

# The Use of Anion Geochemistry in Mapping Groundwater Facies of Yola Area NE Nigeria

**Gabriel Ike Obiefuna<sup>1</sup> and Donatus Maduka Orazulike<sup>2</sup>** <sup>1</sup>Department of Geology, Federal University of Technology, Yola, NIGERIA <sup>2</sup>Geology Programme, Abubakar Tafawa Balewa University, Bauchi, NIGERIA

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### Abstract

This study was aimed at employing anion geochemistry in mapping groundwater facies in Yola area of Northeastern Nigeria. The concentration levels of sulphate were analysed using the HACH Spectrophotometer model No DR/2400 whereas those of  $C\Gamma$ ,  $CO_3^{2-}$  and  $HCO_3^{-}$   $HCO_3^{-}$  were done by titrimetric method. The results of the analysed dissolved anions are recorded as  $HCO_3^-$  (16.2 to 19.2 mg/l),  $C\Gamma$  (0.50 to 0.80 mg/l) and  $SO_4^{2-}$  (1.60 to 3.55 mg/l) for the rainwater and  $HCO_3^-$  (73.30 to 273 mg/l),  $C\Gamma$  (27.90 to 455.20 mg/l) and  $SO_4^{2-}$  (2 to 29.11 mg/l) for the surface water samples. The shallow groundwater and deep groundwater revealed values of  $HCO_3^-$  (19.90 to 240 mg/l), Cl<sup>-</sup> (0 to 170.17 mg/l) and  $SO_4^{2-}$  (0 to 35 mg/l) and  $HCO_3^{-}$  (50 to 207 mg/l),  $Cl^{-}$  (0.004 to 159.40 mg/l) and  $SO_4^{2-}$  (0 to 64.50 mg/l) respectively. The absence of  $SO_4^{2}$  and relatively high concentration of bicarbonate in some of the samples could be attributed to sulphate reduction. The reaction is believed to take place in the presence of sulphate reducing bacteria in the soil zone through which recharge water percolates. The absence of some ions such as  $CO_3^{2-}$  and  $SO_4^{2-}$  and the varied concentration levels in others such as  $C\Gamma$  and  $HCO_3^-$  also affect the types and numbers of mappable facies in surface water and groundwater systems. Mappable groundwater facies for the different water sources are the bicarbonate-chloride-sulphate facies for the rainwater and the chloride-sulphate-bicarbonate for the surface water and groundwater systems respectively. The results further revealed that the groundwater has a local meteoric origin that evolves towards the composition of sea water. It also suggests that their chemical evolution is associated mainly with progressive dissolution and/or weathering of minerals along the flow paths.

Key words: Anion geochemistry, groundwater facies, sulphate reduction, Yola area, NE Nigeria.

### Introduction

Facies are identifiable parts of different nature belonging to any genetically related body or system. Hydrochemical facies are distinct zones that have cation and anion concentrations describable within defined composition categories<sup>1</sup>. Hydrochemical facies can be studied in terms of anions and cations or both. For instance, Chebotarev<sup>2</sup> used anion species only and developed his well-known sequence which states that all ground waters tend to evolve chemically toward the composition of seawater. Toth<sup>3</sup> used anion facies development in mapping groundwater discharge and recharge areas in Canada. Amadi et al<sup>4</sup> used both anion and cation species in mapping the groundwater facies type housed in a north-south direction of some part of the Niger Delta region. Although each option may differ in scope but all are directed towards the definition and delineation of hydrochemical facies types found in groundwater flow systems.

Groundwater flow systems has been mapped and correlated with hydrochemical patterns to varying degrees using hydrochemical facies. As a result certain broad relationship between chemical composition and the flow distribution of groundwater have been established in the process. Consequently, the mapping of groundwater flow systems using hydrochemical facies has aided the separation of potable and non-potable water. Hence, water quality has been related to the hydraulic regime (inflow, through flow, outflow) and the type (local, intermediate, regional) of the flow system<sup>5</sup>. Finally Egboka and Amadi<sup>8</sup> demonstrated the use of anion geochemistry in mapping groundwater facies in the Portharcourt area of the Niger Delta, Nigeria. In this study similar technique was applied in Yola area of Northeastern Nigeria in using anion geochemistry in mapping groundwater and surface water facies.

Study Area: The study area occur at an elevation varying from 152m to 455m above mean sea level and falls within the Upper Benue Basin which has a catchment area of about 203,000km<sup>2</sup>. It is located within longitudes 12°24'E and 12°34'E and Latitudes 9°11'N and 9°24'N and lies about 50km south of the Hawal Massifs. It is bounded to the east by the Republic of Cameroun and to the west by Ngurore town. The northern boundary is demarcated by Gokra town and the southern boundary by the Mandarara town (figures 1). The study area falls within the semi-arid climatic zone of Nigeria in Sub-Saharan Africa is characterized by two distinct seasons; a hot dry season lasting from November to April and a cool rainy season lasting from April to October. The study area receives summer rainfall from the south-western monsoon derived from the Gulf of Guinea. Rainfall during 1963/64-2006/2007 water years averaged 827.7mm per annum while the mean annual evapotranspiration is about 2384.6 mm.

# **Material and Methods**

A total of forty-three (43) water samples were collected from forty-three (43) locations between the months of November and December 2007. Of this forty-three locations (consisting of 27 groundwater, 11 surface water and 5 rainwater samples) were sampled. These samples were designated as SW1 to SW11 for surface water, RW1 to RW5 for rainwater and HW1 to HW45 and BH21 to BH137 for groundwater samples) respectively (figure 1). A global positioning system (GPS), Garment 12, was used for well location and elevation readings. This was supported by topographic sheets made available from the Ministry of Lands and Survey, Adamawa State of Nigeria.

The samples were collected in polyethylene bottles after pumping the sampled wells for about 30 minutes and kept cool until analyses. This was done to remove groundwater stored in the well itself and to obtain representative samples. Various physical parameters were measured in the field using standard equipments. These include Temperature and conductivity (DR 2400), dissolved oxygen (Hach 2400 electronic meter) and pH/Eh (DR 2400 pH meter) measurements were made in the field.

The samples were filtered through a thin polycarbonate membrane with  $0.45\mu$ m pore size and subsequently analyzed in the Laboratory of the Adamawa State Water Board Yola for  $HCO_3^{-1}$  CO<sub>3</sub><sup>2-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and TDS. The chemical analyses were based on the standard methods presented in APHA/AWWA/WPCF<sup>9</sup>. Results of chemical analyses in milligrams per litre were converted to values in milliequivalent per litre and anions balanced against cations as a control check on the reliability of the analyses results. All the samples were assessed for charge balance and were all within the acceptable range of  $\pm 5$ 

The resulting values of  $(\text{HCO}_3^- + CO_3^{2-})$  and those of  $(\text{CI}^- + \text{SO}_4^{2-})$  were then expressed as percentages of all anions. The facies of the resulting percentages were then matched with the guidelines proposed by Back<sup>10</sup> whereas the direction of facies change was determined by fitting the facies types into the anion diamond field of Domenico<sup>11</sup>.

# **Results and Discussion**

Analytical data of the anion values of the sampled rainwater, surface water and groundwater in milligram per litre are provided in tables 1 to 3 whereas their equivalent values in milliequivalent per liter are presented in tables 4 to 6. The values of the sum of  $HCO_3^-+CO_3^{2-}$  and those of  $Cl^- + SO_4^{2-}$  expressed as percentages of all anions are displayed in Tables 7 to 9. The results obtained from these tables were interpreted based on the classification guide given by Domenico<sup>11</sup>, Back<sup>12</sup> and UNESCO/WHO<sup>13</sup> as given in Tables 10 and 11 respectively. Tables 12, 13 and 14 revealed the hydrochemical facies of the sampled rainwater, surfacewater and groundwater obtained in the study area.

**Environmental controls on the Anion Concentration Levels:** Tables 1 to 3 indicate that sulphate anions varies from 1.60 mg/l to 3.55 mg/l in rainwater and 2 mg/l to 29 mg/l in surface water whereas those obtained for the shallow groundwater and deep groundwater varies from 0 mg/l to 35 mg/l and 0 mg/l to 64.50 mg/l respectively. These results indicate completely absent sulphate values in some sampled water to relatively low values in most samples. The absence of  $SO_4^{2^-}$  and relatively high concentration of bicarbonates in some of the samples could be attributed to sulphate reduction resulting from the activities of sulphate reducing bacteria whereas relatively low values obtained in others are due to on-going sulphate reduction.

Chemical reduction of oxidized sulphur ions to sulphate ions or to the sulphide state occurs frequently in groundwater. The reaction is believed to take place in the presence of sulphate-reducing bacteria in the soil zone through which recharge water percolates. The process controls the level of occurrence of  $SO_4^{2-}$  in groundwater. The absence of  $CO_3^{2-}$  in all the sampled water is due to the relatively high acidity of the groundwater system. Tables 1 to 3 revealed pH values ranging from to which are considered unfavourable for the formation of  $CO_3^{2-}$ through the dissolution of bicarbonate. This process according to Davis and DeWiest<sup>14</sup> is only affective above a pH value of 8.2 as indicated in the following reaction which justified the dependence of individual  $CO_2$  forms on pH (table 11).

$$H^{+}+CO_{3}^{2-} = HCO_{3}^{-}$$
 (1)

Thus the pH range of 4.30 to 8.00 recorded for the sampled rainwater, surface water and groundwater favoured the occurrence of bicarbonate ions as opposed to carbonate ions. This is because a pH of 8.2 and less favours the formation of bicarbonate ion by the addition of H<sup>+</sup> to the  $CO_3^{2^-}$  as indicated in equation 1 (table 11).

The mean chloride for the surface water bodies and precipitation are 145.87 mg/l and 0.65 mg/l with ranges of 39.93 mg/l and 455.20 mg/l (surface water) and 0.50 and 0.80 mg/l (precipitation). The mean chloride concentration for the shallow groundwater and deep groundwater are 83.46 mg/l and 75.58 mg/l with ranges of 0 mg/l and 170.17 mg/l (Shallow groundwater) and 0.004 mg/l and 159.40 mg/l (deep groundwater).

The chloride values in precipitation are low in comparison with those obtained for the surface water and the groundwater indicating that pollution is derived from anthropogenic reactions and/or dissolved mineral constituents in the underlying rock formations. It also suggests that chloride behaves as a conservative natural tracer indicating presence of NaCl-type water<sup>15</sup>. Chloride does not react easily with aquifer materials and tends to be closely associated with water molecules (Mercado 1985). These qualities prevent chloride from being easily removed from solution and enhance its solution in groundwater.

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S/N	Location	Date of	Date of	Water	Parameter				
5/1	Location	collection	analysis	table (m)	pН	SO4 <sup>2-</sup>	$CO_{3}^{2-}$	$HCO_3^-$	Cl <sup>-</sup>
1	Rainwater Yola RW1	15/08/09	15/08/09	Nil	7.40	1.60	Nil	18	070
2	Rainwater Yola RW2	15/08/09	15/08/09	Nil	4.30	1.80	Nil	19.20	0.60
3	Rainwater Yola RW3	15/08/09	15/08/09	Nil	7.70	4.50	Nil	16.20	0.65
4	Rainwater Yola RW4	15/08/09	15/08/09	Nil	6.40	2.70	Nil	17.50	0.80
5	Rainwater Yola RW5	15/08/09	15/08/09	Nil	6.20	3.55	Nil	18.73	0.50
6	River Benue SW1	22/11/09	22/11/09	1	7.34	17.00	Nil	148	39.93
7.	River Benue SW2	22/11/09	22/11/09	1	7.55	10.00	Nil	183	27.90
8	Lake Geriyo SW3	22/11/09	22/11/09	1	7.70	11.50	Nil	273	227
9	River Benue TPY SW4	22/11/09	22/11/09	1	7.60	22.10	Nil	133	227.6
10	River Benue TPY SW5	22/11/09	22/11/09	1	7.61	2.00	Nil	73.30	284.50
11	River Benue SW6	22/11/09	22/11/09	1	8.00	24.86	Nil	130	40
12	River Benue SW7	22/11/09	22/11/09	1	7.20	20.06	Nil	145	51.31
13	River Benue SW8	22/11/09	22/11/09	1	7.50	29.11	Nil	162	60.00
14	Lake Njuwa SW9	22/11/09	22/11/09	1	7.70	20.50	Nil	57	455.20
15	River Benue SW10	22/11/09	22/11/09	1	7.80	20.21	Nil	153	147.05
16	River Benue SW11	22/11/09	22/11/09	1	7.30	18.34	Nil	48.50	147.05

Table-1

Anion Concentration and pH levels in rainwater and Surface Water Samples of the Study Area

 Table-2

 Anion Concentration and pH levels in Shallow Groundwater Samples of the Study Area

C/N	Location	Date of	Date of	Water		Parameter				
5/IN	Location	collection	analysis	table (m)	pН	SO4 <sup>2-</sup>	$CO_3^{2-}$	$HCO_3^-$	Cl	
1	Lainde HW 1	19-11-09	19-11-09	24.2	6.90	10.10	Nil	61.90	57.90	
2	Modire HW 4	19-11-09	19-11-09	23.33	6.60	5.20	Nil	99.50	113.80	
3	Girei HW 12	19-11-09	19-11-09	7.27	7.30	12.80	Nil	76	115.0	
4	Wuro Chekke	19-11-09	19-11-09	8.00	7.40	0.00	Nil	89.13	85.30	
5	Jimeta HW 24	19-11-09	19-11-09	1.40	7.30	0.00	Nil	77.00	110.90	
6	Bachure HW25	19-11-09	19-11-09	5.20	6.70	0.00	Nil	51.50	63.30	
7.	Tofare Buhu HW 36	19-11-09	19-11-09	2.12	6.50	29.80	Nil	92.00	170.17	
8	Kabawa	19-11-09	19-11-09	6.70	6.90	17.50	Nil	85.40	112.80	
9	Sebore HW 42	19-11-09	19-11-09	12.00	7.10	2.10	Nil	125.00	110.70	
10	Yolde Patch II HW45	19-11-09	19-11-09	7.88	7.20	35.00	Nil	41.00	64.90	
11	Bajabure Phase II BH21	19-11-09	19-11-09	6.065	7.20	32.50	Nil	93.00	0.00	
12	Jambutu BH 37	19-11-09	19-11-09	4.70	7.10	0.90	Nil	240.00	56.89	
13	Njobboli BH 117	19-11-09	19-11-09	11.00	7.40	1.50	Nil	103.50	66.90	
14	Lainde BH 123	19-11-09	19-11-09	35,00	6.50	16.70	Nil	102.00	132.90	
15	Kofare BH 136	19-11-09	19-11-09	16.00	6.90	10.01	Nil	10.90	0.00	
16	Yolde Patch II BH137	19-11-09	19-11-09	18.00	6.80	0.00	Nil	82.00	73.90	

		Date of	Data of	Water		Parameter				
S/N	Location	collection ana	analysis	table (m)	pН	SO4 <sup>2-</sup>	$CO_{3}^{2-}$	$HCO_3^-$	Cl	
1	Sabare HW14	18/11/09	18/11/09	36.40	6.8	21.10	Nil	77.80	113.90	
2	Karewa HW 26	18/11/09	18/11/09	60	7.10	0.09	Nil	84.00	57	
3	Karewa HW 46	18/11/09	18/11/09	62	7.55	27.5	Nil	104.90	133.60	
4	Karewa HW 47	18/11/09	18/11/09	58	6.80	0.35	Nil	53.50	171.50	
5	Girei BH7	18/11/09	18/11/09	50	6.60	11.88	Nil	153.30	77.00	
6	FUT Yola BH 7	18/11/09	18/11/09	56	6.80	64.50	Nil	207	42.00	
7.	Jimeta BH 10	18/11/09	18/11/09	46	7.40	25.50	Nil	101	11.02	
8	Jimeta BH 75	18/11/09	18/11/09	46	7.50	11.20	Nil	94.90	159.40	
9	Jimeta BH 81	18/11/09	18/11/09	48	7.80	0.00	Nil	99.60	65.90	
10	Demsawo BH 87	18/11/09	18/11/09	37	7.50	0.83	Nil	109	0.004	
11	Yola BH 91	18/11/09	18/11/09	52	7.60	0.02	Nil	50	0.03	

 Table-3

 Anion Concentration and pH levels in deep groundwater sample of the study area

 Table-4

 Anions in meq/l for rainfall and surface water samples

S/N	Location/Parameters	<i>SO</i> <sub>4</sub> <sup>2-</sup>	<i>CO</i> <sub>3</sub> <sup>2–</sup>	HCO <sub>3</sub>	СГ	total
1.	Rainwater Yola RW1	0.03331	Nil	0.29502	0.01975	0.34808
2	Rainwater Jimeta RW 2	0.03748	Nil	0.31469	0.01834	0.3691
3	Rainwater Vinikilang RW 3	0.09369	Nil	0.26552	0.01834	0.37755
4	Rainwater FUT Yola RW 4	0.05621	Nil	0.28683	0.02257	0.36561
5	Rainwater Girei RW 5	0.07391	Nil	0.30698	0.01411	0.395
6	River benue SW 1	0.35394	Nil	2.42572	1.12643	3.90609
7	River Benue SW 2	0.2082	Nil	2.99937	0.78706	3.00463
8	Lake Geriyo SW3	0.23943	Nil	4.47447	6.40367	11.11757
9	River Benue TPy SW4	0.46012	Nil	2.17987	6.42060	9.06059
10	River Benue TPY SW5	0.04164	Nil	1.20139	8.02575	9.26878
11	River Benue SW6	0.51759	Nil	2.1307	1.1284	3.77669
12	River Benue SW7	0.41765	Nil	2.37655	1.44746	4.24166
13	River Benue SW8	0.60507	Nil	2.65518	1.6926	4.95385
14	Lake Njuwa SW9	0.42681	Nil	0.93423	12.84119	14.20223
15	River Benue SW10	0.42077	Nil	2.50767	1.24209	4.17053
16	River Benue SW11	0.38184	Nil	0.79492	4.14828	5.32504

S/N	Location/Parameters	<i>SO</i> <sub>4</sub> <sup>2-</sup>	<i>CO</i> <sub>3</sub> <sup>2–</sup>	HCO <sub>3</sub>	Cl	total
1.	Lainde HW1	0.21028	Nil	1.01454	1.63336	2.85818
2.	Modire HW4	0.10826	Nil	1.63081	3.21030	4.94947
3.	Girei HW 12	0.26650	Nil	1.24564	3.24415	4.75629
4.	Wurochekke HW 22	0.00000	Nil	1.46084	2.40631	3.86715
5.	Jimeta HW24	0.00000	Nil	1.26203	3.12849	4.39052
6.	Bachure HW25	0.00000	Nil	0.84409	1.78569	2.62978
7.	Tafare Buhu HW36	0.62044	Nil	1.50788	4.80050	6.92882
8.	Kabawa HW 38	0.36435	Nil	1.39971	3.18209	4.9465
9.	Sebore HW42	0.04372	Nil	2.04875	3.12285	5.21532
10.	Yolde Patch II HW45	0.7287	Nil	0.67199	1.83083	3.23152
11.	Bajabure Phase II BH21	0.67665	Nil	1.52427	0.00000	2.20092
12.	Jambutu BH37	0.01874	Nil	3.9336	1.60487	5.55721
13.	Njobboli BH117	0.03123	Nil	1.67637	1.88725	3.61485
14.	Lainde BH123	0.34769	Nil	1.67178	3.74911	5.76858
15.	Kofare BH136	0.21028	Nil	0.32616	0.00000	0.53644
16.	Yolde Patch II BH137	0.00000	Nil	1.34398	2.08472	3.4287

Table-5 Anions in meq/l for shallow groundwater samples

 Table-6

 Anions in meq/l deep groundwater samples

S/N	Location/parameter	<i>SO</i> <sub>4</sub> <sup>2-</sup>	CO <sub>3</sub> <sup>2–</sup>	HCO <sub>3</sub>	Cl	total
1.	Sabore HW14	0.43930	Nil	1.27514	3.21312	4.92756
2.	Karewa HW26	0.00187	Nil	1.37676	1.60797	2.9866
3.	Karewa HW46	0.57255	Nil	1.71931	3.76886	6.06072
4.	Karewa HW47	0.00729	Nil	0.87359	4.83802	5.7189
5.	Girei BH7	0.24734	Nil	2.51259	2.17217	4.9321
6.	FUT Yola BH75	1.34289	Nil	3.39273	1.18482	5.92044
7.	Jimeta BH10	0.53091	Nil	1.65539	0.31087	2.19717
8.	Jimeta BH75	0.22944	Nil	1.55541	4.49667	6.28152
9.	Jimeta BH81	0.00000	Nil	1.63244	1.85904	3.49148
10.	Demsawo BH87	0.01728	Nil	1.78651	0.00011	1.8039
11.	Yola BH91	0.00042	Nil	0.8195	0.00085	0.82077

S/N	Location/parameter	$HCO_3^- + CO_3^{2-}(_{\%})$	$CI^{-} + SO_4^{2-}(\%)$
1.	Rainwater Yola RW1	84.756	15.244
2	Rainwater Jimeta RW2	85.259	14.741
3	Rainwater Vinikilang RW3	70.327	29.673
4	Rainwater FUTY Rw4	78.452	21.548
5	Rainwater Girei RW5	77.716	22.284
6	River Benue SW1	62.101	37.899
7	River Benue SW2	75.085	24.915
8	Lake Geriyo SW3	40.247	59.753
9	Rover Benue TPY SW5	24.059	75.941
10	River Benuw TPJ SW5	12.962	87.038
11	River benue Sw6	56.417	43.583
12	River Benue SW7	56.029	43.971
13	River Benue SW8	53.598	46.402
14	Lake Njuwa SW9	6.578	93.422
15	River benue SW10	60.128	39.872
16	River benuw SW11	14.928	85.072

Table-7
Values of $(HCO_3^- + CO_3^{2-})$ and of $(Cl^- + SO_4^{2-})$ as Percentages of all Anions for Rainwater and Surface Water Samples

# Table-8 Values of $(HCO_3^- + CO_3^{2^-})$ and of $(CI^- + SO_4^{2^-})$ as Percentages of all Anions for Shallow groundwater Samples

S/N	Location/parameter	HCO <sub>3</sub> <sup>-</sup> + $CO_3^{2-}$ (%)	$Cl^{-} + SO_4^{2-}(\%)$
1.	Lainde HW1	35.496	64.504
2	Modire HW4	32.950	67.050
3	Girei HW12	26.189	73.811
4	Wurochekke Hw22	37.776	62.224
5	Jimeta HW24	28.744	71.256
6	Bachure HW25	32.097	67.903
7	Tafare Buhu HW36	21.762	78,238
8	Kabawa HW38	28.299	71.701
9	Sebore HW42	39.283	60.717
10	Yolde Patch II Hw45	20.795	79.205
11	Bajabure Phase II BH21	69.256	30.744
12	Jambutu BH37	70.784	29.216
13	Njobboli BH117	46.928	53.072
14	Lainde BH123	28.981	71.019
15	Kofare BH136	60.801	39.199
16	Yolde Patch II BH137	39.198	60.802

#### Table-9

	$(\alpha \alpha^{2})$	$- \alpha \alpha^{2} - \lambda $	e 11 A + e	1 1 4	
values of (HCO <sub>3</sub> +	$-CU_3^-$ ) and of (CI	+ SO <sub>4</sub> ) as Percentage	s of all Anions for (	deep groundwater	C Samples
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S/N	Location/parameter	HCO <sub>3</sub> <sup>-</sup> + $CO_3^{2-}$ (%)	$CI^{-} + SO_4^{2-}(\%)$
1.	Sabore HW14	25.878	74.122
2	Karewa HW26	46.097	53.902
3	Karewa HW46	28.368	71.632
4	Karewa HW47	15.275	84.725
5	Girei BH7	50.944	49.056
6	FUT Yola BH75	57.305	42.695
7	Jimeta BH10	66.291	33.709
8	Jimeta BH75	24.762	75.238
9	Jimeta BH81	46.755	53.245
10	Demsawo BH87	99.036	0.964
11	Yola Bh91	99.845	0.155

 Table-10

 Classification of Hydrochemical Facies<sup>12</sup>

	Percentage of constituents, epm					
	Ca + Mg	Na + K	$HCO_3^- + CO_3^{2-}$	$\mathbf{C}\mathbf{I}^{-} + \mathbf{SO}_4^{2-}$		
Cation Facies						
Calcium – Magnesium	90-100	0<10				
Calcium – Sodium	50-90	10<50				
Sodium – Calcium	10 - 50	50<90				
Sodium – Potassium	0 - 10	90 -100				
Anion Facies						
Bicarbonate			90 - 100	0<10		
Bicarbonate – Chloride – Sulphate			50 - 90	10<50		
Chloride – Sulphate – Bicarbonate			10 - 50	50<90		
Chloride – Sulphate			0 – 10	90 - 100		

 $Table-11 \\ Dependence \ of \ Individual \ CO_2 \ forms \ on \ pH^{13}$ 

	% CO <sub>2</sub> at pH								
CO <sub>2</sub> Forms	4	5	6	7	8	8.3	9	10	11
Free	99.5	95.4	67.7	17.3	2.0	1.0	0.2	-	-
Bicarbonate	0.5	4.6	32.2	82.7	97.4	97.8	94.1	62.5	14.3
Carbonate	-	-	-	-	0.6	1.2	5.7	37.5	85.7

S/N	Location	Hydrochemical facies
1.	Rainwater Yola RW1	$SO_4^{2-} + Cl^-$
2	Rainwater Jimeta RW2	$HCO_{3}^{-} + CO_{3}^{2-}$
3	Rainwater Vinikilang RW3	$HCO_{3}^{-} + CO_{3}^{2-}$
4	Rainwater FUTY Rw4	$HCO_{3}^{-} + CO_{3}^{2-}$
5	Rainwater Girei RW5	$HCO_{3}^{-} + CO_{3}^{2-}$
6	River Benue SW1	$SO_4^{2-} + Cl^{-}$
7	River Benue SW2	$HCO_{3}^{-} + CO_{3}^{2-}$
8	Lake Geriyo SW3	$SO_4^{2-} + Cl^{-}$
9	Rover Benue TPY SW5	$HCO_{3}^{-} + CO_{3}^{2-}$
10	River Benuw TPJ SW5	$HCO_{3}^{-} + CO_{3}^{2-}$
11	River benue Sw6	$HCO_{3}^{-} + CO_{3}^{2-}$
12	River Benue SW7	$SO_4^{2-} + Cl^{-}$
13	River Benue SW8	$SO_4^{2-} + Cl^{-}$
14	Lake Njuwa SW9	$SO_4^{2-} + Cl^-$
15	River Benue SW10	$HCO_{3}^{-} + CO_{3}^{2-}$
16	River Benue SW11	$HCO_{3}^{-} + CO_{3}^{2-}$

 Table-12

 Hydrochemical Facies in Rainwater and Surface Water Samples

Table-13				
Hydrochemical Facies in Shallow groundwater				

S/N	Location/parameter	Hydrochemical Facies
1.	Lainde HW1	$SO_4^{2-} + Cl^-$
2	Modire HW4	$SO_4^{2-} + Cl^-$
3	Girei HW12	$SO_4^{2-} + Cl^-$
4	Wurochekke Hw22	$SO_4^{2-} + Cl^-$
5	Jimeta HW24	$SO_4^{2-} + Cl^-$
6	Bachure HW25	$SO_4^{2-} + Cl^-$
7	Tafare Buhu HW36	$SO_4^{2-} + Cl^-$
8	Kabawa HW38	$SO_4^{2-} + Cl^-$
9	Sebore HW42	$SO_4^{2-} + Cl^-$
10	Yolde Patch II Hw45	$SO_4^{2-} + Cl^-$
11	Bajabure Phase II BH21	$HCO_{3}^{-} + CO_{3}^{2-}$
12	Jambutu BH37	$HCO_{3}^{-} + CO_{3}^{2-}$
13	Njobboli BH117	$SO_4^{2-} + Cl^{-}$
14	Lainde BH123	$SO_4^{2-} + Cl^-$
15	Kofare BH136	$HCO_{3}^{-} + CO_{3}^{2-}$
16	Yolde Patch II BH137	$SO_4^{2-} + Cl^-$

Thus the absence of some ions such as  $CO_{3}^{2-}$  and  $SO_{4}^{2-}$  and the varied concentration levels of others such as  $CI^{-}$  and  $HCO_{3}^{-}$  affect the types and number of mappable facies in groundwater systems<sup>8</sup>.

Table-14Hydrochemical Facies in Deep groundwater C

S/N	Location	Hydrochemical Facies
1.	Sabore HW14	$SO_4^{2-} + Cl^{-}$
2	Karewa HW26	$HCO_{3}^{-} + CO_{3}^{2-}$
3	Karewa HW46	$SO_4^{2-} + Cl^{-}$
4	Karewa HW47	$SO_4^{2-} + Cl^{-}$
5	Girei BH7	$HCO_{3}^{-} + CO_{3}^{2-}$
6	FUT Yola BH75	$HCO_{3}^{-} + CO_{3}^{2-}$
7	Jimeta BH10	$HCO_{3}^{-} + CO_{3}^{2-}$
8	Jimeta BH75	$HCO_{3}^{-} + CO_{3}^{2-}$
9	Jimeta BH81	$SO_4^{2-} + Cl^{-}$
10	Demsawo BH87	$HCO_{3}^{-} + CO_{3}^{2-}$
11	Yola Bh91	$HCO_{3}^{-} + CO_{3}^{2-}$

Anion Facies in the Groundwater: The percentage of anion concentration in rainwater and surface water samples (table 7) and in shallow groundwater and deep groundwater samples (tables 8 and 9) were matched and compared with the guidelines given in table 10. These resulted in groundwater anion facies for the study area as displayed in tables 12, 13 and 14. These tables indicate that while there is a clear dominance of bicarbonate-sulphatechloride facies in the rainwater, the surface water revealed an almost equal percentage of both bicarbonate-sulphatechloride facies and sulphate-chloride-bicarbonate facies respectively. The study also indicated that the shallow groundwater revealed sulphate-chloride-bicarbonate facies whereas the deep groundwater indicated both the sulphatechloride-bicarbonate facies and the bicarbonate-sulphatechloride facies.



Settlement, — Torred Road, ---- Untorred Road, ----- Footpath, O Contour (Ft),
 River/Stream, Sample Points: Π Hand-dug wells, O Borecholes, Δ Surface water.
 Figure-1

Map of the study area showing some well location and sampling points



Figure-2 Geological map of the study area

N 12 W

Strike and Dip



Mediùm coarse grained

Nomenclature for hydrochemical facies: (AFTER: Domenico, 1972)

ALBLAN

SANDSTONE

Figure-4 Anion facies in rainwater environment



Figure-7 Anion facies in deep groundwater environment

Thus when the facies types are fitted into the anion diamond field of Domenico (1972) as indicated in figure 3 there is an indication of the following facies change

HCO 3 50

Rainwater Facies Sequence HCO<sub>3</sub><sup>-</sup> - SO<sub>4</sub><sup>2-</sup> - Cl<sup>-</sup> $\rightarrow$  SO<sub>4</sub><sup>2-</sup> - Cl<sup>-</sup>- HCO<sub>3</sub><sup>-</sup>

 $HCO_{3}^{-} - SO_{4}^{2-} - CI^{-} \rightarrow SO_{4}^{2-} - CI^{-} - HCO_{3}^{-}$ (2) Surface water Facies Sequence

 $HCO_3^- - SO_4^{-2-} - CI^- \rightarrow SO_4^- - CI^- - HCO_3^-$  (3) Shallow groundwater Facies Sequence

HCO<sub>3</sub><sup>-</sup> - SO<sub>4</sub><sup>-</sup> - CI<sup>-</sup>  $\rightarrow$  SO<sub>4</sub>- CI<sup>-</sup> (4) Deep groundwater Facies Sequence

 $HCO_{3}^{-} - SO_{4}^{2} - CI^{-} \rightarrow SO_{4}^{2} - CI^{-} - HCO_{3}^{-}$  (5)

These facies indicate a strong evolution from fresh water to sea water (figures 4, 5, 6 and 7).

The order in which groundwater encounter strata of different mineralogical composition influences the final chemistry of the groundwater (Freeze and Cherry 1979). Thus the chemistry of groundwater not only depends on the processes in the vadose zone but also on the reactions operating along the saturated flow system. Most of the same processes affecting ion concentrations in the unsaturated zone are also operative in the saturated zone including the dissolution and precipitation of various

minerals and cation exchange (Schwartz and Zhang 2003). This conforms with Chebotarev (1955) study that states that all groundwaters tend to evolve chemically towards the composition of seawater which according to him is normally accompanied by the following regional changes in dominant anion species;

Travel along flow path $\rightarrow$ 

$$HCO_{3}^{-} \rightarrow HCO_{3}^{-} + SO_{4}^{2-} \rightarrow SO_{4}^{2-} + HCO_{3}^{-}$$
$$SO_{4}^{2-} + CI^{-} \rightarrow CI^{-} + SO_{4}^{2-} \rightarrow CI^{-}$$
(6)

Increasing Age

These findings are therefore in conformity with the theory and observations (Chebotarev 1955; Toth 1984), that the flow of water from inflow to outflow areas may be attended in general by increases in the total dissolved solids contents (TDS) and Mg<sup>2+</sup>: Ca<sup>2+</sup> ratio, and decreases in the SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup> and Ca<sup>2+</sup>, Na<sup>+</sup> ratios. Furthermore, local systems may be associated with low TDS and a high percentage of Ca<sup>2+</sup>, Mg<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup>; intermediate systems with intermediate TDS and a high percentage of Na<sup>+</sup>,  $SO_4^{2-}$ and Cl<sup>-</sup> and regional systems with high TDS and a high percentage of Na and Cl<sup>-</sup>, relative to the local and intermediate systems. However, complications are brought about by factors such as mobility of the element, temperature, pressure, contact area between rock and water, contact time, length of flow path, amounts and distribution of soluble salts in rocks and antecedent water quality.

### Conclusion

An anion geochemistry was employed in mapping the groundwater facies found in semiarid Yola area NE Nigeria. Groundwater from different water sources such as rainwater (5) surface water (11), shallow groundwater (16) and deep groundwater (11) were analyzed for the relevant anions ( $C\Gamma$ ,  $SO_4^{2-}$ ,  $HCO_3^{-}$  and  $CO_3^{2-}$ ) employing standard methods. The concentration levels of each anions were interpreted and related to the environmental factors that control their availability.

The results indicate that all the other water sources have a local meteoric origin that evolves toward the composition of sea water. They also suggest that their chemical evolution is associated mainly with progressive dissolution and/or weathering of minerals along the flow path.

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