HYDROCHEMICAL ASSESSMENT OF SURFACE WATER IN PART OF SOUTHEASTERN NIGERIA.

A.A ELUEZE, B.E. EPHRAIM, M.E. NTON[a]

ABSTRACT

The area of study occurs mainly within the Calabar Flank and part of the adjacent basement terrain of the Oban Massif. The latter is composed of mainly migmatitic gneisses, phyllites, amphibolites, granites, schists and granodiorites, while the major lithologies of the Calabar Flank include carbonates, shales, claystones and sandstones. This study aims at determining the quality and usability of the water, in addition to ascertaining the possible pollutants and ways to ameliorate their effects.

Results of some physical and hydrochemical parameters have average values of 5.53pH, 77.4mg/l TDS, 17.8mg/l Na^+, 5.5mg/l Ca^{2+}, 13.2mg/l Cl^-, 3.3mg/l SO_4^{2-}, 0.7mg/l NO_3^-, and 49.6ms/cm conductivity. The water hardness and sodium absorption ratio (SAR) are respectively 20.5mg/l and 6.6. The total hardness, Ca^{2+}, SO_4^{2-} are higher for the water draining the carbonate rock environs, while the TDS, Na^+, conductivity and Cl^- are greater in the basement rock areas. Hydrochemical parameters in the piper trilinear diagram, as well as the Gibbs plot, respectively suggest that the water is of sodium bicarbonate facies, and dissolved solids are mostly products of weathering.

Application of R-mode factor analysis suggests that the main components of the water characteristics are related to hydrological, lithological and environmental controls. The factor containing CO_3^{2-} and HCO_3^- is derived from the carbonate rocks in the area, whereas Na^+ and K^+ which are possibly transported in solution as base exchange of clay minerals, notably characterize the basement rocks. The group showing enrichment in Cl^-, Mg^{2+} and NO_3^- is considered to be associated with environmental control, through precipitation of meteoric water, while the presence of SO_4^{2-} is linkable to the aeration of sulfide minerals in the area.

On the whole, the water is slightly acidic with low sodium hazard. It therefore satisfies the World Health Organisation (WHO) standards for domestic, agricultural and other industrial uses requiring usual treatment such as filtration and disinfection.

INTRODUCTION

Throughout the history of humanity, water has always sustained life and communities and the quality of available water is essentially an index of the living standard of any society. In particular, the low level of the socio-economic advancement of most developing countries is sufficiently mirrored by the unsatisfactory or defective harnessing of their water resources.

For instance, abundant surface water resources exist in Nigeria, particularly the southern region lying within the tropical rain forest zone. However, these

[a] Department of Geology, University of Ibadan, Ibadan.

potentials are yet to be adequately exploited for the supply of potable water, due to various limitations. Further, the effective development of the ground water prospects is constrained by geological, economic and political factors. Consequently, the non availability of good quality water persists as a major bane to the survival of most communities, especially in the rural districts.

The southeastern segment (Fig.1) which notably occurs within two major geological domains, namely the basement suite of the Oban Massif and the sedimentary basin of the Calabar Flank, typically exemplifies this rather pathetic situation. Again, it is remarkable that the area is well drained by rivers and streams flowing through fractures, joints and channels within the rocks of both domains. Incidentally, the appraisal of the surface water was virtually neglected before it was realised that the geological complexities could hinder optimum development of the subsurface reserves (Mbuk, 1977). In addition, the southeastern littoral drainage basin supports one of the most dense populations and this has significant effects on land use and urbanization. On the other hand, the increasing industrial, agricultural and mining activities have substantial implications on demand, and the quality of particularly the surface run-off.

In this part of the country, only a small percentage of the rural communities is provided with pipe-borne water. The greater majority relies on supplies from rivers, streams and channels. Since the quality of water is effected by the characteristics of the environment of circulation and occurrence, such sources are invariably exposed to anthropogenic and industrial pollutants.

Consequently, this study is borne-out of the need to evaluate the surface water resources in the area. It particularly aims at determining the quality and usability of the water. In addition, to ascertain the possible pollutants and ways to ameliorate their effects.

PHYSIOGRAPHIC AND GEOLOGICAL SETTING OF THE LOCATION

The study area is bounded by latitudes $5°05'$ and $5°08'N$ and longitudes $8°23'$ and $8°28'E$, and covers approximately $51 km^2$, some kilometres north of Calabar in southeast Nigeria (Fig. 1). The location is part of the drainage basin of the Cross River, the principal river in the region and whose estuary provides the main outlet into the South Atlantic Ocean (Fig. 2). Apart from the important tributaries, numerous interconnected streams and other water courses drain and sculpture their routes within the
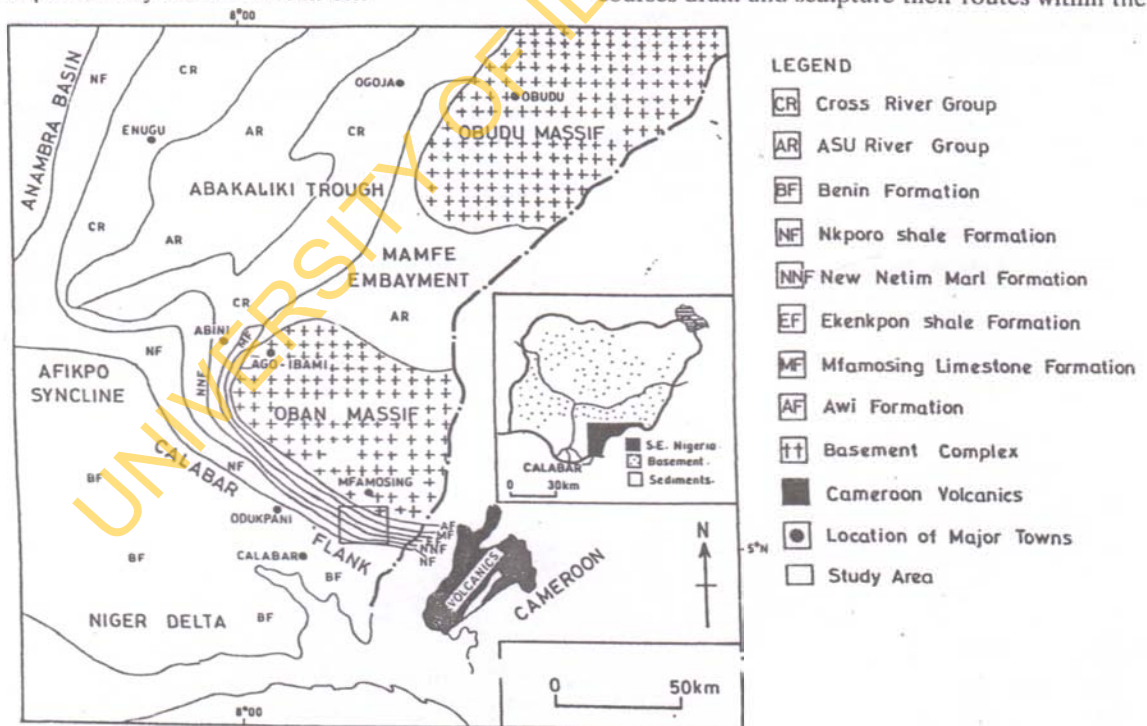

LEGEND

CR — Cross River Group
AR — ASU River Group
BF — Benin Formation
NF — Nkporo shale Formation
NNF — New Netim Marl Formation
EF — Ekenkpon shale Formation
MF — Mfamosing Limestone Formation
AF — Awi Formation
++ — Basement Complex
■ — Cameroon Volcanics
⊙ — Location of Major Towns
☐ — Study Area

FIGURE 1: *Geological sketch map of southeastern Nigeria showing the position of the Calabar Flank and location of study (compiled from Petters 1982 and Ekwueme 1995).*
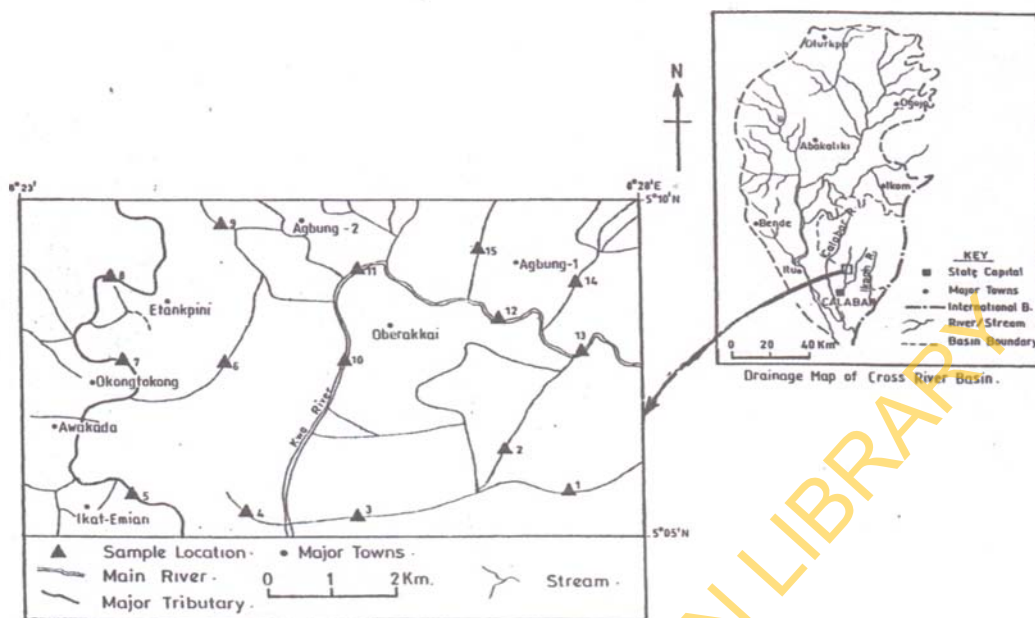
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FIGURE 2: *Drainage and Sample location map of the study area. Inset is the drainage map of Cross River Basin.*

basin. The major rivers are short, with N-S flow direction, while the streams follow southward meandering courses. The drainage pattern is generally dendritic, since the stream network essentially constitute a random system. In particular, the locality of study is traversed by the Kwa River, its tributaries and streams (Fig. 2).

In the study area, there are two main seasons, namely wet and dry. The former or the rainy period is confined to between March and October; while the latter characterised by relatively hot and dusty conditions, covers the duration of November to February. The total monthly rainfall ranges from about 763.6 during the peak, to about 2.1mm in the dry season. The mean annual minimum and maximum temperatures correspondingly vary from 22.6 to 24.6°C and 28.2 to 33.2°C, while the mean monthly humidity is between 81 to 92%.

The geology of the district falls mostly within the Calabar Flank and part of the Oban Massif. Rocks of the Oban Massif are mainly phyllites, schists, gneisses and amphibolites. These are intruded by pegmatites, granites, granodiorites, diorites, tonalites, monazites and dolerites. Associated with these intrusives are charnockites which occur as enclaves in gneisses and granodiorites (Rahman et al. 1981; Ekwueme 1995). Overlying the Oban Massif within the Calabar Flank, is the Awi Formation. It is made up of crossbedded subarkosic sandstones, conglomerates, grits, mudstones, shales and kaolinites cyclically arranged and sourced from

the nearby Oban Massif (Adeleye and Fayose 1978; Nton 1999). This is accordingly succeeded by the Mfamosing Limestone (Petters, 1982), Ekenkpon Shale and New Netim Marl Formations (Petters et al. 1995). Friable Nkporo shales (Reyment, 1965) with bands of marlstones and gypsum, as well as the continental sands of Benin Formation, constitute the younger sequences respectively. The geologic sketch of the area of study and rock distributions are shown in Fig. 3.

METHOD OF STUDY

The field investigation involved the examination of rock outcrops and the distribution of rivers and streams. At locations along the drainage system, mainly determined by accessibility, water samples were collected and stored in labelled clean sterilized polythene bottles. The bottles were thoroughly rinsed with aliquots of the stream water, prior to immersing them well below the surface to collect water samples devoid of the top film. Altogether, 15 representative water samples were selected and analysed for the necessary variables, after effecting relevant precautions.

Parameters such as conductivity, pH, total dissolved solids (TDS), temperature, dissolved oxygen (DO) and turbidity were determined instrumentally in the field. A Hach spectrophotometer (model DR 3000) was used for the determination of total suspended solids (TSS) and colour. Analysis for SO_4^{2-}, Ca^{2+}, Cl^-, Mg^{2+}, CO_3^{2-}

KEY

▨	Nkporo shale Formation
☐	New Netim marl Formation
☶	Ekenkpon shale Formation
⊞	Mfamosing Limestone Formation
⠿	Awi Formation
✝✝	Precambrian Basement
—	Geologic Boundary
⊀	Dip and Strike
	Major Tributary

▲ Sample Location.   ● Major Towns.
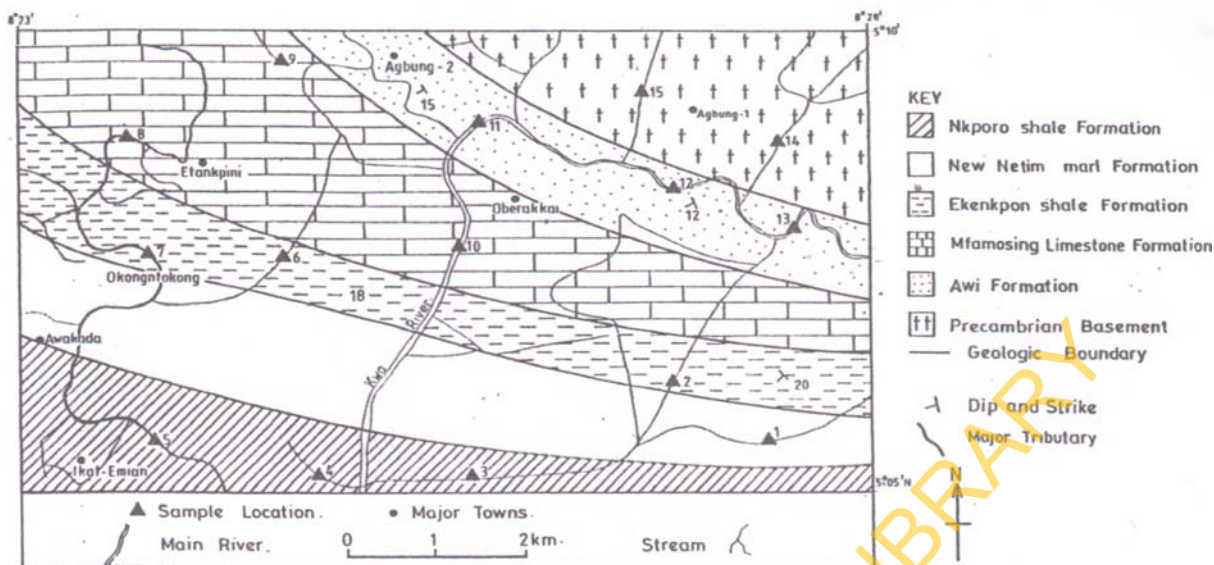
Main River.   0   1   2km.   Stream ⌒

FIGURE 3: *Geology sketch of the study area and rock distributions*

and HCO_3^- were by volumetry technique. EDTA standard solution and murexide indicator were employed for Ca^{2+} and Mg^{2+}, silver trioxonitrate standard and potassium chromate solution were used for Cl^- determination. Hydrochloric acid and standard methyl orange indicator were utilised for CO_3^{2-} and HCO_3^- while colorimetry technique was adopted for SiO_2 (molybdenum yellow method). Other determinations include NO_3^- (copper-cadmium column method), NO_2^- (diazozitization method), PO_4^{3-} (molybdenum blue method) and NH_4^+ (nesslerization method). K^+ and Na^+ concentrations were estimated by standard computation and ionic balance techniques respectively (cf. Sobande, 1991). Further details on analytical methods are presented in Ephraim (1988).

RESULTS AND DISCUSSION

The data for the water analyses, have been grouped into three categories, based on the dominant lithology at the sampling site. Group A data set represents samples obtained from areas in which sandstones, siltstones and shales outcrop. Group B represents those samples from the limestone and marlstone area, while C groups those sampled from areas of grits and basement rocks.

The results and summary of the analytical parameters are represented in Tables 1 and 2. The total dissolve solids (TDS) constitute a greater proportion of the total solid components, with a range from 56.2 to 103.7mg/l, whereas the total suspended solid (TSS) ranges from 3 to 6mg/l. The

TDS average values are 66.0, 81.7 and 84.5mg/l respectively for groups A, B, and C. The total solid content indicates that the water is generally of low mineralization and low suspended solid content. This is borne out of the fact that the TDS concentration falls within the range for fresh water class of Heath (1984). The lowest value of TDS (66mg/l, from the Group A) may likely point to low weatherability of the geological material.

The major dissolve components of the water include Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, HCO_3^-, CO_3^{2-} and SO_4^{2-}. The comparative major ionic components of the different groups is shown in Fig. 4, while the relative compositions of the dissolved solids are shown in Fig. 5. It is clearly seen from both illustrations (Fig. 4 and 5) that Na^+ and HCO_3^- are the most abundant cation and anion, with respective compositions 23% and 28%. CO_3^{2-}, Cl^- and Ca^{2+} are equally of significance with respective percentages 17.0%, 18.0% and 5%. The remaining major solids are comparatively of less significance (Fig. 5).

The minor dissolved solids comprise NH_4^+, NO_3^-, NO_2^-, PO_4^{3-}, and SiO_2 (Tables 1 and 2). The values of NH_4^+, NO_3^- and SiO_2 are generally low (<2mg/l) with the exception of NO_2^- having a value of 4.34mg/l in one of the Group A location (Table 1). However, NO_2^- and PO_4^{3-} are below detection limit. The comparative minor dissolved ionic compositions of the different groups are shown in Fig. 6. The low values of NO_3^- and NH_4^- reflect low pollution status of the water. The very low and/or undetectable

TABLE 1: *Water Analyses Result.*

Water Components	Group A (Siltstone, Sandstone & Shale)					Group B (Limestone & Marl stone)					Group C (Grit & Basement Rock				
Sample Numbers →	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ca^{2+}	2.4	4.8	2.4	3.2	3.2	3.2	15.2	12.4	12.6	6.4	4.0	4.0	2.4	2.4	3.2
Mg^{2+}	1.6	3.2	6.4	1.6	0.6	0.8	0.6	0.4	0.8	0.8	0.0	2.4	0.8	2.4	2.4
Na^+	16.6	20.5	8.3	16.3	14.9	19.1	18.2	7.6	9.0	27.8	26.4	25.5	17.7	17.0	22.8
K^-	0.9	1.2	0.8	0.9	0.8	1.0	1.3	0.9	0.9	1.5	1.3	1.4	0.9	1.0	1.2
Cl^-	9.5	21.5	10.5	10.5	9.2	11.8	13.0	10.9	10.9	20.6	10.9	21.9	8.7	12.2	15.2
HCO_3^-	18.3	18.3	18.4	18.4	15.4	18.3	30.6	15.3	18.3	27.46	27.5	21.4	18.4	18.3	24.4
CO_3^{2-}	11.7	11.7	11.7	11.7	9.7	11.7	19.5	9.9	11.69	17.5	17.5	13.6	11.7	11.7	15.6
SO_4^{2-}	1.4	5.6	1.9	2.1	2.4	3.4	5.2	5.3	5.3	1.62	2.0	6.4	1.9	2.9	1.3
SiO_2	0.91	0.77	0.69	0.92	0.71	1.16	0.82	0.81	0.77	0.33	0.94	1.06	0.9	0.72	0.95
NO_3^-	0.37	4.34	0.54	0.43	0.13	0.1	0.09	0.08	0.08	0.83	0.48	-0.29	0.73	1.0	0.43
NO_2^-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.01	0.01·	0.0	0.0	0.0	0.0	0.0	0.0
NH_4^+	0.08	0.32	0.22	0.36	0.34	0.09	1.87	0.92	0.84	0.07	0.06	0.01	0.21	1.26	0.07
PO_4^{2-}	0.0	0.0	0.0	0.0	0.13	0.004	0.003	0.004	0.004	0.006	0.0	0.001	0.0	0.0	0.0
Dissolved Oxygen	5.0	4.5	4.9	4.5	4.4	3.6	4.0	4.1	4.1	5.2	4.5	4.8	5.0	4.6	5.1
TDS	62.3	86.7	60.3	64.6	56.2	69.3	103.5	62.7	69.5	103.7	89.7	96.6	82.5	67.9	86.0
TSS	5	6	6	4	4	3	4	4	3	3	5	6	6	4	6
Conductivity (Ms/Cm)	39.9	55.5	38.6	41.4	36.0	44.3	66.3	40.1	44.5	66.4	57.4	61.8	52.8	43.5	55.1
Temperature (°C)	28.2	28.3	28.1	28.6	28.6	28.6	28.6	28.7	28.8	28.2	28.4	28.3	28.5	28.5	28.3
pH (pH Unit)	5.72	5.8	5.7	5.3	5.32	5.3	5.66	5.67	5.7	5.86	5.3	6.22	5.05	5.28	5.14
Turbidity (FTU)	1	5	7	9	11	2	33	35	37	2	1	20	8	10	2
Colour (Pt/CO)	25	50	49	81	93	37	270	23	39	22	25	81	62	72	31
Total Hardness (mg/l)	12.6	25.2	32.3	14.6	10.5	11.3	40.5	32.6	34.8	19.3	10.0	19.9	9.3	15.9	17.9

TABLE 2: *Summary of Physical and Chemical characteristics and WHO (1984) Standard for Drinking water.*

Water Components	Measured Parameters	Range	Group A		Group B		Group C		Overall Mean	Acceptance Level [a]	Max. Permissible level [a]
			X*	(r)*	X*	(r)*	X*	(r)*			
Total Solids		Range									
	TSS	3-6	5.0	(0.89)	3.4	(0.49)	5.4	(0.80)	4.6		
	TDS	56.2-103.7	(66.0)	(10.71)	81.7	(18.03)	84.5	(9.55)	77.4		1000.00
Major Dissolved Solids	Na$^+$	7.6-27.8	15.3	(3.97)	16.3	(7.39)	21.9	(3.90)	17.8		200.0
	K$^+$	0.8-1.5	0.9	(0.15)	1.1	(0.15)	1.2	(0.19)	1.06		
	Ca^{2+}	2.4-15.2	3.2	(0.88)	10.0	(0.88)	3.2	(0.72)	5.5	75.0	200.0
	Mg^{2+}	0 - 6.4	2.7	(2.03)	0.7	(2.03)	1.6	(1.01)	1.65		
	Cl$^-$	8.7 - 21.9	12.2	(4.66)	13.4	(4.66)	13.8	(4.57)	13.2		250.0
	HCO$_3$	15.3 - 30.5	17.8	(1.19)	22.0	(1.19)	22.0	(3.50)	20.6		
	CO$_3^{2-}$	9.7-19.5	11.3	(0.78)	14.1	(0.78)	14.0	(2.27)	13.1		
	SO$_4^{2-}$	1.3-6.4	2.7	(1.48)	4.2	(1.48)	2.9	(1.81)	3.3	200.0	400.0
Minor Dissolved Solids	NH$_4^+$	0.01-1.87	0.26	(0.10)	0.76	(0.66)	0.32	(0.51)	0.4		
	NO$_3^-$	0.08-4.34	1.16	(1.60)	0.24	(0.30)	0.59	(0.25)	0.7		10.0
	NO$_2^-$	0-0.01	bdl	***	bdl	***	bdl	***	bdl		
	PO$_4^{2-}$	0 - 0.13	bdl	***	0.01	(0.10)	bdl	***	bdl		
	SiO$_2$	0.33-1.16	0.80	(0.10)	0.78	(0.26)	0.92	(0.11)	0.8		
Dissolved Oxygen and Physical Characteristics	DO	3.6 - 5.2	4.7	(0.24)	4.2	(0.53)	4.8	(0.23)	4.5		
	Temp. (°C)	28.1 - 28.8	28.4	(0.21)	28.6	(0.20)	28.4	(0.12)	28.4		
	pH (pH Unit)	5.05-6.22	5.6	(0.22)	5.6	(0.18)	5.4	(0.86)	5.53	6.5	8.5
	Cond.(Ms/cm)	36.0-66.4	42.3	(6.35)	52.3	(11.54)	54.1	(6.11)	49.6		1400.0
	Turb. (FTU)	1 - 37	6.6	(3.44)	21.8	(16.22)	8.2	(0.80)	12.2		5.0
	Colour (Pt/Co. Unit)	22 - 270	59.6	(24.39)	78.2	(96.15)	54.2	(17.88)	64		15
	Total hardness (mg/l)	9.3-40.5	19.04		27.7		14.6		20.5		

X*   Mean Concentration in Mg/l or other specified units for each group
(r)*   Standard deviation of grouped samples
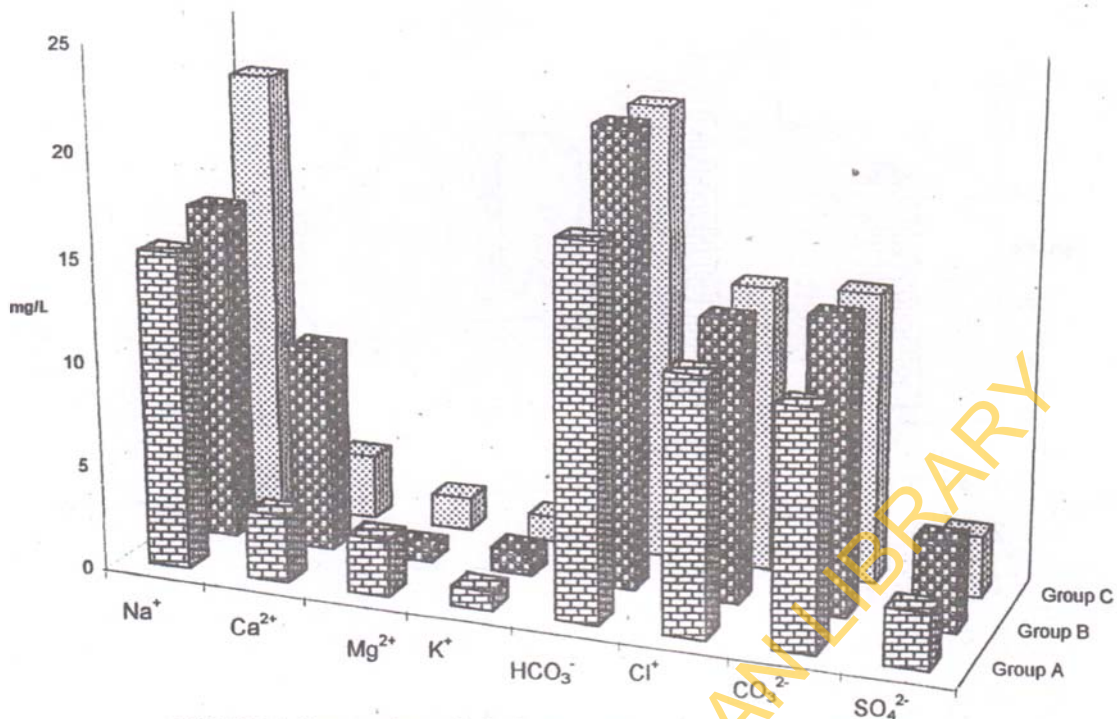***   Below detected limit
a   After WHO (1984)

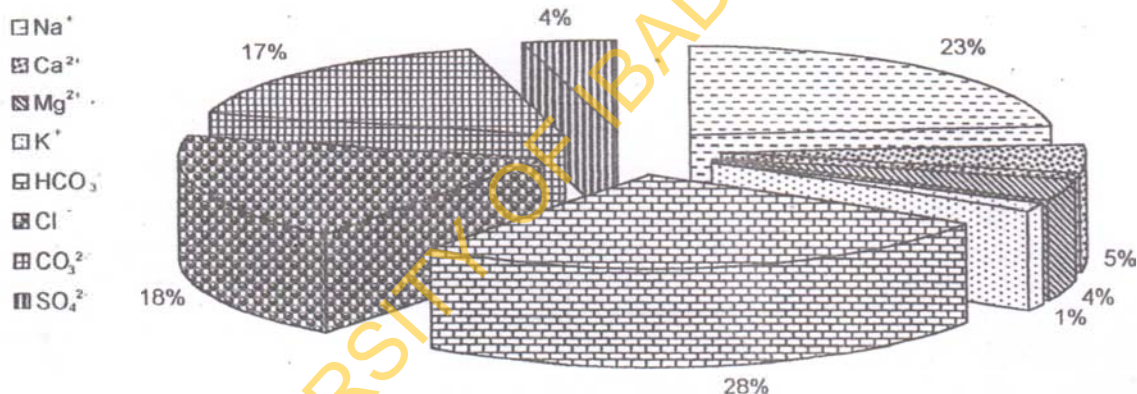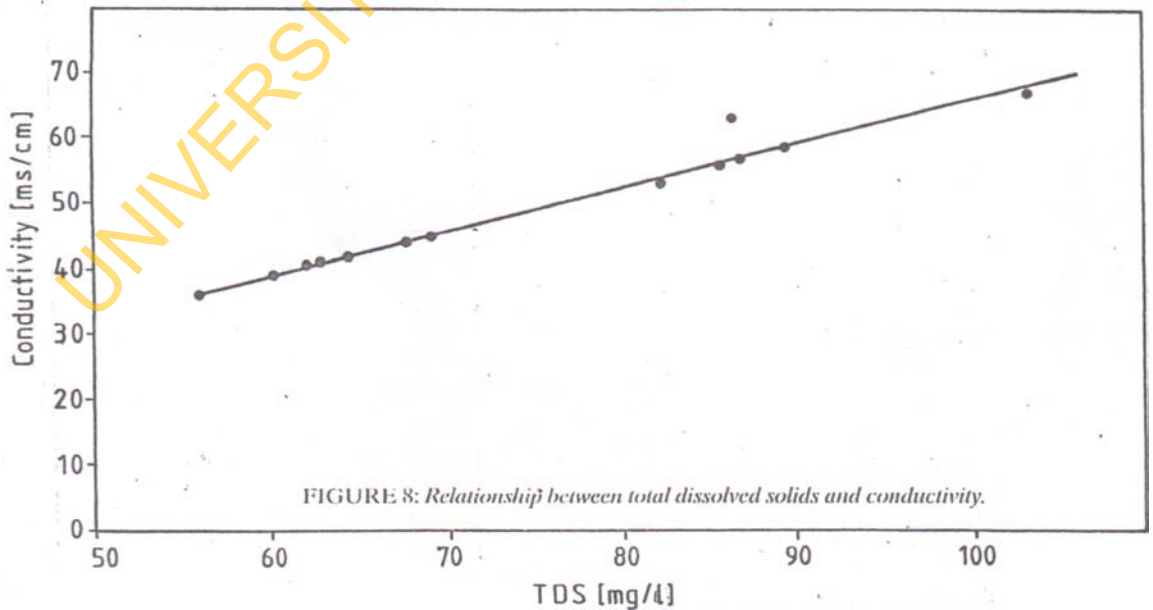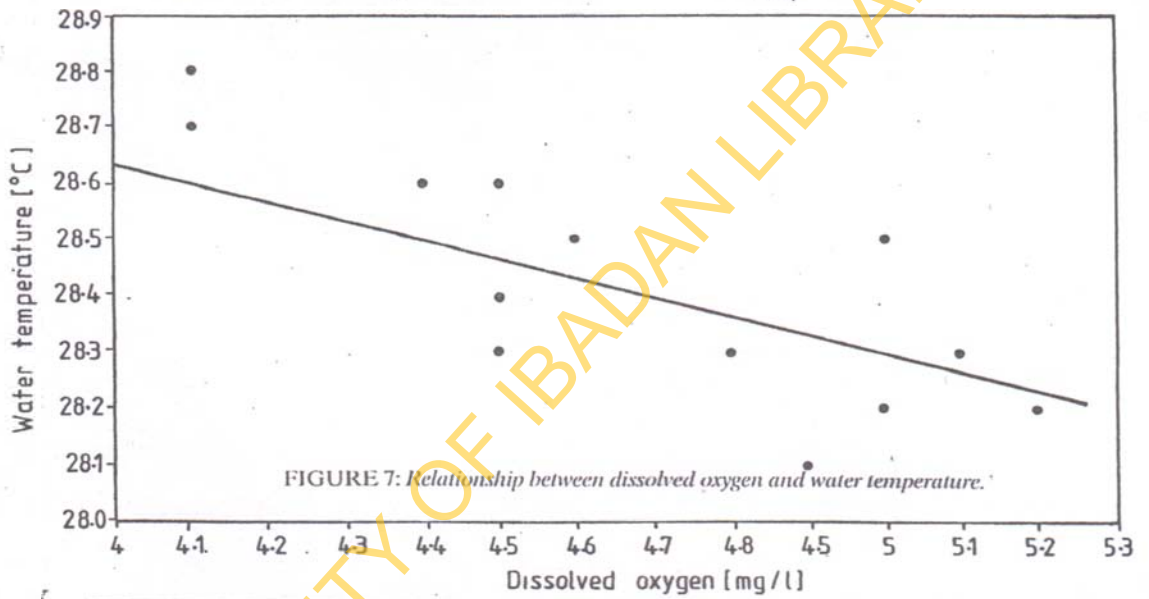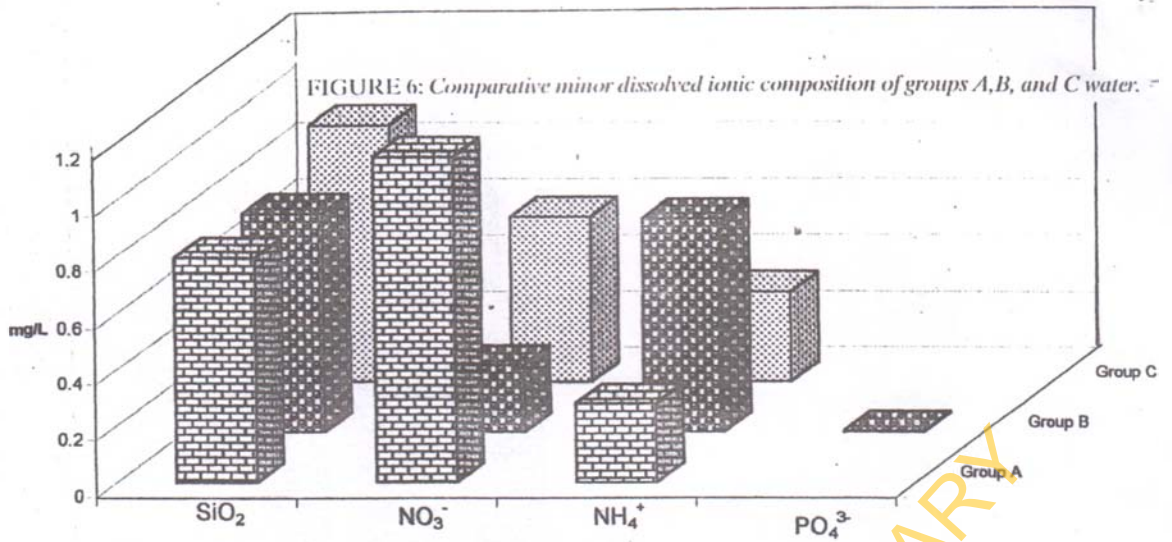FIGURE 4: *Comparative major ionic composition of groups A,B, and C waters.*

FIGURE 5: *Relative composition of the major dissolved solids component of the water.*

concentrations of NO_2^- and PO_4^{3-} are expected since NO_2^- is an unstable phase of nitrogen compound, also the low pH falls below the range favouring the occurrence of phosphoric acid in solution thereby not enhancing the concentration of PO_4^{3-}.

The ranges of dissolved oxygen (DO) and water temperatures are 3.6 to 5.2mg/l and 28.1 to 28.8°C respectively while the relationship between water temperature and dissolved oxygen is shown in Fig. 7. This relationship exists because with higher temperatures, natural waters release their gaseous content into the atmosphere, resulting in lower concentration (Kashef, 1986; Martins and Awokola 1996).

Values for pH show ranges from 5.05 to 6.22 with overall average of 5.53 (Table 2). The values are restricted to a particular rock type; however, the higher value of 6.22 is associated with the grits and basement domain. From the average pH value, the water is slightly acidic. This condition may be attributable to biotic activities that result in the production of CO_2 in the water column. So far, leaching of the organic acids from decaying vegetation and the soils is presumed to be the main biotic activity in this area. This corroborates the views of Ezeigbo (1989). According to Onuoha and Offodile (1995), environmental contaminants resulting from gas flaring in the nearby Niger delta

FIGURE 6: *Comparative minor dissolved ionic composition of groups A,B, and C water.*

FIGURE 7: *Relationship between dissolved oxygen and water temperature.*

FIGURE 8: *Relationship between total dissolved solids and conductivity.*

and volcanic outgassing in the adjacent Cameroon Volcanic Zone may contribute to low pH values. From the location of the study area (Fig. 1) similar conditions are envisaged.

The conductivity values are quite variable, ranging from 36.0 to 66.4ms/cm while the relationship between conductivity and total dissolved solids (TDS) is shown in Fig. 8. Higher conductivity values were observed in the basement and grits domain. The strong correlation of conductivity and dissolved solid is an approximate relationship for most natural water (Richard 1954). Based on Gibb's (1970) plots of TDS against the Na/(Na+Ca) ratio (Fig.9), the water may have acquired its chemistry from the weathered materials from the associated rock types.

The turbidity and colour values are respectively 1 to 37 FTU and 22 to 270Pt/Co in ranges. It is observed that the turbidity values are higher in the carbonate area. However an abnormal colour value of 270 Pt/co measured at one location within the carbonate terrain may be associated with the logging activity that was on going at the time of sampling. This may also have some effect on the seemingly high turbidity in this location.

Computed values of water hardness and sodium absorption ratio (SAR) are represented in Table 3. These values show ranges 9.3 to 40.5mg/l and 1.2 to 13.2 for water hardness and SAR respectively. Higher values of hardness in the carbonate area
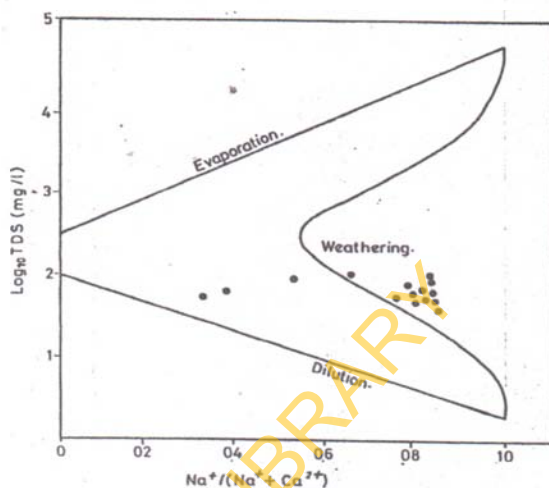

FIGURE 9: *Plot of log TDS against Na/(Na + Ca) ratio (after Gibbs 1970).*

(11.3 to 40.5mg/l) are expected. With an overall average of 20.5mg/l for the hardness, and majority of SAR being <10 (with exception of 11.1 and 13.2 values recorded in the grits and basement area), the water in the area of study fits mainly into the soft and low sodium hazard grouping (Sawyer and McCarthy 1967; Todd 1980; Hem 1985 and Leeden et al, 1990). (See Table 3).

Water Types

Plots of hydrochemical parameter on Pipers (1944)

TABLE 3: *Computed Water hardness (H_t) and sodium absorption ratio (SAR) VALUES.*

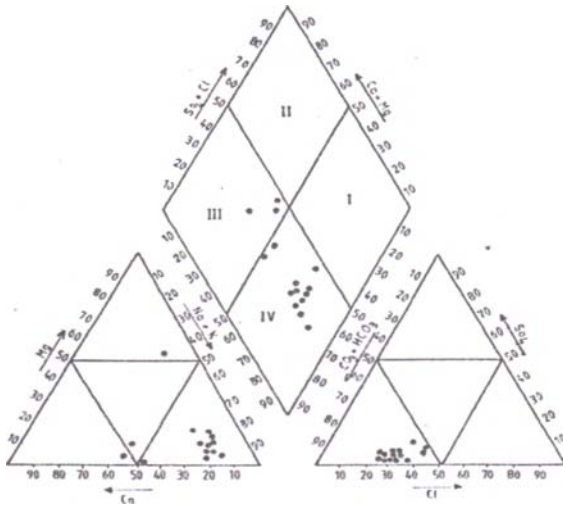| Group	Sample Nos.	H_t (mg/l) $CaCO_3$	SAR	REMARK
	1	12.6	8.1	Soft waters of low sodium hazard
	2	25.2	5.1	»
A	3	32.3	1.9	»
	4	14.6	6.8	»
	5	10.5	7.8	»
	6	11.3	9.6	Soft waters of low Sodium hazard
	7	40.5	2.3	»
B	8	32.6	1.2	»
	9	34.8	1.3	»
	10	19.3	7.7	»
	11	10.0	13.2	Soft waters of low Sodium hazard
	12	19.9	8.0	»
C	13	9.3	11.1	»
	14	15.9	7.1	»
	15	17.9	8.1	»

FIGURE 10: *Trilinear Piper diagram showing the chemical characteristics of surface waters in southeastern Nigeria.*

trilinear diagram (Fig. 10) indicate that the points concentrate within 2 fields that have been interpreted after Levin (1981) as follows:

Field III: $(Ca^{2+} + Mg^{2+})$ >50% and
 $(HCO_3^- + CO_3^{2-})$ >50%
Field IV: $(Na^+ + K^+)$ >30% and
 $(HCO_3^- + CO_3^{2-})$ >50%

Since field IV, has the highest concentration of the plotted points, the water is classified as being predominantly of sodium bicarbonate $(Na^+ - HCO_3^-)$ facies. This corroborates the comparative major ionic component of the different groups (Fig. 4).

According to Lohnert (1970), the sodium bicarbonate water type is an indication of cation exchange processes, and such water is referred to as 'exchange water'. This implies that the bicarbonate (HCO_3^-) anion is in excess of the total alkaline earths $(Ca^{2+} + Mg^{2+})$ concentration. The former is therefore available to act as scavenger in the release of cations, notably alkalis $(Na^+ + K^+)$, through exchange reaction with clay minerals. Such activity may account for the nature of the water of the study area.

Water Quality and Usability

The chemical character of any water determines its quality and utilization. The 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). Hence, there

are different water quality standards for the various uses of water (WHO standard 1984).

Drinking water standards are generally based on two main criteria (Davis and De Weist 1966). These are:

(1) Presence of objectionable taste, odour and colour.
(2) Presence of substances with adverse physiological (health) effects.

The chemical analysis results show that the surface water in the southeastern Nigeria has the various ionic concentration and parameters such as NO_3^-, Cl^-, TDS, Ca^{2+}, Na^+, SO_4^{2-}, conductivity, pH all falling within the maximum acceptable limit of the WHO standard (Table 2). According to Ezeigbo (1987) the presence of excessive suspended sediment (high turbidity) in streams used for recreation could be controlled by dam construction while those in the surface water used for domestic water supply could be controlled through filtration. The latter case seems applicable to this study. Based on the work of Leeden et. al. (1990), the ranges of additional parameters such as SAR, hardness, etc are consistent with domestic supplies, recreation, wildlife propagation, irrigation and most industrial requirements. Apart from the water meeting WHO (1984) standard, the concentration of the parameters fit into the class designated "good source of water supply requiring usual treatment such as filtration and disinfection" in the standard for raw water used as source of domestic supplies (Leeden et al 1990).

On the other hand, irrigation water criteria are dependent on water conductivity, sodium-absorption ratio (SAR), type of plants, amounts of irrigation water used, soil and climate. Using Wilcox model (Table 4), the surface water in the study area could be regarded as excellent – good with low SAR. Out of a total of 15 water samples, 13 samples (more than 86%) show low values of SAR < 10. The other two values are within medium salinity hazard of good water class (Table 4).

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 (Todd 1980; Hem 1985; Leeden et al., 1990).

Sources of Possible Pollutants

R-mode factor analysis is a multivariate statistical

TABLE 4: *Modified Wilcox Quality Classification of Irrigation Waters.*[a]

Water Class	Elect. Conduct. (Ms/cm)	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

a Source: Todd 1980

technique that is widely used to aid interpretation of geochemical data and enhance subtle but significantly single-element anomalies (Garret and Nichol 1969). Application of R-mode factor analysis data in water chemistry has been reported in literature (Dalton and Opchurch 1978). Similarly, Imeokparia (1984); Elueze and Olade (1985) have reported successful applications of R-mode factor analysis in lithogeochemical and stream sediment reconnaissance studies respectively. In this study, R-mode factor analysis was used to process the data

in an effort to determine the sources of pollutants, their controlling factors and ways to ameliorate them. All computation of the R-mode factor analysis are by means of statistical package for social sciences software (SPSS) (Nie et al. 1975). The results of factor analysis are summarised in a factor matrix (Table 5), while the requirements and details are discussed in Ephraim (1998).

According to Reyment and Joreskorg (1993), Malinowski, (1991), careful data selection is a crucial requirement for successful factor analysis operation. In this study, data which are self consistent and provide new information are the ones included in the matrix. The parameters selected as most reliable include conductivity, total dissolved solids, temperature, dissolved oxygen (DO), Mg^{2+}, Na^+, K^+, Ca^{2+}, Cl^-, HCO_3^-, CO_3^{2-}, SiO_2, NH_4^+, NO_3^- and SO_4^{2-}.

After inspection of the various factor models that were computed, a four-factor model that accounted for 82.7% of the data variance was considered to be the most consistent with known hydrological, geological and environmental processes and appropriate to the limits of analytical precision. Only variables with loading greater than 0.55 were considered significant members of a particular factor. These different factors are discussed below:

Factor 1 (Conductivity, K^+, TDS, HCO_3^-, Na^+,

TABLE 5: *R - Mode varimax factor matrix*

	FACTOR 1		FACTOR 2		FACTOR 3		FACTOR 4	
Loading	Conductivity	0.97	Ca^{2+}	0.93	SO_4^{2-}	0.86	NO_3^-	0.82
	K^+	0.96	NH_4^+	0.80	SiO_2	0.76	Cl^-	0.70
	TDS	0.95	Temp.	0.61	DO	0.72	Mg^{2+}	0.58
	HCO_3^-	0.89						
	Na^+	0.85						
	CO_3^{2-}	0.80						
Eigenvalue	5.60		3.48		1.72		1.61	
Percent of Total Variance	37.3		23.3		11.4		10.7	
Cummulative Percentage	37.3		60.6		72.0		82.7	

CO_3^{2-}) accounts for 37.3% of total data variance. The high loading of Na^+, K^+, HCO_3^- and CO_3^{2-} reflect geochemical interactions of transported foreign materials with those occurring within the study area. The southward hydraulic gradient and the general relief of the area permit transportation and weathering products such as clays from the adjoining basement into the drainage basin of the study area. Foster (1950); Krothe and Parizek (1970) agree that sodium bicarbonate waters exist in drainage basins that had or are presently experiencing cation exchange, provided all of calcium carbonate, organic deposits and base exchange minerals are present beneath such drainage channels. The cation exchange operation that probably occurred in the area is explained accordingly by the following sets of reaction;

$$CH_2O + O_2 \qquad = CO_2 + H_2O \dots\dots\dots (1)$$
$$CaCO_3 + CO_2 + H_2O = Ca^{2+} + 2HCO_3^- \dots (2)$$
$$Ca^{2+} + Na_2\ Clay = 2Na^+ + Ca\ Clay \dots (3)$$

Reaction (3) drives the carbonate dissolution equilibrium to the right by absorbing Ca^{2+} and Mg^{2+} on the exchange sites, thereby concentratiing Na^+ and HCO_3^- and probably K^+ and CO_3^{2-} It is obvious, from already known geological information that Ca^{2+}, HCO_3^- and CO_2 are sourced from carbonate rocks of the study areas while Na^+ and K^+ are transported in solution or in base exchange minerals occuring in clays from the adjoining basement area. From the plot of the $\log_{10}$ TDS against the Na/(Na + Ca) ratio shown earlier (Fig. 9), it is apparent that the water in the area may have acquired its chemistry from the weathered materials derived from the associated rocks. Nton (1999) had earlier reported the presence of kaolinite clays within the Awi Formation of the Calabar Flank to be sourced from the Oban Massif by weathering of feldspathic rocks in warm humid environment. This further affirms that much of the dissolved solids/pollutants in the water are traceable to hydrological processses. The conductivity, which is related to the overall component of the TDS is similarly effected.

Factor 2 (Ca^{2+}, NH_4^+, Temperature). This accounts for about 25.3% of the total data variance. The high loading of Ca^{2+}, NH_4^+ and temperature in this grouping reflects weathering and decomposition. Decomposition of the organic deposits probably involved the breakdown of complex protein into amino acids with the release of NH_3 according to the reaction.

$$R - NH_2 + H_2O \rightarrow NH_3 + R - OH + energy$$
(Amino – N). Here the NH_3 released is hydrolyzed to NH_4^+.
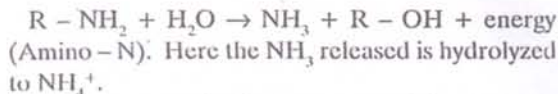
This interpretation is borne out of the fact that abundant deposits of limestones, marlstones and organic shale deposits outcrop in the area. Temperature is a very important factor in weathering process and its inclusion in this factor grouping supports the interpretation. The presence of Ca^{2+} is related to the geology.

Factor 3: (SO_4^{2-}, SiO_2, DO) accounts for about 11.6% of the total data variance. The inverse association of SO_4^{2-} with DO in the group may suggest environmental and hydrological controls by the oxidation of sulphide minerals such as pyrite. Hem (1970) has reported that when sulphide minerals weather in contact with aerated water, sulphur is oxidized to yield sulphate ions which go into solution. It is envisaged that this is the mode of acquisition of SO_4^{2-} in this area as there are reported occurrence of pyrites minerals within the organic shales of the Calabar Flank (Reyment, 1965, Adeleye and Fayose, 1978, Nton, 1999). SiO_2 may be derived from natural sources such as feldspars, ferromagnesium and clay minerals (Todd, 1980). DO is associated with natural geochemical cycle of the water.

Factor 4: (NO_3^-, Cl^-, Mg^{2+}) accounts for 10.7% of the data variance. The ionic assemblages in this grouping clearly indicate environmental control. NO_3^- can be obtained from the atmosphere, plants debris etc. Mg^{2+} may be associated with amphiboles, olivine, pyroxene or even clay minerals from the adjoining basement terrain. Indications are that most if not all of Cl^-, Mg^+ and the low NO_3^- concentrations are derived from environmental and atmospheric precipitation.

CONCLUSIONS

Hydrochemical and statistical reduction methods have been used to investigate the surface waters of the Calabar Flank and part of adjacent Oban-Massif. Results of the water qualities show that the water is slightly acidic of low mineralisation and suspended solids and generally dominated by Na^+ and HCO_3^- water type. Computed values of water hardness and sodium absorption ratio indicate that the water is generally soft and with low sodium (alkali) hazard. Gibbs plots show that the dissolved solids are products of weathering. Application of R-mode factor analysis indicate a 4 factor model showing that the main components of the water characteristics

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are related to hydrological, lithological and environmental controls. Generally, the hydrochemical parameters satisfy the WHO standard for domestic, agriculture and other industrial uses requiring usual treatments such as filtration and disinfection.

Using this study as a basis, it could be suggested that the surface water reserve be developed to supplement subsurface water supply in the region. With this background information, further investigation could span a wide scope in terms of time and space so that the temporal and spatial variations could be better understood. Such investigations would be most meaningful if heavy metals and isotopic compositions of the water are incorporated.

REFERENCES

ADELEYE, D. R. and FAYOSE, E.A. 1978. Stratigraphy of the type section of Awi Formation, Odukpani area, southeastern Nigeria. J. Min. Geol. 15(1): 33-37.

DALTON, M.G. and UPCHURCH, S. B. 1978. Interpretation of hydrochemical facies by factor analysis. Groundwater, 16(4): 228-233.

DAVIES, S.N. and DEWIEST, R.J.M. 1966. Hydrology, Wiley, N.Y.

EKWUEME, B.N. 1995. The Precambrian geology of Oban Massif, southeastern Nigeria. In B.N., Ekwueme, E.E., Nyong and S.W. Petters (eds), Geological Excursion guidebook to Oban Massif, Calabar Flank and Mamfe Embayment, southeastern Nigeria. Dec. Ford Publishers Ltd, Calabar, 36p.

ELUEZE, A. A. and OLADE, M.A. 1985. Interpretation through factor analysis of stream sediment reconnaissance data of gold exploration in Ilesha greenstone belt southwest Nigeria. Trans Instn. Min. Metall. (Sec. B. Appl. Earth Sci). 94: B155-B160.

EPHRAIM, B.E. 1998. Water Chemistry evaluation in parts of the Calabar Flank, southeastern Nigeria. M.Sc. Dissertation, Department of Geology, Univ. of idatan, 90p.

EZEIGBO, H.I. 1987. Quality of water resources in Anambra State, Nigeria. Nig. Journ. Min. Geol. Vol. 23 Nos 1 and 2 pg. 97-103.

EZEIGBO, H.I. 1989. Groundwater quality problems in parts of Imo State, Nigeria. Nig. J. Min. Geol. 25 (1 & 2): 1-10.

FOSTER, M.D. 1950. The origin of high sodium bicarbonate in the Atlantic and Gulf coastal plains, Geochim Cosmochim, Acta 1:33-48.

GARRETT, R.G. and NICHOL I. 1969. Factor analysis as an aid in the interpretation of regional geochemical stream sediment data. Col. Sch. Mines Q, 64 No 1, pp. 245-264.

GIBBS, R.J. 1970. Mechanisms controlling world water chemistry. Science 170: 1088-1090.

HEALTH, R.C. 1984. Basic groundwater hydrology. U.S. Geological Survey water supply paper 2220.

HEM, J.D. 1985. Study and interpretation of the chemical characteristics of natural water. 3rd ed.; U.S. Geological Survey water supply paper 1473.

IMEOKPARIA, E.G. 1984. Factor analysis as an aid in the interpretation of bedrock geochemical data. Nig. J. Min. Geol. 21 (1 & 2): 191-202.

KASHEF, A.L. 1987. Groundwater Engineering. McGraw - Hill Book Company, N.Y. 512p.

KROTHE, N.C. and PARIZEK, R.R. 1979. An anomalous occurrence of sodium bicarbonate waters in a flood plain in carbonate terrain. Groundwaater, 17(6): 595-603.

LEEDEN, F.V.D., TROISE, F.L. and TODD, D.K. 1990. The water encyclopedia. Geraghly and Miller groundwater series. Lewis Publishers, Inc. U.S.A. 417-493.

LEVIN, M. 1981. The geology, hydrology and hydrochemistry of an area between the Kuruman and Orange rivers,

northwestern Cape. Trans. Geol. Soc., South Africa, 84 (2). 177-190.

LOHNERT, E.P. 1970. Groundwasserchemismus and kationentausch in norddeuschen Flachland Zditsch Geol. Ges Sondesh, Hydrologeol. Hydrogeochem. No. Voll. November: 139-159.

MALINOWSKI, E.R. 1991. Factor analysis in Chemistry. Wiley – Interscience publication. John Wiley and sons, Inc., N.Y. 350p.

MARTINS, O. and AWOKOLA, O.S. 1996. Total dissolved solids of selected rivers in southwestern Nigeria.J. Min. Geol. Vol. 32(2) pp. 113-119.

MBUK, I.N. 1997. Rural Water Supply in the Cross River State of Nigeria – geological problems and solutions 33rd Annual Conference Nig. Min. Geo. Soc. Book of Abstracts.

NIE, N.H., HILL, C.H., JENKINS, I.G., STEINBRENNER, K. and BENT, D.N. 1975. Statistical package for the social Sciences. McGraw Hill, N.Y. 2nd ed. 675p.

NTON, M.E. 1999. Sedimentology and Depositional Environmental of Awi Formation, Calabar Flank, southeastern Nigeria. Jour. of Min. and Geol. Vol. 35(1) p. 23-36.

NYONG, E.E. 1995. Cretaceous sediments in the Calabar Flank. In B.N. Ekwueme, E.E. Nyong and S.W. Petters (eds) Geological Excursion Guidebook to Oban Massif and Mamife Embayment, southeastern Nigeria. 31st Annual Conf. Nig. Min. and Geosciences society Calabar Dec – Ford Pub. Ltd. Calabar 36p.

ONUOHA, K.M. and OFFODILE, M.E. 1995. Proceedings of the International Workshop in natural and man-made hazards in Africa. An N.M.G.S. Contribution to the Nigeria Programme for the United Nations decade for National disaster reduction, Awka Anambra State. 1990 – 1999, 362p.

PETTERS, S.W. NYONG, E.E., AKPAN, E.B. and ESSIEN, N.U. 1995. Lithostratigraphic, revision for the Calabar Flank, S.E. Nigeria. In Proc. Of the 31st Ann. Conf. Of N.M.G.S.Calabar.

PETTERS, S.W. 1985. Central West African Cretaceous – Tertiary benthic foraminifera and stratigraphy. Palaeontographica A. 1975; p. 1-104.

PIPER, A.M. 1994. A graphical procedure in geochemical interpretation of water analysis. Trans. Am. Geophys, Union 25. 914 – 923.

RAHMAN, A.A.M.S., UKPONG, E.E. and AZMATULLAH, M. 1981. Geology of part of the Oban Massif, southeastern Nigerian. Journ. Min. Geol. 18(1) p. 60-65.

REYMENT, R.A. 1965. Aspects of the geology of Nigeria, Ibadan Univ. Press, Ibadan Nigeria. 145p.

REYMENT, R. and JORESKOG, K.G. 1993. Applied Factor analysis in the natural sciences. Cambridge Univ. U.S.A. 370p.

RICHARDS L.A. 954. Diagnosis and improvement of saline and alkali soils. Agric Handbook 60, U.S. Dept. Agric. Washington, D.C. 160p.

SAWYER, C.N. and McCARTY, P.L. 1967. Chemistry for sanitary engineers. 2nd ed. McGraw Hill New York.

SOBANDE, A.A. 1991. Hydrogeological evaluation of Cretaceous shale aquifers in the Lower Benue trough, Nigeria. Unpublished Ph.D., Dissertation. Univ. of Ibadan, 261p.

TIJANI, M.N. 1994. Hydrochemical assessment of ground water in Moro area, Kware State, Nigeria. Environmental Geology vol. 24p. 194-202.

TODD, D.K. 1980. Groundwater hydrology, 2nd ed. New York, John Wiley & sons 535p.

WHO (WORLD HEALTH ORGANISATION, 1984). Guideline for drinking water quality, Vol. 1 Recommendations Geneva. WHO.