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ARTICLE

Re-examination of Hydrochemistry and Groundwater Potentials of Cross River and Imo-Kwa-Ibo Intersecting Tropical Basins of South-South Nigeria

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ABSTRACT

This review attempted a detailed description of geological and hydrogeological configurations of Cross River and Imo-Akwa Ibo basins. It presented a synthesis of hydrochemistry and a description of the hydrogeological configurations of the two basins. Hydrogeologically, most areas under Cross River and Imo-Kwa-Ibo are poor in terms of groundwater potentials. Based on the hydrochemistry, the basins hold water of excellent quality. Groundwater sources fall in soft to moderately hard classes. The entire sources groundwater has a TDS concentration of less than 500 mg/l. Groundwater classification based on electrical conductivity (EC) showed EC levels were less than 500 μS/cm. Most of the examined cations and anions are within WHO reference guidelines for drinking water quality. However, no broad analysis of water quality based on water quality indices. Also, studies modeling pollution or the impact of land use changes on groundwater quality are wanting. Thus, further analysis of the hydrochemistry of groundwater aquifers is recommended.

1. Introduction

Groundwater is under stress in the tropical basins consequent of climate change, pollution, population growth, urbanization, and industrialization, as well as land use, all of which are changed by anthropogenic activities [1-6]. These pressures are expected to have great environmental concerns. Therefore, understanding hydrogeological and hydrochemical configurations plays an important role in the functioning of the tropical basins under the current era of human impact on the entire components of the natural environment [7]. Hydrogeochemical processes that operate within the tropical basins are anticipated to accelerate as land use changes and the capacity of the aquifers to regulate natural geological process (including rock weathering and ion exchange process) and increased anthropogenic activities (such as overexploitation of aquifers, application of agrochemicals, municipal

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and industrial wastes), with its consequent depletion of groundwater [8-11]. Groundwater is polluted in many ways as illustrated in Figure 1.

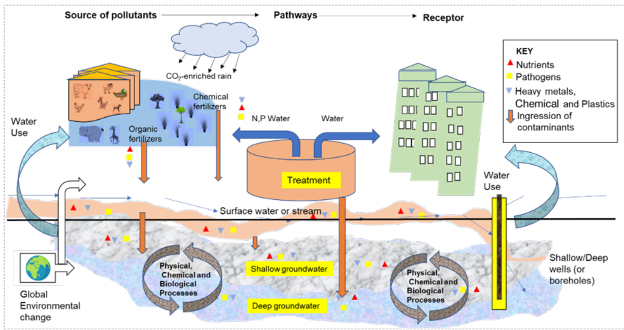

Figure 1. Sources of groundwater contamination [12]

Understanding the major hydrogeochemical interactions at basin scale is constrained geographically and relies on limited filed observations [13-18]. Improved understanding of interactions within the basins is required for the stakeholders to actively focus on mitigation and adaptation strategies for anthropogenic pollution and land use changes. Of special concern are the interactions among pollutants and groundwater near-surface and subsurface water table (including shallow aquifers), and solutes transport, streamflow, and sediments [19-22]. The current state of awareness underlines the need for a detailed review of hydrogeology and hydrochemistry of tropical basins and indicates research approaches that would aid the interpretation of hydrogeochemical processes in the tropical basins within the context of precipitously changing ecological environments, and it affects groundwater quality.

There is need for three focal research areas related to (1) nutrient cycling - additional explicit consideration to cohesive modeling, measuring and understanding of nutrients fluxes between surface and groundwater [7,23-25]; (2) basin processes- highlighted the necessity for a vibrant understanding of how anthropological land modifications affect chemical transport and flow to streams and aquifers [7,26-30]; and (3) acquisition of long-term hydrogeochemical data- there is a need for consolidative field studies that concurrently evaluate nutrients contents in streams and aquifers [7,31-36]. This review seeks to identify the groundwater potentials and hydrochemistry of groundwater in the humid tropical basins of South-South Nigeria.

2. Cross River and Imo-Kwa-Ibo Basins

2.1 Cross River Basin

Cross River Basin (CRB) is located in the eastern part of Nigeria. It occupies most parts of Cross River State [37-42]. The basin is characterized by poor groundwater potentials. This attributed to low permeability shale bedrock which underlain the basin [37,43]. In most remote communities, accessibility to potable water from groundwater sources is very difficult. Besides, the water supply in most of these rural communities is almost exclusively through shallow wells and surface water. The basin is bounded to the north by the Lower Benue Basin covering most of Otukpo and Igumale areas to the north, down to Calabar in the south (Figure 2). The basin covers an area of about 68,000 km^2 and is drained by the Cross River and its tributaries [44].

The climate type is tropical (Am) based on The Köppen-Geiger climate classification. Throughout the year, there is considerable precipitation and a brief dry season. The basin has a mean yearly temperature of 26.2 °C. The annual precipitation is about 2741 mm [39]. The drainage pattern is dendritic and discharges its headwaters into the Atlantic Ocean. The longer tributaries which include the Onwu, Konshisha, and Aboine rises from the Enugu escarpment [44]. The River Calabar which is smaller arises from the Oban Massif in the east of the basin [45-48]. In terms of topography, the CRB is gently sloping, the surface rises at a low gradient from less than 200 meters above sea level, in the west and the southwest, to the uppermost points above 350 meters in the south-eastern parts, at the Oban hills and the northeast, at the Boji hills [44].

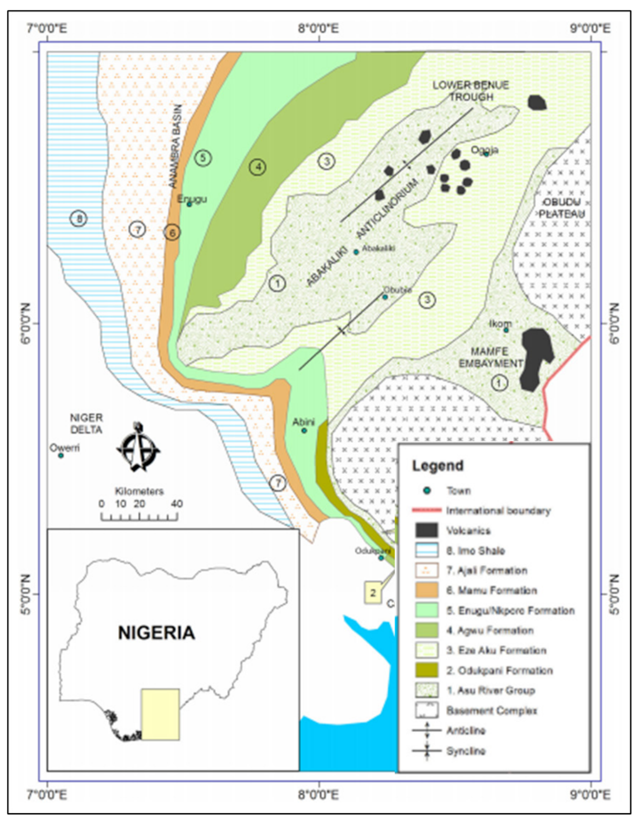

Figure 2. Geological map of Cross River Basin [43]

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2.2 General Hydrogeological Characteristics

The age of the geological formations of Cross River Basin (CRB) ranged from Precambrian through Cretaceous to Tertiary with an unconformity from Upper Coniacian to Lower Campanian [37,43,49]. The catchment is composed of sandstone, limestone, shale, and marl, or marlstone, which is a calcium carbonate or lime-rich mud or mudstone, containing largely variable amounts of clays and silt. The dominant carbonate mineral in most marls is calcite, but other carbonate minerals such as aragonite, dolomite, and siderite may be present. The Abakaliki Shale is the oldest formation and lies unconformably on the Basement Complex, notably Oban massif and Obudu plateau [46,47,50-53]. It is characterized by bluish-grey black and black shales, sandy shales, fine micaceous and calcareous sandstone, and siltstone with limestone interbedding [43,54-56]. The Cenomanian Odukpani Formation overlies the Asu River Group and is made of black shales with slight inter beddings of limestone and sandstone [57,58]. The Turonian to early Santonian Eze-Aku Formation [59] contains black shales separated within sandy units and shelly limestones overlie the Odukpani Formation. The Eze-Aku shale is overlain by the Conacian Agwu shale and is made up of black shale with minor separations of limestone and sandstone [60,61].

Superimposing the Agwu Formation is the Campanian to Maastrichtian Enugu/Nkporo Formation comprising mostly of shale, limestone, and sandstone [62-64]. The youngest unit (Imo Formation) is found in the Tertiary Niger Delta [65,66]. The black shale interbedded with clay and sandstone constitutes the major rock formation. The Cretaceous sediment was transformed by tectonics activities (folding/faulting) during the pre- and post-Turonian times [37,43]. The outcrop pattern of geologic formations and major structural elements in the Cross River Basin is shown in Figure 2. Tectonism was trailed by magmatism which caused the formation of volcanic rocks in the Asu River and Eze Aku Groups [59, 67-69]. This is illustrated in Figure 3. These intrusive rocks have been detected in Obubra and Iyametet [43].

Cross River Basin falls into three hydrogeological assemblies of south-eastern Nigeria: lower, middle, and upper [43]. The lower hydrogeological group is lying beneath the Shale rocks of the Abakaliki Formation, Odukpani Shale, Eze-Aku Shale, Agwu Shale, Nkporo Shale, and Enugu Shale. The middle hydrogeological group is established in the interior of the Mamu, Ajali, and Nsukka Formations, which is comprised of sandy dispositions [43,70,71]. The upper hydrogeological group is made up of Imo Shale, Bendi-Ameki, Ogwashi-Asaba, and the Benin Formations [43].

AGE	BASIN	FORMATION	THICKNESS	HYDRO STRATIGRAPHIC UNIT	HYDROGEOLOGICAL GROUP
PLIOCENE					
MIOCENE					
OLIGOCENE					
EOCENE	Niger Delta	Imo Shale Group	314	Imo Shale Aquitard	
PALEOCENE		Nsukka Formation	233	Nsukka Aquitard	
MAASTRCTIAN		Ajali Formation	450	Ajali Sandstone Aquifer	Middle
		Mamu formation		Mamu Aquiclude	
CAMPANIAN		Enugu Shale		Enugu Shale Aquitard	
		Nkporo Shale	1829	Nporo Shale Aquitard	
SANTONIAN					
	Cross River				
CONIACIAN					
		Agwu Shale		Agwu aquitard	Lower
TURONIAN					
		Eze Aku Group	3000	Asu River Aquitard	
		Abakaliki Shale		Abakaliki Aquitard	
CEROMANIAN					
ALBIAN					
APTIAN					
PRECAMBRIAN	Oban Massif			Basement Aquifer	

Figure 3. Stratigraphic and hydrogeologic components of the Cross-River Basin [43]

The most important characteristic of the lower hydrogeological group in the CRB is the existence of a thin shallow but extensive unconfined groundwater aquifer. The aquifer is molded by the upper worn layer within the fractured shales and sandy layers. The shallow aquifer is tapped mostly by hand-dug wells [43,49]. Groundwater is primarily found in tabular partings at shallow depths of between 10 and 40 meters [43,72-74]. The shales of the Asu River Group are known to have high transmissivity [43,75-77], perhaps associated with the depths and low-grade metamorphism of the shale host rock. The Agwu Shale, which is not splintered has low transmissivity, consequently making it difficult to tap the aquifer [43,78,79]. The saturated thickness is less than 50 meters and yields of boreholes are generally less than 0.3 l/s [43].

The middle hydrogeological group occurred in the Mamu, Ajali, and Nsukka Formations [43,80]. This hydrogeological cluster contains a massive sandy aquifer. The hydrogeology of Mamu, Ajali, and Nsukka Formations are detailed in the literature [43,81-84]. The upper group consists of the Tertiary Imo Shale of Palaeocene age [43,79,85,86]. It is characterized by deposits of shales, clay stones, calcareous mudstones, siltstones, ironstones, and lenses of sandstones. The shales are fissile and sporadically interbedded with sandstone layers producing the confined aquifer-aquitard system [43]. The stratigraphic and hydrogeologic units of CRB is presented in Figure 4.

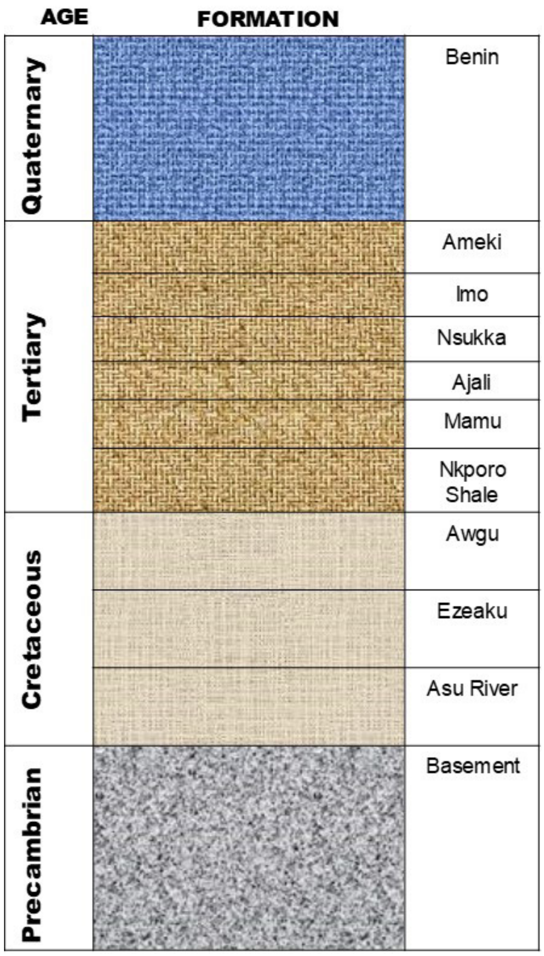

Figure 4. Hydrogeology of Cross River Basin

The hydrogeology of CRB comprises of a sequence of rocks leading from Basement (Precambrian) through Cretaceous and Tertiary sediments beds [43,44]. Most of CRB is underlain by Cretaceous Sediments of the Ameki, Asu River, Awgu, Ajali, Benin, Ezeaku, Imo, Nkporo, and Nsukka Formations [43,87-89], with the oldest (Asu River Formation) underlain by Basement Complex Formation. All these hydrogeologic units are poor aquifers except Awgu and Ezeaku Formations [43,44,90]. The Basement Complex is confined south-eastward, on the Oban hills and the northeast-ward along the Boji hills. Groundwater in these areas has not been fully explored, though the situation is expected to be like in the other sections of the Basement Complex areas. Groundwater condition in this area is typical of Nigeria's Basement Complex. There are published data on the hydrogeology of the Basement Complex of Nigeria [91-96].

2.3 The Asu River, Ezeaku, Awgu, Mamu and Nkporo Assemblages

Albian in age, the Asu group can be subdivided into three formations:

(1) Over 200 meters bluish grey to olive-brown shales and sandy shales;

(2) Fine-grained micaceous and calcareous sandstones and some patches limestones; and

(3) Small dikes, sills, and several igneous intrusive rocks.

The Asu River group lies beneath greater parts of eastern Enugu, Imo, and larger parts of Ebonyi State [43,97-100]. The Okposi, Uburu, and Abakaliki are the main outcrop areas, which are dominated by Abakaliki anticlinorium which runs coarsely north-southwest [43,44]. Around Enyiba, Uburu and Okposi, the Asu Formation is highly weathered and large quantities of saliferous groundwater were pumped out during lead-zinc mining activities. In less weathered sections the Asu Formation cannot be well-thought-out for groundwater exploration [43,74,101,102]. But in the weathered sections, for example, the Abakaliki regions, groundwater is found in large quantities, although with high drawdowns as a result of the limitations in the extent of the aquifers, caused by impermeable shale-clay boundaries [103,104].

Bordering the Asu River Group, and plummeting northwestward and south-west, are outcrops of the Ezeaku formation, with its facies member, the Amasiri sandstones [105,106]. The formation of about 100 meters thick passes laterally into sandstones and sandy limestones in some locations. Groundwater aquifers are found mainly within the coarser, less cemented sandstones, weathered limestones with solution cavities and channels [44]. This geological group comprises of granites and has a thin lenticular shale, layers of grits, and gravelly stones. The textural classes are mostly coarse in texture. The Awgu Formation outcrops in the southern areas close to Awgu, where it is referred to as "Awgu sandstone". This formation reaches about 450 meters in thickness [107,108]. The hydrogeology of Awgu formation has been described in the literature [107,109-111].

The Mamu and Nkporo groups were superimposed by the Awgu Group, successively are not excellent groundwater aquifers [44]. Entirely these poor aquiferous formations lie beneath the CRB and have added to the hydrogeological complications of the basin [112-114]. Abakaliki, Enugu, and Afikpo are the Major cities affected. In contrast, the extreme southeast corner, where Cross River flows into the sea, lies beneath by more promising younger aquifers, notably, the Ajali and Benin Formations which outcrops around Utapate, Etinan, Oron and Calabar areas [44]. Most of the deep wells constructed in CRB seemed to be positioned on the Benin Formation, as the outcrops of the Ajali Formation is narrow. The aquifers of Benin Formation

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are confined in some places producing artesian conditions [44,115-118]. As a result of poor groundwater conditions in CRB, people largely depend on surface water sources, waterborne diseases like guinea worm contagion, is rather widespread, especially in Abakaliki, Enyimba, and Uburu areas [44].

2.4 The Akwa-Ibo-Imo River Basin

This small basin covers an aerial extent of about 12000 km^2, forming a rectangular basin, extended in the northwest-southeast direction [78,119]. The basin is bordered by the Southern Trunk of the River Niger, just south of Onitsha extending to the northwest, and Atlantic coast, to the south and southeast. The basin is drained by River Imo and River Akwa-Ibo. The two rivers run virtually parallel to each other. The River Imo had its source from the Igboukwu-Orlu-Okigwe highlands, just southeast of Umuahia. Both rivers flow southeastward directly into the Atlantic Ocean [44]. The River Imo is joint by its major tributary-the River Otamiri. River Orashi had its origin from Orlu-Okigwe and also runs virtually parallel to River Niger. The river appears to join the Deltaic network to the south [44].

The basin covers most parts of Imo State, southern Anambra State, southwestern areas of Akwa Ibom and the Cross-River States. The basin also extended to the north-eastern parts of Rivers State [44]. Major towns include Abak, Eket, and Opobo in the coastal areas. Towns in the hinterland include Aba, Umuahia, and Owerri. Rainfall is highly localized and is strongly influenced by the ocean factor. Mean annual rainfall ranges from 1000-2000 mm near the coast [44]. The relative humidity is very high with a mean potential annual evapotranspiration of less than 1400 mm. The topography of the basin is shaped by the Igbouku-Orlu-Okigwe ridge, extending from northwest to southeast and sloping from a just over 300 meters above sea level down to about 150 meters to the northwest of Umuahia, and gradually to sea level in the extensive coastal area of the basin, proximal to the Atlantic Basin [44].

2.5 General Hydrogeological Characteristics

Geologically the basin is characterized by the Miocene Akata Formation (shales, intercalated sands, and Silestone) [120], Miocene-Pliocene Agbada Formation (sands and sandstones, intercalated with shales) [121-123] and the Pliocene Benin Formation (coarse-grained sand, gravelly sands with minor inter-beddings of clays and shales), from top to bottom [124-127]. The middle and the upper sand units of the Benin Formation form the major aquiferous units in the area. Average boreholes depths in the area range from 42-172 meters in depth [128-130]. The static water level ranges from 1-55 meters, and saturated thickness ranged from 39-100 meters. On the other hand, transmissivity is about 216-5304m^2/day. A drawdown ranging from 1.2-42.5 meters was recorded in Ikot Ekpene, and storage coefficient of 0.10-0.30 [44].

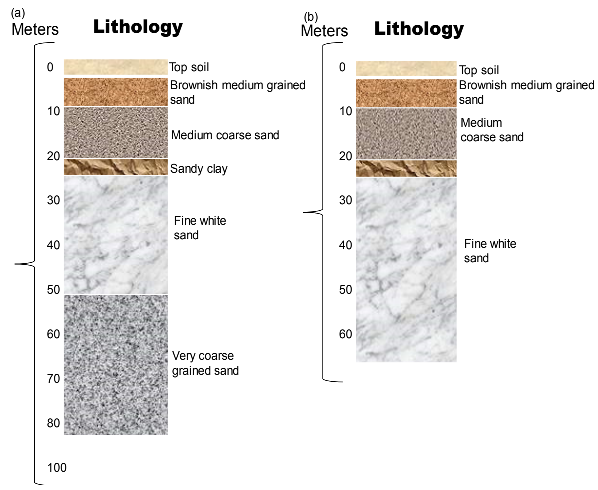

Figure 5. The lithology of Southern Ukanafun, Akwa Ibom State, (a) Borehole 1, and (b) Borehole 2

The water table varies from 1.3-52 meters in the area [128-130]. These formations are comprised of continental sand and gravel, deposited in an upper deltaic plain environment [44]. The grain sizes range from coarse to fine in texture and are poorly sorted. They are also thick and friable with minor intercalations of clay, silts, and sandstones. The alternate assemblage builds up multiple-aquifer systems with various thicknesses. Consequently, the aquifer systems are a combination of the different grain sizes of sand [44]. Figure 5 shows the lithology of Southern Ukanafun Local Government Area, Akwa Ibom State. In all the five layers within the maximum electrode, the separation was identified with each having its distinct thickness and resistivity range as shown in Figure 4. The upper layer, which is medium-grained sand, is generally very thin and it overlies medium coarse-grained sand layer [44,77,131,132]. This layer shows an increasing resistivity with depth. The fine sand layer overlies the very coarse-grained sand layer. This layer shows resistivity inversion with depth. The fine sand and the very coarse-grained sand layers which are sandwiched with a thin bed of clay formed the major shallow productive aquifers in the area. The bottom layer at the maximum current electrode separation is sandstone whose thickness cannot be defined within the maximum current electrode separation (Table 1).

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Table 1. Resistivity and depths obtained by correlations of VES and the nearby logged boreholes at Ukanafun [131]

Types of rocks	Resistivity (Ωm)	Depth to Bottom of layers (m)
Medium grained sand	385-6860	0.40-3.00
Medium-coarse grained sand	1425-8800	0.70-26.47
Fine Sand	207-2530	4.40-40.00
Very coarse sand (gravelly)	46870-30700	30.00-60.00
Sandstone	15,700-163000	31.00-

The depth to the first aquifer compared favorably with the static water levels, which are 20.16 and 18.32 meters, respectively. These layers have very good potential for freshwater based on their high resistivities and the aquifers may not likely to be contaminated due to their depths. The shallow aquifers are characterized by insignificant hydraulic gradients due to the slight variation in the static water levels [131]. The Imo Basin is underlain by the following geologic sequence (Figure 6). The principal water-bearing formations are the Ameki and Benin Formations. The Ameki Formation is confined by the Imo Shale in the northern edge of the basin. However, in the southern part of the basin, both the Ameki and Benin Formations, as well as the sedimentary deposits the River Niger, seem to be hydrologically connected and therefore, provide combined aquiferous horizons [44].

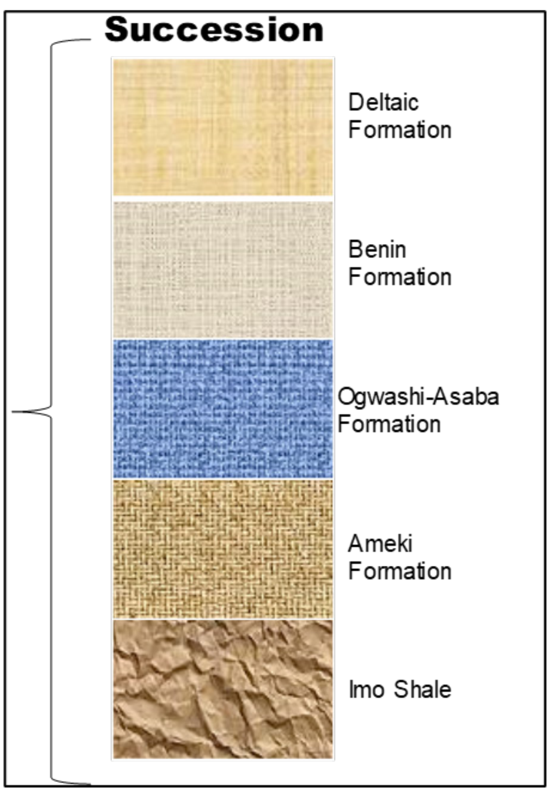

Figure 6. Geologic progressions in Imo Basin

Groundwater is chiefly found under water-table conditions. However, the water table is very deep in some places including Akata, Orlu-Ezima, Umuahia, Atta, Awomama Umuma circle where the depth of water table varies from less than 50 meters along the Awomama Umuma circle to over 75 meters towards the center of the Orlu ridge [44]. Along the area south of Owerri and Abba, closer to the lower plains, the water table depth increases to between 6 meters close to the coast to 30 meters inward. Groundwater recharge is primarily by precipitation in most parts of the basin, through the profuse porous sands of the Benin Formation [133-136]. Groundwater is assumed to be flowing from the northern highland areas of the basin towards the coastal areas in the south and beyond under the sea. The alluvial deposits and deltaic formation is formed by the Imo River [137,138], it's tributary the Otamiri River, the River Kwa Ibo and the extensive valley of the Niger River and its tributary, the Orashi River are marked by wide sedimentary deposits which store large quantities of groundwater [139-141]. The groundwater potential of the areas is high and can be utilized for irrigation farming. The thickness of the alluvium range from a few meters to 20 meters, along with the river courses [44]. Along the coastal margin, are the deltaic formations of the Imo Basin, where the River Imo and River Kwa Ibo empty their flows into the sea.

3. General Hydrochemical Characteristics

The two basins are hydrochemically and geographically comparable, thus are treated jointly in this section. Physical parameters of groundwater (pH, temperature, EC, TDS, alkalinity, TSS, DO, turbidity, and salinity) were synthesized from the literature and were used to characterize the physical chemistry of groundwater. The cation and anion chemistry was depicted using chemical parameters including Al, Ba, Ca, Mg, Mn, Cd, Pb, Cu, Fe, Zn, NO_2, NO_3, PO_4, and SO_4. The concentrations of heavy metals in the harbor or estuarine deposits within the study area are generally high owing to substantial anthropogenic metal loadings carried by upstream of the tributary [142]. The alluvium serves as a metal pool that can release metals to the overlying water through natural or anthropogenic processes, which may impact the ecosystem. Besides, marine biota can take up metals, which in turn increases the potential of some metals entering into the food chain [142]. Evaluation of chemical parameters of water quality is important due to their deviating sources. At a level above the recommended limits, these elements may render groundwater sources unfit for human use. Chemical elements such as Ca, Mg, Cu, Cd, B, Al, and As, are primarily derived from rocks. But elements such as Cl, NO_3, and SO_4 are added to groundwater from anthropogenic sources. Thus, under-

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standing the origin and concentration level of chemical elements in groundwater is very important for groundwater management.

3.1 Physical Chemistry of Groundwater

Groundwater is expected to meet all the physical requirements for drinking: tasteless. colorless and odorless [143]. In assessing the physical quality of drinking-water, consumers rely largely on their senses [144,145]. It is important to note that, the microbial, chemical and physical characteristics of water may impact its appearance, odor, or taste [146], and the water users tend to measure the quality and acceptability of the water-based on these principles. Even if these rudiments may not impact human health, very turbid groundwater is usually colored and may have an objectionable taste or odor. Consequently, it is important to be aware of considering both health-related guideline values and aesthetic criteria when assessing groundwater sources and develop-

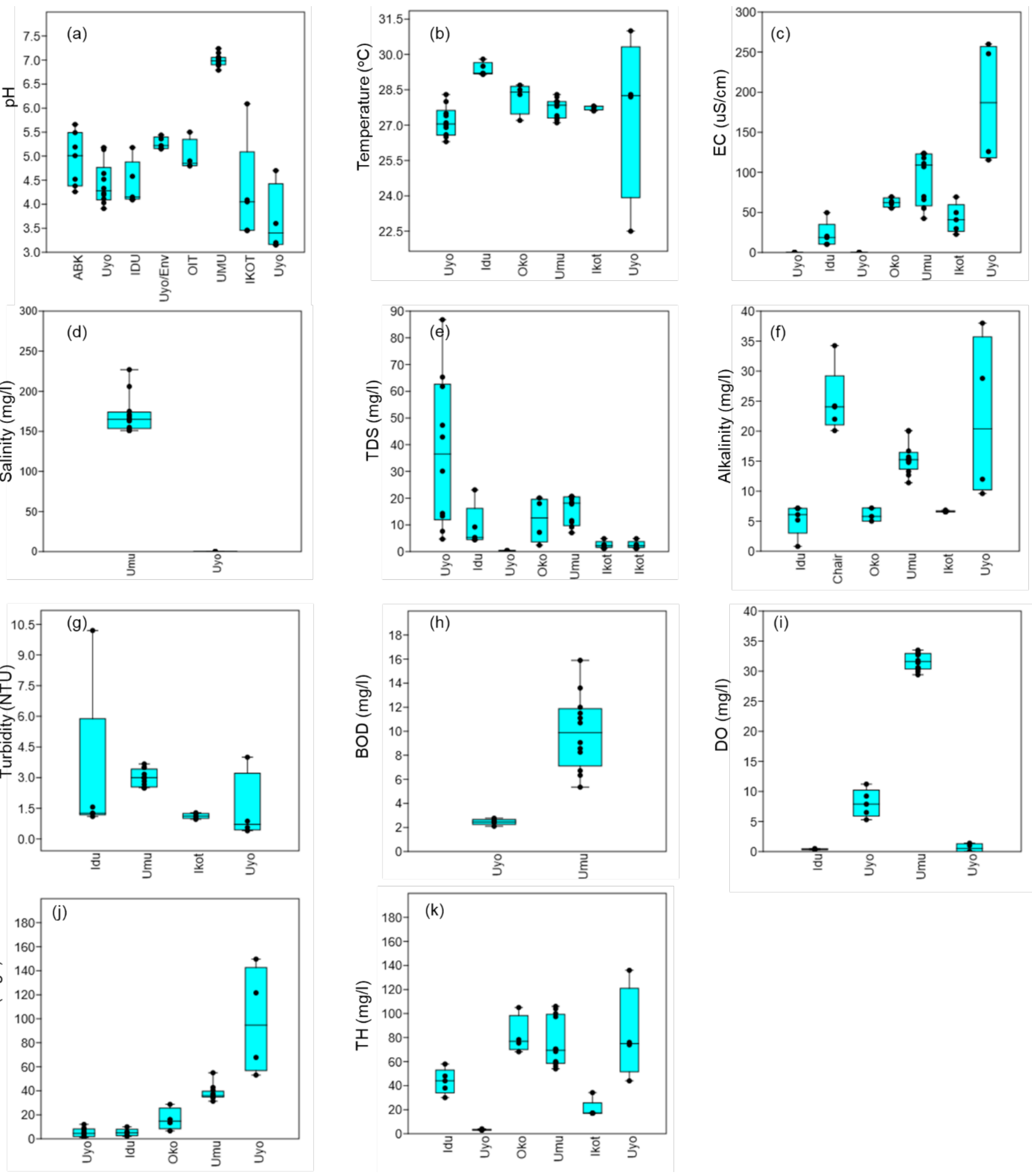

Figure 7. a-k physical characteristics of groundwater

Note: Ikot=Ikot Effanga, Ebo=Ebonyi, Idu=Idu Uruan, Oko= Okorette, Iko Town, Umu=Umuahia North ing principles and criteria for different uses. Changes in the normal color, taste, or odor of groundwater source may be an indicator of variations in the quality of the water source. Figure 7 (a-k) summarized the physical chemistry of groundwater in the study area. Based on 78.57% of groundwater sources are acidic as indicated in Figure 7a and Table 2d. The underlying reasons for low pH in the basins need to be understood. Total hardness ranged from 2.9-136 mg/l. Hardness less than 75 mg/l is especially required for drinking. Evaluation of total hardness (TH) from 35 locations revealed that 74% of groundwater sources in Cross River-Akwa-Ibo-Basin fall in soft class, and 26% fall in moderately hard class (Table 2a).

The total dissolved solids (TDS) concentration from 46 locations revealed that 100% of groundwater sources in the basin have a TDS concentration of less than 500 mg/l (Table 2b). The mean TH is 55.05 mg/l. TDS ranged from 0.13-23.1 mg/l. The Mean TDS is 8.82 mg/l. Conductivity (EC) ranged from 0.03-260 µS/cm. Mean EC is 72.94 µS/cm. Generally, the EC level is low. EC levels from 45 locations were less than 500 µS/cm (Table 2c). This is especially required for drinking. Except for the acidity of groundwater sources, groundwater in Cross River-Akwa-Ibo Basins is good for drinking Based on physical parameters.

Table 2. Groundwater classification based on total hardness, TDS, EC and pH

(a) Hardness ($CaCO_3$) mg/l	No. sites	Percentage (%)	Classification
0 - 75	26	74.29	Soft
75 - 150	9	25.71	Moderate Hard
150 - 300	0	0	Hard
>300	0	0	Very Hard
Total	35	100	
(b) TDS (mg/l)			
Less than 500	46	100	Essential for drinking
500-1000	0	0	Required for drinking
1000-3000	0	0	Suitable for drinking
Greater 3000	0	0	Unsuitable for drinking and irrigation
Total	46	100	
(c) Conductivity (µS/cm)			
250-750	45	100	Good for drinking
750-2250	0	0	Permissible
Greater than 2250	0	0	Doubtful
Total	145	100	
(d) pH			
Less than 6.5	44	78.57	Acidic
6.5-8.5	12	21.43	Neutral
Greater than 8.5	0	0	Alkaline
Total	56	100	

3.2 The Cation Chemistry

Figure 8 summarized the cation chemistry of groundwater. There are very few studies on aluminum (Al), ammonia (NH_4), and arsenic (As), from the study area [147,148]. Al ranged from 0-230.2 mg/l. Mean Al is 59.85 mg/l. NH_4 concentration ranging from 0.07-0.08 mg/l with an average value of 0.074 mg/l [148]. Barium (Ba) concentrations ranged from 0-6 mg/l Ba, with an average value of 2.82 mg/l. Calcium (Ca) ranged from 8.2-116 mg/l with an average value of 43.73mg/l. Elevated levels of Ca in drinking water may be beneficial and groundwater sources that are rich in calcium will tend to have good taste. There is an indication that the incidence of heart disease is minimized in locations having groundwater aquifers with a high level of hardness, the primary component of which is calcium so that the existence of the component in a water supply is helpful to health. At reasonable levels, Ca in drinking water is beneficial. Nonetheless, high Ca levels in combination with Mg can form carbonate hardness ($CaCO_3$). The significance of Ca in hydrochemical analysis relates to hardness. Calcium is found naturally in various environmental settings and occurs widely in groundwater aquifers [149-151]. It is an integral component of coral and is found in high concentrations (400mg/l) in brine. In lime regions, Ca attain 100 mg/l. Elementary calcium at normal temperature can react with water, based reaction process indicated by Eq. 1:

$$Ca_{(s)} + 2H_2O_{(g)} \rightarrow Ca\left(OH\right)_{2(aq)} + H_{2(g)} \quad (1)$$

Dissolved calcium hydroxide forms soda and hydrogen gas. It typically occurs when CO_2 is freed, resulting in the development of carbonic acid, affecting Ca compounds. The carbon weathering reaction and the total reaction are defined in equations 2 and 3, respectively.

$$H_2O + CO_2 \rightarrow H_2CO_3 \text{ and } CaCO_3 + H_2CO_3 \rightarrow CaH(CO_3)_2 \quad (2)$$

$$CaCO_{3(s)} + CO_{2(g)} + 2H_{2(l)} \rightarrow Ca^{2+}_{(aq)} + 2HCO^{-}_{3(aq)} \quad (3)$$

Consequently, calcium hydrogen carbonate is produced. Groundwater aquifers can be affected by changes in temperature since Mg is a relatively low reducing element. Thus, rising oxygen can increase the reduction process. Additionally, Mg can react with water vapor to produce hydrogen gas or magnesium hydroxide as defined in Eq. 4.

$$Mg_{(s)} + 2H_2O_{(g)} \rightarrow Mg\left(OH\right)_{2(aq)} + H_{2(g)} \quad (4)$$

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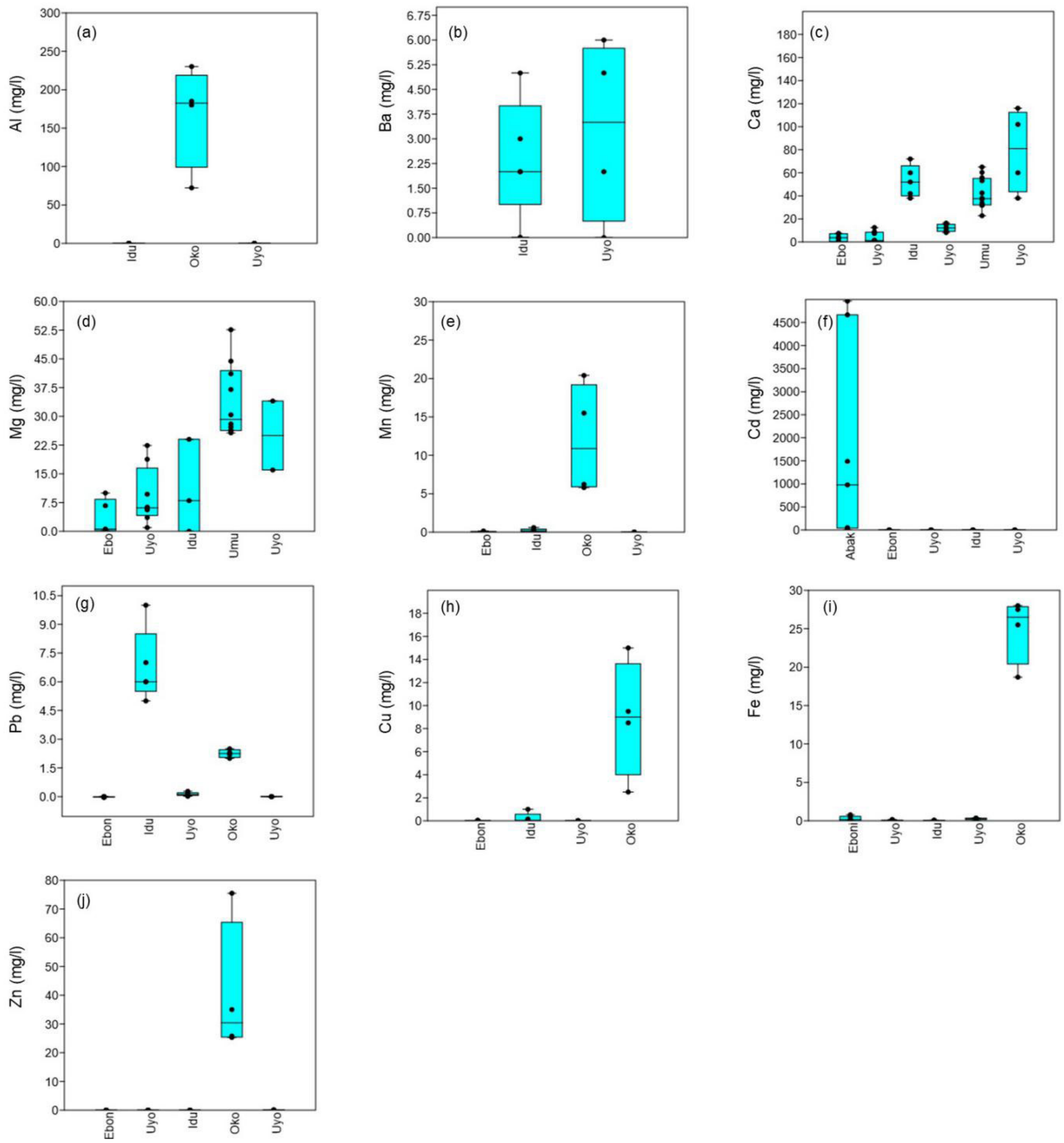

Figure 8. a-j the cation chemistry of groundwater

Note: Ebo=Ebonyi, Idu=Idu Uruan, Oko= Okorette, Iko Town, Umu=Umuahia North.

Magnesium (Mg) ranged from 0-52.6 mg/l with an average value of 16.57 mg/l. Like Ca, Mg is also profuse in natural waters and an important nutritional prerequisite for humans - 0.3-0.5 g/day. It is the second major constituent of hardness and it generally comprises 15-20% of the total hardness. Its absorption is very important when measured in combination with that of sulfate [152,153]. The significance of Mg is that it constitutes a second major component of hardness ($CaCO_3$). Dolomite and magnesium carbonate are primary sources of Mg in aquifers [154-156]. The concentration of manganese (Mn) in drinking water is above 0.1 mg/l, which may cause an unwanted taste in drinks and stains sanitary ware and laundry. The existence of Mn in drinking water may cause the accumulation of deposits in the distribution system. At levels, less than 0.1 mg/l is generally satisfactory to consumers. However, under some environments, Mn can be at levels above 0.1 mg/l and may go on in solution for a longer period compared with its usual solubility in most drinking water [143]. Mn ranged from 0-20.4 mg/l, with an average value of 3.17 mg/l.

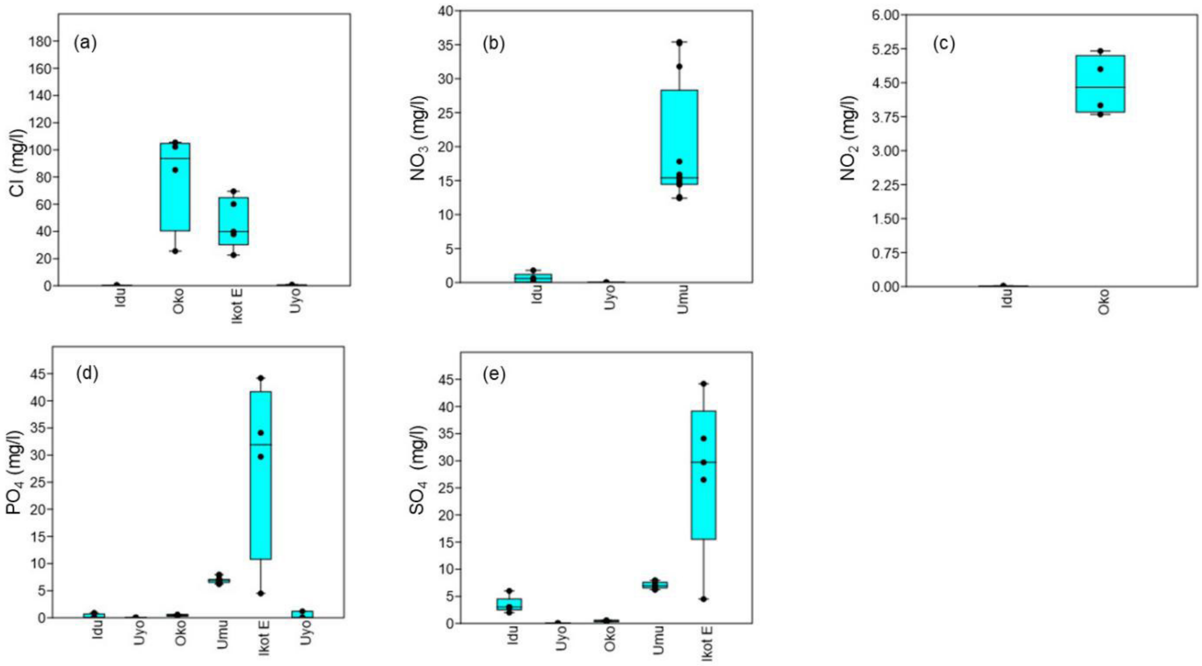

Figure 9. a-e the cation chemistry of groundwater

Note: Ebo=Ebonyi, Idu=Idu Uruan, Oko= Okorette, Iko Town, Umu=Umuahia North.

Mean sodium (Na) was 18.46 mg/l and ranged from 13-24.1mg/l [157]. Na concentrations are very low at some locations [158]. The taste verge concentration of Na in water rest on the accompanying anion and the temperature of the solution. At room temperature, the average taste threshold for Na is about 200 mg/l [143]. Potassium (K) ranged from 0.04-0.2 mg/l with an average value of 0.09 mg/l [158]. Potassium occurs widely in the environment, including all-natural waters. But K occurs in natural waters at levels far below those of health concern. The recommended daily requirement is above 3000 mg/l. Cadmium (Cd) ranged from 0-4966 mg/l with an average value of ~591.77 mg/l. The WHO, 1963 standards for drinking water quality recommended 0.01mg/l Cd, as a maximum permissible limit based on health concerns. In 1971 this value was as a tentative higher concentration limit, based on the lowest concentration that could be appropriately measured. In 1984, a guideline value of 0.005mg/l was recommended for Cd in drinking water, which was further reduced to 0.003 mg/l in the 1993 Guidelines [159]. Fluoride (F) was not widely reported in the literature. The F concentration was 0.01 mg/l at Uyo [148]. Lead (Pb) ranged from -0.032-10 mg/l with an average value of 1.98 mg/l. In drinking water, Pb is generally less than 5mg/l [159].

Nickel (Ni) ranged from -0.032 to 0.011 mg/l with an average value of -0.019 mg/l in Abakaliki [160]. Like F, Ni was not widely reported. Nickel is another metallic element that is limited in drinking water because of possible carcinogenicity as far as humans are concerned; it also has variable detrimental effects on aquatic life. Nickel is toxic to plant life and is a danger to fish [152]. Copper (Cu) ranged from 0.001-15 mg/l, with an average value of 2.26 mg/l. The threshold for the effects of Cu in drinking water on the gastrointestinal tract occurs, but then there is still some hesitation concerning the long-term effects of Cu on sensitive populations, such as carriers of the gene for *Wilson Disease* and other metabolic disorders of copper homeostasis [159]. Iron (Fe) ranged from 0-28 mg/l with an average value of 3.98 mg/l [147,157,158,160,161]. Iron is available in natural freshwaters at levels ranging from 0.5 to 50mg/l [159]. At levels above 0.3 mg/l, Fe stains laundry, and plumbing fixtures. There is generally no obvious taste at iron concentrations below 0.3 mg/l, although turbidity and color may form [162]. Zinc (Zn) ranged from 0-75.5 mg/l with an average value of 7.92 mg/l. Water containing Zn at concentrations more than the range of 3 to 5 mg/l may look opalescent and form an oily film on boiling. Natural waters seldom contain Zn at levels above 0.1 mg/l [162].

3.3 Anion Chemistry

Figure 9(a-e) summarized the anion chemistry of groundwater. Chloride (Cl) ranged from 0-105.5 mg/l with an average value of 32.8 mg/l. Elevated Cl in groundwater results in a salty taste [143]. Taste verges for the Cl rest on the accompanying cation and is in the range of 200-300 mg/l for Na, K, and calcium chloride. At levels, above

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250 mg/l are increasingly likely to be detected by taste. Nitrate (NO_3) ranged from 0.02-35.4 mg/l with an average value of 11.44 mg/l. Nitrate occurs naturally in the environment and is a vital plant nutrient. It is found at varying levels in all plants and is a part of the nitrogen cycle [159]. Nitrate is primarily derived from organic matter, chemical fertilizers, and oxidation of ammonia. High NO_3 levels in aquifers can be related to past pollution by anthropogenic activities. Diverse sources of NO_3 in aquifers is illustrated in Figure 10. Nitrite (NO_2) is not usually present in large quantities except in a reducing condition since nitrate is the most stable oxidation state, which can be formed by the microbial reduction of nitrate [159]. The most important source of human exposure to NO_3 and NO_2 is through vegetables and meat in the diet. Nitrite ranged from 0.003-5.2 mg/l with an average value of 2.09 mg/l.

Phosphate (PO_4) ranged from 0-44.2 mg/l with an average value of 7.35 mg/l. The consequence of phosphorus (P) is primary concerning the phenomenon of eutrophication (over-enrichment) of lakes and, to a lesser extent, rivers. Phosphorus gaining access to such water bodies, along with nitrogen (N) as nitrate, promotes the growth of algae and other plants leading to blooms, littoral slimes, diurnal dissolved oxygen variations of great magnitude and related problems [152]. Sulfate (SO_4) ranged from 0.03-44.2 mg/l with an average value of 8.67 mg/l. The existing data do not identify a level of SO_4 in the Cross River-Anambra Basin that is likely to cause adverse human health effects. Nevertheless, because of the gastrointestinal effects resulting from the ingestion of drinking-water containing high SO_4 levels, it is recommended that sources of drinking water that contain sulfate concentrations more than 500mg/l [159].

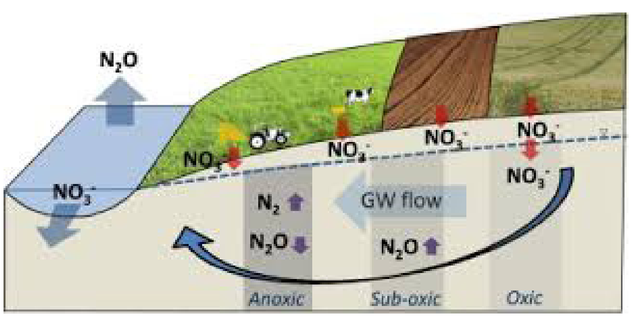

Figure 10. Potential sources of nitrate in groundwater [163]

4. Conclusion

In this reassessment, a detailed explanation of the geological and hydrogeological setting of Cross River-Akwa Ibo basins was attempted. The review also presented a summary of synthesis data on hydrochemistry of the Cross River-Akwa Ibo basins. Data on 26 physicochemical parameters were fused and presented, to provide the reader with a clear picture of general physicochemical characteristics of groundwater. Based on the hydrogeological and hydrochemical analysis, the following remarks can be made:

(1) The hydrogeological analysis showed most geologic formations in Cross River and Imo-Kwa-Ibo are poor in terms of groundwater potentials;

(2) Based on total hardness, 74% of groundwater sources fall in soft class and 26% fall in moderately hard class;

(3) The entire sources groundwater have TDS concentration less than 500 mg/l;

(4) Groundwater classification based on EC showed that EC levels were less than 500 µS/cm. In contrast, 78.57% of groundwater sources in the basin are acidic;

(5) Studies on Al, As, Ba, and NH4 are rare, making it difficult to make an inference. Consequently, further evaluations are required;

(6) Calcium ranged from 8.2-116 mg/l with an average value of 43.73mg/l. Magnesium ranged from 0-52.6 mg/l with an average value of 16.57 mg/l. Mn ranged from 0-20.4 mg/l, with an average value of 3.17 mg/l;

(7) Sodium concentration is generally low. Na ranged from 0.01-0.15 mg/l with an average value ~0.062 mg/l;

(8) Cadmium concentrations are above WHO reference guidelines. Lead concentration ranged from -0.032-10 mg/l with an average value of 1.98 mg/l;

(9) Nickel range of -0.032 to 0.011 mg/l with an average value of -0.019 mg/l in Abakaliki. In Ebonyi, Idu Uruan, Uyo, and Iko Town indicate Cu concentration ranged from 0.001-15 mg/l. Iron (Fe) ranged from 0-28 mg/l. Zinc concentration ranged from 0-75.5 mg/l;

(10) Mean chloride (32.8 mg/l) is less than WHO reference guidelines. Nitrate ranged from 0.02-35.4 mg/l. Nitrite ranged from 0.003-5.2 mg/l. Phosphate ranged from 0-44.2 mg/l. Sulfate ranged from 0.03-44.2 mg/l.

The physicochemical composition of groundwater showed that the two basins hold water of excellent quality. However, analysis of the hydrogeochemical evolution of groundwater in lacking. No broad studies of water quality based on water quality indices. Also, studies modeling pollution or the impact of land use changes on groundwater quality are wanting. Thus, further analysis of hydrochemistry of shallow and deep aquifers is recommended.

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