

Hydrogeochemical Investigation of Groundwater Resources in Umunya and Environs of the Anambra Basin, Nigeria

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ABSTRACT

The study area falls within the Anambra Basin in southeastern Nigeria. The lithostratigraphic units within the study area are the Imo Shale (Paleocene) and the Ameki Formation (Eocene). This paper takes a closer look at the physico-chemical analyses of the groundwater discharge from the prolific Nanka Sands reservoir.

A total of twenty-one (21) water samples were obtained from the groundwater sources and were analyzed for their physico-chemical characteristics with the aim of assessing their quality and usability. Result of some physical and hydrochemical parameters show mean values of 5.75 pH, 46.98 mg/l TDS; 10.86 mg/l Ca^{2+} , 7.50 mg/l Na^+ ; 3.29 mg/l K^+ , 1.46 mg/l Mg^{2+} , 25.74 mg/l HCO_3^- ; 16.70 mg/l Cl^- , 0.09 mg/l Fe^{2+} , 4.65 mg/l NO_3^- and 72.36 $\mu\text{S}/\text{cm}$ conductivity. The water hardness and Sodium Absorption Ratio (SAR) are respectively, 34.74 mg/l and 0.73. Statistical analyses, using the product moment coefficient of correlation, indicate very strong correlation between the following pairs of parameters: Total Hardness and TDS ($r = 0.94$); TDS and E_c ($r = 0.99$); Ca^{2+} and HCO_3^- ($r = 0.83$); Ca^{2+} and Mg^{2+} ($r = 0.70$); Na^+ and K^+ ($r = 0.57$); pH and TH ($r = 0.52$) while negative correlation was observed between pH and Cl^- ($r = -0.77$).

Five water groups were identified based on characterization in the piper trilinear diagram. These include Ca-Na+K- HCO_3^- , Na+K- HCO_3^- , Na+K- HCO_3^- -Cl, Ca-Cl- HCO_3^- , and Ca-Na+K- SO_4 . They reflect diverse effects of bedrock lithologies, base exchange processes, precipitation and weathering. The groundwater source is strongly to weakly acidic fresh water with the exception of water sample (WS2) showing slightly alkaline fresh water. The water samples are generally soft with low sodium content. The groundwater quality is good and satisfies the World Health Organization (WHO) guidelines and the Nigeria

Standards for Drinking Water Quality (NSDWQ) for domestic, agricultural and other industrial uses requiring minor treatment.

(Keywords: groundwater, quality, physico-chemical analyses, lithostratigraphic, formation, geochemistry)

INTRODUCTION

The urban and suburban population in Anambra State depend greatly on the development of groundwater resources in the area. The groundwater resources occur in form of springs and boreholes while in some places it may be in the form of hand dug wells. The increasing demand for groundwater resources in the area is due to the inability of the municipal authorities to provide sufficiently treated water for the consumption of the populace.

Presence of any component such as major ions in excess concentration with respect to background values prescribed by World Health Organization (WHO), 2004 will result in water unsuitable for irrigation, domestic or industrial uses. Physical and chemical parameters such as temperature, ionic concentration (pH), electrical conductivity (EC), total dissolved solids, sodium, potassium, calcium, magnesium, total alkalinity, total hardness, sulphate, chloride, nitrate and fluoride of groundwater play a significant role in classifying and assessing water quality.

It has also been established that geology has a role to play in the chemistry of subsurface water (Abimbola, et al., 2002; Olatunji, et al., 2001). The mineralogical composition of the underlying rocks, secondary products (e.g. clay) and the nature of the surface run-offs are also important factors that affect quality of groundwater (Olatunji et al., 2001 and Tijani, 1990). Consequently shallow groundwater is prone to pollutant elements than groundwater from very deep

aquifer. However, this study is borne-out of the need to evaluate the groundwater sources in the area. It is particularly aimed at determining the quality and usability of the water in addition to ascertaining possible pollutants and ways to ameliorate their effects.

Study Location and Geology

The study area is situated in the southeastern, Nigeria and falls within latitudes 6°10'N and 6°15'N and longitudes 6°48'E and 7°00'E (Figure 1). It covers an area of about 209.52km² with major settlements such as Nkwelle Ezunaka, Ogbunike, Umunya, Umunachi, Awkuzu, Nogu, Ukpo-Akpu, Ifite-Ukpo, and Abagana. The area belongs to the third tropical climatic region, characterized by alternating wet and dry season. The wet season usually lasts from April to October and is dominated by heavy rainfall, while the dry season begins in November to March. The annual rainfall ranges from 1,875mm to 2,500mm while the average annual temperature is about 27°C

with a pressure range of 1010 to 1012.9 millibars (Inyang and Monanu, 1975). High humidity (generally above 80%) and long wet season ensures adequate supply of water and continuous presence of moisture in the air.

The groundwater supplies are mainly from the borehole reservoirs and springs. The springs are commonly observed in areas where the aquiferous sandstone units are in contact with shale units. The mapped area is occupied by the Imo Shale (Paleocene) and the Ameki Formation (Eocene). The Imo Shale is represented by the shale unit while the Ameki Formation is made up of a sandstone unit. The contact between the Imo Shale and Ameki Formation was established by a marked lithologic and topographic changes as well as the attitude of the beds. The Imo Shale shows higher dip value of about 24° as compared with lower dips of the Ameki Formation (6 - 8°). The pebble morpho-analysis and lithofacies changes suggest that the depositional environment ranges from beach to shallow marine.

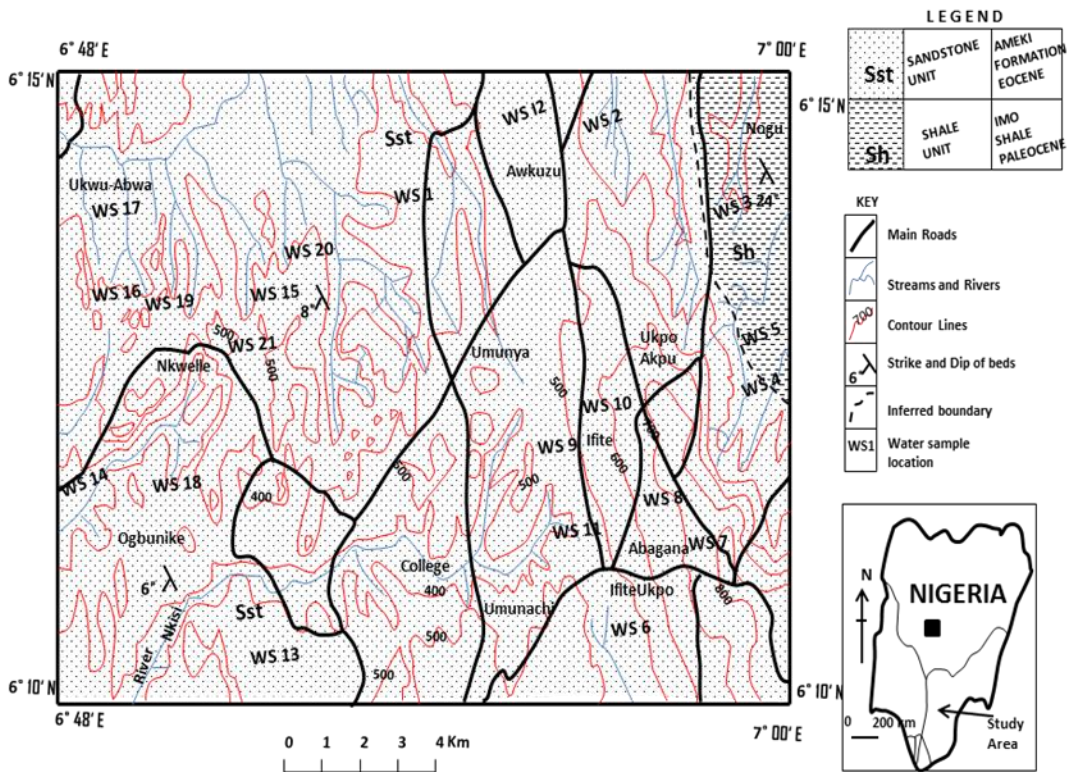


Figure 1: Geological Map of Umunya and Environs.

MATERIALS AND METHODS

Twenty-one groundwater samples were obtained for the study. The water samples were taken from boreholes and springs. Soil samples were observed visually for color, texture and presence of fines while rock samples were obtained for petrography observation of the mineralogy. The water samples were collected in duplicate for every location in two liter white plastic containers. The samples were adequately labelled in the field.

The sample meant for cations determinations were acidified with HNO₃ to prevent the ions from adhering to the surface of the container and to allow them remains in solution. The samples meant for anions determination were not acidified. The electrical conductivity, total dissolved solids (TDS), temperature were measured in the field using a digital conductivity meter WTWL 95 model. The analyses of the water samples were undertaken at the laboratory in the Oyo State Ministry of Environment and Habitat, Ibadan.

Parameters that were analyzed for include Na⁺, Ca²⁺, Mg²⁺ and Fe²⁺ for cations, HCO₃⁻, NO₃⁻, Cl⁻ and SO₄²⁻ for anions. Also, hardness, salinity, pH and alkalinity were determined using standard titrimetric, turbimetric and colorimetric methods. The results obtained from the various forms of analyses were statistically evaluated and interpreted to ascertain the hydrochemical character of the groundwater of the study area.

RESULTS AND DISCUSSION

The data for the physico-chemical parameters of groundwater in the study area are presented in Tables 1 and 2. The summary of the various parameters, their mean values as compared to the values of World Health Organisation (WHO, 2006) guidelines and the NSDWQ (2007) standard for drinking water is shown in Table 3.

Table 1: Results of Physical Characteristics of Groundwater in the Study Area.

Sample No.	Water source	pH	Temp °C	EC	TH	TDS	SAR
WS 1	GW	6.60	25.70	30.60	20.00	19.89	0.69
WS 2	GW	7.42	26.10	321.00	160.00	208.70	0.52
WS 3	GW	6.39	26.10	50.40	32.00	32.76	0.44
WS 4	GW	6.06	26.20	38.40	22.00	24.96	1.21
WS 5	GW	6.00	26.10	51.30	28.00	33.35	0.49
WS 6	GW	6.94	25.90	98.60	50.00	64.09	0.50
WS 7	GW	5.90	26.10	73.60	30.00	47.84	0.62
WS 8	GW	5.93	26.10	41.90	25.00	27.24	0.96
WS 9	GW	6.81	26.20	70.80	34.00	46.02	0.75
WS 10	GW	5.98	26.30	24.81	22.00	16.13	0.59
WS 11	GW	5.51	26.0	30.70	24.00	19.96	3.35
WS 12	GW	5.88	26.40	34.70	24.00	22.56	2.10
WS 13	GW	5.67	29.90	45.80	32.00	29.77	0.23
WS 14	GW	5.59	29.80	28.20	6.00	18.33	0.18
WS 15	GW	4.39	30.10	105.50	44.00	68.56	0.33
WS 16	GW	4.96	28.90	23.90	14.00	15.54	0.35
WS 17	GW	4.65	29.90	21.40	12.50	13.93	0.37
WS 18	GW	4.64	29.70	24.80	10.00	16.12	0.55
WS 19	GW	4.89	29.80	158.10	33.00	101.47	0.53
WS 20	GW	4.62	28.80	90.10	24.00	58.57	0.36
WS 21	GW	5.89	29.90	154.90	83.00	100.69	0.19

TH = Total Hardness, mg/l CaCO₃;
 TDS = Total Dissolved Solids, mg/l
 EC = Electrical Conductivity, μs/cm;
 SAR = Sodium Absorption Ratio;
 GW = groundwater

Table 2: Results of Chemical Characteristics of Groundwater in the Study Area.

Sample No.	Water source	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Fe ⁺	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	NO ₃	PO ₄ ²⁻
WS 1	GW	6.40	0.98	7.11	5.00	ND	16.00	3.99	8.00	3.96	0.00
WS 2	GW	48.80	9.32	15.00	9.00	1.52	144.00	4.98	13.00	2.80	0.00
WS 3	GW	11.20	0.98	5.67	4.00	0.09	28.00	5.98	3.00	3.06	0.01
WS 4	GW	6.40	1.47	13.00	3.00	ND	24.00	6.97	8.00	4.01	0.00
WS 5	GW	8.80	1.47	6.01	4.00	ND	24.00	7.97	6.00	4.62	0.00
WS 6	GW	17.60	1.47	8.09	4.00	0.02	28.00	5.98	10.00	3.09	0.04
WS 7	GW	10.40	0.98	7.77	4.00	0.08	44.00	7.97	14.00	4.13	0.11
WS 8	GW	8.00	1.23	11.09	5.00	ND	24.00	9.96	8.00	4.55	0.00
WS 9	GW	12.00	0.98	10.11	4.00	ND	28.00	4.98	11.00	3.04	0.00
WS 10	GW	6.40	1.47	6.34	7.00	ND	20.00	4.98	7.00	3.13	0.00
WS 11	GW	1.23	0.98	20.54	4.00	ND	24.00	8.97	8.00	4.05	0.00
WS 12	GW	1.23	0.98	12.84	3.00	0.01	20.00	2.99	8.00	3.01	0.00
WS 13	GW	11.20	0.98	3.00	1.00	0.00	10.00	23.00	0.00	5.72	0.00
WS 14	GW	2.40	0.00	1.00	0.00	0.00	5.00	21.00	0.00	1.32	0.00
WS 15	GW	16.00	0.98	5.00	3.00	0.02	25.00	44.00	12.00	15.85	0.12
WS 16	GW	4.00	0.98	3.00	0.00	0.00	5.00	31.00	0.00	3.52	0.01
WS 17	GW	4.00	0.61	3.00	3.00	0.00	30.00	30.00	6.00	4.84	0.00
WS 18	GW	3.20	0.46	4.00	1.00	0.00	10.00	65.00	4.00	4.40	0.02
WS 19	GW	12.00	0.73	7.00	2.00	0.02	0.44	25.00	0.00	0.00	0.00
WS 20	GW	8.00	0.98	4.00	1.00	0.00	1.00	19.00	1.00	9.68	0.21
WS 21	GW	28.80	2.68	4.00	2.00	0.21	30.00	17.00	5.00	8.80	0.00

All parameters in mg/l; GW = Groundwater, ND = Not Detected.

The pH of all the water samples ranges from 4.39–7.42, indicating a strongly to weakly acid fresh water with the exception of the water sample (WS2) in Nkwelle which is slightly alkaline. Temperature varies between 25.70°C-30.10°C while the electrical conductivity (EC) ranges from 21.40 μs/cm-321.00 μs/cm (Table 1). Total hardness (total hardness as CaCO₃) values from 6.00 mg/l-160.00 mg/l were recorded while sodium absorption ratio (SAR) and total dissolved solids (TDS) range, respectively, from 0.18-3.35 and 13.93 mg/l-208.70mg/l (Table 1).

The ranges of the chemical parameters in mg/l are as follows: Ca²⁺ (1.23-48.80); Mg²⁺ (0.00-9.32); Na⁺ (1.00-20.54); K⁺ (0.00-9.00) and Fe⁺ (0.00-1.52) while others include HCO₃⁻ (0.44-144.00); Cl⁻ (2.99-65.00); SO₄²⁻ (0.00-14.00); PO₄²⁻ (0.00-0.21) and NO₃⁻ (0.00-15.85) (Table 2). The mean concentration of the cations therefore is in the order Ca²⁺ > Na⁺ > K⁺ > Mg²⁺ > Fe²⁺ while for the anions, it is: HCO₃⁻ > Cl⁻ > SO₄²⁻ > NO₃⁻ > PO₄²⁻ (Table 2).

Applying the Pearsonian product moment correlation coefficient showed positive correlation between some pairs of parameters except in the parameter between pH and Cl⁻ which indicated a

negative correlation (Table 3). There are relatively strong correlations between TH and TDS (r = 0.94), TDS and EC (r = 0.99), Ca and HCO₃⁻ (r = 0.83), Ca and Mg (r = 0.70). Weaker correlations were obtained between Na and K (r = 0.57) while pH and TH (r = 0.52). Negative correlation was observed between pH and Cl⁻ (r = -0.77).

Table 3: Correlations between some of the Hydrochemical Parameters.

Variable	Correlation Coefficient
TH and TDS	0.94
Na and K	0.57
TDS and Ec	0.99
Ca and HCO ₃ ⁻	0.83
Ca and Mg	0.70
PH and TH	0.52
PH and Cl ⁻	-0.77

A plot of the TDS against the $\frac{Na}{(Na + Ca)}$ ratio (Fig. 2) showed that the groundwater in the study area is influenced by rock and weathering activities.

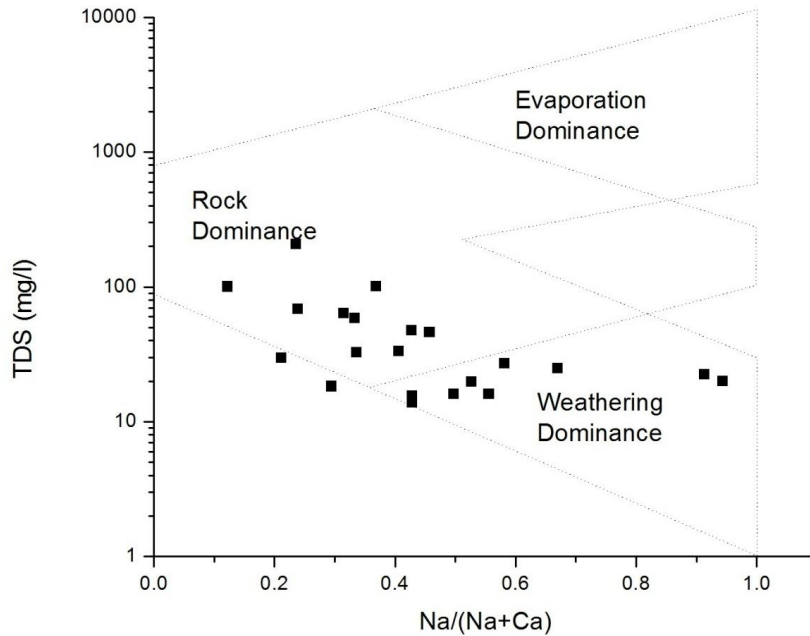


Figure 2: Plot of TDS against the $\left(\frac{Na}{Na + Ca} \right)$ Ratio (after Gibbs 1970).

The majority of the samples plot in the center of Gibbs (1970) diagram, which points to rock as the main pollutant. The Gibbs (1970) showed that about 60% rock dominance indicating short residence time of water rock interaction. Calcium is both abundant in the Earth's crust and extremely mobile in the hydrosphere. It is also one of the most common ions in the subsurface water (Davis and Dewiest, 1966). In this study, Ca^{2+} has the highest cation mean concentration value of 10.86 mg/l and may either be attributed to its abundance in the Earth's crust or is released as weathering product of feldspars and clay minerals.

The sources of HCO_3^- with mean concentration of 25.74mg/l in the sample can be attributed to CO_2 charge recharge (Tijani, 1994). In general, the warm temperature (up to 27.62°C mean) may also cause marked dissolution of the percolating water, leading to a build-up of H^+ that is responsible for cation exchange reaction. The equally high Cl concentration of 16.70mg/l suggests that the chemical characteristics of the water are influenced by recharge from interactions of transported foreign material with those occurring in the area. The presence of Mg^{2+} in the groundwater of the area may be explained by the occurrence of magnesium with calcium carbonate cement in the detrital sedimentary formation or even clay minerals.

The analysis of both radial and stiff diagrams (Figures 3 and 4) on the water samples showed that the water sample (WS1) is Ca-Na- HCO_3 which is essentially a mixed water type.

The water sample (WS2) showed Ca-Mg- HCO_3 water type which is an indication of a hard water. The water samples (WS3, WS4) showed Ca- Na- HCO_3 and Na-Ca- HCO_3 water types which is interpreted as mixed water. Moreover, the water samples WS5, WS6, WS7, WS8 and WS9 showed Ca- Na- HCO_3 , Ca - Na - HCO_3 , Ca- Na- HCO_3 , Na - Ca - HCO_3 and Ca - Na - HCO_3 , water types respectively and are interpreted as a mixed water type. In addition, the water samples WS10, WS11, WS12 and WS15 showed Ca - Na - HCO_3 , Na - HCO_3 , Na - HCO_3 and Ca - Cl - HCO_3 water types which are interpreted as a mixed water type. More so, water samples WS13, WS14, WS16, WS18, WS19 and WS 20 indicate a Ca- Cl water type and are interpreted as saline and hard water. Finally, the water samples WS17, WS19, WS20 and WS21 showed Ca - Cl - HCO_3 , Ca - Na - Cl, Ca - Na - Cl, Ca - HCO_3 - Cl water types and are interpreted as a mixed water type.

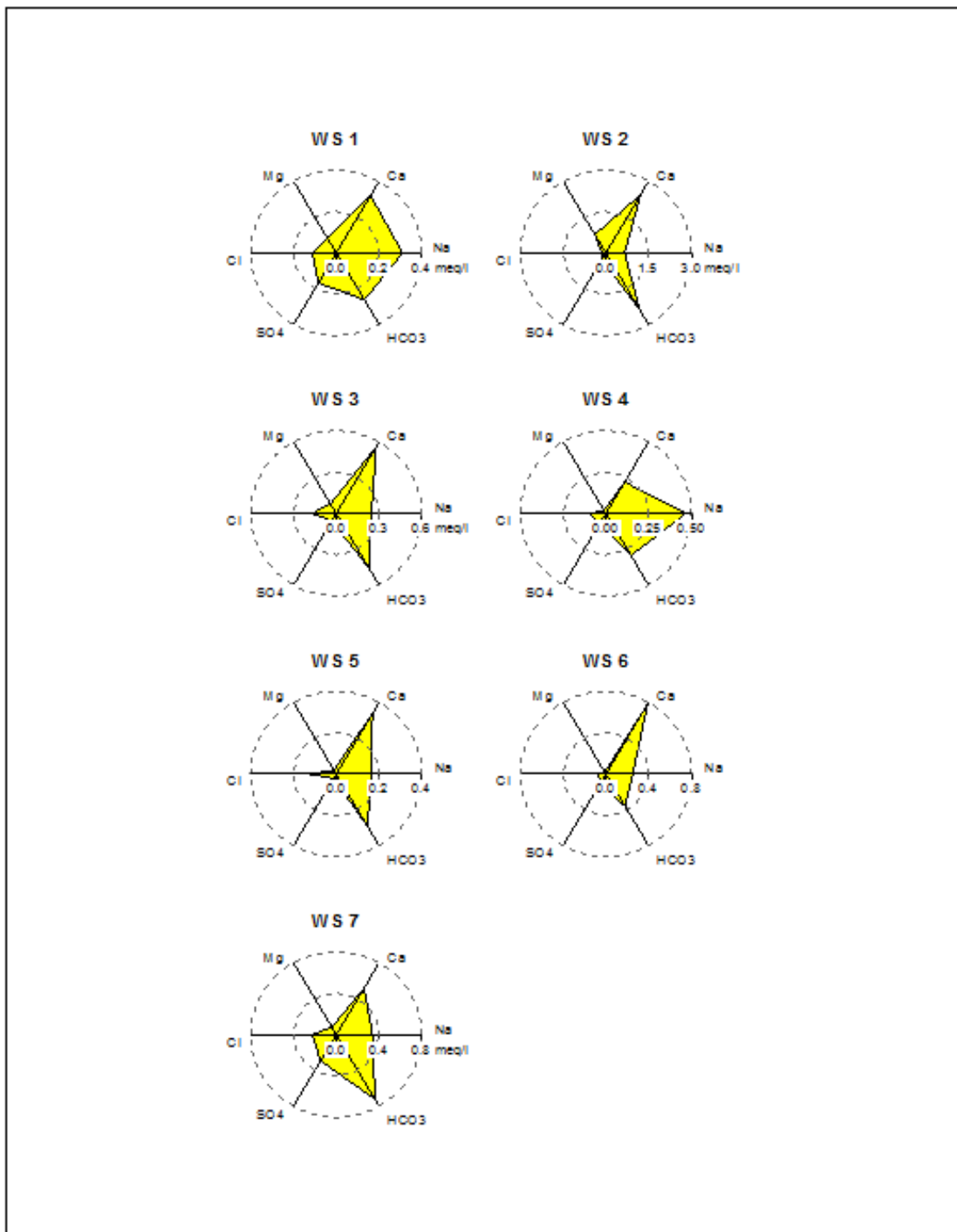


Figure 3a: The Radial Diagrams of the Water Samples (1 – 7) in the Study Area.

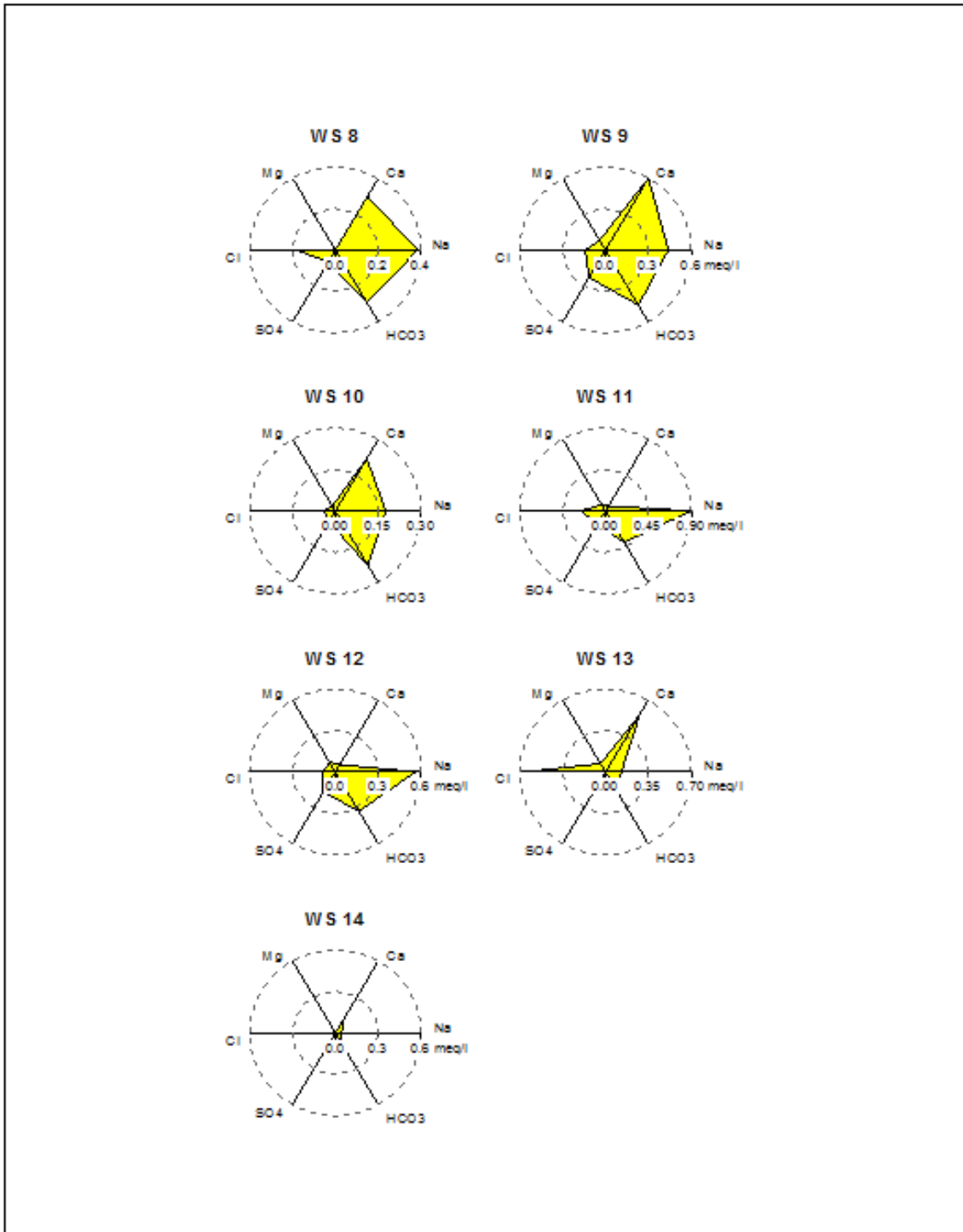


Figure 3b: The Radial Diagrams of the Water Samples (8 – 14) in the Study Area.

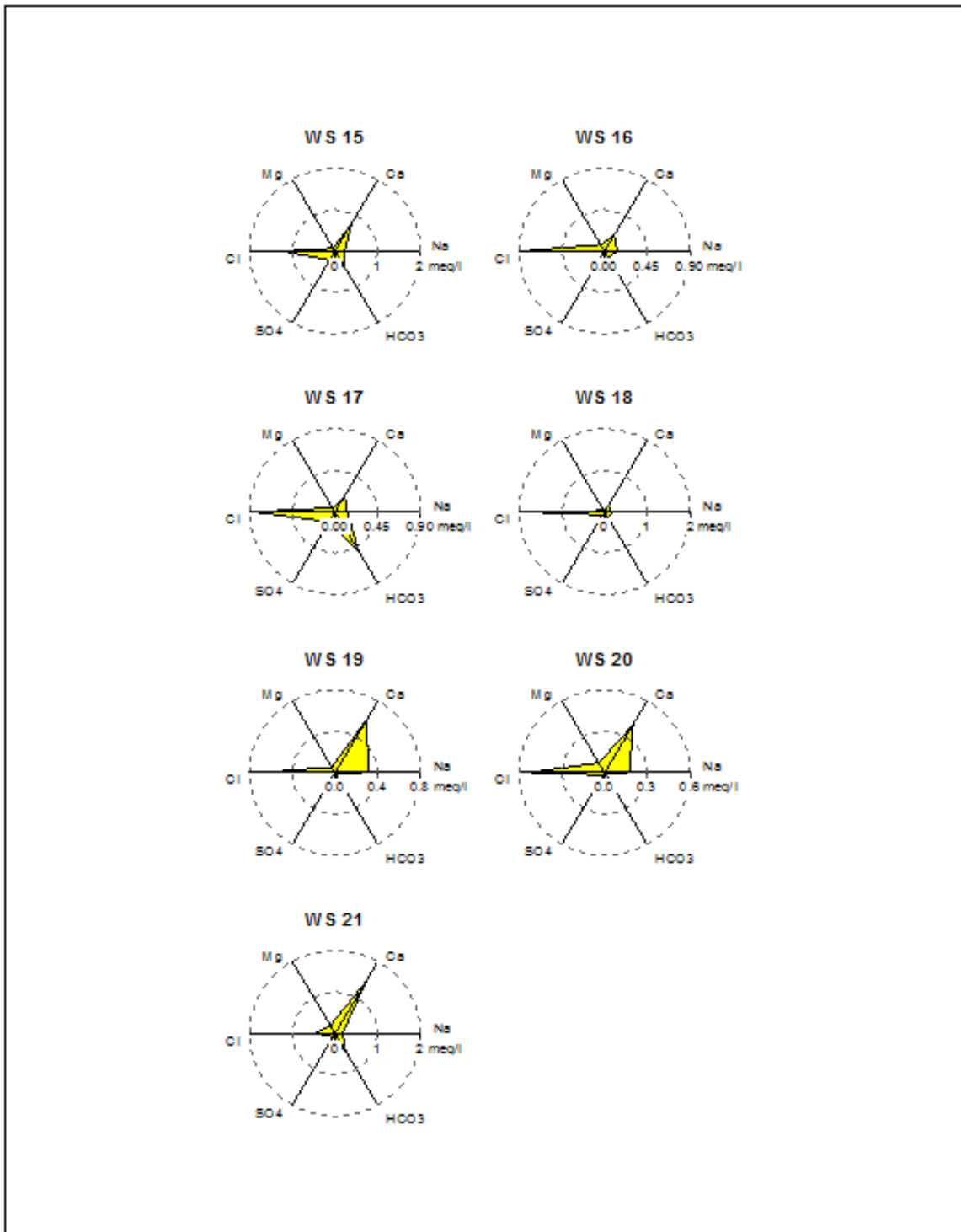


Figure 3c: The Radial Diagrams of the Water Samples (15 – 21) in the Study Area.

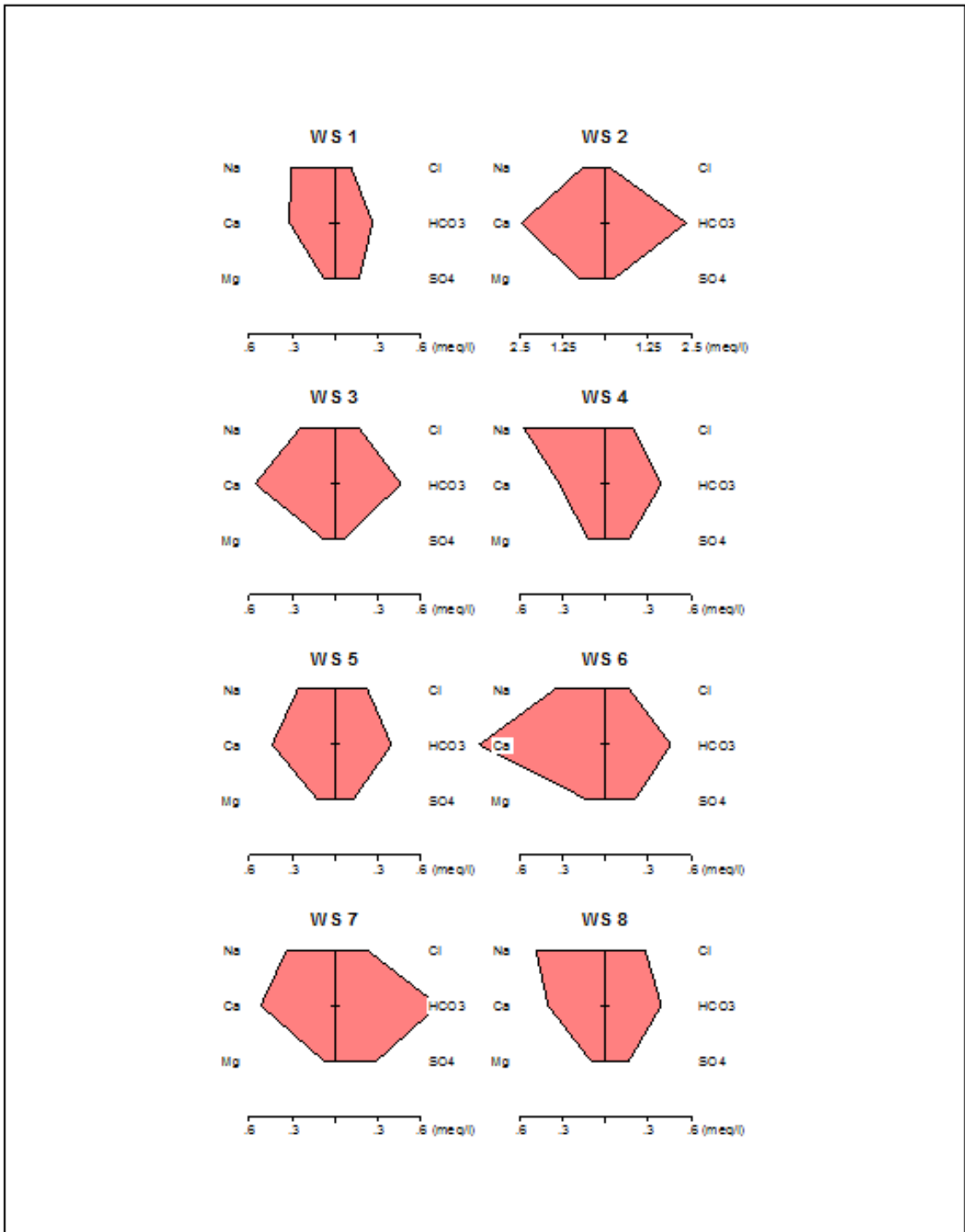


Figure 4a: The Stiff Diagrams of the Water Samples (1 – 8) in the Study Area.

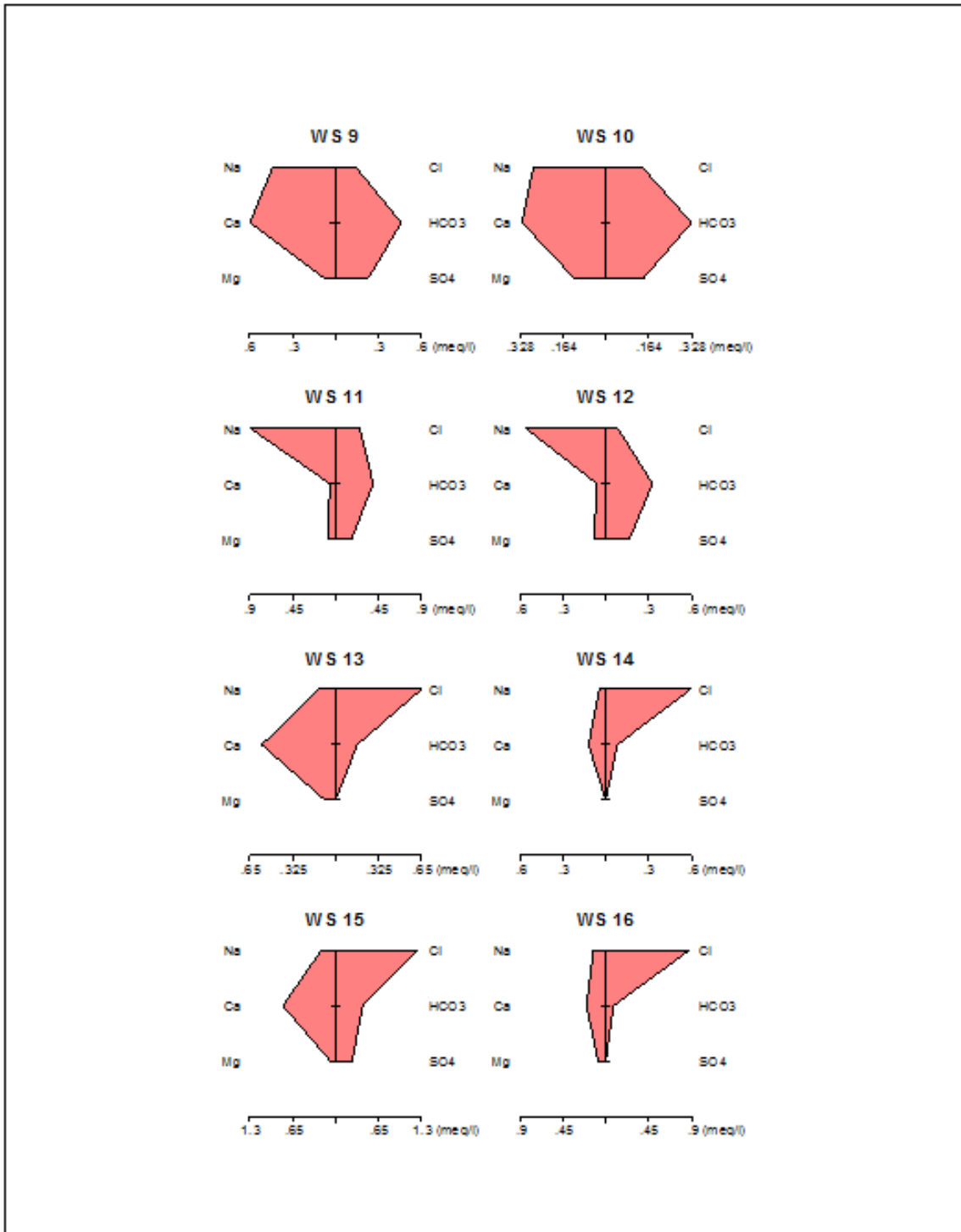


Figure 4b: The Stiff Diagrams of the Water Samples (9 – 16) in the Study Area.

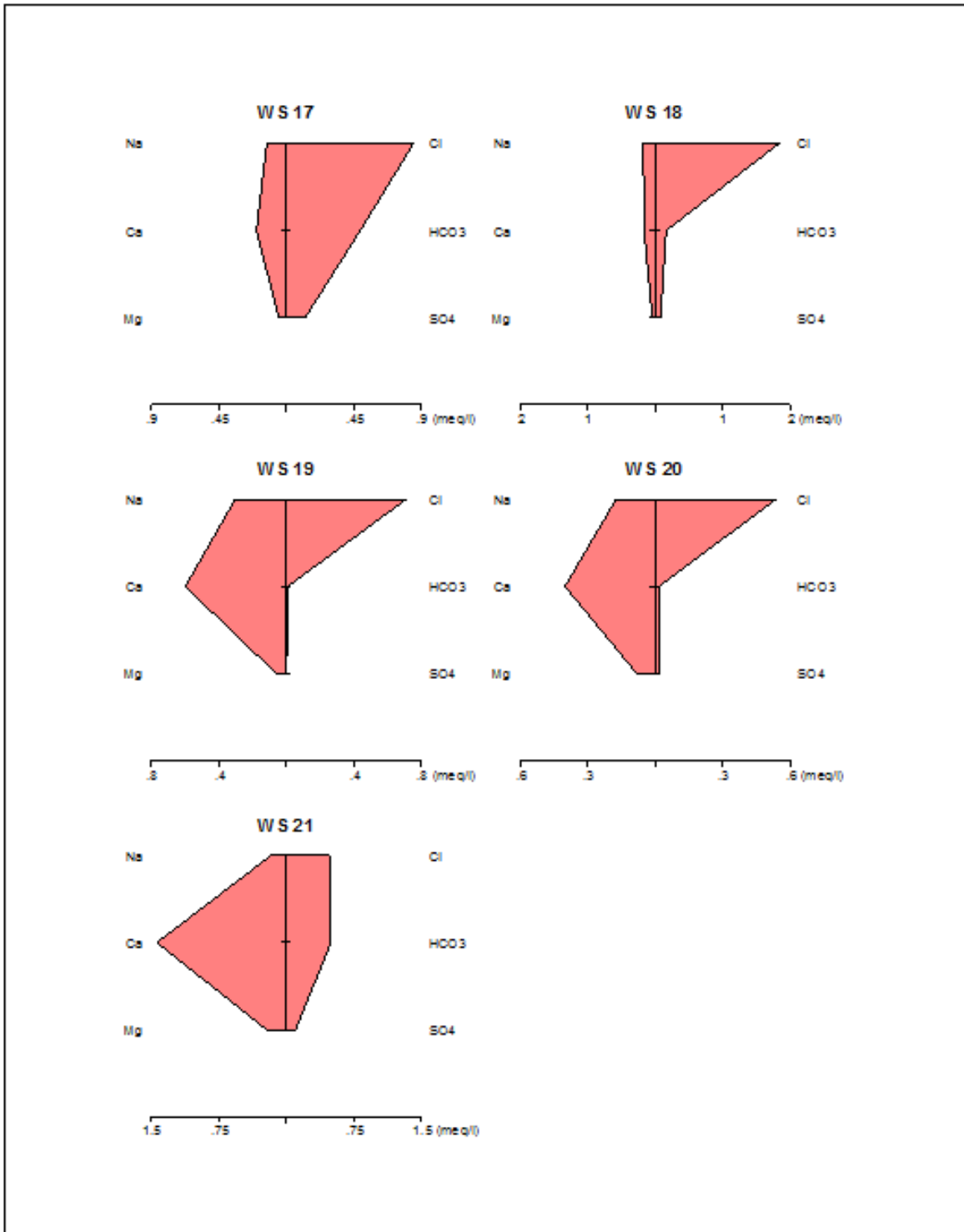


Figure 4c: The Stiff Diagrams of the Water Samples (17 – 21) in the Study Area.

Plots of the hydrogeochemical parameters of the groundwater on Piper (1944) trilinear diagram are shown in Figure 5 which identified five different water facies. The five water facies are predominantly made up of Calcium bicarbonate ($\text{Ca} - \text{HCO}_3$).

These five important water types and their percentages of occurrence in the study area are shown in Table 4.

Also the result from the Durov curve of water quality (Figure 6) further confirmed this five water types as shown below:

Water Types

- i. $\text{Na} + \text{K} - \text{HCO}_3$
- ii. $\text{Ca} - \text{Na} + \text{K} - \text{HCO}_3$
- iii. $\text{Ca} - \text{Na} + \text{K} - \text{Cl} - \text{HCO}_3$
- iv. $\text{Ca} - \text{HCO}_3$
- v. $\text{Ca} - \text{Cl}$.

Table 4: Water Types and their Percentages of Occurrence in the Study Area.

S/N	Water Types	Percentage of Occurrence In The Area
i.	$\text{Ca} - \text{Na} + \text{K} - \text{HCO}_3$	29%
ii.	$\text{Na} + \text{K} - \text{HCO}_3$	14%
iii.	$\text{Na} + \text{K} - \text{HCO}_3 - \text{Cl}$	10%
iv.	$\text{Ca} - \text{Cl} - \text{HCO}_3$	33%
v.	$\text{Ca} - \text{Na} + \text{K} - \text{SO}_4$	14%

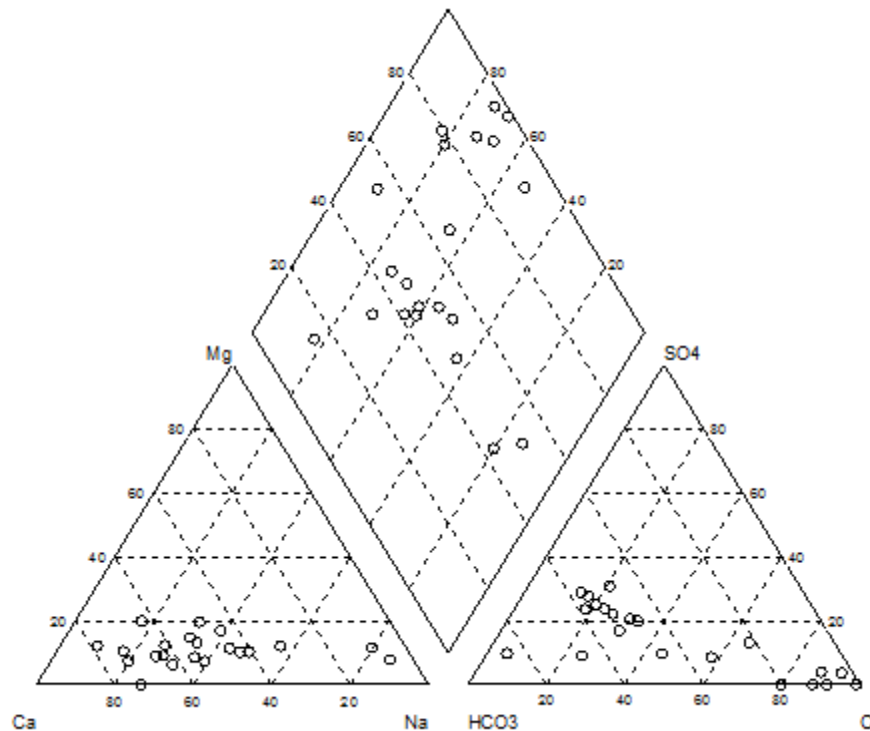


Figure 5: Piper Trilinear Plots of the Chemical Character of the Sampled Water.

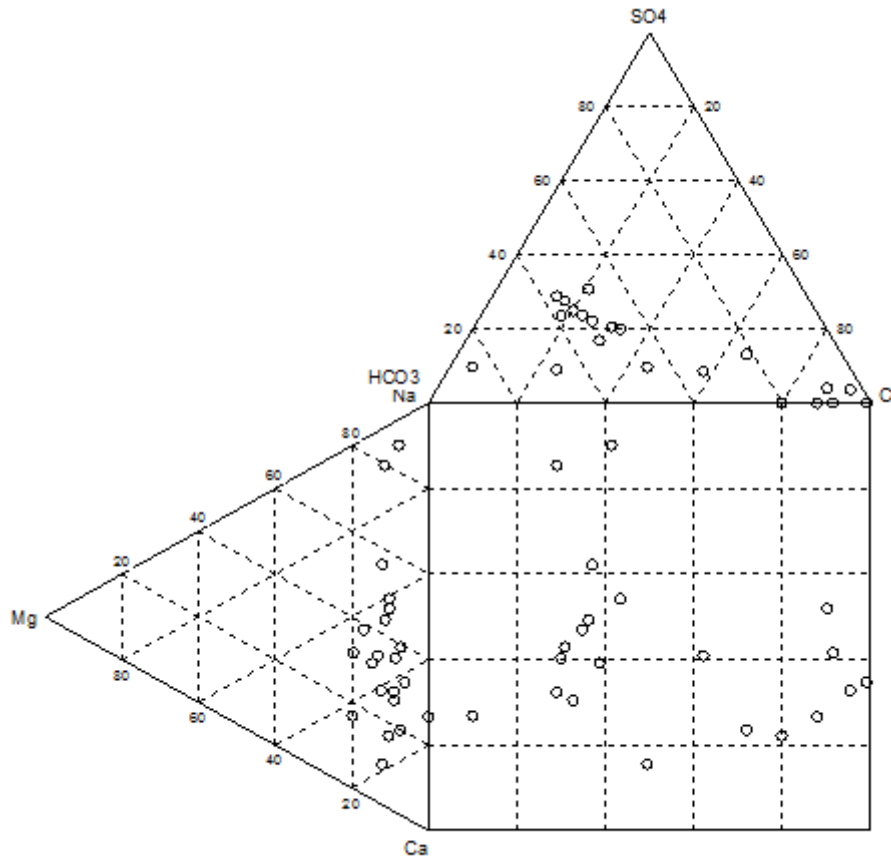


Figure 6: Durov Curve of Water Quality.

The Schoeller Semi – logarithmic plots of the data further confirmed this water type (Figure 7). The peaks indicate the dominant ions in the water samples while the troughs indicate the less dominant ions. In this study, the dominant ions in the water sample include Ca – Na + K – HCO₃ – Cl .

Quality and Usability

The Chemical character of any water determines its quality and utilization. The water quality is a function of the physical, chemical and biological parameters and could be subjective since it depends on a particular intended use (Tijani, 1994). The World Health Organization (2006) has prescribed the quality of drinking water worldwide.

Comparing the various analyses with the prescribed standards, most of the water samples are within the specified standards. The physical parameters such as pH, E_C, TDS are within the acceptable limit of the WHO (2006) guidelines (Table 5).

Also, the chemical characteristics such as Ca²⁺, Mg²⁺, Na⁺, Fe²⁺, Cl⁻, SO₄²⁻ and NO₃⁻ have concentration within the acceptable limit of the WHO (2006) guidelines (Table 5) . The water samples in the study area are classified as fresh water based on the proportion of total dissolved solids (TDS) which falls between 0- 1000 mg/l (Carroll, 1962) . According to Mandel and Shiftan (1991), water containing sodium absorption ratio (SAR) of 0 to 10 can be applicable on all agricultural soils while, that having SAR range from 18 to 26 may produce harmful effects and requires good soil management.

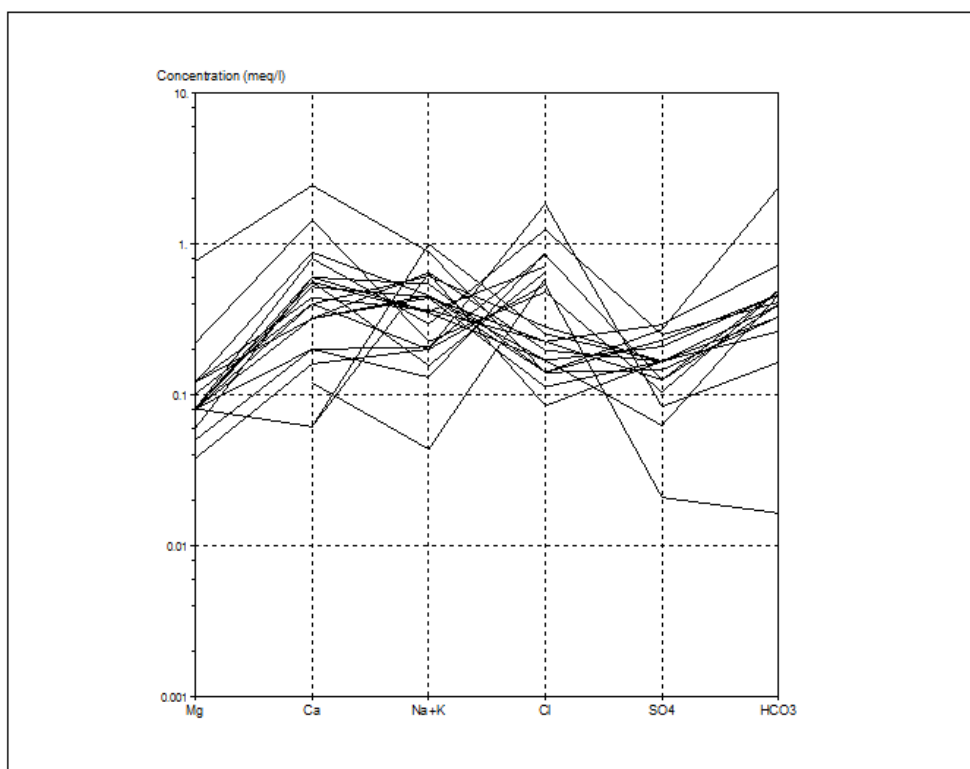


Figure 7: Scholler Semi-Logarithmic Diagram showing Relative Abundance of Cations and Anions.

Table 5: Summary of Physical and Chemical Characteristics of the Water Samples, WHO (2006) Guidelines and NSDWQ (2007) Standards for Drinking Water.

Measured Parameter	Range	Groundwater Mean Concentration Overall Mean	WHO (2006) Guidelines	NSDWQ (2007) Standards
Temp °C	25.70 – 30.10	27.62	25	Ambient
pH (pH unit)	4.39 - 7.42	5.75		
EC(µs/cm)	21.40 - 321.00	72.36	500	1000
TH (mg/l)	6.00 - 160.00	34.74	500	150
TDS (mg/l)	13.93 - 208.70	46.98	1000	500
SAR (mg/l)	0.18 - 3.35	0.73		
Ca ²⁺ (mg/l)	1.23 -48.80	10.86	200	75
Mg ²⁺ (mg/l)	0.00 – 9.32	1.46	150	0.20
Na ⁺ (mg/l)	1.00 – 20.54	7.50		
K ⁺ (mg/l)	0.00 – 9.00	3.29	15	NG
Fe ⁺ (mg/l)	0.00 – 1.52	0.09	0.3	0.3
HCO ₃ ⁺ (mg/l)	0.44 – 144.00	25.74	500	NG
Cl ⁻ (mg/l)	2.99 – 65.00	16.70	250	250
SO ₄ ²⁻ (mg/l)	0.00 – 14.00	6.29	400	100
PO ₄ ²⁻ (mg/l)	0.00 – 0.21	0.02	10	NG
NO ₃ (mg/l)	0.00 – 15.85	4.65	10	50

NG = Not Given

Table 6: Modified Wilcox quality classification of irrigation water.

Water Class	Electrical Conductivity	Salinity Hazard	SAR
Excellent	< 250	Low	0 – 10
Good	250 – 750	Medium	10 – 18
Permissible	750 – 2000	High	18 – 26
Doubtful	2000 – 3000	Very high	26 – 30

Sodium absorption ratio range of 26 -100 is unsuitable for irrigational purposes. Based on the above, the Total Hardness (TH) and Sodium Absorption Ratio (SAR) (Richard, 1954; Sawyer and McCarthy, 1967) shows that the water is soft, and has low sodium content. On the other hand, irrigation water criteria are dependent on water conductivity (E_c), Sodium Absorption Ratio (SAR), type of plants, and amounts of irrigation water used, soil and climate. Using Wilcox model (Table 6), the groundwater is excellent with low saline content.

However, two principal effects of sodium are a reduction in soil permeability and a hardening of the soil. In this study, such effects are ruled out because of low SAR. Hence, it can be used to irrigate most plants (crops) and on most soils (Hem, 1985; Leeden *et al.*, 1990). Based on the work of Leeden *et al.*, (1990), the ranges of additional parameters such as SAR, TH, etc. are consistent with domestic supplies, recreation, wildlife propagation, irrigation and most industrial requirements.

CONCLUSIONS

The result of hydrogeochemical studies of groundwater in the study area show that the water is strongly to weakly acid fresh water with the exception of water sample (WS2) indicating slightly alkaline, with the following water facies; Ca – Na + K – HCO_3 , Na+ K – HCO_3 , Na + K – HCO_3 - Cl, Ca – Cl – HCO_3 , and Ca – Na + K – SO_4 . These may reflect contribution of diversity of bedrock types and consequently also, the product of weathering.

Computed values of water hardness and SAR indicate that the water is generally soft with low sodium content. The groundwater quality is good and satisfies the WHO guidelines and the Nigeria Standard for Drinking Water Quality for domestic, agricultural and other industrial uses. It may be

recommended that the groundwater resources in the study area be developed to supplement the existing ones. Further studies should include microbial investigation, heavy metal and isotopic compositions, to ascertain other quality parameters and perhaps the prescription of necessary treatment measures.

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