# THE USE OF ANION GEOCHEMISTRY IN MAPPING GROUNDWATER FACIES IN THE PORT HARCOURT AREA OF THE NIGER DELTA, NIGERIA.

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# ABSTRACT

The groundwater system of the Port Harcourt area is home to three anion facies, the  $CI - SO_4$ , the  $CI - SO_4 - HCO_3$ and the  $HCO_3 - CI - SO_4$ . The first two types exist in both shallow – and deep – groundwater environments while the third is restricted to the deep environment. Although there are natural intermittent and, in some cases, continuous interactions between shallow and deep groundwaters, this paper establishes that the quality and facies types of the groundwaters are not exactly alike. 28 groundwater samples (12 from hand-dug wells; 16 from boreholes) were analysed for CI,  $SO_4$ ,  $HCO_3$  and  $CO_3$ . The concentration levels of  $SO_4^{2^2}$  were analysed using the HACH Spectrophotometer equipment, model No DR/2000 while those of  $CI^{-}$ ,  $CO_3^{2^{-}}$  and  $HCO_3^{-}$  were by titrimetric method, using the Titro Process Dosimat 665 equipment. The results indicate that, for the hand-dug wells,  $SO_4^{2^{-}}$  levels ranged from 0.00mg/l to 67.0mg/l with an average of 16.5mg/l;  $HCO_3^{-}$  from 12.2 to 36.6 with an average of 15.25, while  $CI^{-}$ ranged from 11.332 to 121.905 with an average of 41.22mg/l. No  $CO_3^{2^{-}}$  was detected in all the samples. For the borehole samples, the respective figures for  $SO_4^{2^{-}}$ ,  $HCO_3^{-}$  and  $CI^{-}$  are 0.00 to 33.0 with an average of 2.13; 12.2 to 24.4 with an average of 12.96, and 5.490 to 72.306 with an average of 17.037 mg/l. Again, no  $CO_3^{2^{-}}$  was detected. The total absence of  $CO_3^{2^{-}}$  conforms with the relatively high acidity of the groundwater environment of the Port Harcourt Area; and the diminutive level of  $SO_4^{2^{-}}$ , is associated with the effect of the bacteria catalysed reduction of the ion. This absence of some ions and the low levels in others do affect the number and type of mappable facies in groundwater systems. With the results obtained, the paper notes that:

- (1) The shallow groundwater environment embedded less number of mappable facies than the deep groundwater environment;
- (2) Facies sequences mapped are tending towards the composition of seawater; and concludes that the existence of different groundwater facies is an evidence that groundwater encounters strata of different mineralogical compositions along its flow path.

# KEY WORDS: Anion facies, Hand-dug well, Mappable, Acidity, Sulphate reduction.

# INTRODUCTION

Hydrogeological practice in the Port Harcourt area of the Niger Delta has centred mainly on drilling for water supply. Details of water quality are rare except for some scanty qualitative details that appear in Amajor (1991), Etu-Efeotor (1981), Abibo (1988) and Akujieze *et al.* (2003). There is hitherto no literature on the aspect of groundwater facies for the Port Harcourt region.

# **Hydrochemical Facies**

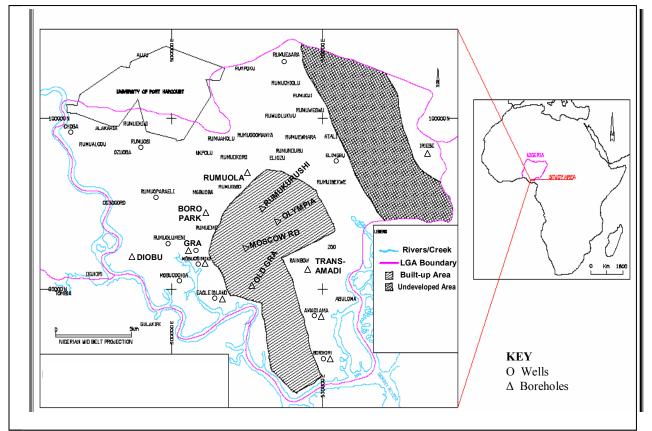
Facies are identifiable parts of different nature belonging to any genetically related body or system. Hydrochemical facies are distinct zones that have cation and anion concentrations describable within defined composition categories. Domenico (1972) notes that although specific details concerning methodology vary somewhat, the facies are studied in much the same manner as lithofacies in geology, with Piper's (1944) trilinear diagram, or some slight modification, used to identify the various chemical types. The areal distribution of constituents is shown by fence diagrams, hydrochemical facies can be studied in terms of anions, or cations, or both. These various options of study may be in consideration for the scope of the research involved or of the possible unavailability of relevant equipment or both. For example, Chebotarev (1955) used anion species only and developed his well-known sequence which states that all groundwaters tend to evolve chemically toward the composition of seawater; similarly Toth (1966b) used anion facies development in mapping groundwater discharge and recharge areas in Canada; and Amadi et al.; (1989) used both anion and cation species in mapping the groundwater facies-types housed in a north-south direction of some part of the Niger Delta region. Each option defines its scope but is directed towards achieving the same objective, that is, the delineation of facies - types embedded in groundwater systems. There is no significant advantage of one option over the others. The thrust of this paper is 156

of the Port Harcourt area, using only anion species of groundwater samples from both the shallow groundwater – and deep groundwater environments of

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The study area comprises two Local Government Areas, namely, the highly industrialized Port Harcourt Local Government Area (PHALGA) and the rapidly expanding lies between latitudes  $4^042^\prime$  and  $4^057^\prime N$  and longitudes  $6^053^\prime$  and  $7^008^\prime$  E (Fig. 1) and covers an area of about  $313 km^2$  within the Niger Delta sedimentary basin. Its



Obio/Akpor Local Government Area (OBALGA), both of which are together designated as the Port Harcourt Metropolis, or Greater Port Harcourt. The Metropolis

characteristic area, shown in Fig. 2, lies between the freshwater swamp area that is seasonally flooded and the saltwater swamp area that is tidally flooded.

Fig 1: Location Map Showing Positions of Wells and Boreholes

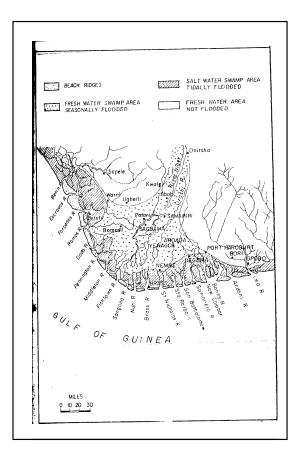


Fig.2 Characteristic Areas (NEDECO, 1959)

# METHODOLOGY

Considering the objective of this work, groundwater samples were collected with scrupulously clean polyethylene plastic bottles. The samples were unacidified but were filtered through a  $0.45\mu$ m pore size disposable filter paper, and collected in pre-cleaned plastic bottles. To accommodate both shallow – and deep-groundwater environments, 12 samples were collected from hand-dug wells and 16 from boreholes. The target species were  $SO_4^{2^\circ}$ ,  $CI^\circ$ ,  $CO_3^{2^\circ}$  and  $HCO_3^\circ$ . The concentration levels of  $SO_4^2$  were determined using the HACH Spectrophotometer equipment model No. DR/2000 while those of CI,  $CO_3^2$ , and  $HCO_3$  were by titrimetric method, using the Titro Process Dosimat 665 equipment. All analyses were carried out at the

Production Chemistry Laboratory of the Shell Petroleum Development Company, Nigeria Limited, Port Harcourt.

### STAGES IN MAPPING GROUNDWATER FACIES

Four stages were followed in mapping the groundwater facies.

**Stage (i):** Results of the chemical analyses in milligrams per litre were converted to values in milliequivalents per litre.

**Stage (ii):** The resulting values of  $(HCO_3 + CO_3)$  and those of  $(CI + SO_4)$  were then respectively expressed as percentages of all anions.

**Stage (iii):** To define the facies, the resulting percentages were matched with the guidelines proposed by Back (1996), using the anion column in Table 7. **Stage (iv):** The direction of facies change was thereafter determined by fitting the facies types into the anion diamond field of Domenico (1972), (Fig.3).

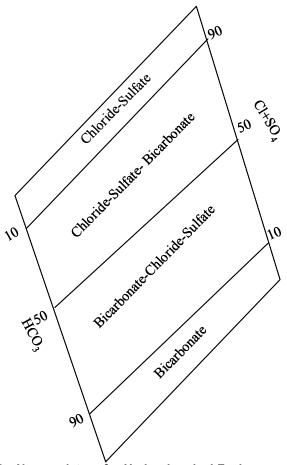


Fig. 3 Nomenclature for Hydrochemical Facies. (Domenico, 1972)

# **RESULTS AND DISCUSSION**

The anion values of the sampled wells and boreholes are presented in Tables 1 and 2 respectively; and the results converted to values in milliequivalents per litre are presented in Tables 3 and 4. Values of  $(HCO_3 + CO_3)$  and those of  $(CI + SO_4)$  as percentages of all anions are presented in Tables 5 and 6. Domenico (1972) notes that hydrochemical facies can be studied in terms of anions, or cations, or both and Back (1966) gives a classification guide shown in Table 7.

# Environmental Controls on the Anion Concentration Levels

Tables 1 and 2 show that among the anions,  $SO_4^{2^-}$  was detected in only 50% of the 12 well samples and in only 12.5% of the 16 borehole samples. While no  $CO_3^{2^-}$  was detected in all 28 samples,  $HCO_3^{-}$  and  $C\Gamma$  were detected in all. The  $SO_4^{2^-}$  values in the 50% of well

borehole samples ranged from 1mgl/l to 33 mgl/l with an average of 17mgl/l. The absence of SO42- in some of the samples could be attributed to sulphate - reduction, a process engineered by certain bacteria. Davis and DeWiest (1966) note that some types of sulphatereducing bacteria are found in soil horizons and that groundwater may contain less than 1 ppm of sulphate if sulphate-reducing bacteria are active in the soil through which recharge water percolates. Domenico (1972) notes that sulphate reduction accounts for diminishing quantities of sulphate in groundwater. This process therefore controls the level of occurrence of  $SO_4^{2-}$  in groundwater. For CO322, its absence in all 28 samples conforms with the relatively high acidity of the groundwater system of the Port Harcourt region. In Table 1, the pH range is from 4.46 to 6.30; in Table 2, the range is 4.15 to 6.14. These pH values are not favourable for the formation of  $\text{CO}_3^{2^\circ}$  via the

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Table

S/No	1	2	3	4	5	9	7	8	6	10	11	12
Location	Eagle Island	Rumuosi	Rumuolumeni <sup>(s)</sup>	Rumuolumeni <sup>(d)</sup>	Choba	Borokiri	Amadi- Ama	Elimgbu	Rumuesara	Mgbuo- shimini	Mgbu- odohia	GRA
Date of collection		<b>26-02-09</b> 01-03-09 <b>03-03-09</b>	03-03-09	03-03-09	05-03-09	15-03-09	18-03-09	19-03-09	19-03-09	22-03-09	23-03-09	07-04-09
Date of analysis		<b>26-02-09</b> 01-03-09 <b>03-03-09</b>	03-03-09	03-03-09	05-03-09	15-03-09	15-03-09 18-03-09	19-03-09	19-03-09	22-03-09	23-03-09	07-04-09
Watertable (m)	2.240	10.50	4.20	5.565	11.230	2.805	5.040	7.620	8.505	5.30	5.233	5.50
Parameter					Ani	Analytical Results	ults					
Hq	4.89	5.81	4.48	<i>L</i> .4	4.46	4.53	4.48	5.27	4.72	6.30	5.73	4.66
$\mathrm{SO_4}^{2-}$	16	0.00	00.00	00'0	0'.79	20.0	00.0	1.00	0.00	61.0	33.0	0.00
$CO_3^{2-}$	Nil	Nil	Nil	liΝ	Nil	Nil	Νil	Nil	Nil	Nil	Nil	Nil
HCO <sub>3</sub> -	12.2	12.2	12.2	12.2	12.2	24.4	12.2	12.2	12.2	36.6	12.2	12.2
CI <sup>-</sup>	21.629	12.636	28.869	28.644	112.237	63.583	11.332	28.599	11.332	121.905	42.538	11.332
s = shallow well	well											

s = shallow well d = deep well concentrations in mg/l

# Table 2 Anion Concentration and pH Levels in Boreholes

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# Table 3 Anions in meq/1 for Well Samples

	Parameter					
	Location	SO4 <sup>2-</sup>	CO32-	HCO <sub>3</sub>	CI	TOTAL
1.	Engle Island	0.33312	-	0.19996	0.61015	1.14323
2.	Rumuosi	-	-	0.19996	0.35646	0.55642
3.	Rumuolumeni <sup>(s)</sup>	-	-	0.19996	0.81439	1.01435
4.	Rumuolumeni <sup>(a)</sup>	-	-	0.19996	0.80805	1.00801
5.	Choba	1.39494	-	0.19996	3.16621	4.76111
6.	Borokiri	0.4164	-	0.39992	1.79368	2.61
7.	Amadi-Ama	-	-	0.19996	0.31968	0.51964
8.	Elimgbu	0.02082	-	0.19996	0.80678	1.02756
9.	Rumuesara	-	-	0.19996	0.31968	0.51964
10.	Mgbuoshimini	1.27002	-	0.59987	3.43894	5.30883
11.	Mgbuodohia	0.68706	-	0.19996	1.20	2.08702
12.	GRA	-	-	0.19996	0.31968	0.51964

# Table 4 Anions in meq/1 for Borehole Samples

	Parameter					
	Location	SO4 <sup>2-</sup>	CO3 <sup>2-</sup>	HCO₃ <sup>-</sup>	CI	TOTAL
1.	Eagle Island	-	-	0.19996	1.04027	1.24023
2.	Boro Park	-	-	0.19996	0.30825	0.50821
3.	Rumuola	-	-	0.19996	0.15487	0.35483
4.	Moscow Road	-	-	0.19996	0.30952	0.50948
5.	Trans-Amadi	-	-	0.19996	0.61777	0.81773
6.	Olympia	-	-	0.19996	0.45666	0.6566
7.	Diobu	-	-	0.19996	0.30698	0.50685
8.	Rumukurushi	-	-	0.19996	0.32599	0.52595
9.	Eagle Island <sup>(P)</sup>	-	-	0.19996	0.31841	0.51837
10.	Old GRA	-	-	0.19996	0.30571	0.50567
11.	Borokiri <sup>(P)</sup>	0.68706	-	0.19996	2.03975	2.92677
12.	Borokiri <sup>(P)</sup>	0.02082	-	0.19996	0.33361	0.55439
13.	Amadi-Ama <sup>(P)</sup>	-	-	0.19996	0.32475	0.52471
14.	Mgbuoshimini <sup>(P)</sup>	-	-	0.19996	0.190276	0.390236
15.	Iriebe <sup>(P)</sup>	-	-	0.19996	0.167455	0.36742
16.	GRA <sup>(P)</sup>	_	-	0.3992	0.48964	0.88884

# Table 5 Values of (HCO<sub>3</sub>+CO<sub>3</sub>) and of (Cl + SO<sub>4</sub>) as percentages of all Anions for Well Samples

	Parameter		
	Location	HCO <sub>3</sub> +CO <sub>3</sub>	CI + SO₄
1.	Engle Island	17.49	82.509
2.	Rumuosi	35.9368	64.063
3.	Rumuolumeni <sup>(s)</sup>	19.713	80.287
4.	Rumuolumeni <sup>(d)</sup>	19.837	80.163
5.	Choba	4.1998	95.896
6.	Borokiri	15.322	84.677
7.	Amadi-Ama	38.480	61.520
8.	Elimgbu	19.459	80.540
9.	Rumuesara	38.480	61.520
10.	Mgbuoshimini	11.299	88.70
11.	Mgbuodohia	9.581	90.490
12.	GRA	38.480	61.520

	Parameter		
	Location	HCO <sub>3</sub> +CO <sub>3</sub>	CI + SO <sub>4</sub>
1.	Engle Island Eagle	16.123	83.877
2.	Boro Park	39.346	60.654
3.	Rumuola	56.354	43.646
4.	Moscow Road	39.248	60.752
5.	Trans-Amadi	24.453	75.547
6.	Olympia	30.454	69.549
7.	Diobu	39.452	60.566
8.	Rumukurushi	38.019	61.981
9.	Eagle Eagle Island	38.575	61.425
10.	Old GRA	39.544	60.456
11.	Borokiri <sup>(P)</sup>	6.832	93.168
12.	Borokiri	36.068	63.932
13.	Amadi-Ama <sup>(P)</sup>	38.109	61.891
14.	Mgbuoshimini <sup>(P)</sup>	51.241	48.759
15.	Iriebe <sup>(P)</sup>	54.423	45.576
16.	GRA <sup>(P)</sup>	44.912	55.088

# Table 6 Values of (HCO<sub>3</sub>+CO<sub>3</sub>) and of (CI+SO<sub>4</sub>) as percentages of all Anions for Borehole Samples

# Table 7 Classification of Hydrochemical Facies.

	Percentag	e of Constit	uents, epm	
	Ca+Mg	Na+K	HCO <sub>3</sub> +CO <sub>3</sub>	CI+SO <sub>4</sub>
Cation facies:				
Calcium-Magnesium	90-100	0<10		
Calcium-Sodium	50-90	10<50		
Sodium-Calcium	10-50	50<90		
Sodium-potasium	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
·				(Back, 19

dissociation of  $HCO_3^-$ . According to Davis and DeWriest (1966) the process is only effective largely above a pH of 8.2 below this pH, most of the  $CO_3^{2^-}$  add H<sup>+</sup> to become  $HCO_3^-$ :

$$H^+ + CO_3^{2-} = HCO_3^{-}$$
.

In fact, the dependence of individual  $CO_2$  forms on pH is shown in Table 8.

# Table 8: Dependence of Individual CO<sub>2</sub> forms on pH

				9	6 CO₂ at p	Н			
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

# (UNESCO/WHO, 1978)

It is therefore not surprising that  $CO_3^{2^-}$  is completely undetected in all the samples. The occurrence of  $HCO_3^-$  in all samples (Tables 1 and 2) is favoured by the pH conditions of the groundwater system.

In the shallow groundwater environment (the wells),  $HCO_3$  values range from 12.2mg/l to 36.6 mg/l with an average of 15.25mg/l while the range in the

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It is known that below pH of 8.2,  $HCO_3^-$  forms  $CO_3^{2-}$  by addition of H<sup>+</sup>. The maximum pH value recorded in this research for the shallow and deep water environments are 6.30 and 6.14 respectively (Tables 1 & 2) and this favours the occurrence of the bicarbonate ion. The relatively high values of Cl<sup>-</sup> in all samples is tied to the fact that irrespective of its source, Cl<sup>-</sup> is

conservative. It does not react easily with aquifer materials and tends to be closely associated with water molecules (Mercado, 1985). These qualities preclude CI<sup>-</sup> from being quickly removed from solution and enhances its relatively easy occurrence in groundwater. In the shallow water environment (Table 1) the ion ranges from 11.332mg/l to 121.905mg/l with an average of 41.22mg/l. The respective values in the deep water environment (Table 2) are 5.490 to 72.306 with an average of some ions and the varied concentration levels of others should affect the types and number of mappable facies in groundwater systems.

### Anion Facies in the Groundwaters

The percentage of anions concentration in well samples (Table 5) and in borehole samples (Table 6) when matched with the guidelines in the right hand column of Table 7, resulted in the following groundwater anion facies as presented in Tables 9 and 10 respectively. Both tables show that there is a clear dominance of the  $CI - SO_4^2 - HCO_3$  facies over others. Over 80 per cent of the wells and 75 percent of the boreholes are dominated by this facies-type. When the facies types are fitted into the anion diamond field of Domenico (1972), as shown in Fig. 3, there is indication of a facies change, for the well water, from CI - SO<sub>4</sub>- $HCO_3$  type toward the Cl - SO<sub>4</sub> type, (Fig. 4). In the borehole environment, there is also a facies change from the  $HCO_3 - CI - SO_4$  type, again towards the CI -SO<sub>4</sub> type as shown in Fig. 5. Chebotarev (1955), using anion species only, develops his well-known sequence which states that all groundwaters tend to evolve chemically towards the composition of seawater, an evolution which according to him is normally accompanied by the regional changes in dominant anion species:

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Travel along flow path HCO_3 \rightarrow HCO_3 + SO_4^{2^-} \rightarrow SO_4^{2^-} \rightarrow SO_4 + CI \rightarrow CI^- + SO_4^{2^-} \rightarrow CI^-
Increasing age \longrightarrow
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Location	Hydrochemical Facies
Eagle Island	chloride – sulphate – bicarbonate
Rumuosi	chloride – suphate – bicarbonate
Rumuolumeni <sup>(s)</sup>	chloride – sulphate – bicarbonate
Rumuolumeni <sup>(d)</sup>	chloride – sulphate – bicarbonate
Choba	chloride – sulphate
Borokiri	chloride – sulphate – bicarbonate
Amadi-Ama	chloride – sulphate – bicarbonate
Elimgbu	chloride – sulphate – bicarbonate
Rumuesara	chloride – sulphate – bicarbonate
Mgbuosimini	chloride – sulphate – bicarbonate
Mgbuodohia	chloride – sulphate
GRA	chloride – sulphate – bicarbonate

**Table 9 Hydrochemical Facies in Wells** 

Location	Hydrochemical Facies
Eagle Island	Chloride – sulphate – bicarbonate
Boro Park	Chloride – sulphate – bicarbonate
Rumuola	Bicarbonate – chloride – sulphate
Moscow Road	Chloride – sulphate – bicarbonate
Trans-Amadi	Chloride – sulphate – bicarbonate
Olympia	Chloride – sulphate – bicarbonate
Diobu	Chloride – sulphate – bicarbonate
Rumukoroshe	Chloride – sulphate – bicarbonate
Eagle Island <sup>(P)</sup>	Chloride – sulphate – bicarbonate
Old GRA	Chloride – sulphate – bicarbonate
Borokiri <sup>(P)</sup>	Chloride – sulphate
Borokiri	Chloride – sulphate – bicarbonate
Amadi – Ama <sup>(P)</sup>	Chloride – sulphate – bicarbonate
Mgbuoshimini <sup>(P)</sup>	Bicarbonate – chloride – sulphate
Iriebe <sup>(P)</sup>	Bicarbonate – chloride – sulphate
GRA <sup>(P)</sup>	Chloride – sulphate – bicarbonate



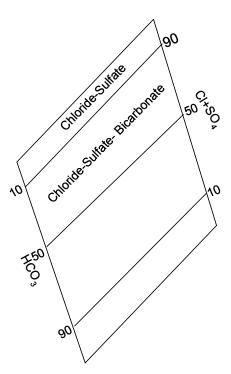


Fig. 4 Anion Facies in shallow groundwater

and Toth (1966b), from investigations in Canada, describes the anion facies development and reports a general tendency for a shift from a pure  $HCO_3^-$  facies in recharge areas to a  $SO_4^{2^-}$  facies in discharge areas. Within the scope of this work, it is noted that purely  $HCO_3^-$  water does not exist in the Port Harcourt region. The facies defined in the present work do indicate that the groundwaters are actually tending towards the composition of seawater in some direction (Figs. 4 and 5). This work also reveals that in general, the shallow groundwaters house less number of mappable facies than the deep groundwaters as is obvious from their respective facies:

Hand dug well facies sequences:  $CI - SO_4^2 - HCO_3 \rightarrow CI - SO_4$ Borehole facies sequences:

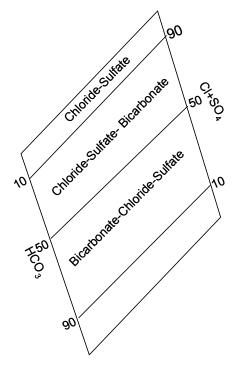


Fig. 5 Anion Facies in deep groundwater environment

$$HCO_3 - CI - SO_4^2 \rightarrow CI - SO_4^2 - HCO_3 \rightarrow CI - SO_4^2$$

The evolution of these groundwater facies can be reasonably explained by the order of encounter proposed by Freeze and Cherry (1979). This theory briefly states that the order in which groundwaters encounter strata of different mineralogical composition can exert an important control on the final water chemistry. As groundwater flows through strata of different mineralogical composition, the water composition undergoes adjustments caused by the mineralogically controlled imposition of new thermodynamic constraints. Domenico (1972) observes that the type of facies that develops is controlled largely by the mineralogy of the rocks and its distribution is controlled by the flow pattern.

# CONCLUSIONS

In this work, the use of anion geochemistry has aided in mapping the groundwater facies embedded in the Port Harcourt region of the Niger Delta, Nigeria. Both shallow and deep groundwater environments were accommodated and that informed the use of hand-dug wells and boreholes within the same geographical environment. 28 water samples (12 from wells and 16 from boreholes) were analysed for the relevant anions Cl,  $SO_4^{2-}$  HCO<sub>3</sub> and  $CO_3^{2-}$  using standard equipment. The concentration levels of each ion have been discussed and related to the environmental controls on their availability. The result of the analyses show that the groundwater system of the Port Harcourt region is home to three anion facies:  $CI - SO_4$ , the  $CI - SO_4 - SO_4$  $HCO_3$  and the  $HCO_3$ -  $CI - SO_4$ . Over 80% of the wells and over 75% of the boreholes, house the  $CI - SO_4$  -HCO<sub>3</sub> facies. The paper finally draws three conclusions that:

- (1) The shallow groundwater environment embedded less number of mappable facies than the deep groundwater environment.
- (2) the existence of different groundwater facies is an evidence that groundwater encounters strata of different mineralogical compositions along its flow path and that
- (3) The facies sequences mapped are tending towards the composition of seawater.

However, the mapped facies sequences and the tendency towards the seawater composition must be viewed, like many others in the geological sciences, in terms of scale and with the normal provisions for interruption and incompletion.

# ACKNOWLEDGEMENT

Our primary acknowledgements are to the imaginative and creative scientists of many nations, who, over the past several decades, have shaped and reshaped the ideas of hydrochemical facies as we now know them. We are grateful to the Shell Petroleum Development Company (Nig.) Ltd, for the sponsorship of the analysis of our water samples.

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# **FIGURE CAPTIONS**

Figure 1	Location map showing positions of wells and boreholes	
Figure 2	Characteristic areas	
Figure 3	Nomenclature for hvdrochemical facies	
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# Figure 5 Anion facies in boreholes