2-} scatter plot (Fig. 7b) revealed data points distribution in two clusters. The first cluster plotted near the gypsum dissolution line or 1:1 equiline is indicative of a simultaneous increase of calcium and sulphate ions. This pattern indicates contribution most likely from the dissolution of gypsum and or anhydrite (Garrels and Mackenzie 1971), which is confirmed by the linear evolution of both gypsum and anhydrite SI and the sum of calcium and sulphate (Fig. 7c). The second cluster is situated below the 1:1 line which about 72.5% of these samples had Ca^{2+}/SO_4^{2-} ratios widely lower than 1. The SO_4^{2-} excess relative to Ca^{2+} could be due to precipitation of calcite, gypsum dissolution, and the loss of Ca^{2+} instead of Na⁺ during the cation exchange reaction.

According to Hui et *al.* (2020), the source of Na⁺ and Cl⁻ can be traced using the Na⁺/Cl⁻ ratio. If the ratio is unity (1), the ions source from halite dissolution; contrary to this, the ions originate from silicate dissolution, ion exchange, etc. Therefore, since the Na/Cl ratio in the study area ranges from 0.16-7.00 meq/l, they reflect inputs from sources other than halite dissolution such as silicate weathering, ion exchange, and anthropogenic sources (Table 3). The abundance of Na⁺ may signify that cation exchange and halite dissolution are plausible in the area (Mapoma et al. 2017; and Merkel and Planer-Friedrich 2005). However, silicate weathering and cation exchange are more responsible for the observed levels of Na⁺ and Cl⁻ ions in water samples from Uburu-Okposi saline field areas (Fig. 7c). Though contributions from halite dissolution cannot be ruled out as a possible source of Na⁺ and Cl⁻ in the area, the excess Cl⁻ relative to Na⁺ in the water samples could also possibly emanate from irrigation returns through the infiltration of runoffs or must have been in the fluid since deposition as chloride ion is conservative. Moreover, infiltrating waters transiting diverse subsurface horizons tend to leach evaporites constituents of the formation thereby contributing to the elevated Na⁺ levels in groundwater.

Ion Exchange Process

Groundwater chemistry can be well understood via careful study of its interaction with rocks-soil through which it percolates/resides. According to Schoeller (1977), Chloro-Alkaline Index (CAI) suggested ionic exchange between groundwater and its host environment during residence time or travel times. It can be estimated using equations 4 & 5 below:

$$CAI-I=\frac{(Cl-(Na-K))}{Cl} \qquad(4)$$

$$CAI-II = \frac{Cl - (Na - K)}{SO_4 + HCO_3 + CO_3 + NO_3}$$

Positive CAI values suggest that Na⁺ and K⁺ of groundwater are exchanged with Ca²⁺ and Mg²⁺ of host rocks, and vice-versa. Table 3 reveals CAIand CAI-II range from – 6.22 to 0.78 (average = -0.3) and – 20.05 to 4.03 (average= -0.55) respectively. Although about 65% of the samples had positive CAI values, illustrating direct base-exchange reaction (Fig. 8), their average values of -0.3 and – 0.55 indicate that indirect base-exchange reaction is the principal factor controlling water chemistry in the study area. This is because monovalent cations (Na⁺ and K⁺) from the host rocks are exchanged with the divalent cations (Ca²⁺ and Mg²⁺) in the water resulting in significant enrichment in the alkaline metals. The Ca²⁺ ions are substituted by Na⁺ ions on the solid surface, as illustrated in Eq. 6 below.

$$Na - X\frac{1}{2}Ca \rightarrow Na + \frac{1}{2}Ca \dots (6)$$

X is regarded as the soil exchanger when the groundwater encounters Na, which originated from seawater or NaCl (halite minerals) that precipitated on the aquifer matrix. The Na⁺ replaces the Ca²⁺ thereby becoming dominant in the groundwater via cation exchange. Thus, Na⁺ increases in the groundwater solution (Isa et al. 2012), while Cl⁻ remains unchanged due to its ability to resist changes (Kura *et al.* 2013).

	T Statistical Sun	Fable 3 nmary of I	onic ratic	DS
S/N	lonic ratios	Min.	Max.	Ave.
1	CAI-I	-6.22	0.78	-0.30
2	CAI-II	-20.05	4.03	-0.55
3	Na ⁺ /Cl ⁻	0.16	7.00	1.18
4	Ca ²⁺ /Mg ²⁺	0.68	15.00	2.93
5	Mg ²⁺ /Na ⁺	0.00	1.34	0.42
6	Ca ²⁺ /Na ⁺	0.00	6.08	1.20
7	HCO3-/Na+	0.00	3.82	0.74
8	Ca ²⁺ /SO ₄ ²⁻	0.00	718	28.85

Hydrogeochemical Facie Types and Water-Rock Interaction Characteristics

Hydro-chemical characterization of the water samples was carried out to identify the water types while Gibb's diagram revealed the dominant geochemical control on the water chemistry in the study area.

The Piper trilinear diagram (Fig. 9a) showed that 35% of the samples were characterized as Na-Cl type, 15% were Na-HCO₃ type, 25% were Ca-Mg-Cl type while 25% classified as Ca-Na-HCO₃ type (temporarily hard). These samples' temporary hardness was further proven by their alkalinity being greater than their Total Hardness. The heterogeneities characteristic of the aquifers is responsible for the different water types observed. Triangular cationic field showed that 15% of the samples fell into (Ca) dominant type, and 67.5% of samples fell in Na + K type; only 12.5% of the samples fell into the no dominant cation domain. Furthermore, Fig. 9aalso revealed that 65% of the samples fell in fields 2, 4, and 7, suggesting that alkalis (Na⁺ and K⁺) exceed alkaline earth (Ca²⁺ and Mg²⁺), strong acids (SO₄²⁻ and Cl⁻) exceed weak acids (CO₃²⁻ and HCO₃⁻) and non-carbonate hardness dominated. The anionic triangle showed 35% of the samples fell within the HCO₃⁻ field, 65% of the samples fell into Cl⁻ type. While none of the samples fell into the no-dominant field.

The chemical attributes of water and the relative abundance of its chemical constituents may be used to determine the origin of most of the dissolved ions and the processes governing the groundwater chemistry in an area. The principal sources of dissolved ions in inland water are atmospheric deposition, weathering of rock minerals, and anthropogenic inputs (Subramanian 1987). Rock–water interaction or precipitation-based effect were inferred using Gibbs classification. Gibb's plot showed that 92.5% of the water samples plotted in the rock–water interaction field while only 7.5% of the samples (15, 16, and 31) fell into the evaporation-precipitation field (Fig. 9b). This observation is a pointer to the earlier assertion that carbonate and silicate minerals dissolution largely control the groundwater chemistry in the study area. The rock–water interaction process may include the chemical weathering of rocks, dissolution–precipitation of secondary carbonates, and ion exchange between water and clay minerals (Subba Rao, 2006; and Kumar *et al.* 2014).

Multivariate Factor Analyses

According to Hallouche et al. (2017) and Badana et al. (2018), further evaluation of groundwater mineralization mechanisms and the effects of water-rock interactions on the geochemical process can be done using the principal component analysis (PCA). The laboratory results were subjected to PCA using the SPSS statistical tool, version 20. PCA is a multivariate statistical tool used in mapping out association patterns among variables (Xiao et al. 2019).

Here, the PCA approach of statistical data reduction was applied on the chemical parameters using the Varimax rotation with Kaiser Normalization (KN), which considers only the Eigenvalues (EV) that exceeded 1 (Table 4). That is, Principal Component (PC) results were retained for the Eigenvalues greater than 1 (Xu et al. 2019 and Emenike et al. 2020). The scree plot was plotted to also demarcate the Eigenvalues that are greater than 1; these represent the straight line segment that contains the first four points (Fig. 10a). Moreso, the factors were plotted in rotated space (Fig. 10b); to show the relationship between the chemical constituents and if possible to show those with common sources. Four (4) principal component factors were extracted for the Eigenvalues of more than 1, making up 85.34% of the total variance.

In Table 4, the first principal component loading range from -0.13 to 0.97 which accounts for 33.50% of the total variance with a positive but strongly loaded with Ca²⁺ (0.97), Mg²⁺ (0.92), Na⁺ (0.92) and K⁺ (0.96); and moderately loaded with HCO₃⁻ (0.52) respectively. Sources of these elements in the water samples could be mainly from weathering of silicate minerals; carbonate dissolution and cation exchange processes with

very minor inputs from pastoral activities in the area. The second component portrays a contribution of 63.04% total variance and is strongly positively loaded with pH (0.83), EC (0.97), TDS (0.97), and salinity (0.93) in the groundwater samples reflective of recharge via infiltration and dissolution of carbonate materials and organic matter decomposition.

The third factor characterised with a total variance of 76.78% is also strong and positively loaded with Cl⁻ (0.79) and NO₃⁻(0.79) respectively linked with the NaCl dissolution, effluents from sewage, and agro-pastoral activities in the area. By and large, the fourth principal component revealed a very strong loading of PO₃²⁻ (0.96) pointing to irrigation return flow as its likely source due to the application of N.P.K fertilizer on farmlands.

S/N	Parameters	PC1	PC2	PC3	PC4
1	PH	-0.08	0.83	-0.37	-0.02
2	EC	0.04	0.97	0.18	0.03
3	TDS	-0.00	0.97	0.18	-0.06
4	Salinity	0.01	0.93	0.12	0.17
5	Ca ²⁺	0.97	-0.00	0.04	-0.14
6	Mg ²⁺	0.92	0.00	0.26	-0.10
7	Na ⁺	0.92	-0.07	-0.08	-0.03
8	K ⁺	0.96	-0.04	0.11	0.13
9	CI⁻	0.29	0.18	0.79	-0.21
10	HCO ₃ [−]	0.52	0.11	-0.32	-0.10
11	NO ₃ ⁻	-0.13	0.05	0.80	0.28
12	P04 ³⁻	-0.08	0.08	0.07	0.96
13	Eigen Value	4.02	3.55	1.65	1.03
14	% Variance	33.48	29.56	13.74	8.57
15	%Cumulative	33.48	63.04	76.78	85.34

Table 4	
Principal Component	Loadin

5. Conclusion

This study assessed the influence of hydrogeochemical factors vis-à-vis weathering, rock-water interaction, ion exchange; carbonate dissolution, and precipitation on the chemical status of forty (40) groundwater samples from Uburu-Okposi areas. Physico-chemical parameters results revealed a slightly acidic (6.69), and fresh-blackish (122-4,670) water. Cation abundance followed the trend Na⁺ > Ca²⁺ > K⁺ > Mg²⁺ while anions is in $Cl^- > HCO_3^- > NO_3^- > SO_4^{2-} > PO_4^{3-} > CO_3$ trend with Na⁺ and Cl⁻ constituting more than 75% each of the total cation and anion concentration.

Modeling of the geochemical process via SI suggests that groundwater is saturated to oversaturated with Calcite (CaCO₃), Aragonite (CaCO₃), Dolomite (MgCO₃)₂, and Magnesite (MgCO₃) but undersaturated with Thernadite, Nahcolite (NaHCO₃), and Halite (NaCl). Bivariate plots such as HCO_3^{-}/Na^+ vs Ca^{2+}/Na^+ and Mg^{2+}/Na^+ vs Ca^{2+}/Na^+ and lonic ratios like Na^+/Cl^- , Ca^{2+}/Mg^{2+} , Ca^{2+}/Na^+ , Ca^{2+}/SO_4^{-2-} , indicated that ion exchange, mineral weathering, and salinization processes are the hydrogeochemical factors controlling groundwater chemistry in the study area.

However, other factors include evaporation and anthropogenic activities (domestic wastewater discharge, use of fertilizer, septic tank discharge, and industrial wastewater). On the other hand, Piper trilinear diagram revealed varying hydrochemical facies types such as Na-Cl (35%), 15% as Na-HCO₃, 25% as Ca-Mg-Cl (permanently hard waters) while 25% were temporarily hard falling into the Ca-Mg-HCO₃ water types. Furthermore, the Piper diagram also pointed out that 65% of the samples had alkaline metals (Na⁺ and K⁺) composition exceeding alkaline earth (Ca²⁺ and Mg^{2+}), strong acids (SO_4^{2-} and Cl^-) exceed weak acids (CO_3^- and HCO_3^-) and non-carbonate hardness dominated. To better understand the influence of natural hydrogeochemical processes on the groundwater chemical composition, Gibbs plots show that rock-water interaction (about 92.5% of the samples) and evaporation (about 7.5% of the samples) are key controlling factors. Lastly, PCA revealed four components factors with the first three components factors vis-à-vis Factor 1, 2, and 3 accounting for more than 75% of the total variation. Each PC loading/factor reflects water-rock interactions in the geochemical process.

Declarations

Tijani Moshood: Supervision//Conceptualization

Tunbosun Owolabi: Formal Analysis, and Writing- Original Draft Preparation

Nnamdi Obini: Investigation, Formal Analysis, Writing- Review and Editing

Compliance with Ethical standards: This research work was conducted under every known ethical standard(s).

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Ethical standards: This work was conducted under all acceptable ethical and professional conduct.

Availability of data and materials: The data and materials used for this research are readily available.

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Figures



Figure 1

Map of the Benue Trough of Nigeria (Modified from Obaje et al. 1999)





Pie-chart showing lonic distribution (a) Cation and (b) Anions

Figure 4

a-j Relationship between different hydrochemical parameters



a-f Saturation level of samples 1 - 40





Bi-plots (a) HCO_3^-/Na^+ (meq/l) (b) Mg^{2+}/Na^+ Vs Ca^{2+}/Na^+ (meq/l)

Figure 7

Bi-plots (a) $Ca^{2+} + Mg^{2+} Vs HCO_3^{-} (meq/I)$ (b) $Ca^{2+} Vs SO_4^{2-} (meq/I)$ and; (c) SI Anhydrite Vs $Ca^{2+} / SO_4^{2--} (meq/I)$



CAI plot for analyzed samples



- **a.** Piper diagram for the study water samples showing the facies types
- b. Gibbs diagram for geochemical factors controlling water chemistry in the study area



Graphical Plot PCA Results (a) Scree plot and; (b) Rotated space plot