

Review

Groundwater chemistry and quality of Nigeria: A status review

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Accepted 21 December, 2011

The present work is a review on the quality characteristics of groundwater in Nigeria. The aim was to collate, synthesize and analyse hydrochemical data from available literature in order to evaluate the physical and chemical character, quality and determine the sources of ions. The review process covered four major groundwater sedimentary basins viz Benin, Benue, Niger Delta, Sokoto and the Crystalline Basement Complexes. The issue of saline groundwater in parts of Benue and Niger Delta Basins were given attention. In general, data show that on the average, TDS for the groundwater from the different basins was < 250 mg/l compared to the saline groundwater with average TDS as high as 15700 mg/l. The high salinity was attributed to dissolution of salts and seawater intrusion. Nitrate concentration on the average is high especially, for Sokoto Basin indicating anthropogenic pollution. Descriptive and multivariate statistics together with cross plots indicate that the major geologic controls on the groundwater chemistry are chloride dissolution, weathering (silicate and carbonate) and ion exchange. With respect to agricultural and irrigation purposes, the groundwater are excellent besides the water from the saline groundwater from Benue Basin and the coastal aquifers.

Key words: Groundwater, chemistry, quality, Nigeria.

INTRODUCTION

Nigeria is blessed with large quantity of groundwater resources. For instance, Rijswijk (1981) estimated the amount of groundwater resource in Nigeria to be 6×10^{18} m³. The resource plays an important role in the social and economic life of the people in terms of domestic, industrial and agricultural use. However, little is done to assess and understand the quality of groundwater especially within the different aquifer systems. Most literature on groundwater quality of Nigeria is localized, small scale and scattered. Besides, no known publication to date has been highlighted on quality alongside the sources and processes responsible for the water chemistry for the entire nation as an entity.

Available literature both published and unpublished are skewed towards comparing analytical results with existing national and international standards for drinking, domestic and agricultural purposes. Besides, geologic

input is not given consideration in the quality assessment while most of the works are routine and does not seek to address any geologic problem.

The present work uses published work to document for the first time the quality status of groundwater in Nigeria bearing in mind natural and anthropogenic inputs. This consisted of gathering information on the groundwater geology of Nigeria; collate the information, synthesis and analysis the physicochemical data to assess their quality and sources of the ions bearing the local geologic setting of the major groundwater basins in Nigeria. The overall objectives of this review work are three-fold as follows:

1. To describe the distribution of physicochemical parameters in order to bring the groundwater quality problem to the attention of the population.
2. To identify the major pollutants in groundwater.
3. To identify the major sources of ions in water.

The available published works on groundwater quality and chemistry of Nigeria are on specific issues and

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generally localized in terms of area coverage. One widely addressed issue is on quality assessment for drinking, domestic, agricultural and industrial uses in some cities (Lagos, Orlu, Calabar, Ijebu Ode, Warri, Agila, Ede, Yenogoa, Mubi, Akure, Agbor, Igbora, Bama, Iddo,); local government areas (Calabar, Port Harcourt, Khana, Gokana, Tai-Elleme, Jemaa and Umuahia); states (Akwa Ibom, Anambra and Ondo) and some geologic terrains (parts of Sokoto Basin, Eastern and Western Niger Delta, Basement of Central Nigeria, Obudu Plateau and Oban massif). These studies are documented in the work of Longe et al. (1987), Otezie (1991), Edet (1993), Olarewaju et al. (1997), Udom et al. (1998), Ajayi (1998), Ajayi and Obot (1998), Erah et al. (2002), Ahirakwem and Ejimadu (2002), Ogunbayo (2004), Olobaniyi and Owoyemi (2004), Ozoko (2004), Udom et al. (2004), Adediji and Ajibade (2005), Ofoma et al. (2005), Efe et al. (2005), Edet and Okereke (2005), Alagbe (2006), Udom and Amah (2006), Abulude et al. (2007), Olobaniyi et al. (2007), Olobaniyi and Efe (2007), Adekunle et al. (2007), Jatau and Bajeh (2007), Chukwu (2008a), Boboye (2008), Adebo and Adetoyinbo (2009), Babatunde et al. (2009) and Nganje et al. (2010a).

Another area of concern in literature include bacterial contamination in groundwater in Benin City and Eastern Niger Delta (Tekwa et al., 2006; Ejechi et al., 2007), determination of natural background levels for parts of Cross River Basin (Offiong and Edet, 1998a, b; Edet et al., 2003; Edet, 2004) and groundwater dating of surface and subsurface waters in Sokoto Basin (Oteze, 1993; Adelana et al., 2003; Goni, 2006).

Other works in literature were on the interaction of groundwater with the host rock in Anambra State, parts of Niger Delta, northern parts of Ibadan, Warri Metropolis, Owerri Town and the Lower Benue Trough, (Ezeigbo, 1987; Amadi et al., 1989; Abimbola et al., 2002a; Olobaniyi and Owoyemi, 2006; Edet and Ekpo, 2008; Nganje et al., 2010; Amadi et al., 2010).

Impact of human activities received some attention on the groundwater situation in Nigeria. Most of the impacts were due to poor sanitation and agricultural practices, petroleum related activities and mining. Examples of these studies as documented in literature are nitrates in shallow aquifers of Sokoto and acid mine drainage pollution in Enugu. Others are on impact of waste dumps on groundwater quality in Orita-Ibadan, Oramiriukwa River Basin-Owerri, Minna, Benin and Lagos (Uma, 1993; Ezeigbo and Ezeanyim, 2006; Abimbola et al., 2002b; Tijani et al., 2002; Ibe sr and Sowa, 2002; Chukwu, 2008b; Yerima et al., 2008; Omo-Irabor et al., 2008; Edet, 2009; Omofonmwan and Ezeigbe, 2009).

Saline groundwater problem has also been given prominent attention in Cross River Basin and Niger Delta (Uma et al., 1990; Uma, 1997; Awalla and Ezeigbo, 2002; Frank-Briggs, 2005; Edet, 2009; Amadi et al., 2010; Edet and Okereke, 2001a, b; Edet et al., 2011).

From the above, as stated earlier, these studies were

localized. Hence the need to assemble the available works in literature as a prelude to give an overall status of the quality of groundwater in Nigeria. In achieving this, emphasis is placed on the major sedimentary basins and the basement complex bearing in mind the local geologic setting.

Location of Nigeria

Nigeria is situated south of the Sahara Desert in West Africa. It is bordered by Niger and Chad to the north, Benin in the west, Cameroon in the east and Gulf of Guinea in the south (Figure 1). The country lies between latitude 4° 10 to 13° 48 North and longitude 2° 50 to 14° 20 East covering an estimated area of 923, 768 km². The climate of Nigeria varies from equatorial in the south through tropical in the central to arid to the north. Nigeria experiences consistently high temperatures throughout the year. The temperature ranges between 21 and 33°C (Iloeje, 1981). The mean annual rainfall along the coast is more than 4000 mm while it is less than 250 mm in the north with an average of 1180 mm (BGS, 2003).

GEOLOGY AND GROUNDWATER BASINS

The geology of Nigeria consists of two main lithological units. These are the Precambrian Crystalline Basement and Cretaceous-Tertiary sedimentary rocks (Figure 2). The basement complex rocks are of metamorphic-igneous-volcanic origin. The main rock types include units include: Migmatite-Gneiss Complex (migmatites, gneisses), Schist Belts (schists, quartzites, metaconglomerates, amphibolites, phyllites), Older Granites (granites) and Younger Granites (basalts, rhyolites, tuff), Oyawoye (1970).

The sedimentary basins include the northern inland sedimentary basins consisting of the Sokoto and Chad Basins while the middle belt and southern coastal basins is made up of the Nupe, Benue, Benin and Niger Delta Basins. The sedimentary sequences in these basins were broadly divided into basal non marine sandstones, siltstones, and mudstones; a middle marine shales and limestones intercalated with sandstones and siltstones and an upper sandstone sequence that is continental or paralic (Petters, 1982).

The Sokoto Basin of northwestern Nigeria is the southern sector of the lullemeden Basin transboundary aquifer shared by Mali, Niger, and Algeria. The depth of water level in the Sokoto Basin aquifers is typically in the range 15 to 75 m (BGS, 2003), while the Gwandu aquifer has an estimated yield of 10 to 35 L/s (Akujeze et al., 2003).

The Chad Basin consist of three main aquifers: an upper aquifer at 30 to 100 m depth with yield of 2.5 to 30 L/s, a middle aquifer about 40 to 100 m thick having a



Figure 1. Map of Nigeria showing the different states and surrounding countries (<http://www.mapsofworld.com/nigeria/nigeria-political-map.html>).

yield of 24 to 32 L/s and a lower aquifer consisting of sands and clays at a depth of 425 to 530 m with yield of 10 to 35 L/s (Akujeze et al., 2003; BGS, 2003).

In the Benue Basin, three broad hydrogeological groups were identified in the southern Benue Basin (Uma and Onuoha, 1990; Adelana et al., 2008). These include the first hydrogeological group underlain predominantly by shaly formations. The thickness is in the range of 10 to 40 m and water levels are generally < 20 m. The second hydrogeological group consists of mainly sandy and shaly horizons with yield in the range of 3 - > 30 L/s while the lower hydrogeological group consists predominantly of sands, sandstones and clays. The upper Benue Basin has the Gombe Sandstone and Kerri Kerri Formations as

the main aquifers. These aquifers consist of coarse grained and highly permeable materials. The Kerri Kerri aquifer has yield of 1.25 to 9.5 L/s (Akujeze et al., 2003).

The Nupe Basin contains significant groundwater resources with occasional artesian conditions. Good aquifers are present in the Tertiary and Quaternary sediments of the southern coastal areas (Benin and Niger Delta Basins). The water level varies between 0 and 9 m while, the specific capacities, were in the range 90 to 1400 m³/d/m, Offodile (1992).

The groundwater storage in the crystalline basement is small. Groundwater availability is largely limited to fracture zones and areas of deep weathering (Ajayi and Hassan, 1990; Olorunfemi, 1990; Edet, 1992; Edet and

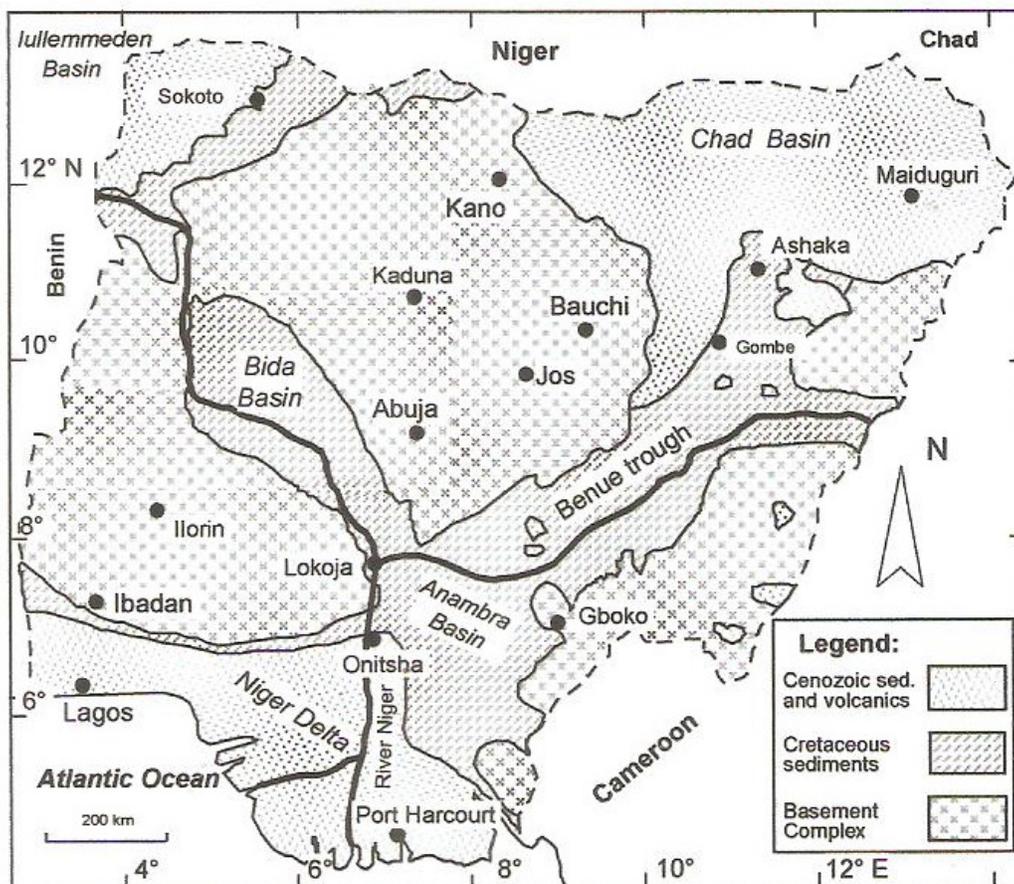


Figure 2. Generalized geological map of Nigeria including the basement complex and some sedimentary basins (Adapted from Adelana et al., 2008).

Okereke, 1997; Edet et al., 1998; Okereke et al., 1998). Generally, the principal source of groundwater is from hand dug wells. Details on the hydrogeology of Nigeria are contained in Offodile (1992), Akujieze et al. (2003), BGS (2003) and Adelana et al. (2008). A summary of the hydrostratigraphic units in Nigeria is presented in Table 1.

DATA GATHERING

In the present work, available literature were gathered and categorized on the basis of the different groundwater provinces. In categorizing these works, only literature with complete physical (temperature, electrical conductivity, total dissolved solids and pH), basic cation (sodium, potassium, calcium and magnesium) and anions (chloride, bicarbonate, sulphate and nitrate) were selected. This was in addition to iron and manganese. The data were then subjected to descriptive statistics (mean, median, minimum, maximum, standard deviation), correlation and factor analyses. In addition, cross plots were made between different ions. The cross plots together with correlation and factor analyses were used

to determine the source of ions in groundwater bearing in mind the lithologic units under consideration. The data were also compared with national and international standards to assess their suitability for domestic, industrial and agricultural applications. The cross plots were made with Microsoft Excel while the multivariate statistics were made with the software STATISTICA®. The locations and sources of data for the present review work are presented in Table 2.

OVERVIEW OF GROUNDWATER QUALITY IN NIGERIA

A number of groundwater quality studies have been carried out in Nigeria, though generally on local basis with few numbers of chemical constituents. This accounts attempt to make a summary of the groundwater characteristics. BGS (2003) noted that the shallow aquifers are vulnerable to pollution from domestic, agricultural and industrial waste. Oil spillages are known to have some impact on groundwater a good example being the recent report on the environmental assessment

Table 1. A summary of the hydrostratigraphic units of Nigeria^a.

Age	Benin Basin	Niger Delta Basin	SE Benue Trough	NE Benue Trough	Chad Basin	Nupe Basin	Sokoto Basin
Quaternary	Alluvial aquifer Deltaic aquifer				Chad aquifer		
Pliocene							
Miocene							
Oligocene	Benin aquifer	Benin aquifer	Benin aquifer	Kerri Kerri aquifer	Kerri Kerri aquifer	Patti aquifer	
Eocene	Ilaro aquifer Akimbo/Oshosun aquifers	Agbada aquifer	Ogwash-Asaba aquifer Nanka sand aquifer Ameke aquitard				Gwandu aquifer Kalambaina aquifer
Paleocene	Imo Shale aquitard Ewekoro aquifer	Akata Shale aquitard	Imo Shale aquitard				Dange aquiclude Wurno aquifer
Maastrichtian	Nkporo Shale aquitard	Nkporo Shale aquitard	Nsukka aquitard Ajali Sandstone aquifer Mamu aquiclude Nkporo Shale aquitard Enugu Shale aquitard	Gombe Sandstone aquifer	Gombe Sandstone aquifer	Lokoja Sandstone aquifer	Dukumaje aquiclude Taloka aquifer
Campanian							
Santonian			Agwu aquitard	Lamja Sandstone aquifer	Fika Shale aquitard		
Coniancian	Abeokuta aquifer		Agbani Sandstone aquifer Amaseri Sandstone aquifer New Netim marl aquitard	Numanha aquifer Sukuliye aquifer Jessu aquifer Gulani aquifer			
Turonian			Ekenkpon shale aquitard Eze Aku aquitard Markurdi Sandstone aquifer Agala aquifer Ezillo aquifer	Pindiga aquitard	Gongila aquifer		
Cenomanian			Odukpani aquitard	Yolde aquifer			
Albian			Asu River aquitard	Bima Sandstone aquifer	Bima Sandstone aquifer		Illo-Gundumi aquifer/aquiclude
Pre-Albian	Basement Complex	Basement Complex	Basement Complex	Basement Complex	Basement Complex	Basement Complex	Basement Complex

^a Based on the work of Petters (1982), Offodile (1992), Akujize et al. (2003), Adelana et al. (2008)

of Ogoni land (UNEP, 2011).

Natural water quality problems have also been noted especially, in relation to dissolution of evaporate minerals in the Benue Basin (Ekwere and Ukpong, 1994; Uma, 1998; Tijani, 2008).

Overexploitation of coastal aquifers, tidal

influences and shallow wells in the coastal parts of Nigeria has led to problems with saline intrusion. This is noted around Lagos, Ondo, Delta, Bayelsa, Rivers, Akwa Ibom and Cross Rivers States.

Problems of acid mine drainage have also been

reported in some areas especially, the coal mining areas in Enugu (Nganje, 2010, 2011).

A summary of groundwater for a total of 600 samples is given in Table 3. The data indicate that the average concentrations of most elements investigated are present in concentrations lower

Table 2. Location characteristics and data source.

State	Code	Age	Basin	Formation (Aquifer)	Sample size (n)	Source
Abia	AB	Oligocene	Niger Delta	Benin	27	Ukandu (2009)
Akwa Ibom	AK				75	Edet (1993), Ajayi and Obot (2006)
Bayelsa	BAY				27	Amadi et al. (1989)
Cross River	CR-1				7	Edet et al. (2009)
Delta	DEL				34	Olobanyi et al. (2001)
Lagos	LAG				12	Longe et al. (1987)
Rivers	RIV				54	Udom et al. (1999), Frank-Briggs (2003)
Imo	IM	Eocene		Ogwashi Asaba	10	Ahiarakwem and Ejimmadu (2002)
Ogun	OG-1	Paleocene	Benin	Ewekoro	7	Tijani (2003)
Ogun	OG-2	Coniacian		Abeokuta	15	Ogunbanjo (2004)
Anambra	ANAM	Eocene	Benue Trough	Nanka Sands	4	Ogbukagu and Akujieze (1990)
Enugu	ENU	Maastrichian		Enugu Shale	44	Onwuka et al. (2004)
Benue	BNE-1	Turonian		Agila	12	Ozoko (2004)
Ebonyi	EBY	Albian		Asu River	17	Awalla and Ezeigbo (2002)
Sokoto	SOK-1	Eocene	Sokoto	Gwandu	19	Uma (1993), Alagbe (2006)
	SOK-2	Eocene		Kalambina	30	Alagbe (2006)
FCT-Abuja	FCT-KD		Basement Complex	North Central	53	Etu-Efeotor (1998 a, b), Alagbe (2002)
Adamawa	ADAM			Adamawa Hills	3	Onugba and Eduvie (2005)
Ondo	ON-OY			South West	74	Ajayi (1998), Abimbola et al. (2002), Ogunbajo and Kolajo (2003), Boboye (2008)
	CR-2			Oban massif	18	Ekwere (2011)
	CR-3			Obudu plateau	27	Edet and Okereke (2005)
Akwa Ibom/Bayelsa/Rivers	AK-BAY-RIV	Quaternary	Seawater	Benin	12	Edet and Okereke (2001a, b)
Benue	BNE-2	Turonian	Saline	Markurdi Sandstone	4	Uma (1998), Uma et al. (1990), Tijani et al. (1996)
Benue	BNE-3	Albian		Awe	5	Tijani (2008)
Cross River/Ebonyi States	CR-EBY	Albian		Asu River	11	Ekwere and Ukpong (1994)

Source: Abimbola et al. (2002) and JMG {2001: 37(1)}.

than the WHO (1993) guideline values for domestic and agricultural uses. This excludes the saline groundwaters which have concentrations higher than the WHO (1993) guideline. In the next section, details of concentrations and variations within the different groundwater basins are discussed.

DISTRIBUTION OF IONS ACCORDING TO GROUNDWATER BASINS

The distribution of ions in groundwater of sedimentary and basement complex areas (excluding the saline water) indicate comparable concentrations with EC, Na, K, Mg, and Cl higher

in the sedimentary area relative to the basement complex. No geographical bias to the distribution is observed but on local basis, the water tends to reflect the lithology. The distribution of ions in the sedimentary area is as follows $\text{Na}^+ > \text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+}$ and $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ and for the basement area the sequence is $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$ and $\text{HCO}_3^- >$

Table 3. Summary of major ions data for groundwater in Nigeria (n = 600), excluding the saline groundwater.

Parameter	Unit	Mean	Med	Min	Max	SD	WHO [1993]
Temp	°C	28.27	28.03	26.46	30.79	1.04	
pH		6.04	6.12	4.86	7.05	0.58	6.5-8.5
EC	μS/cm	270.63	225.83	30.16	635.36	181.04	1500
TDS	mg/l	164.83	131.95	10.00	413.92	131.70	1000
Hardness	mg/l	78.38	60.92	0.01	316.70	77.67	500
Na ⁺	mg/l	30.35	12.27	0.00	202.09	47.49	200
K ⁺	mg/l	8.07	3.05	0.02	52.29	12.02	30
Ca ²⁺	mg/l	20.16	13.15	1.04	55.60	17.00	200
Mg ²⁺	mg/l	9.98	5.98	0.20	46.01	11.77	150
Cl ⁻	mg/l	25.34	17.27	0.87	82.55	23.17	250
HCO ₃ ⁻	mg/l	71.50	44.57	4.64	237.79	67.20	380
SO ₄ ²⁻	mg/l	21.03	12.64	0.00	87.38	25.61	400
NO ₃ ⁻	mg/l	18.38	10.09	0.00	97.22	24.99	10
Fe	mg/l	1.28	0.32	0.04	12.01	2.87	0.3
Mn ²⁺	mg/l	0.20	0.16	0.05	0.58	0.15	0.1

SO₄²⁻ > Cl⁻.

The Niger Delta Basin

The aquifers within the Niger Delta Basin are the most prolific and exploited in Nigeria. These are the Oligocene Benin and the Eocene Ogwashi/Asaba aquifers. These aquifers are composed of alternating layers of gravels, sands, silts and clays thus giving rise to a multi-aquifer system (Okereke et al., 1998; Ibe snr and Sowa, 2002). The Benin aquifer underlies the coastal states of Lagos, Ogun, Ondo, Edo, Delta, Bayelsa, Rivers, Akwa Ibom and Cross River States (Figure 1). Groundwater chemistry data for this aquifer were obtained from the work of Longe et al. (1987), Amadi et al. (1989), Edet (1993), Ajayi and Obot (1998), Udom et al. (1999), Olobaniyi et al. (2007), Edet and Okereke (2001a,b; 2002), Edet et al. (2003), Frank-Briggs (2003), Bolaji (2009) and Ukandu (2009).

From the work of these authors (Table 4), the mean groundwater temperature is between 27.35 and 29.43°C, while the mean pH is less than 7.00. The average value of total dissolved solids (TDS) is less than 150 mg/l and hardness, less than 75 mg/l of CaCO₃. The pH indicates acidic condition and outside the WHO (1993) acceptable limit of 6.5 to 8.5. According to Freeze and Cherry (1979) reference values, the groundwater is fresh (TDS < 1000 mg/l) and soft (Hardness < 75 mg/l). The average ions values show that for the Benin Aquifer the sequence is as follows: Na⁺ > K⁺ > Ca²⁺ > Mg²⁺ and Cl⁻ > HCO₃⁻ > SO₄²⁻ for the anions. The data indicate that the concentrations of Na, Ca, Mg, Cl and SO₄ were within the WHO (1993) acceptable limit of 200 mg/l (Na), 200 mg/l (Ca), 150 mg/l (Mg), Cl (250 mg/l) and 400 mg/l (SO₄) respectively for

drinking water. The lowest values were observed from the inland state of Abia while the highest values were mainly from the coastal states of Akwa Ibom, Bayelsa, Cross River, Delta, Lagos, Ondo and Rivers due to saline water intrusion.

The water types (Table 5) in the Benin Aquifer are not uniform and consist of the following: Na⁺-Cl⁻ (Abia and Cross River States), Ca²⁺-Na⁺-Cl⁻ (Delta State), Ca²⁺-Mg²⁺-Na⁺-Cl⁻ (Rivers State), Ca²⁺-Mg²⁺-Na⁺-Cl⁻-HCO₃⁻ (Akwa Ibom State), Na⁺-Ca²⁺-Mg²⁺-Cl⁻-SO₄²⁻ (Bayelsa State) and Ca²⁺-Na⁺-Mg²⁺-SO₄²⁻-Cl⁻ (Lagos State). The variations are mainly due to differences in number of samples used for the review and locations of data in terms of distance from the Gulf of Guinea.

The work of Ahirakwem and Ejimadu (2002), documented the characteristics of the Ogwashi/Asaba aquifer in parts of Imo State. The major components of the unconfined aquifer are sands, clays, shales and lignite. The groundwater here is acidic, fresh and soft. The cation concentration show that, Na⁺ > Ca²⁺ > Mg²⁺ > K⁺ while, the anion are HCO₃⁻ > SO₄²⁻ > Cl⁻. The water type in this aquifer is Na⁺-Ca²⁺-Mg²⁺-SO₄²⁻-Cl⁻ (Table 5).

The Benin Basin

The Benin Basin is situated in the southwestern part of Nigeria covering most of Ondo and Ogun States extending to the Republic of Benin. Two aquifers, the Coniancian Abeokuta (Shale, Limestone) and the Paleocene Ewekoro (Limestone, Shale) aquifers were considered based on the work of Tijani (2003) and Ogunbanjo (2004).

The average groundwater temperature for the aquifers ranged from 27.97 to 28.47°C, while the mean pH is in

Table 4. Physicochemical characteristics of groundwater for some aquifers in Nigeria.

Basin	Formation (Aquifer)	Code	Temp (°C)	pH	EC (µS/cm)	TDS (mg/l)	TH (mg/l)	Na ⁺ (mg/l)	K ⁺ (mg/l)	Ca ²⁺ (mg/l)	Mg ²⁺ (mg/l)	Cl ⁻ (mg/l)	HCO ₃ ⁻	SO ₄ ²⁻
Niger Delta	Benin	AB	29.43	4.86	30.16	14.58	3.46	2.67	0.36	1.04	0.20	5.54	33.81	0.00
		AK	27.74	6.12	86.24	52.22	60.92	9.50	2.36	13.15	6.73	28.32	18.53	3.38
		BAY	27.35	6.60	353.34	252.04	49.59	23.29	12.96	10.01	5.89	54.21	39.84	18.02
		CR-1	27.98	6.35	225.83	116.58	6.98	18.81	2.30	2.11	0.41	10.75	44.57	2.84
		DEL	28.95	5.27	53.24	21.98	13.67	4.92	1.42	3.81	1.00	8.58	4.64	1.35
		LAG		5.46		10.00	12.95	3.08	0.73	2.75	1.75	5.58	27.86	12.64
		RIV	27.74	6.20	258.31	141.99	51.78	12.69	2.24	10.74	5.98	54.78	42.07	6.13
	Ogwashi Asaba	IM		5.62		28.08	20.05	5.36	0.42	3.87	2.49	6.51	18.90	13.25
Benin	Ewekoro	OG-1	27.97	5.63	95.00	59.71	37.75	37.04	1.54	12.39	1.63	42.86	50.00	0.43
	Abeokuta	OG-2	28.47	6.80	161.07		211.78	7.86	8.32	26.27	35.07	0.87	51.67	12.69
Benue Trough	Nanka Sands	ANAM		5.50	313.25	153.75	163.33	0.00	3.05	39.50	15.50	53.25	13.50	8.00
	Enugu Shale	ENU		5.31	635.36	413.92	98.91	80.26	23.16	11.56	17.19	82.55	119.10	79.37
	Agila	BNE-1		6.61	625.38	372.53	0.01	0.25	0.02	46.40	19.29	23.42	237.79	35.75
	Asu River	EBY	28.76	6.49	539.18	283.78	316.70	97.20	20.86	50.00	46.01	59.56	192.08	87.38
Sokoto	Gwandu	SOK-1		5.89	180.82	117.84	67.06	57.84	9.31	16.99	3.97	13.71	27.09	7.50
	Kalambina	SOK-2		7.05	364.71	402.50	106.80	202.09	52.29	55.60	14.89	17.27	156.93	25.52
Basement Complex	North Central	FCT-KD	26.46	6.13	185.87	136.32	80.95	12.27	4.07	18.57	8.29	12.00	81.38	42.69
	Adamawa Hills	ADAM	30.79	6.64	334.07	320.03	119.56	27.68	9.25	30.59	10.34	8.06	183.06	5.09
	South West	ON-OY	28.07	6.57	377.36	177.72	88.72	27.88	8.46	24.30	6.71	22.59	92.98	14.96
	Oban massif	CR-2	28.62	5.91	123.68	93.39	27.44	2.63	3.62	6.23	2.84	1.89	18.43	6.09
	Obudu plateau	CR-3	27.44	5.89	199.03	127.59	107.61	3.98	2.67	37.41	3.38	19.86	47.27	58.62
Saline water	Benin	AK-BAY-RIV	27.64	6.68	4551.33	2395.44	790.16	508.02	46.58	134.09	109.18	1206.68	187.86	114.79
	Markurdi Sandstone	BNE-2	31.85	6.83	27722.00	17641.25	1271.44	6136.75	243.15	390.58	70.80	10278.75	406.05	
	Awe	BNE-3	35.70	7.06	15441.20	9119.40	660.70	3371.00	110.44	201.58	37.62	4814.60	524.10	17.17
	Asu River	CR-EBY	29.12	6.58	50203.91	33715.14	3875.83	11528.27	283.03	1216.95	200.03	20147.18	219.85	179.36
WHO (1993)			6.5-8.5	1500	1000	500	200	30	200	150	250	380	400	

TH-Total hardness.

the range 5.63 to 6.80. This indicates that the groundwater in this basin is acidic. However, the water is fresh with total dissolved solid (TDS) is less than 1000 mg/l while, the hardness varies between soft and hard. The average concentration of ions was in the order: Na⁺ > Mg²⁺

> Ca²⁺ > K⁺ for the cations and HCO₃⁻ > Cl⁻ > SO₄²⁻ for anions. The data in Table 4 indicate that the mean concentrations of Na, K, Ca, Mg, Cl and SO₄ are within the WHO (1993) acceptable limit for domestic purposes. The main types of water are respectively, Mg²⁺-Ca²⁺-HCO₃⁻-SO₄²⁻ and Na⁺

Ca²⁺-Cl⁻ for the Ewekoro and Abeokuta Aquifers.

The Benue Basin

The Benue Basin comprises four aquifers which are Nanka sands, Enugu Shale, Agala Sandstone

and Asu River Group (Ogbukagu and Akujieze, 1990; Okeke and Igboanua, 2003; Onwuka et al., 2004; Ozoko, 2004; Awalla and Ezeigbo, 2002).

The groundwater of Benue Basin is acidic and fresh. The hardness of the different groundwater bodies in the Benue Basin ranges from moderately hard for the Enugu Shale, through hard for the Agala Sandstones and very hard for the Asu River Group aquifer.

The average concentrations of Na^+ ranged from 0.25 for Agala Sandstone to 97.20 mg/l for Asu River Group; K^+ , 0.02 (Agala Sandstone) – 23.16 mg/l (Enugu Shale), Ca^{2+} , 11.56 (Enugu Shale) – 50.0 mg/l (Asu River Group) and Mg^{2+} , 17.19 (Enugu Shale) – 46.01 mg/l (Asu River Group). In all cases, the cation values are within the WHO (1993) permissible limits for domestic purposes. The concentration of chloride vary from 23.42 (Agala Sandstone) – 82.55 mg/l (Enugu shale), while the bicarbonate concentrations range from 13.50 mg/l for Nanka Sands to 237.79 mg/l for the Agala Sandstone. Sulphates mean concentration is in the range 8.00 mg/l for Nanka Sands – 87.38 mg/l for Asu River Group. The main groundwater types are $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-Cl}^-$, $\text{Na}^+\text{-Cl}^-$ - SO_4^{2-} , $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-SO}_4^{2-}\text{-Cl}^-$ and $\text{Na}^+\text{-Mg}^{2+}\text{-Ca}^{2+}\text{-SO}_4^{2-}\text{-Cl}^-$ - HCO_3^- respectively, for Nanka Sands, Enugu Shales, Agala Sandstones and Asu River Group (Table 5). These variations in the water types reflect the complex lithologic types in the Benue Basin.

The Sokoto Basin

The work of Uma (1993) and Alagbe (2006) were used in respect of the Eocene Gwandu (Shale, Limestone) and the Paleocene Kalambina (Limestone, Marly limestone) aquifers of the Sokoto Basin.

The groundwater in the Sokoto Basin are acidic-basic, fresh and soft (Gwandu Aquifer) to moderately hard (Kalambina Aquifer). The mean concentrations of cations are as follows: $\text{Na}^+ > \text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+}$. The anions are in the order $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$. The main types of groundwater for the Sokoto Basin are $\text{Mg}^{2+}\text{-Na}^+\text{-SO}_4^{2-}\text{-Cl}^-$ and $\text{Na}^+\text{-K}^+\text{-Cl}^-$ - SO_4^{2-} for the Gwandu and Kalambina Aquifers respectively (Table 5).

Basement complex

The mean groundwater temperature for the basement complex is uniform with mean values ranging from 26.4 to 30.79°C. The mean pH, TDS and ions values (Table 4) indicate that the groundwater is acidic and fresh while the groundwater hardness vary from soft, to hard. The concentrations of Na^+ and K^+ are in the range 2.63 to 27.88 mg/l and 2.67 to 8.46 mg/l while, Ca^{2+} and Mg^{2+} are 6.23 to 34.31 mg/l and 2.84 to 10.34 mg/l respectively. The anions are in the following ranges for Cl^- , HCO_3^- and SO_4^{2-} as 1.89 to 22.59 mg/l, 18.43 to 183.06 mg/l and

5.09 to 58.62 mg/l respectively. The dominant water types of the basement complex are $\text{Ca}^{2+}\text{-Na}^+\text{-SO}_4^{2-}\text{-Cl}^-$ for the north central basement complex (Etu-Efeotor, 1998a, b; Alagbe, 2002), $\text{Ca}^{2+}\text{-Na}^+\text{-Cl}^-$ - HCO_3^- - SO_4^{2-} for Adamawa Hills and northwestern basement complex (Onugba and Eduvie, 2005), $\text{Ca}^{2+}\text{-Na}^+\text{-Cl}^-$ - HCO_3^- - $\text{SO}_4^{2-}\text{-HCO}_3^-$ for the southwestern basement complex (Ajayi, 1998; Abimbola et al., 2002a; Ogunbanjo and Kolajo, 2004; Tijani, 2003; Boboye, 2008) and $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-SO}_4^{2-}\text{-Cl}^-$ - HCO_3^- and $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-SO}_4^{2-}\text{-Cl}^-$ respectively, for the Oban massif and Obudu plateau in in southeastern basement Complex (Edet and Okereke, 2005; Edet and Ekpo, 2008; Ekwere, 2011).

Saline groundwater

The occurrence of groundwater with very high salinity has been documented in some parts of Nigeria. These occurrences were reported from the Albian Asu River Group in Cross River and Ebonyi States, Albian Awe and Turonian Markurdi Sandstones aquifers in Benue State (Benue Basin). The TDS, Na, K, Ca, Mg, Cl, HCO_3^- and SO_4 concentrations are as high as 33715.14mg/l, 11528.27mg/l, 283.03mg/l, 1216.95mg/l, 200.03mg/l, 20147.18mg/l, 219.85mg/l and 179.36mg/l respectively (Table 4). These high values are unacceptable for domestic and agricultural purposes. The source of the salinity in groundwater has been attributed to dissolution of chloride minerals (Uma et al, 1990; Ekwere and Ukpong, 1994; Uma 1998; Tijani et al., 1996; BGS, 2003; Tijani 2008).

Coastal aquifers in Nigeria straddling from Lagos State in the west to Cross River State in the east (Figure 1) have been reported to be affected by sea water intrusion. Some of these are presented in the works of Amadi et al (1989), Edet and Okereke (2001a, b), Frank-Briggs (2003), Olobaniyi and Owoyemi (2006), Edet (2008, 2009, 2010), Edet and Worden (2009), Adebo and Adetoyinbo (2009), Olufemi et al., (2010) and Edet et al., (2011). The sequences of ion concentration are as follows $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ for cations and $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-}$ for the anions. A summary of the chemical characteristics including some standards for the different basins are presented in Table 6.

GROUNDWATER EVOLUTION

Correlation

Correlation coefficient is a commonly used measure to assess the relationship between two variables. It is a simple measure to exhibit how well one variable predicts the other (Bahar and Reza, 2010). The correlation matrix for the different variables is shown in Table 7. The data illustrate that EC and TDS show statistically high positive

Table 5. Hydrochemical facies and quality characteristics of groundwater for some aquifers in Nigeria.

Basin	Formation (Aquifer)	Code	Facies	NO ₃ ⁻ (mg/l)	Fe (mg/l)	Mn ²⁺ (mg/l)	SAR	Na (%)	RSC
Niger Delta	Benin	AB	Na ⁺ -Cl ⁻	0.00	0.10		0.78	72.05	0.48
		AK	Ca ²⁺ -Mg ²⁺ -Na ⁺ -Cl ⁻ -HCO ₃ ⁻	2.41	0.51	0.18	0.64	31.71	-0.91
		BAY	Na ⁺ -Ca ²⁺ -Mg ²⁺ -Cl ⁻ -SO ₄ ²⁻	0.57	2.54	0.17	1.43	46.88	-0.34
		CR-1	Na ⁺ -Cl ⁻	27.24			3.79	88.71	0.59
		DEL	Ca ²⁺ -Na ⁺ -Cl ⁻	1.14	0.32	0.07	0.53	45.57	-0.20
		LAG	Ca ²⁺ -Na ⁺ -Mg ²⁺ -SO ₄ ²⁻ -Cl ⁻	1.76	12.01	0.12	0.37	28.10	0.01
		RIV	Ca ²⁺ -Mg ²⁺ -Na ⁺ -Cl ⁻	0.17	1.37	0.15	0.70	28.56	-0.35
		IM	Na ⁺ -Ca ²⁺ -Mg ²⁺ -SO ₄ ²⁻ -Cl ⁻	0.94	0.33	0.05	0.56	39.98	-0.09
Benin	Ewekoro	OG-1	Mg ²⁺ -Ca ²⁺ -HCO ₃ ⁻ -SO ₄ ²⁻	18.93	0.04		2.84	68.48	0.06
	Abeokuta	OG-2	Na ⁺ -Ca ²⁺ -Cl ⁻	4.76	2.43		0.24	13.04	-3.39
Benue Trough	Nanka Sands	ANAM	Ca ²⁺ -Mg ²⁺ --Cl ⁻	2.10	0.18	0.35	0.00	3.05	-3.05
	Enugu Shale	ENU	Na ⁺ -Cl ⁻ -SO ₄ ²⁻	27.50			4.26	70.79	-0.03
	Agila	BNE-1	Ca ²⁺ -Mg ²⁺ -SO ₄ ²⁻ -Cl ⁻	17.49	0.25	0.58	0.01	0.73	-0.03
	Asu River	EBY	Na ⁺ -Mg ²⁺ -Ca ²⁺ -SO ₄ ²⁻ -Cl ⁻ -HCO ₃ ⁻	40.26	0.29		2.49	40.95	-3.19
Sokoto	Gwandu	SOK-1	Mg ²⁺ -Na ⁺ -SO ₄ ²⁻ -Cl ⁻	70.72			0.52	41.02	-1.22
	Kalambina	SOK-2	Na ⁺ -K ⁺ -Cl ⁻ -SO ₄ ²⁻	97.22	0.14		2.28	65.68	-1.72
Basement Complex	North Central	FCT-KD	Ca ²⁺ -Na ⁺ -SO ₄ ²⁻ -Cl ⁻	10.09	0.49		0.66	42.23	-0.28
	Adamawa Hills	ADAM	Ca ²⁺ -Na ⁺ -Cl ⁻ -HCO ₃ ⁻ -SO ₄ ²⁻	5.29			1.12	40.15	0.61
	South West	ON-OY	Ca ²⁺ -Na ⁺ -Cl ⁻ -HCO ₃ ⁻ -SO ₄ ²⁻ -HCO ₃ ⁻	26.09	0.57	0.18	1.45	43.04	-0.25
	Oban massif	CR-2	Ca ²⁺ -Mg ²⁺ -SO ₄ ²⁻ -Cl ⁻ -HCO ₃ ⁻	17.11	0.12		0.20	26.97	-0.25
	Obudu plateau	CR-3	Ca ²⁺ -Mg ²⁺ -SO ₄ ²⁻ -Cl ⁻	14.08	0.05	0.15	0.20	14.16	-1.38
Saline groundwater	Benin	AK-BAY-RIV	Na ⁺ -Cl ⁻	3.81	3.10	0.38	7.80	53.91	-12.72
	Markurdi Sandstone	BNE-2	Na ⁺ -Cl ⁻				73.77	91.38	-18.77
	Awe	BNE-3	Na ⁺ -Cl ⁻				58.88	92.38	-4.62
	Asu River	CR-EBY	Na ⁺ -Mg ²⁺ -Cl ⁻				88.40	84.82	-73.91
WHO (1993)			10	0.3	0.1				

correlation at 95% confidence limit with Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻ and SO₄²⁻. These correlations indicate that the ions are derived from the same source. The high positive correlation between Na⁺-Cl⁻, may represent influence of saline water. The high positive correlation between Na⁺-Ca²⁺, Mg²⁺-SO₄²⁻ and Ca²⁺-SO₄²⁻ may represent ion exchange and gypsum dissolution and the relation between Ca²⁺-HCO₃⁻ and Ca²⁺-Na⁺ may represent

contributions from silicate and carbonate weathering. The correlation between K⁺-NO₃⁻ may represent poor sanitation conditions including application of fertilizer.

Factor analysis

Factor analysis is a multivariate statistical method

which yields the general relationship between measured chemical variables by showing multivariate patterns that may help to classify the original data. The geological interpretation of factors gives an insight into the main processes, which may govern the distribution of hydrochemical variables. Factor analysis can identify several pollution factors reasonably but the interpretation of these factors in terms of

Table 6. Overview of physicochemical and quality characteristics of groundwater for some basins in Nigeria.

Basin	pH	SEC ($\mu\text{S/cm}$)	TDS (mg/l)	Na ⁺ (mg/l)	K ⁺ (mg/l)	Ca ²⁺ (mg/l)	Mg ²⁺ (mg/l)	Cl ⁻ (mg/l)	HCO ₃ ⁻ (mg/l)	SO ₄ ²⁻ (mg/l)	NO ₃ ⁻ (mg/l)	Fe (mg/l)	Mn (mg/l)	TH (mg/l)	SAR	Na (%)	RSC
Niger Delta	5.89	136.27	87.93	10.77	3.05	6.24	3.35	23.67	32.23	8.04	4.73	2.41	0.10	29.39	1.18	48.00	-0.09
Benin	6.21	128.03	29.86	22.45	4.93	19.33	18.35	21.86	50.84	6.56	11.84	1.23	0.00	124.76	1.54	40.76	-1.66
Benue Basin	5.89	338.11	203.15	29.18	7.59	23.03	15.02	43.47	89.57	33.70	13.12	2.36	0.21	119.75	1.29	31.49	-0.96
Sokoto Basin	6.53	411.95	215.19	17.25	83.31	43.57	11.80	16.15	110.18	28.70	58.78	0.00	0.04	158.09	0.78	26.97	-1.36
Basement Complex	6.23	244.00	171.01	14.89	5.61	23.42	6.31	12.88	84.62	25.49	14.53	0.25	0.07	84.86	0.72	33.31	-0.31
Saline groundwater and coastal aquifer	6.79	24479.6	15717.8	5386.0	170.8	485.8	104.4	9111.8	334.5	77.8	0.95	0.78	0.09	1649.53	57.21	80.62	-27.51
WHO (1993)	6.5-8.5	1400.00	1000.00	250	10	200	100	250		400	10	0.3	0.1	< 75			
Freshwater				30.00	3.00	50.00	7.00	20.00	52.00	8.30							

Table 7. Correlation matrix between major ions.

	EC	TDS	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	HCO ₃ ⁻	SO ₄ ²⁻	NO ₃ ⁻
EC	1.000									
TDS	0.997	1.000								
Na⁺	0.983	0.979	1.000							
K⁺	0.266	0.252	0.249	1.000						
Ca²⁺	0.875	0.870	0.833	0.266	1.000					
Mg²⁺	0.946	0.941	0.952	0.230	0.912	1.000				
Cl⁻	0.990	0.984	0.983	0.217	0.838	0.925	1.000			
HCO₃⁻	0.456	0.489	0.439	0.052	0.633	0.579	0.361	1.000		
SO₄²⁻	0.692	0.697	0.713	0.182	0.733	0.794	0.640	0.628	1.000	
NO₃⁻	-0.110	-0.131	-0.103	0.662	0.073	-0.036	-0.195	0.238	0.171	1.000

actual controlling sources and processes is highly subjective (Matalas and Reihner, 1967; Bahar and Reza, 2010).

R-mode factor analysis on the combined data sets provided two factors with eigenvalue > 1 that can explain approximately 83.57% of the variability of the data (Table 8). Factor 1 has an eigenvalue of 6.644 and explains 66.44% of the total variance and shows high loadings on EC, TDS, Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, HCO₃⁻ and SO₄²⁻.

The high loading for EC, TDS, Na⁺ and Cl⁻ indicates high salinity due to saline water influence.

The Na⁺, Ca²⁺ and Mg²⁺ and SO₄²⁻ may reflect the contributions of other hydrochemical processes (ion exchange, gypsum dissolution, silicate and carbonate weathering). Factor 2 has an eigenvalue of 1.71 and explains 17.14% of the total variance with high loading on K⁺ and NO₃⁻. This reveals pollution sources attributed to the

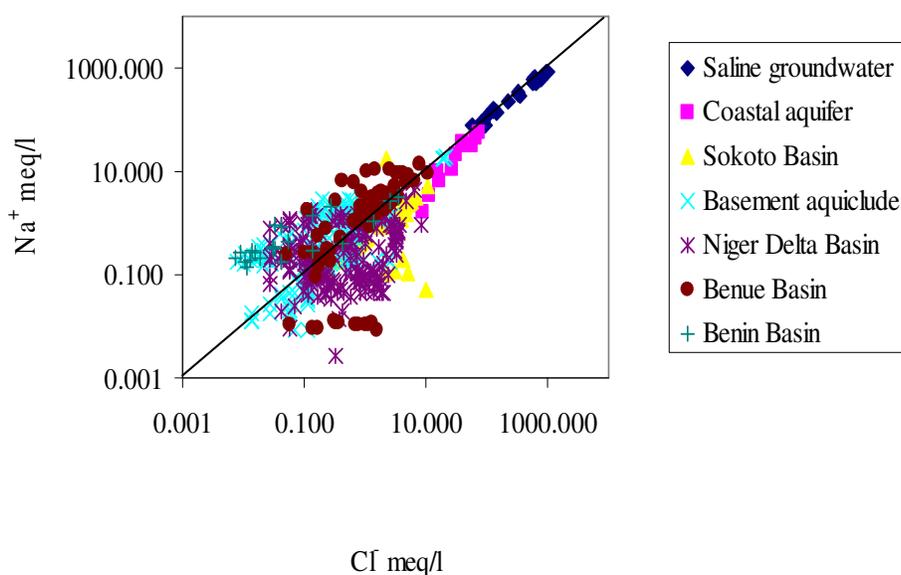
poor sanitation and application of fertilizer.

Cross plots

The Na-Cl relationship has often been used to identify mechanisms for acquiring salinity and saline intrusions (Dixon and Chiswell, 1992; Garcia et al., 2001). In addition, the simultaneous enrichment in both ions indicates dissolution of

Table 8. Varimax factor loading.

Parameter	Factor	
	1	2
EC	0.982	0.005
TDS	0.983	-0.007
Na ⁺	0.974	0.000
K ⁺	0.191	0.814
Ca ²⁺	0.914	0.180
Mg ²⁺	0.979	0.074
Cl ⁻	0.965	-0.086
HCO ₃ ⁻	0.565	0.301
SO ₄ ²⁻	0.780	0.251
NO ₃ ⁻	-0.115	0.958
Eigen value	6.64	1.71
% Total variance	66.44	17.14
Cumulative Eigen value	6.64	8.36
Cumulative % total variance	66.44	83.57

**Figure 3.** Plot of Na⁺ versus Cl⁻ based on data from literature for the different basins.

chloride salts or concentration by evaporation process (Jalali, 2005). This is responsible for the relatively high Na⁺ and Cl⁻ contents in the saline groundwater and coastal groundwater in the Benue Basin and coastal aquifers. Figure 3 shows the plot of Na⁺ as a function of Cl⁻ based on data from literature. The dissolution of halite in groundwater releases equal concentration of Na and Cl in the solution due to dissolution of salt horizons (Uma, 1998; Uma et al., 1990; Ekwere and Ukpogon, 1994; Tijani et al., 1996; Tijani, 2008) and coastal groundwater affected by sea water intrusion (Amadi et al., 1989; Edet and Okereke, 2001a, b; Frank-Briggs, 2005; Edet, 2008c, 2009, 2010; Edet et al., 2011).

The plot of Na-Cl (Figure 3) also show that some samples deviate from the expected 1:1 relation indicating that a fraction of Na is associated with another anion. A Na⁺/Cl⁻ ratio greater than 1 reflects Na⁺ released from silicate weathering reaction (Meybeck, 1987). Silicate weathering is the probable source for Na⁺ in groundwater in parts of Niger Delta Basin, Benin Basin, Benue Basin and the Basement Complex. In Sokoto Basin, the ratio of Na⁺/Cl⁻ < 1 meaning another source is contributing chloride to the groundwater. Generally water containing significant amount of chloride whose drainage has few salty rocks or evaporate as in Sokoto Basin, is considered to be derived from the atmosphere (Al-

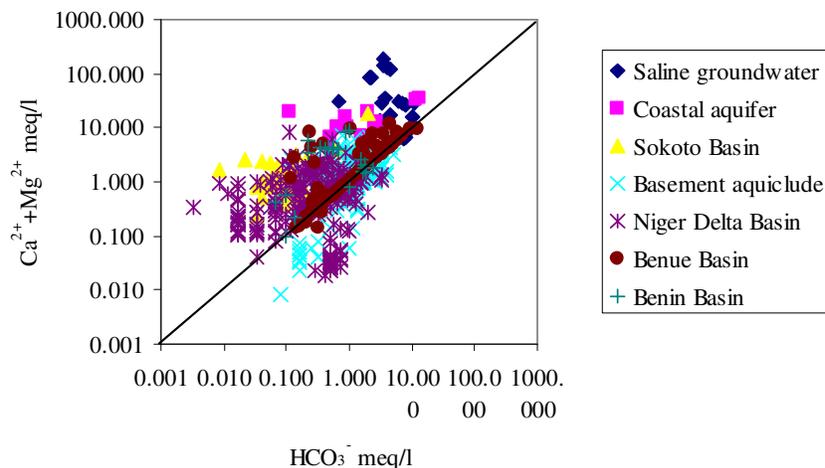


Figure 4. Plot of $\text{Ca}^{2+}+\text{Mg}^{2+}$ versus HCO_3^- based on data from literature for the different basins.

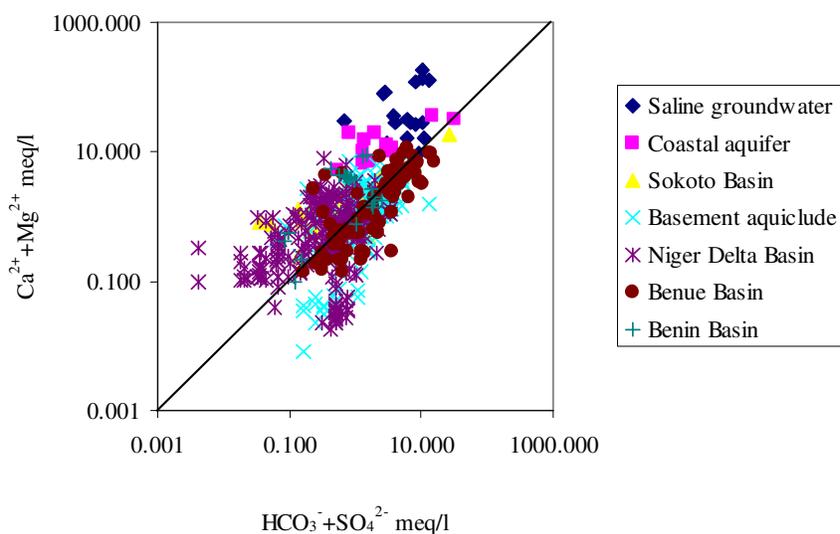


Figure 5. Plot of $\text{Ca}^{2+}+\text{Mg}^{2+}$ versus $\text{HCO}_3^-+\text{SO}_4^{2-}$ based on data from literature for the different basins.

Mikhlafi et al., 2003).

The $\text{Ca}^{2+}+\text{Mg}^{2+}/\text{HCO}_3^-$ ratio marks the upper limit of bicarbonate input from weathering of carbonate rock (Stallard and Edmond, 1983). In Nigeria, most basins show excess of $\text{Ca}^{2+}+\text{Mg}^{2+}$ over HCO_3^- indicating some extra source of Ca^{2+} and Mg^{2+} . However, $\text{Ca}^{2+}+\text{Mg}^{2+}$ was less than HCO_3^- (Figure 4), due to other sources contributing extra HCO_3^- in parts of Niger Delta Basin and the Basement Complex.

In Figure 5, a plot of $\text{Ca}^{2+}+\text{Mg}^{2+}$ versus $\text{HCO}_3^-+\text{SO}_4^{2-}$ shows that for the Niger Delta Basin, Benin Basin, Sokoto Basin Basement Complex, saline groundwater and coastal groundwater, most of the data points are above the 1:1 equiline. Further a plot of $\text{Ca}^{2+}+\text{Mg}^{2+}$ versus total

cations (TC), Figure 6 shows that the plotted points for all the basins fall below the equiline reflecting an increasing contribution of Na^+ and K^+ . From the above, it is clear that the groundwater chemistry is likely to be from dissolution of silicate and carbonate minerals. Thus the concentrations of major elements is controlled by the congruent weathering of carbonate and incongruent weathering of silicates (Garrels and Mackenzie, 1971; Stumm, 1992; Zhang et al., 1995; Al-Mikhlafi, 2003; Garcia et al., 2001; Jalali, 2005).

The ion exchange process is characterized by an $(\text{HCO}_3^-+\text{SO}_4^{2-})$ excess over $(\text{Ca}^{2+}+\text{Mg}^{2+})$, while the reverse ion exchange is marked by an excess of $(\text{Ca}^{2+}+\text{Mg}^{2+})$ over $(\text{HCO}_3^-+\text{SO}_4^{2-})$ (Cerling et al., 1989;

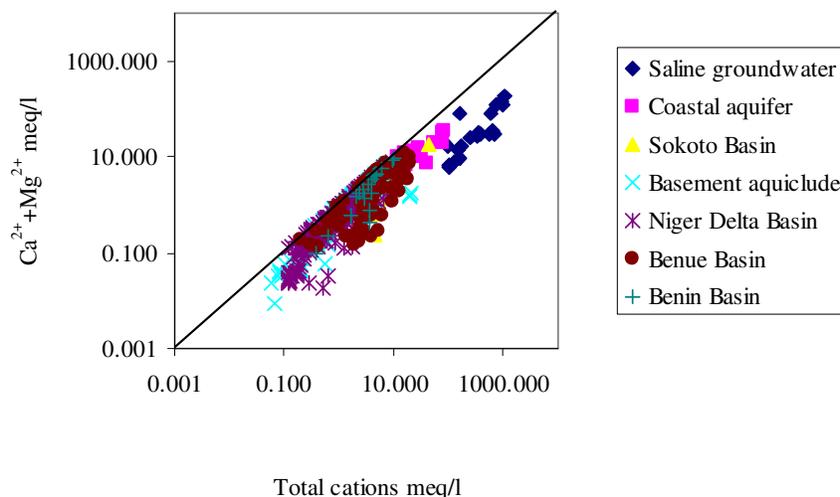


Figure 6. Plot of $\text{Ca}^{2+}+\text{Mg}^{2+}$ versus total cation $\text{HCO}_3^-+\text{SO}_4^{2-}$ based on data from literature for the different basins.

Fisher and Mulican, 1997). The ratio, $(\text{Ca}^{2+}+\text{Mg}^{2+})/(\text{HCO}_3^-+\text{SO}_4^{2-}) > 1$, in Niger Delta Basin, Benin Basin, Sokoto Basin, parts of the Basement Complex and saline groundwater indicating a reverse ion exchange process. However, for Benue Basin and parts of the Basement Complex, the ratio $(\text{Ca}^{2+}+\text{Mg}^{2+})/(\text{HCO}_3^-+\text{SO}_4^{2-}) < 1$, indicating an ion exchange process. The significance here is that two processes, ion exchange and reverse ion exchange are simultaneously contributing to the water chemistry in the basement complex.

GROUNDWATER QUALITY

Here we focus on special areas of groundwater pollution due to natural and anthropogenic sources. The saline groundwater noted above from Benue and Cross River states are unacceptable for domestic uses with concentrations of indicators parameters exceeding national and international standards (Table 2). Water from the other basins is acidic, fresh and soft. High concentrations of potassium were recorded in Sokoto Basin. In some basins including Sokoto, Benue, Benin and the Basement complex, elevated levels of nitrate were recorded from some wells and boreholes.

Iron and Manganese

The occurrence of high iron and manganese in groundwater of some aquifers in Nigeria has been reported (Longe et al., 1987; Ajayi and Obot, 1998; Oteze, 1991; Edet, 1993; Amadi et al., 1989; Abimbola et al., 2002; Awalla and Ezeigbo, 2002; Ibe Sr and Sowa, 2002; Tijani et al., 2002; Udom et al., 2002; Akujieze et al., 2003; Edet et al., 2003; BGS, 2003; Olobaniyi and

Owoyemi, 2004; Ozoko, 2004; Olatunji et al., 2005; Alagbe, 2006; Udom and Amah, 2006; Olobaniyi and Efe, 2007; Olobaniyi et al., 2007; Adebo and Adetoyinbo, 2009; Nganje et al., 2010). Concentrations of Fe up to 3.10 mg/l were reported for the coastal parts of the Niger Delta Basin (Edet, 1993; Ajayi and Obot, 1998; Amadi et al., 1989; Udom et al., 1999; Olobaniyi et al., 2001; Frank-Briggs, 2003; Edet et al., 2009; Ukandu, 2009). Fe concentrations up to 2.43 mg/l were found in the groundwater of Abeokuta aquifer (Ogunbanjo, 2004). Some workers found average concentrations of Fe and Mn in the range 0.18 to 0.29 mg/l and 0.35 to 0.58 mg/l for the Benue Basin (Awalla and Ezeigbo, 2002; Onwuka et al., 2004; Ozoko, 2004; Tijani, 2003). Fe concentrations of up to 12.01 mg/l were reported for the Benin Aquifer around Lagos State (Longe et al., 1987). Generally, for the Benin Aquifer, iron concentration range from 0.1 to 2.54 mg/l while manganese varies from 0.07 to 0.18 mg/l (Ajayi, 1998; Ete-Efeotor, 1998a, b; Bala and Onugba, 2001; Alagbe, 2002; Abimbola et al., 2002; Ogunbajo and Kolajo, 2003; Edet and Okereke, 2005; Onugba and Eduvie, 2005; Boboye, 2008; Ekwere, 2011). The maximum values observed for both elements in these aquifers are well over the WHO (1993) guideline values of 0.30 and 0.10 mg/l for Fe and Mn respectively.

Nitrate pollution

Elevated concentration (> 5 mg/l) of nitrate in waters is an indication that the waters are at the risk of pollution (McNeely et al., 1979; Sahinci, 1991; Atabey, 2005a, b). The levels of nitrate in waters are of particular importance for use in drinking water. Studies have shown that high nitrate in water can lead to 'blue disease' (methemoglobinaemia) in babies (Lahl et al., 1983; WHO,

1984), cancer (WHO, 1984, Uslu and Turkman, 1987), urinary tract diseases (Pontius, 1993, Wasik et al., 2001, Polat et al., 2007). Groundwater with nitrate pollution (> 10 mg/l) is noted for Benin Aquifer (Niger Delta Basin). The mean value of 27.27 mg/l is documented for Cross River State while the concentrations generally less than 10 mg/l characterizes Abia, Akwa Ibom, Bayelsa, Delta and Lagos and the Ogwashi/Asaba aquifer in Imo State.

High nitrate concentrations have been recorded within the different groundwater basins. For instance, the average nitrate value was as high as 58.78 mg/L for Sokoto Basin (Table 8). The average concentrations for the other basins were respectively, 4.73, 11.84, 13.12 and 14.53 mg/L for the Niger Delta, Benin, Benue Basins and the Basement complex. These values were however, not very high relative to the WHO (1993, 2006) standard of 10 mg/l for domestic purpose.

The elevated nitrate values were attributable to land use practices especially, in Sokoto Basin (Uma, 1993). Other factors responsible for high nitrate concentrations in other basins include soil leaching and nitrogenous organic waste (Ozoko, 2004), poor well completion (Edet and Okereke, 2005), improper waste disposal, handling and applications of organic and inorganic fertilizers (Alagbe 2006),

Agricultural applications

In respect of agricultural uses, groundwaters from the different basins are of low salinity and low alkalinity hazard. This indicates the usability of these waters for irrigation in most soil and crops with little danger of development of exchangeable sodium and salinity. Considering sodium percentage (%Na), the groundwater of the different basins suggest good to excellent quality and can be used for irrigation purposes (Richards, 1954).

Based on the classification of United States Department of Agriculture's Salinity using electrical conductivity and sodium adsorption ratio, SAR (Lloyd and Heathcote, 1985), the water of the Niger Delta and Benin Basins belong to the low salinity hazard-low sodium hazard (C_1-S_1) class. The SAR data for Benue Basin, Sokoto Basin and the Basement Complex fall in the C_2-S_1 class. This represents a medium salinity hazard-low sodium hazard. The saline groundwater and coastal aquifers water fall into very high salinity hazard-very high sodium hazard. The residual sodium carbonate, RSC (Ragunath, 1987) values (Table 5) indicates that the waters are suitable as irrigation water ($RSC < 1.25$, Eaton, 1950). Generally, the saline groundwater and coastal aquifers are not suitable for agricultural and irrigation purposes.

CONCLUSION

The review considered published data on groundwater

chemistry and quality in Nigeria for some basins including the Crystalline Basement complex, Sokoto, Niger Delta, Benin and Benue Basins. In addition, data for saline and coastal groundwater were also considered. Groundwaters in these basins are acidic, fresh and generally hard. Excluding the saline groundwater, the average concentrations of sodium, calcium, magnesium, potassium, chloride and sulphate for the different basins are generally within the limits stipulated by WHO (1993) for domestic purposes. However, the average concentration of potassium is high in the Sokoto Basin. The most mineralized groundwater is found from the saline and coastal groundwater in Benue and Niger Delta Basins, while the least mineralized is the groundwater in Benin Basin. The geology is the principal factor controlling the chemistry of groundwater in term of the water types and the processes. The main processes include chloride dissolution for saline and coastal groundwater aquifers and a combination of silicate, carbonate weathering and ion exchange for the different aquifers in the various basins and the basement complex areas.

High concentrations of iron and manganese characterize all the basins. Nitrate level is high in the entire basin with the exception of the Niger Delta Basin indicating input from anthropogenic sources. In respect of agricultural uses, groundwaters from the different basins are of low salinity and low alkalinity hazard, good to excellent quality for irrigation on the basis of %Na, SAR and RSC. This thus indicates the usability of these waters for irrigation in most soil and crops with little danger of development of exchangeable sodium and salinity. However, the saline groundwater in the Benue and Niger Delta Basins are not suitable for agricultural and irrigation purposes.

In Benue and Niger Delta Basins where saline groundwater are present, all the parameters exceed the stipulated standards for drinking, domestic and agricultural purposes.

ACKNOWLEDGEMENTS

Authors thank Alexander von Humboldt, Bonn (Germany) for providing fellowship to the first author to Germany where part of this work was done. H. Madkour and two anonymous reviewers are acknowledged for their suggestions.

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