

Hydrochemical characteristics of groundwater of a coastal aquifer in Southsouth Nigeria

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ABSTRACT

The hydrochemical characteristics and quality of the shallow groundwater of the Warri coastal aquifer were studied by using chemical composition (groundwater chemistry), graphical plots, ionic ratios, and estimation of ionic delta and seawater mixing index of the groundwater samples. Twenty groundwater samples were collected from hand dug wells and analyzed for major cations like Ca^{2+} , Mg^{2+} , K^+ and Na^+ , anions like SO_4^{2-} , HCO_3^- , NO_3^- and Cl^- ; and heavy metals like Pb^{2+} , Ni^{2+} and Cd^{2+} . Results of the analysis revealed that rock weathering, cation exchange processes and anthropogenic processes are the major contributors to the chemical compositions of the groundwater. The groundwater classified into two water types namely, $CaHCO_3$, and $NaCl$ water types. The estimated seawater fraction ranged from -0.746 to 0.4887 with a mean of 0.34% for $NaCl$ -type water and a mean of -0.105 % for $CaHCO_3$ -type water. Seawater mixing indexes ranged from 0.244 to 1.127. Ionic delta, seawater fraction and seawater mixing indices revealed that the groundwater from areas closer to the coast is more impacted by seawater-freshwater interactions than that from the upland areas. Among the physiochemical and biological parameters measured (pH, EC, TDS, TH, SO_4 , Cl, HCO_3 , NO_3 , Ca, Mg, Na, K, Pb, Ni, Cd, fecal coliform, total bacterial,) only nitrate (NO_3), sulphate (SO_4) and total bacteria (Bac.) have concentrations below the stipulated WHO (1993) guideline values, indicating that the groundwater of the area is not suitable as drinking water.

Keywords: Groundwater quality, salinization, seawater ratio, ionic ratio, Warri.

INTRODUCTION

Coastal environments globally are characterized by increased urbanization, increased industrialization, overpopulation, over abstraction of water wells and salinization problems [1-7] reported that over 80% of the world's population live along the coast and utilize local aquifers for their water supply. In West Africa for example, the coastal cities are densely populated (Lagos-17.5million, Port Harcourt-1.3million, Accra-2.2million, Abidjan-7.1million, Dakar-2.4million, Monrovia- 970,824). Also, most of the countries' industries are located in the coastal cities/areas (Accra for Ghana, Lagos, Port Harcourt and Warri for Nigeria, Dakar for Senegal and Monrovia for Liberia). High population pressure, intense human activities, inappropriate resource use and absence of proper management practices lead to the deterioration of groundwater resources in most coastal environments [8].

The current study area, Warri, is a coastal town located strategically in the Niger Delta area of Nigeria and it is an operational base for many of the oil producing and servicing companies in Nigeria. Its population is estimated to be over a million people. The potable water supply in the city both from the government agency (state public water utilization board) and individuals is predominantly from groundwater. As urbanization and industrialization continue to increase so does the generation of domestic and industrial wastes, increased construction of individual domestic septic tanks, indiscriminate drilling of boreholes with its attendant over-abstraction and possible saline water

intrusion into the groundwater resources. Previous works on the coastal aquifer in Warri area centered mainly on the determination of the suitability and potability of groundwater resources for drinking and domestic uses. For example, [9] linked high concentrations of iron, lead and nickel in dug-well water from the Warri area to contamination from petroleum chemicals. [10] found a high coliform count in the bacteriological determination of groundwater from the Deltaic Plain Sands aquifer underlying Warri. [11] showed elevated levels of lead (0.56mg/l) and low pH values ranging from 5.10 – 6.35 in rain water collected in Warri and environs. This present work is aimed at determining the hydrochemical characteristics of the coastal aquifer so as to understand the nature and degree of occurrence of salinization in the area. This knowledge will aid in the groundwater management practices of the area.

The Study Area

Warri is located between latitude 5°35' N and 5°35' N and longitudes 5°29' E and 5°48' E. It is within the oil rich province of Nigeria, some 30 km away from the shores of the Atlantic Ocean. It is a nearly flat, low-lying area with very gentle slope towards River Warri and its tributaries that empty their water into the Atlantic Ocean (Figure 1).



Figure 1: Google Earth map of Warri showing groundwater sampling stations

The mean elevation above sea level is six meters. The climate of the area is the tropical equatorial type dominated by two seasons, a long wet season (April to October) and a short dry season (November to March), in response to the interplay between the southwest and northeast trade winds that blow over Nigeria. Annual rainfall is usually in excess of 3000mm, as no month of the year is entirely devoid of rainfall. The mean annual temperature is above 28°C and humidity is about 80% [12].

Niger Delta region is underlain by a sequence of sedimentary formations about 800meters thick, and includes from bottom to top, the Akata Formation, the Agbada Formation, the Benin Formation and the SomeBieiro Warri Deltaic Plain Sands (Table 1; [13]; [14]).

The Akata Formation rests unconformably on the Migmatite –Gneiss basement complex and forms the basal unit of the Niger Delta stratigraphic pile. This formation consists of an open marine facies unit dominated by high-pressured carbonaceous shales. It ranges in age from Paleocene to Eocene and its thickness could exceed 1000m in places. The Agbada Formation consists of a sequence of alternating deltaic sands and shales. It is Eocene to Oligocene in the Niger Delta Basin. The Benin Formation is Oligocene to Plistocene in age and consists essentially of massive and highly porous sands and gravels with a few thin clay intercalations. The uppermost section of the formation is the Quaternary deposit which is about 40 – 150m thick and comprises rapidly alternating sequences of sand and silt/clay with the later becoming increasingly more prominent seawards [15]. The Benin Formation houses

the most productive and hence most tapped aquifer in the Niger Delta region, especially in areas north of Warri where it is at shallow depth.

Table 1: Geologic units of the Niger Delta (after Etu-Efeotor&Akpokodje 1990)

GEOLOGIC UNIT	LITHOLOGY	AGE
Alluvium	Gravel, Sand, Clay, Silt	Recent
Freshwater backswamp, meander belt.	Sand, Clay, some Silt, Gravel	
Mangrove and salt water/backswamps.	Medium fine-grained sands, clay and some silt	
Active/abandoned beach ridges	Sand, Clay and some Silt	Quaternary
Sombeiro –Warri deltaic plain	Sand, clay and some silt	
Benin Formation.	Coarse – medium sand with subordinate silt and clay lenses	Miocene
Agbada Formation	Mixture of sand, clay and silt	Eocene
Akata Formation	Clay	Paleocene

Some Breiro-Warri Deltaic Plain Sands which is Quaternary to Recent in age directly underlies the study area and consists of fine to medium unconsolidated sands that are often feldspathic and occasionally gravelly. The sequence is locally stratified with peat and lenses of soft and plastic clay that could be sandy and shaly. It generally does not exceed 120m in thickness and is predominantly unconfined.

Local hydrogeological setting indicates that Warri city is underlain by the Some Breiro-Warri Plain sand aquifer which consists of fine to medium and coarse grained unconsolidated sands and shales. The aquifer, in most cases unconfined, has thickness that ranges from 60 to 95m and hydraulic conductivity that varies from 8.82×10^{-3} to 9.0×10^{-2} cm/s. Specific capacities recorded from different locations outside Warri city where the unit has been penetrated vary from 6700 lit/hr/m to 13500 lit/hr/m, [16].

MATERIALS AND METHODS

A total of twenty groundwater samples from 20 hand-dug wells within Warri city (Figure 1) were collected in two-liter plastic containers during the month of February. The depths of wells range from 4.1m to 5.4m below ground level. Physical parameters (pH, temperature, total dissolved solids (TDS) and electrical conductivity (EC)) were measured in the field by EC/TDS meter, (Wissenschaftliche Technische Werkstätten (WTW) LF 91 Model) while colour and turbidity were determined with Hach DR/2000 Spectrophotometer. Other parameters were determined in the laboratory and included total hardness (TH) which was determined with Hach Digital Titrator; sodium (Na^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+) and iron (Fe^{2+}) which were analyzed using Atomic Absorption Spectrophotometer (Perkin – Elemer AAS 3110); bicarbonate (HCO_3^-), chloride (Cl^-), nitrate (NO_3^-) and sulphate (SO_4^{2-}) which were analyzed using the colorimetric method with UV spectrophotometer (WPAS110). Lead (Pb), nickel (Ni), and cadmium (Cd) were determined with digital bulk 205 Atomic Absorption Spectrophotometer (AAS) while total bacteria and fecal coliform were determined by Multiple Tube Fermentation Technique.

Seawater mixing index (SMI) was estimated for water of all the sampling locations in order to understand the relative degree of seawater mixing. SMI was estimated using the relation [17]:

$$\text{SMI} = a \times \frac{C_{\text{Na}}}{T_{\text{Na}}} + b \times \frac{C_{\text{Mg}}}{T_{\text{Mg}}} + c \times \frac{C_{\text{Cl}}}{T_{\text{Cl}}} + d \times \frac{C_{\text{SO}_4}}{T_{\text{SO}_4}} \dots\dots\dots 1$$

where

a, b, c and d are constants and represent the relative concentration proportion of Na, Mg, Cl and SO₄ respectively (a = 0.31, b = 0.04, c = 0.57, d = 0.08 –see [17],

C_{Na} , C_{Mg} , C_{Cl} and C_{SO_4} represent concentrations of Na, Mg, Cl and SO₄ respectively measured in groundwater samples expressed in mg/l and

T_{Na} , T_{Mg} , T_{Cl} and T_{SO_4} represent threshold values of Na, Mg, Cl and SO₄ which were estimated from interpretation of cumulative probability curves.

To understand and differentiate the sources of salinization, Ionic delta (Δ) were obtained for all the major ions (Na, K, Mg, Cl, HCO_3^- and SO_4^{2-}) using the mathematical relations described by [18, [19], [20]. For example, Ionic delta (Δ) was calculated using the following relations

$$\Delta C_i = C_{i\text{sample}} - C_{i\text{mixed}} \dots\dots\dots 2$$

where

ΔC_i is the ionic delta of ion i in the groundwater sample,

$C_{i\text{sample}}$ is the measured concentration of the ion i in the groundwater sample,

$C_{i\text{mixed}}$ is the theoretical concentration of the ion iforconservative mix of freshwater and seawater.

The theoretical mixing concentrations ($C_{i\text{mixed}}$) for each ion were calculated using the relation:

$$C_{i\text{mixed}} = f_{\text{sea}} \times C_{i\text{sea}} + (1 - f_{\text{sea}}) \times C_{i\text{fresh}} \dots\dots\dots 3$$

where

f_{sea} isthe seawater content of chloride ion,

$C_{i\text{sea}}$ is the seawater concentration of the ion i, and is $C_{i\text{fresh}}$ is the freshwater concentration of the ion i.

The seawater contribution from the chloride concentration (f_{sea}) wasobtained from the relation:

$$f_{\text{sea}} = \frac{(C_{\text{Clsample}} - C_{\text{Clfresh}})}{(C_{\text{Clsea}} - C_{\text{Clfresh}})} \dots\dots\dots 4$$

where

C_{Clsample} is the chloride concentration in the groundwater sample,

C_{Clfresh} is the freshwater chloride concentration C_{Clsea} is the seawater chloride concentration.

In these calculations chloride was used because it is considered as a conservative tracer [21]; it is usually not removed from the aquifer system due to its high solubility[22]. The only inputs are either from the aquifer matrix salts or from a salinization source like seawater intrusion.

The spatial distribution maps for selected ions were prepared using Rockworks 2006 edition software.

RESULTS AND DISCUSSION

Physiochemical characteristics

The results of the physiochemical and biological analyses of the groundwater samples are presented in Table 2. The pH value varies from 6.45 to 7.80 with an average of 7.03 which reveals that the groundwater is slightly acidic to slightly alkaline. Total dissolved solids values ranged from 328mg/l to 857mg/l with an average value of 492mg/l indicating that the groundwater of the area is all of the fresh water type [23]. The relative abundance of cations and anions is in the order; $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$ and $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-}$ respectively (Figure 2). Calcium and chloride are the most dominant ions with average concentration values of 3.063meq/l and 3.852meq/l, respectively while potassium and sulphate have the least average concentrations of 0.819 and 0.124meq/l, respectively among the major ions.

TDS and major ions showed very low ranges and low standard deviation (SD). This indicates that the groundwater chemical composition is impacted by non-complex hydrochemical processes[17]. The spatial distribution of TDS is presented in Figures 3 and shows that high values of TDS (> 600mg/l) are observed at the western part of the area close to the coast. The high TDS values at this part of the area may be resulting from ingression of saline water and or from cation exchange processes. Low values are observed at the central and eastern parts of the area and these areas denote areas of freshwater and recharge zones.

Table 2: Physico-chemical and bacteriological content values of the shallow groundwater in Warri coastal area

Location	pH	EC [#]	TDS ^a	TH ^a	Bac [‡]	Coli ⁺	SO ₄	Cl	HCO ₃	NO ₃	Ca	Mg	Na	K	Fe	Pb ^a	Ni ^a	Cd ^a	Water type
1	7.02	850	516	150	3	0	0.089	5.533	1.839	0.201	1.179	1.232	4.000	0.431	0.22	0.01	0.006	0.001	NaCl
2	6.45	1010	520	125	6	0	0.105	5.673	2.559	0.201	1.400	1.105	4.000	0.344	0.24	0.01	0.021	0.001	NaCl
3	6.85	805	622	74	4	0	0.108	7.050	2.793	0.424	1.168	0.314	4.938	0.764	0.42	0.00	0.011	0.000	NaCl
4	7.50	1002	701	231	3	0	0.133	6.994	3.332	0.336	2.905	1.711	4.709	0.906	0.40	0.04	0.032	0.002	NaCl
5	6.72	920	707	154	5	1	0.142	6.751	3.970	0.561	1.249	1.844	3.924	1.197	0.42	0.03	0.040	0.003	NaCl
6	6.84	912	857	155	7	0	0.142	6.492	3.116	0.466	1.358	1.752	3.680	1.959	0.40	0.04	0.038	0.004	NaCl
7	6.62	790	613	114	6	3	0.140	6.064	3.553	0.484	1.038	1.243	1.985	1.622	0.34	0.02	0.028	0.004	NaHCO ₃
8	6.60	602	598	205	8	2	0.140	4.219	3.835	0.469	2.246	1.860	1.689	1.756	0.38	0.02	0.022	0.006	NaHCO ₃
9	7.12	600	538	228	9	3	0.142	3.950	3.442	0.426	2.894	1.677	1.706	1.952	0.24	0.02	0.009	0.005	NaHCO ₃
10	6.90	504	539	155	6	0	0.142	2.888	3.248	0.230	2.276	0.989	1.741	1.535	0.28	0.01	0.016	0.018	NaHCO ₃
11	6.80	480	510	184	4	0	0.129	2.544	2.963	0.244	3.000	0.693	1.966	0.903	0.30	0.01	0.012	0.016	NaHCO ₃
12	6.92	492	518	194	5	1	0.130	2.668	2.924	0.324	3.207	0.674	1.744	0.794	0.25	0.01	0.019	0.008	NaHCO ₃
13	6.84	440	450	229	6	0	0.125	1.980	3.090	0.259	3.523	1.053	0.875	0.514	0.30	0.02	0.011	0.009	NaHCO ₃
14	6.96	585	462	298	3	1	0.125	2.549	2.725	0.273	4.912	0.840	0.512	0.394	0.29	0.01	0.002	0.001	NaHCO ₃
15	6.88	645	468	316	7	0	0.125	2.488	3.160	0.227	4.990	1.316	0.454	0.261	0.36	0.01	0.015	0.003	NaHCO ₃
16	7.44	423	440	275	0	0	0.104	1.698	3.606	0.246	4.292	1.215	0.442	0.210	0.38	0.01	0.013	0.002	NaHCO ₃
17	7.32	460	358	272	6	1	0.105	2.002	3.248	0.163	4.413	1.013	0.401	0.162	0.26	0.00	0.012	0.006	NaHCO ₃
18	7.50	410	410	328	8	0	0.117	2.375	2.524	0.168	5.894	0.650	0.278	0.164	0.28	0.01	0.010	0.004	NaHCO ₃
19	7.80	362	340	289	7	0	0.119	1.416	1.954	0.246	5.096	0.679	0.437	0.257	0.25	0.00	0.014	0.001	NaHCO ₃
20	7.20	342	328	253	8	1	0.117	1.705	1.693	0.238	4.225	0.834	0.554	0.257	0.27	0.01	0.021	0.002	NaHCO ₃
Mean	7.03	621	492	198	5.5	0.65	0.124	3.852	2.981	0.309	3.063	1.135	2.002	0.819	0.31	0.01	0.018	0.005	NaHCO ₃
SD	0.35	220	132	72	2.21	0.99	0.016	2.033	0.627	0.119	1.552	0.45	1.61	0.633	0.08	0.01	0.01	0	
CV	4.98	34.9	25.2	34	39.4	152	12.66	52.78	21.06	38.59	50.65	39.62	80.36	77.24	21.3	79	58.01	100.6	
Sea*	8.10	53	n.a	n.a	n.a	n.a	59.60	503.6	1.844	n.a	21.34	105.3	413.2	9.976	n.a	n.a	n.a	n.a	

*values obtained from the off coast of Warri (n=2); #- $\mu\text{S/cm}$; a-mg/l; ‡-total bacteria (/100ml); +-fecal coliform (/100ml), other parameters are measured in meq/l; n.a- not available

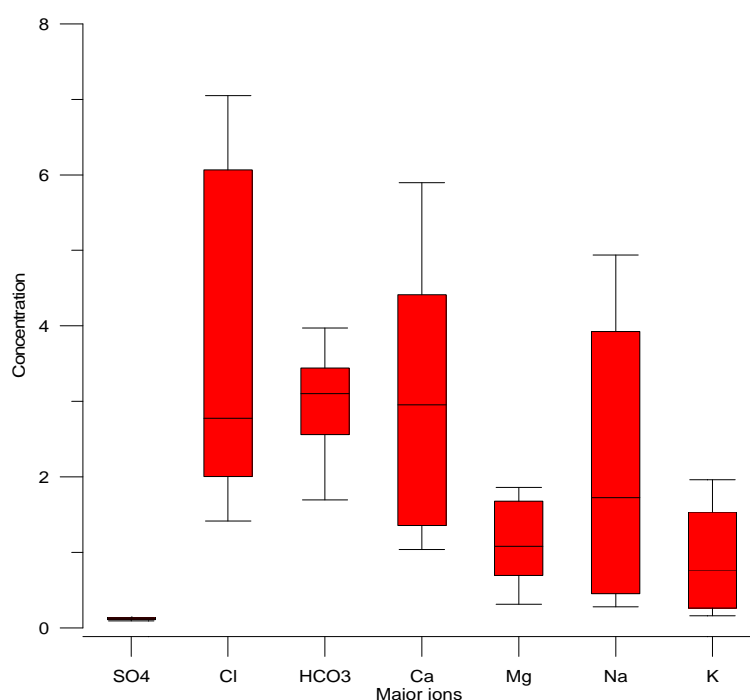


Figure 2: Boxplots of major elements concentration in groundwater samples

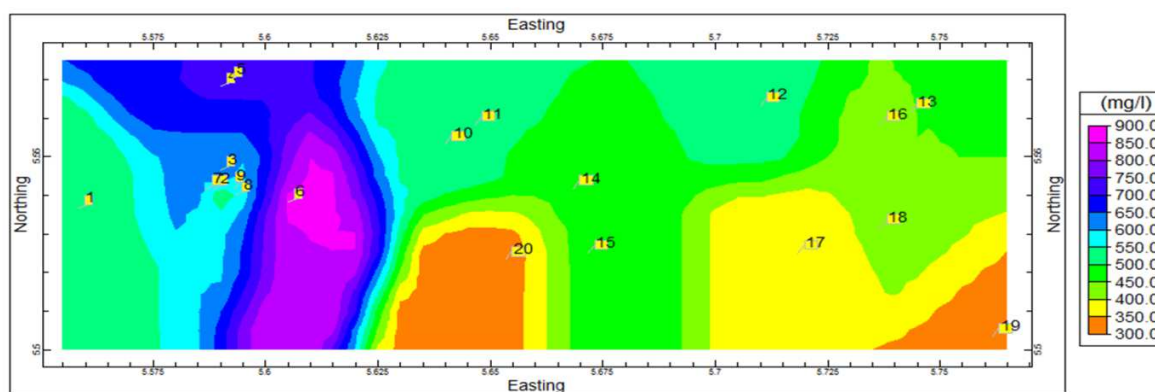


Figure 3: Spatial distribution of TDS in groundwater

In order to evaluate the processes that control the chemical composition of groundwater from the entire study area, the hydrochemical data of all the groundwater samples were plotted in Gibbs Diagram (Figure 4). The diagram reveals that groundwater chemistry or chemical composition is controlled dominantly by rock weathering processes. The differences in concentrations of the various ions in the groundwater may be attributed to the amounts of ions in the rock matrix, reaction characteristics and transport history.

Heavy metals concentrations of Pb, Ni and Cd in the groundwater range from 0 to 0.04mg/l, 0.002 to 0.04mg/l and 0 to 0.018mg/l respectively. Pb concentration exceeds [24] stipulated guideline value at 7 locations (5, 6, 7, 8, 9, 10 and 14) which are all located in the western part of the study area and close to the petrochemical industry. The source is suspected to be from the petrochemical industries in the area and adsorption of marine sediments. Figure 5 shows the spatial distribution of Pb in the area. Nickel concentrations in groundwater samples of the area are below the [24] guideline value; nickel is known to be released into groundwater through water distribution equipment (pipes and installations) and weathering of rocks (Hem 1985).

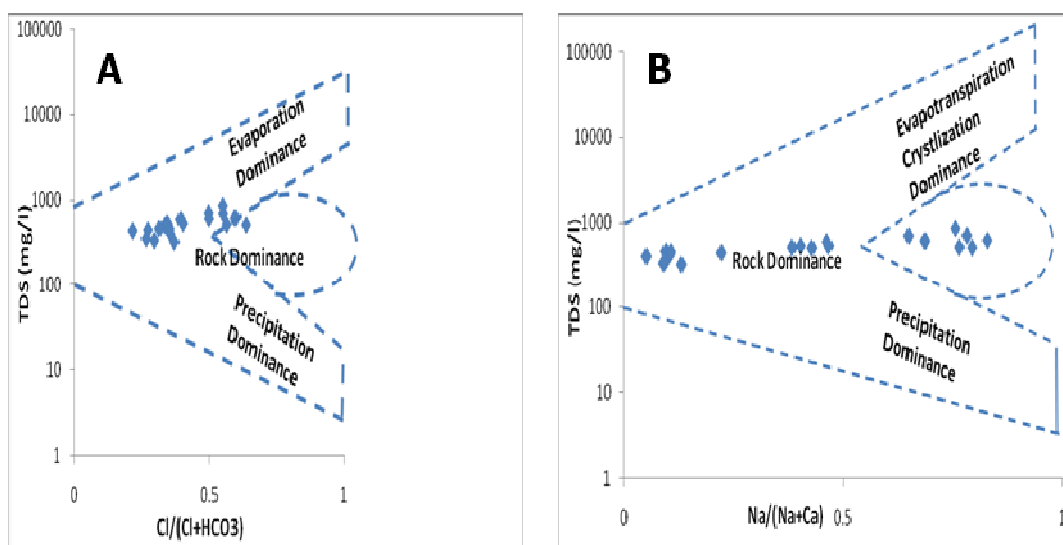


Figure 4: Gibbs Diagram (A-anionic and B-cationic) showing the groundwater chemical composition controlling processes

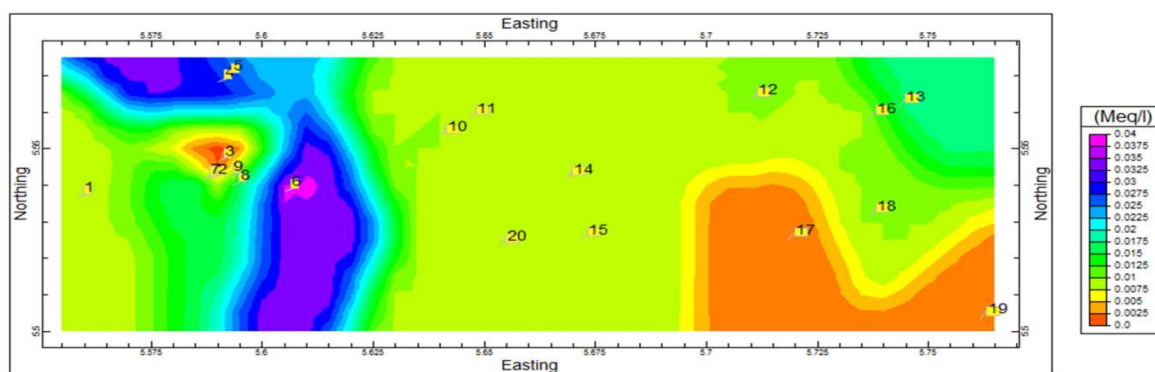


Figure 5: Spatial distribution of lead in groundwater

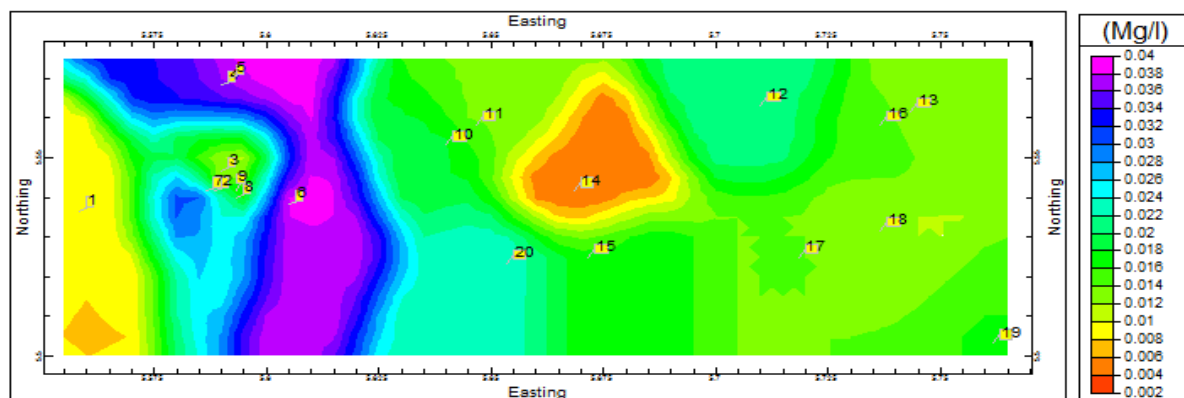


Figure 6: Spatial distribution of nickel in groundwater

Spatial distribution of nickel shows that very high concentration (> 0.035mg/l) is also observed in the western part (precisely locations 4, 5 and 6) of the area(Figure 6). More than half (55%) of the groundwater samples has cadmium concentration above the [24]guideline value. Cadmium is thought to be released into groundwater through both domestic wastewater and industrial wastewater emanating from the steel industry. Cadmium distribution in the area is quite different from those of lead and nickel; it has its highest concentration observed at northern parts of the

area-locations 10 and 11 (Figure 7) which are low in lead and nickel concentrations. Thus cadmium concentration distribution may have been influenced by multiple sources.

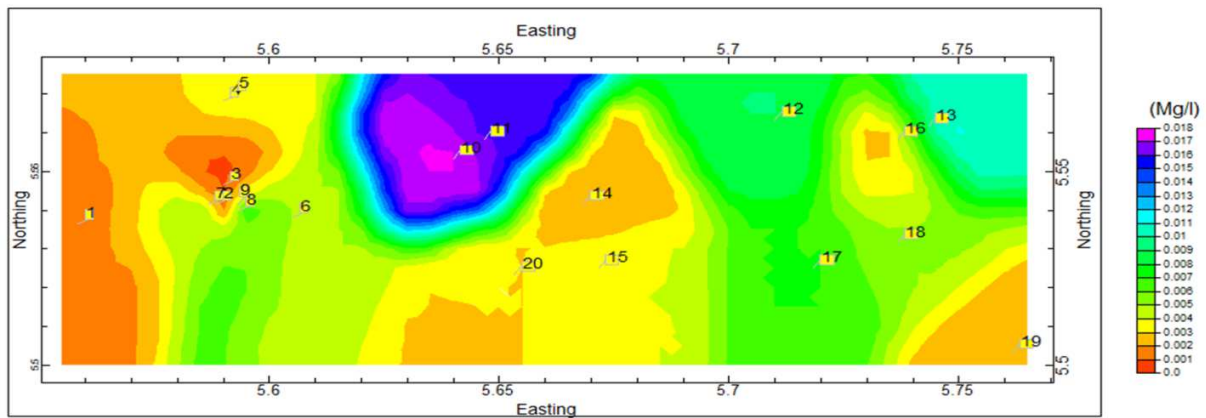


Figure7: Spatial distribution of cadmium in groundwater

Hydrochemical facies

The 20 groundwater samples analyzed were classified using the Piper diagram (Figure 8). The ions classified by the diagram are Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , Cl^- and SO_4^{2-} . Two groups of groundwater types emerged from the classification namely: calcium bicarbonate ($Ca(HCO_3)_2$) water type, and sodium chloride ($NaCl$) water type. The $Ca(HCO_3)_2$ water type reflects groundwater of recharge zone area that is characterized with low EC and TDS, while the $NaCl$ water type reflects groundwater of the discharge zone area that is generally characterized with high EC and TDS.

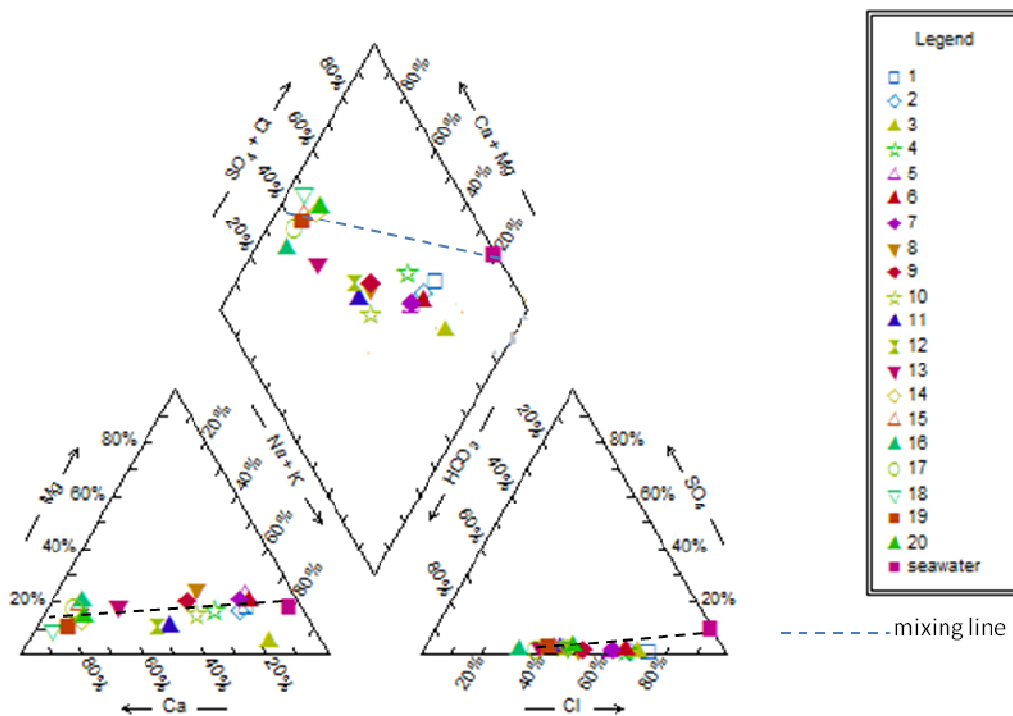


Figure 8: Piper Diagram showing the water types and mixing line

The distribution of the groundwater types reveals that the $NaCl$ water type is closest to the low lying sea shore while the $Ca(HCO_3)_2$ water type is confined to the upland area (Table 2 and Figure 1). [25] observed that the composition

of fresh groundwater in coastal area is often dominated by Ca^{2+} and HCO_3^- ions, which in this particular case have resulted from recharge from precipitation and weathering of host rocks. The question now is:

Any ongoing salinization processes?

The presence of sodium chloride water type in the Warri area suggests possible salinization of groundwater in the area. The possible sources of salinization were investigated using the concentrations of the major ions, graphical plots, ionic ratios, ionic changes (ΔC) and seawater mixing index (SMI). Several authors such as [26], [27], [28], [29], [30], [31], [17] and [32] and [20] have shown that these criteria can be used to work out the contributing sources of saline water in coastal aquifers.

Comparison of the various ionic ratios (Na/Cl, Na/K, Ca/Cl, Ca/Na, Ca/Mg, Mg/Ca and HCO_3^-/Cl) of the studied groundwater with standard seawater ionic ratios reveals great differences in ionic ratios between the two water sources (groundwater and seawater). The difference between each ionic ratio and its standard seawater ratio is smaller for samples taken from areas very close to the coast (samples 1 to 7) than those of the upland areas (8 to 20) (Table 3 and Figure 1). The values of the ionic ratios suggest that groundwater from areas very close to the coast is more impacted by salinization process than those of the upland areas.

Low Na/Cl ratio has been attributed to evaporation of sea water and subsequent halite precipitation while high Na/Cl (≈ 1) is attributed to halite dissolution [32]. In this study, the high Na/Cl ratios (>6.0) of groundwater samples 10, 11 and 12 is attributed to excess of Na^+ released from cation exchange processes.

Table 3: Ionic ratios of the shallow groundwater in Warri coastal area

	Na/Cl	Na/K	Ca/Cl	Ca/Na	Ca/Mg	Mg/Ca	HCO_3^-/Cl
1	0.722935	9.280742	0.213085	0.29475	0.956981	1.044953	0.332369
2	0.705094	11.62791	0.246783	0.35	1.266968	0.789286	0.451084
3	0.700426	6.463351	0.165674	0.236533	3.719745	0.268836	0.39617
4	0.673291	5.197572	0.415356	0.616904	1.697838	0.588985	0.476408
5	0.581247	3.278195	0.18501	0.318298	0.677332	1.476381	0.588061
6	0.566852	1.878509	0.209181	0.369022	0.775114	1.290133	0.479975
7	0.327342	1.223798	0.171174	0.522922	0.835076	1.197495	0.585917
8	0.400332	0.961845	0.532354	1.329781	1.207527	0.828139	0.908983
9	0.431899	0.873975	0.732658	1.696366	1.725701	0.579475	0.871392
10	0.602839	1.134202	0.788089	1.307295	2.301314	0.434534	1.124654
11	0.772799	2.177187	1.179245	1.525941	4.329004	0.231	1.164701
12	0.653673	2.196474	1.202024	1.838876	4.75816	0.210165	1.095952
13	0.441919	1.702335	1.779293	4.026286	3.345679	0.298893	1.560606
14	0.200863	1.299492	1.92703	9.59375	5.847619	0.17101	1.069047
15	0.182476	1.739464	2.005627	10.99119	3.791793	0.263727	1.270096
16	0.260306	2.104762	2.52768	9.710407	3.53251	0.283085	2.123675
17	0.2003	2.475309	2.204296	11.00499	4.356367	0.229549	1.622378
18	0.117053	1.695122	2.481684	21.20144	9.067692	0.110282	1.062737
19	0.308616	1.700389	3.59887	11.66133	7.505155	0.133242	1.379944
20	0.324927	2.155642	2.478006	7.626354	5.065947	0.197396	0.992962
SSW ^b	0.85300	46.9700	0.03700	0.04400	0.200000	5.533000	0.02-0.05

b: standard sea water (data from Collins)

Evidence for cation exchange processes is provided by the plot of $(\text{Ca}+\text{Mg})-(\text{HCO}_3+\text{SO}_4)$ against $(\text{Na}+\text{K})-\text{Cl}$ (Figure 9). From the figure, samples 10 and 11 fall in the region of excess Na^+ , which authors like [33] and [34] have attributed to cation exchange processes. The high Na/Cl ratios (> 7.0 , Table 3) of groundwater samples 1, 2 and 3 may be attributed to a different signature other than those of groundwater samples 10, 11 and 12. Majority of the groundwater samples fall under the excess $\text{Ca}+\text{HCO}_3^-$ region. The excess Ca^{2+} may be attributed to recharge from precipitation and weathering of host rocks. Graphical plots (Figure 10) of the major ions against conservative chloride ion reveal low regression coefficients for all the ions (<5.0) except Na^+ (0.8493) and Ca^{2+} (0.6767). The very high regression coefficients of Na and chloride show that the two ions have similar sources and similar ionic distribution characteristics.

Figure 9: Graphical plot of exchange parameters depicting exchange processes

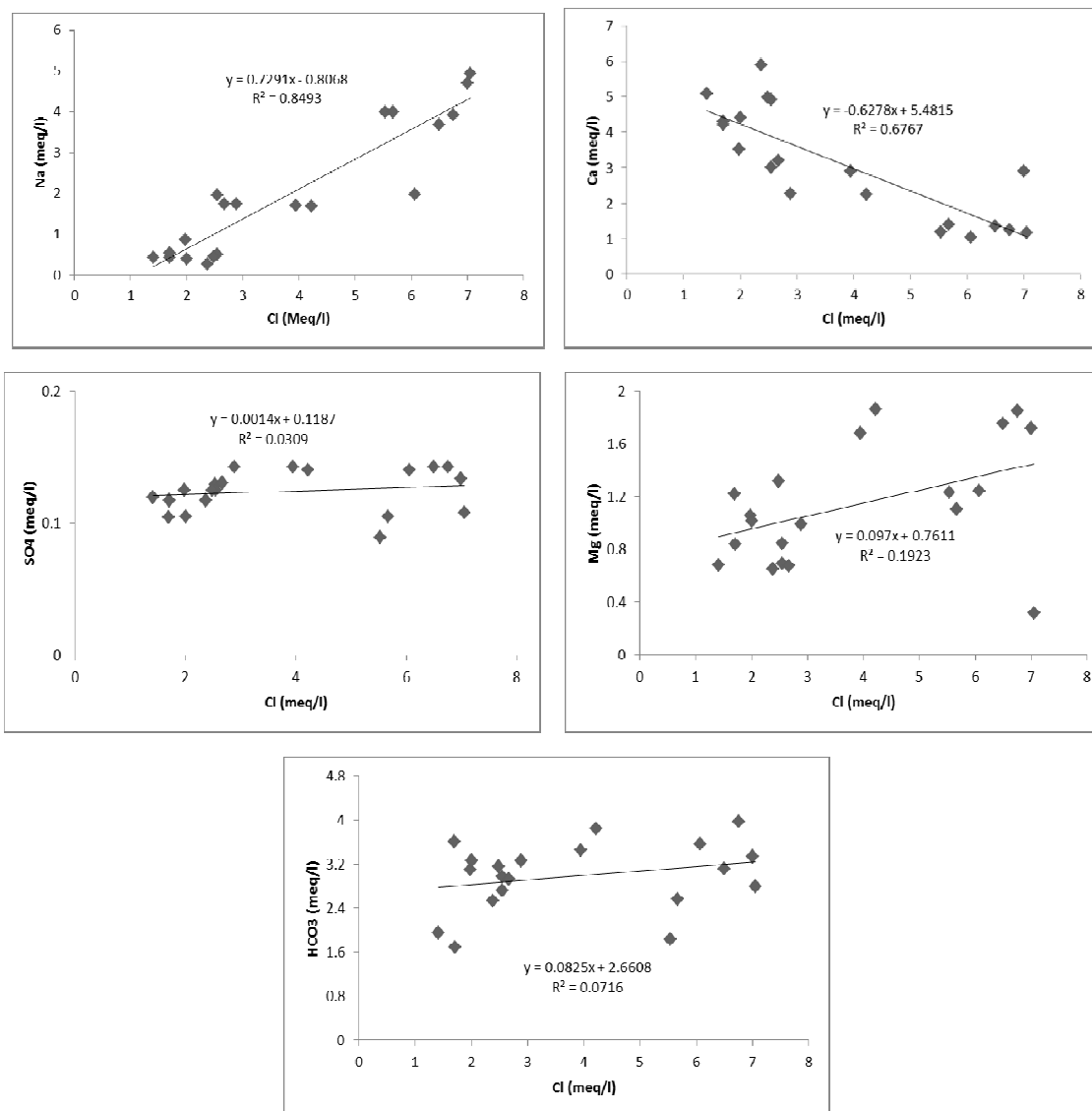
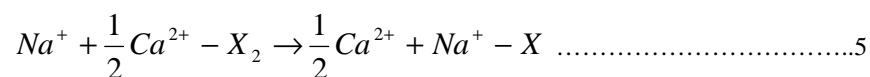


Figure 10: Graphical plots of major ions against conservative chloride

Results of ionic deviations and the seawater fraction of a conservative mixing, $f_{sea}(\%)$ for the major ions are presented in Table 4. From the table, it is observed that the groundwater samples close to the coast and which also belong to the NaCl-type water have positive seawater mixing fraction (mean 0.34%) while those farther away from the coast, and which are of the Ca(HCO₃)₂-type water have negative seawater mixing fraction (mean -0.13%). With respect to the ionic delta for ionic species i (ΔC_i), positive value indicates that the groundwater is enriched with the ion while a negative value indicates depletion of the ions species in the groundwater[35]. From the table, it is clearly shown that all the ions are depleted in areas dominated by NaCl water type (areas closer to the coast). The most depleted ion is the sodium ion. The ionic depletion could be explained in terms of ionic exchanges between freshwater and seawater. For example, when seawater intrudes into a coastal fresh groundwater aquifer, the following exchange reaction takes place:



where X stands for the soil exchanger

Table 4: Percentage of seawater fractions and ionic deltas of groundwater samples

s/n	$f_{\text{sea}} (\%)$	ΔSO_4^{2-}	ΔCl^-	ΔHCO_3^-	ΔMg^{2+}	ΔNa^+	ΔCa^{2+}	ΔK^+
1	0.15626	-7.76802	-70.587	-3.31283	-4.65051	-171.983	-4.67525	-1.38286
2	0.186943	-9.1318	-84.447	-2.45967	-5.73817	-206.53	-5.00683	-1.80246
3	0.488724	-22.6999	-220.77	-0.91594	-15.978	-545.386	-10.6739	-4.65377
4	0.476451	-22.123	-215.226	-0.4302	-14.1967	-531.796	-8.71589	-4.37873
5	0.423196	-19.7191	-191.169	-0.02333	-12.3963	-472.618	-9.41276	-3.51044
6	0.366434	-17.1665	-165.528	-1.12368	-10.711	-408.95	-8.28147	-2.13314
7	0.272634	-12.9503	-123.156	-1.09377	-8.28316	-305.03	-6.91213	-1.45335
8	-0.13171	5.2332	59.499	-2.56664	4.99398	149.9542	1.578178	3.063785
9	-0.19067	7.88635	86.13	-3.2155	6.656822	216.3508	3.287935	3.898843
10	-0.42341	18.35297	191.268	-4.41962	13.25612	478.4493	6.861703	6.004818
11	-0.49881	21.73029	225.324	-5.03182	15.3206	563.5611	8.943489	6.190053
12	-0.47163	20.5092	213.048	-4.95287	14.45073	532.7404	8.661054	5.786468
13	-0.62241	27.28483	281.16	-5.44126	19.55069	701.6451	11.69263	7.140937
14	-0.49771	21.67701	224.829	-5.26506	15.43329	560.8733	10.83575	5.669174
15	-0.51108	22.2782	230.868	-4.88808	16.32787	575.8679	11.15452	5.681091
16	-0.68421	30.0431	309.078	-5.19349	21.64774	770.7996	13.57469	7.50688
17	-0.61759	27.04801	278.982	-5.26234	19.35973	695.7423	12.49579	6.736672
18	-0.53584	23.38388	242.055	-5.63156	16.43726	603.5763	12.50454	5.852543
19	-0.74602	32.83737	336.996	-7.11371	23.04679	840.3821	15.49176	8.223822
20	-0.68268	29.98711	308.385	-7.09983	21.21871	769.1842	13.48006	7.53725

s/n- groundwater samples locations

In this reaction, Na^+ is taken up by the exchanger, whereas Ca^{2+} is released into the water. Because Cl^- in groundwater is highly soluble and remains the same, a depletion of Na^+ relative to Cl^- in groundwater is therefore observed when seawater intrudes the previously fresh aquifer [19], [34] and [20]. According to [36], these processes are controlled largely by the soil properties of the aquifer.

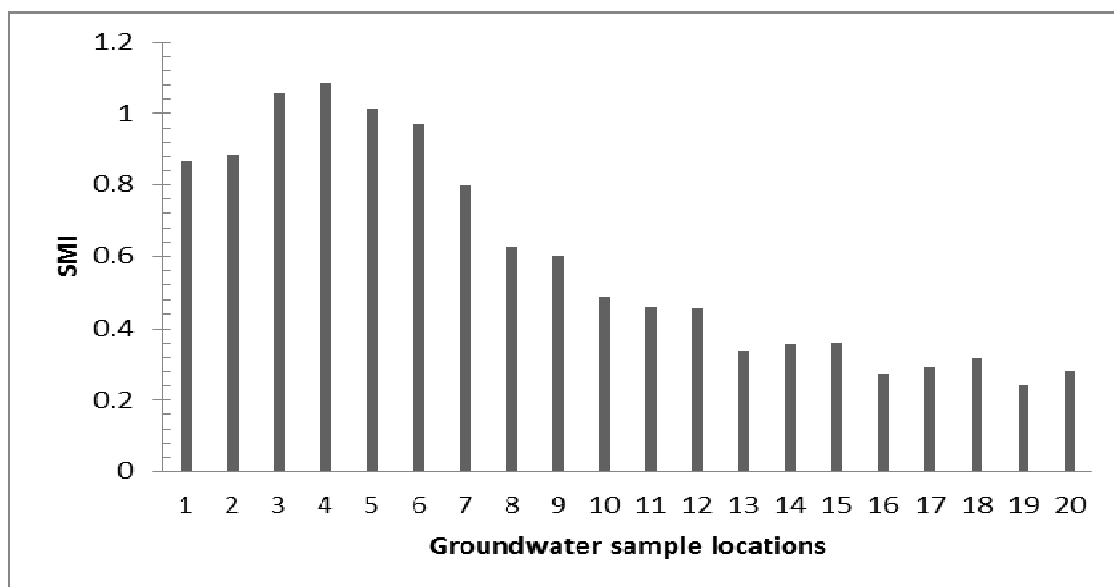


Figure 11: Chart showing the SMI across the study area

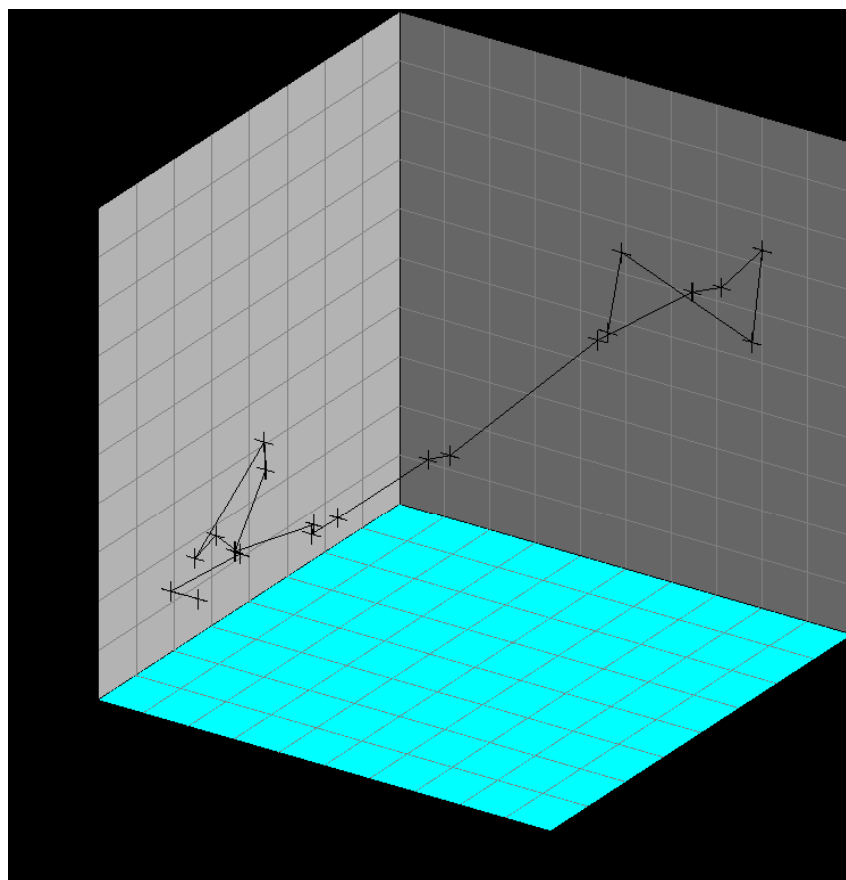


Figure 12: 3D line/scatter diagram of SMI against EC ($\mu\text{S}/\text{cm}$) and Cl (meq/l)

Seawater mixing indexes (SMI) for all the groundwater samples are presented in Figure 11. The SMI values in all the groundwater samples ranged from 0.244 to 1.127 and EC 340 to 1010 $\mu\text{S}/\text{cm}$. Whereas, the SMI of the NaCl-type water varied from 0.896 to 1.127 (mean 1.012) and EC, from 850 to 1010 $\mu\text{S}/\text{cm}$ (916.5 $\mu\text{S}/\text{cm}$), the SMI of the $\text{Ca}(\text{HCO}_3)_2$ -type water varied from 0.244 to 0.799 (mean 0.434) with EC, varying from 342 to 790 $\mu\text{S}/\text{cm}$ (509.6 $\mu\text{S}/\text{cm}$). The 3D plot of SMI against EC and Cl is presented in Figure 12. Although these results imply that no seawater intrusion is apparent in the area as revealed by the results ($\text{EC} < 3000 \mu\text{S}/\text{cm}$ and $\text{SMI} < 1.18$) at the time of present investigation it cannot be ruled out in future as present values of f_{sea} (%) and SMI indicate that future occurrence is possible. Over abstraction of groundwater in the area may trigger the occurrence of seawater intrusion especially in areas very close to the coast where the NaCl-type water presently dominates.

Groundwater Quality for Drinking Purposes

Total hardness measured ranged from 74mg/l to 328mg/l with an average of 198mg/l. Hardness classification of groundwater (after [37]) reveals that the Warri groundwater falls into the four categories, namely soft, moderately hard, hard and very hard with 5% of the samples being soft, 15% moderately hard, 70% hard and 10% very hard (Table 5). Table 6 presents a comparison of the results of the biological and physiochemical analysis of groundwater of the area with the standard guideline values recommended by the World Health organization [24] for drinking water purposes.

Table 5: Groundwater classification based on total hardness after Sawyer and McCarty (1967)

Total hardness as CaCO_3 (mg/l)	Water type	Sample number	Number of Samples	Percentage of samples (%)
<75	Soft	3	1	5
75-150	Moderately hard	1, 2 and 7	3	15
150-300	Hard	4, 5, 6, 8, 9, 10, 11, 12, 13, 14, 16, 17, 19 and 20	14	70
>300	Very hard	15 and 18	2	10

Table 6: Ground water indices and WHO, 1993 stipulated guideline values

Water quality Index	WHO (1993) guideline value (mg/L)	Samples exceeding guideline values	Percentage of samples exceeding guideline values
TDS	500	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12	60
Total bacteria ^a	10	nil	0
Fecal coliform ^a	0	5, 7, 8, 9, 12, 14, 17, 20	40
SO ₄ [*]	4.16	nil	0
Cl [*]	5.64	2, 3, 4, 5, 6, 7	30
NO ₃ [*]	0.73	nil	0
Pb	0.01	4, 5, 6, 7, 8, 9, 13	35
Cd	0.03	6, 7, 8, 9, 10, 11, 12, 13, 17, 18	50
Ni	0.03	1, 2, 3, 4, 5, 6, 7, 8	40

a - measured in /l ooml; *measured in meq/l

It is observed from the Table that 60% of the samples show TDS values above the guideline value of 500mg/l. while 35%, 50% and 40% of the samples are contaminated by the heavy metals of Pb, Cd and Ni, respectively. Also, 40% and 30% of the groundwater samples have fecal coliform and Cl concentrations respectively above the stipulated guideline values. All the groundwater samples, however, have total bacteria, SO_4^{2-} and NO_3^- concentrations below guideline values for drinking water.

CONCLUSION

This work has presented the hydrochemical characteristics and water quality of a coastal aquifer. The chemical composition of the groundwater of the area is strongly influenced by weathering of the litho units of the rocks of the area along with anthropogenic processes (domestic and industrial wastes). Groundwater of the area are slightly acidic to slightly alkaline in nature and also classed as soft, moderately hard, hard and very hard with about 70% of the water being hard.

Two groundwater types were recorded namely, calcium bicarbonate water type and sodium chloride water type with the sodium chloride type being closest to the low-lying sea shore while the calcium bicarbonate type is confined to the upland area. Results showed that the area dominated by NaCl-type water represents the groundwater discharge zone while the area dominated by $CaHCO_3$ -type water represents the recharge zone. Ionic ratios of major ions (Na, K, Ca, Mg, Cl, SO_4 and HCO_3) of the NaCl-type water showed lesser deviations when compared with their standard seawater ionic ratios while those of the $Ca(HCO_3)_2$ -type water showed large deviations when compared with their standard seawater ratios. This variation is thought to reflect the higher degree of the influence of freshwater-seawater interactions at the sea coast/shore relative to that in the upland area. Graphical plots of the major ions against chloride showed that the ionic distribution and sources of the major ions are quite dissimilar from those of the conservative chloride ion for the two water types except for sodium. The estimated ionic delta revealed a mean seawater mixing rate of 0.34% for the NaCl-type water and -0.105 % for the $Ca(HCO_3)_2$ -type water. The seawater mixing index (SMI) of the groundwater ranged from 0.244 to 1.127 with the NaCl-type water having higher values than the $Ca(HCO_3)_2$ -type water thus showing that the former (NaCl) are more impacted by seawater intrusion effects than the latter.

Groundwater quality indices such as TDS, fecal coliform, Cl, Pb, Cd and Ni have concentrations above the stipulated [24] guideline values, indicating that the groundwater of the area is not suitable as drinking water.

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