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The Water Quality Index (WQI) and Hydrochemical Characterization of Groundwater Resources in Hydrocarbon Polluted Sites in the Niger Delta

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Abstract
The quality of groundwater resources is as important as their quantity. Hydrochemical studies are a useful tool which can help in managing quality of water resources. The aim of this study is to evaluate the hydrochemical characteristics, water quality, contamination as well as sources of contamination of groundwater. Water quality assessment was carried out on groundwater to appraise the levels of Heavy metals in Khana and Gokana LGAs of Rivers State and ascertain the suitability of the groundwater resources in the area for human domestic consumption and irrigation purpose. A random sampling approach was employed for groundwater sampling and samples were collected from a total of twenty-two (22) boreholes in the area. A total of ten (10) residential boreholes were sampled in Khana area and twelve (12) in Gokana local government area, Rivers State, Nigeria. Standard sampling and analytical methods were used. The study revealed that cations such as Ca, Na, Mg, and K showed concentrations within WHO regulatory standards in all the samples analyzed and generally in order of decreasing concentration; Ca > Na > Mg > K in groundwater from the area. Anions such as SO_4, Cl and HCO_3 were within permissible standard except NO_3 that showed concentrations above the regulatory limit of 5.0mg/L in both Khana and Gokana Local Government Areas of Rivers State. The results from the Water Quality Index (WQI) ranged from 53.55 to 103.32 in Khana area, denoting poor, very poor and unsuitable water quality for consumption. Similarly, in Gokana area, WQI ranged from 72.71 to 112.92, indicating poor, very poor and unsuitable water quality for consumption. Based on the deteriorated quality of groundwater in the study area as revealed by this study, there is therefore the need of an urgent remediation of oil impacted areas to mitigate further impact on the water table. This study provides a qualitative measure of the water quality around the study locations which suggests the necessity of the remedial actions to the contaminated sources in order to keep the water safe and reliable for present and future consumption. The main innovative things of this study is that Water Quality Index (WQI) has been used which ultimately help us to understand the water quality in the study areas. Moreover, it will be helpful in monitoring activities and for further water quality management to prevent the pollution.

Keywords: *Water quality index, hydrochemistry, groundwater, borehole, pollution, oil producing areas.*

Introduction

Groundwater is the primary source of water for domestic, agricultural and industrial uses in many countries, and its contamination has been recognized as one of the most serious problems (Belkhiri *et al*., 2010). Groundwater moves through pore spaces within rocks and reacts with minerals that make up the rocks in the course of migration (Amadi *et al*., 2012; Boateng *et al.,* 2016). Groundwater quality in any locality takes after the chemical composition of the aquifer through which it migrates in accordance with the hydrological cycle and flow direction (Offodile 1983; Amadi *et al*., 2010; Boateng *et al.,* 2016). The intensive use of natural resources and increased human activities are posing great threat to groundwater quality (Foster, 1995). Groundwater quality assessment can be a complex process undertaking multiple parameters capable of causing various stresses on overall groundwater quality.

Numerous water quality indices have been formulated all over the world which can easily judge out the overall water quality within a particular area promptly and efficiently (Bharti & Katyal, 2011; Nwankwoala & Udom, 2011a). Water Quality Index (WQI) is a technique of rating that provides the composite influence of individual water quality parameters on the overall quality of water for human consumption (Tiwari *et al.,* 1985; WHO, 1993). Water quality indices are tools to determine conditions of water quality and, like any other tool require knowledge about principles and basic concepts of water and related issues (Nikbakht, 2004). WQI is a well- known method as well as one of the most effective tools to express water quality that offers a simple, stable, reproducible unit of measure and communicate information of water quality to the policy makers and concerned citizens. It thus, becomes an important parameter for the assessment and management of groundwater (Venkata and Reddy, 1995; Chauhan *et al*., 2010; Edet, 2010).

Horton (1965) first introduced and defined it as mathematical form of WQI by selecting, rating and integrating the significant physical, chemical and biological parameters of water in a simple, yet scientifically defensible manner. Then it was developed and improved by Brown *et al*., (1970). The development of WQI for groundwater is described by several studies on WQI of groundwater (Backman *et al.,* 1998; Soltan, 1999; Stigter *et al*., 2006a, b; Saeedi *et al*., 2009).

Hydrocarbon exploration/exploitation is one of the major anthropogenic activities which are liable for deteriorating the quality of water, soil as well as the environmental ecosystem in the surrounding area. Anthropogenic activities can adversely affect water quality by introducing contaminants, such as metals and metalloids. The availability of good quality water is vital for life, wellbeing, food and socio-economic development of mankind and it is generally obtained from two principal natural sources: surface water such as fresh water lakes, rivers, streams etc. and groundwater such as borehole water and well water (Boateng *et al.,* 2016). To manage a groundwater resource, we should not only concern about the water quantity and what happens to it, but we should also take care of the quality. Deterioration of groundwater quality may result in serious restrictions on its usages especially when it is used for domestic purposes. This is because poor contaminated water can be a threat to health, more over to the subsistence. In the study area, owing to the numerous hydrocarbon exploration activities, there is the need for the assessment of groundwater quality to ascertain its suitability for drinking purposes. This study therefore, is aimed at evaluating hydrochemical characteristics of the area involving presentation of geochemical data in the form of graphical charts like Piper and Durov diagrams to assess the geochemical processes controlling the water chemistry and to delineate variation in hydrochemical facies.

Location and Geologic Environment of the Study Area

The study area is the oil producing communities within Khana and Gokana Local Government Areas in Rivers State, Nigeria. The area is located geographically within Latitude $4^{0}36^{'}36.51^{''}$N -- $4^{0}43^{'}42.21^{''}$N and Longitude $7^{0}15^{'}12.00^{''}$E -- $7^{0}26^{'}42.97^{''}$E. The study area falls within the Niger Delta region of Nigeria.

The climate of an area plays a major role in determining the vegetation of the locality. Generally, the vegetation of Niger Delta can be described by two major regions, namely the swampy forest region (coastal environment) and the rain forest region (fluvial environment). The swamp forest region can further be subdivided into the mangrove or saltwater swamp forest and the freshwater swamp forest (Abam, 1999). The saltwater swamp forest is characterized by the presence of several varieties of mangrove trees. This region forms the zone of brackish water i.e. the mixture of salt water and fresh water (Ngerebara & Nwankwoala, 2008; Nwankwoala, 2011). The freshwater swamp forest is formed from the influence of the tidal water. This region is characterized by raffia palms that cover the whole of the central portions of the Delta.

Geology of Study Area

The study area is Khana and Gokana L.G.A. of Rivers State (Figure 1), located within the Niger Delta region of Nigeria, situated in the Gulf of Guinea, therefore, has same geology as the Niger Delta. The Niger Delta Basin is perhaps the most prolific basin in Sub-Saharan Africa with respect to its petroleum resources (Short and Stauble, 1967). The Niger Delta is composed of marine shale as the base of its stratification, overlying it is an intercalation of sand and shale as the intermediate layer, then the topmost layer is sandstone (Etu-Efeotor, 1990; Amajor, 1991). The groundwater occurrence is a multi-aquifer system because of the presence of certain clayey strata in formations of various thicknesses that acts as confining layer between two distinct aquiferous rock strata (Ngah, 1990; Nwankwoala, 2013; Nwankwoala & Ngah, 2014). The present-day Niger Delta was formed during the Tertiary period as a result of the interplay between subsidence and deposition arising from a succession of transgression and regression of the three-tertiary subsurface litho-stratigraphic units of Akata, Agbada, and Benin Formations (Short and Stauble, 1967). Further studies and evidence from deep wells drilled in the Niger Delta has also proven that the Niger Delta has a three litho-stratigraphic depositional succession (Akata, Agbada and Benin Formations) with an approximate average thickness of over 5000m of sediment body (Amajor, 1991; Ngah, 2009).

Hydrogeology of the Study Area

Although the Agbada Formation has a sandy unit with aquifer qualities and confirmed water saturation, its depth has made it an unsuitable source for groundwater in the region. Aquifers of the Benin Formation bear the ground water needs of the region (Nwankwoala & Nzaga, 2017). The poorly sorted Benin coastal sands become increasingly sandy and unconsolidated towards the surface. These parameters increase the porosity and permeability and thus, the increase in storage coefficient of the aquifer. The region is composed of multiple aquifer system due to the presence of thin clayey or silty layers acting as confining layer and boundary between distinct aquifer formations (Akpokodje, 2005; Nwankwoala & Ngah, 2014). The groundwater in the area is recharged either by a nearby water body such as surface water or a more prolific aquifer and extensive percolation from rainfall. This has resulted to a prolific

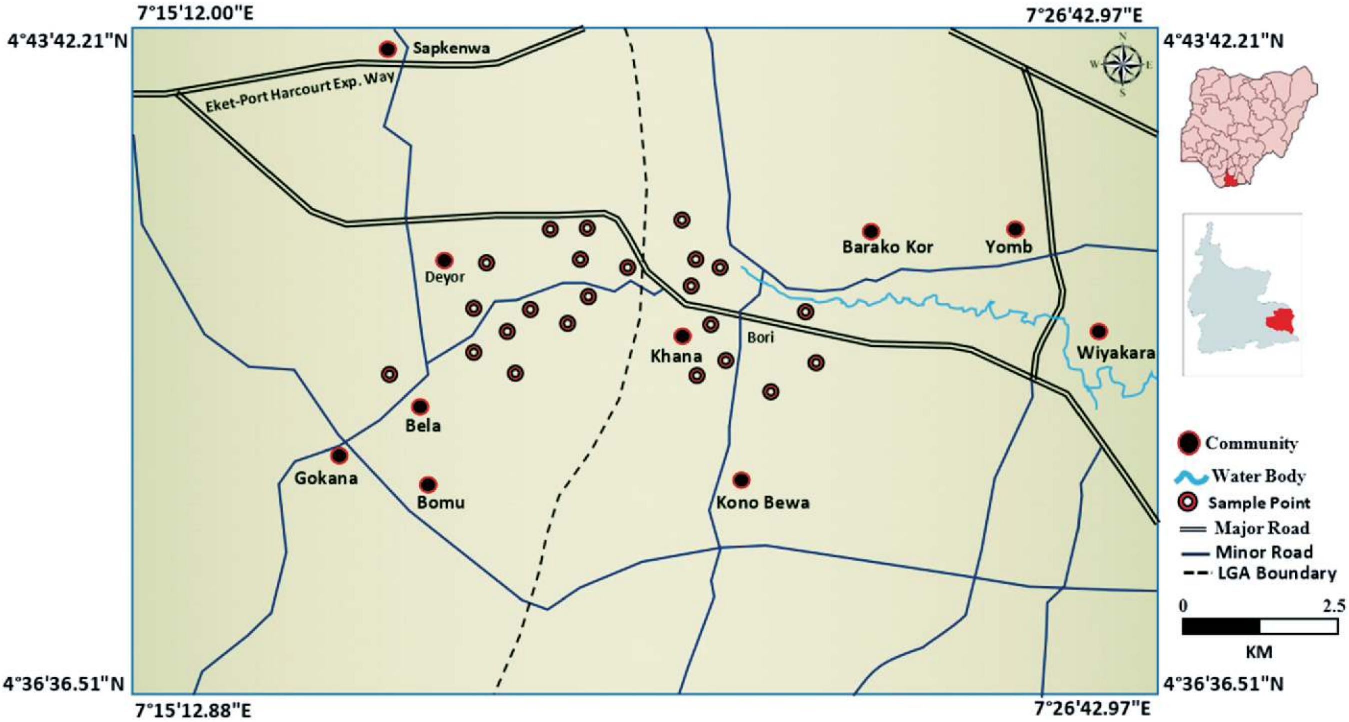

Fig. 1: Map showing sample points in the study locations.

hydrologic unit with depth to water table ranging between 0.3m - 15m (Offodile, 2002; Nwankwoala & Udom, 2011b).

Methods of Study

Field Investigation and Samples Collection

A random sampling approach was adopted in groundwater sampling in Khana and Gokana Local Government Areas of Rivers State, Nigeria. Groundwater samples were collected from a total of twenty-two (22) boreholes in the areas (Table 1). Ten (10) residential boreholes were sampled in Khana while 12 boreholes were sampled in Gokana Local Government Area. At each borehole where water samples were to be collected, the sterilized sample bottles were thoroughly rinsed with the water to be sampled before actual samples were collected. The water was allowed to flow freely for about 5 minutes in order to clear all dissolved solids that may be stuck to the walls of the pipes and well head. The sample bottles were allowed to fill to the brim and corked immediately to minimize escape of dissolved oxygen.

Samples were collected in duplicates for analyses of physicochemical parameters, heavy metals and petroleum hydrocarbon compounds. Samples for physicochemical and heavy metal analysis were collected in plastic bottles, while samples for hydrocarbon compounds determination were collected in glass bottles. Water samples for the determination of physicochemical parameters and heavy metals were stabilized by adding few drops of diluted hydrochloric acid to them after collection. Unstable groundwater parameters such as pH, total dissolved solids (TDS) and electrical conductivity (EC) were analyzed in-situ in order to preserve the integrity of the water samples. All sampling bottles were neatly labelled after sample collection and stored in an ice tight chest for onward transport to the laboratory for analysis. All sampling locations were noted with the aid of a global positioning system (GPS).

Water Quality Index (WQI)

Water Quality Index (WQI) is a single value expression that numerically summarizes multiple water quality parameters. It is calculated from the point of view that a lower value of it signifies less deviation from the recommended values of parameters included and more good quality water for human consumption or vice versa. WQI is defined as a rating that reflects the composite influence of different water quality parameters (Sahu and Sikdar 2008; Amadi *et al.,* 2012). It is an important parameter for assessing groundwater quality and its suitability for drinking purposes (Tiwari and Mishra 1985; Pawar *et al*., 2014; Boateng *et al.,*

Table 1: Sampling location and geographic references for the sampled boreholes

Location	Borehole ID	Easting	Northing
Khana L.G.A.	BH1	318428.88	515856.14
	BH2	317976.04	516741.85
	BH3	320007.51	517190.53
	BH4	318200.19	517703.40
	BH5	319181.86	515201.95
	BH6	320215.87	516128.46
	BH7	317566.83	517306.79
	BH8	317724.13	518146.85
	BH9	317774.02	515758.14
	BH10	317370.54	518766.95
Gokana L.G.A	BH11	311415.80	515607.34
	BH12	314641.10	518751.29
	BH13	316157.97	517409.62
	BH14	315540.04	518848.68
	BH15	315304.79	517898.21
	BH16	315401.34	516504.62
	BH17	313590.93	515734.83
	BH18	313148.27	516222.46
	BH19	313803.46	516453.13
	BH20	313094.83	517074.10
	BH21	314237.74	517104.54
	BH22	313385.94	518168.20

2016). WQI is one of the most effective tools to communicate information on the quality of water to the concerned citizens and policy makers (Ramakrishnaiah *et al*., 2009). It is a dimensionless number that combines multiple water quality factors into a single number by normalizing values to subjective rating curves (Miller *et al.,* 1986). It gives an overall assessment of the water quality in any given area. Weighted arithmetic water quality index method classified the water quality according to the degree of purity by using the most commonly measured water quality variables. The method has been widely used by the various scientists (Dhakad *et al.,* 2008; Chauhan *et al.,* 2010; Rao *et al.,* 2010; Chowdhury *et al*., 2012; Balan *et al*., 2012).

Thirteen parameters were utilized in calculating WQI for the study area. Each parameter was assigned a given weight (wi) based on the perceived health effect or the importance of the parameter on the overall water quality for drinking purposes (Vasanthavigar *et al.,* 2010). Parameters that were considered not to be harmful to health were assigned a value of 1 while parameters that had the most impact on health were assigned a value of 5. Based on overall impact, other parameters were

Table 2: Analytical methods used for groundwater samples analysis

Class	Parameter	Symbol	Unit	Type of Test	Laboratory Standard
Physicochemical parameters	pH	pH		In-situ	APHA 4500-H^+B
	Total Dissolved Solids	TDS	mg/L	In-situ	APHA 2540C
	Electrical Conductivity	EC	uS/cm	In-situ	APHA 2510B
	Sodium	Na	mg/L	Laboratory	APHA 3111B
	Calcium	Ca	mg/L	Laboratory	APHA 3111D
	Magnesium	Mg	mg/L	Laboratory	APHA 3111B
	Potassium	K	mg/L	Laboratory	APHA 3111B
	Sulphate	SO4	mg/L	Laboratory	APHA 4500/SO_4-E
	Nitrate	NO_3	mg/L	Laboratory	APHA 4500/NO_3-E
	Chloride	Cl	mg/L	Laboratory	APHA 3111B
	Bicarbonate	HCO_3	mg/L	Laboratory	APHA 3111B
Heavy Metals	Iron	Fe	mg/L	Laboratory	APHA 3111B
	Zinc	Zn	mg/L	Laboratory	APHA 3111B
	Manganese	Mn	mg/L	Laboratory	APHA 3111B
	Chromium	Cr	mg/L	Laboratory	APHA 3111D
	Lead	Pb	mg/L	Laboratory	APHA 3111B
	Nickel	Ni	mg/L	Laboratory	APHA 3111B
	Cadmium	Cd	mg/L	Laboratory	APHA 3111B
	Copper	Cu	mg/L	Laboratory	APHA 3111B
Hydrocarbon compounds	Polycyclic Aromatic Hydrocarbons	PAH	ug/L	Laboratory	US EPA 8015
	Total Petroleum Hydrocarbons	TPH	ug/L	Laboratory	US EPA 8015

assigned values between 1- 5. The method adopted for WQI determination in this study was based on Dhakad *et al.,* (2008). The method involves first calculating the quality of the parameters (qi) as follows;

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Water Quality Index (WQI) is a single value expression that numerically summarizes multiple water quality parameters. It is calculated from the point of view that a lower value of it signifies less deviation from the recommended values of parameters included and more good quality water for human consumption or vice versa. WQI is defined as a rating that reflects the composite influence of different water quality parameters (Sahu and Sikdar 2008; Amadi *et al.,* 2012). It is an important parameter for assessing groundwater quality and its suitability for drinking purposes (Tiwari and Mishra 1985; Pawar *et al*., 2014; Boateng *et al.,* 2016). WQI is one of the most effective tools to communicate information on the quality of water to the concerned citizens and policy makers (Ramakrishnaiah *et al*., 2009). It is a dimensionless number that combines multiple water quality factors into a single number by normalizing values to subjective rating curves (Miller *et al.,* 1986). It gives an overall assessment of the water quality in any given area. Weighted arithmetic water quality index method classified the water quality according to the degree of purity by using the most commonly measured water quality variables. The method has been widely used by the various scientists (Dhakad *et al.,* 2008; Chauhan *et al.,* 2010; Rao *et al.,* 2010; Chowdhury *et al*., 2012; Balan *et al*., 2012).

Thirteen parameters were utilized in calculating WQI for the study area. Each parameter was assigned a given weight (wi) based on the perceived health effect or the importance of the parameter on the overall water quality for drinking purposes (Vasanthavigar *et al.,* 2010). Parameters that were considered not to be harmful to health were assigned a value of 1 while parameters that had the most impact on health were assigned a value of 5. Based on overall impact, other parameters were assigned values between 1- 5. The method adopted for WQI determination in this study was based on Dhakad *et al.,* (2008). The method involves first calculating the quality of the parameters (qi) as follows;

$$qi = \frac{v_a}{v_s} \times 100 \quad \text{.......(1)}$$

Where; qi – quality rating of each parameter for n number of samples
v_a – value of parameter as obtained from laboratory analysis
v_s – value of parameter obtained from WHO water quality standard reference

The relative weight (Wi) was calculating as follows;

$$Wi = \frac{w_i}{\sum w_i} \quad \text{.......(2)}$$

Water Quality Index was determined as follows;

$$WQI = \sum(q_i w_i) \quad \text{.......(3)}$$

The WQI was then used to classify water quality in the area based on data from Vasanthavigar *et al.,* (2010) as follows; 0-25 (Excellent), >25 – 50 (Good), >50 – 75 (Poor), >75 – 100 (Very poor), > 100 (Unsuitable for drinking purposes).

Results and Discussions

Physicochemical Characteristics of Water Samples

The physicochemical parameter analysis is the preliminary study by which the nature, quality and types of water can be identified. The pH of groundwater in the area ranges from 5.43 to 6.61 with a mean and standard deviation (SD) of 6.10 ± 0.39 in Gokana, pH in groundwater ranges from 5.43 to 6.67 with mean and SD of 6.12 ± 0.37 in Khana. This shows that groundwater in the area is acidic. Based on WHO (2012) and NSDWQ (2007) regulatory guidelines for pH concentration in potable groundwater (pH = 6.5 - 8.5), the average pH values recorded in this study shows that groundwater in the area is unsafe for oral consumption.

Total dissolved solids (TDS) and electrical conductivity (EC) ranged from 29 to 439 mg/L and 58 to 878 uS/cm in groundwater from Khana area. Similarly, TDS and EC ranged from 34.54 to 652 mg/L and from 69.08 to 1304 uS/cm. The average TDS and EC in groundwater from Khana are 135.30 mg/L and 270.60 uS/cm, and 276.05 mg/L and 552.10 uS/cm in Gokana area. Apart from BH18 and BH20 in Gokana area, all other boreholes had TDS and EC values within the stipulated regulatory guidelines of 500 mg/L and 1000 uS/cm. On average, TDS and EC in groundwater had concentration within the regulatory guidelines, suggesting that the water samples are potable for consumption.

For the cations, the average concentration of Na, Ca, Mg and K are 6.55 ± 3.22 mg/L, 7.68 ± 1.33 mg/L, 5.87 ± 1.30 mg/L and 1.21 ± 0.94 mg/L in Khana, and 5.98 ± 2.10 mg/L, 8.29 ±1.96 mg/L, 6.74 ± 2.10 mg/L and 1.23

± 0.75 mg/L in Gokana area, respectively. These values are within WHO regulatory guidelines for potable drinking water (Na =200 mg/L; Ca =75 mg/L; Mg =30 mg/L and K =55 mg/L). Hence, groundwater is safe for consumption in the area. Generally, in order of decreasing concentrations: Ca > Na > Mg > K in groundwater from the area.

For the anions, the average concentration of SO_4, NO_3, Cl and HCO_3 are 18.64 ± 24.19 mg/L, 8.47 ± 2.81 mg/L, 50.91 ± 35.36 mg/L and 16.44 ± 9.25 mg/L in Khana, and 16.26 ± 6.92 mg/L, 8.18 ± 5.13 mg/L, 58.44 ± 32.15 mg/L and 16.63 ± 7.46 mg/L in Gokana area. These values are within WHO regulatory guidelines for potable drinking water (SO_4 = 500 mg/L; Cl =250 mg/L; Mg = 600 mg/L). Only nitrate exceeded the regulatory limit of 5.0 mg/L in both Khana and Gokana areas. Hence, groundwater is safe for consumption in the area based on SO_4, Cl and HCO_3 concentration, but unsafe for consumption based on nitrate content. Generally, in order of decreasing concentration: Cl > SO_4 > HCO_3 > NO_2 in groundwater from the study area.

For heavy metals, Fe ranges from 0.01 mg/L to 0.70 mg/L with mean and SD of 0.37 ± 0.19 mg/L in Khana area, whereas in Gokana, Fe ranged from 0.18 to 063 mg/L with mean and SD of 0.32 ± 0.13 mg/L respectively. In Khana area, BH2, BH4, BH5, BH7, BH8, BH9 and BH10 had iron concentration exceeding WHO and NSDWQ regulatory limits of 0.30 mg/L; whereas in Gokana area, BH11, BH12, BH14, BH17, BH19 and BH20 had iron content exceeding the regulatory requirement. These results show that iron concentration in groundwater within the study area is significantly high to render the groundwater unsuitable for oral ingestion.

Zinc concentration ranges from 0.40 to 3.76 mg/L with mean and SD of 1.23 ± 1.27 mg/L in Khana, and from 0.23 to 0.95 mg/L with mean and SD of 0.59 ± 0.20 mg/L in Gokana area. Generally, WHO standard for Zn in potable drinking water is set at 5.0 mg/L. All the groundwater samples revealed Zn concentrations which are within the regulatory guideline. These results show that zinc is not a possible source of contamination of groundwater in the area.

Manganese ranged from 0.02 to 0.39 mg/L and from 0.01 to 0.43 mg/L in Khana and Gokana areas. The WHO standard for Mn in potable drinking water is set at 0.20 mg/L. In Khana area, only BH3, BH6 and BH9 exceeded this limit, while only BH16 exceeded the regulatory limit in Gokana area. All other boreholes had Mn concentrations within WHO regulatory limit for potable drinking water.

Chromium and Lead ranged from 0.0t to 0.08 mg/L and from 0.001 to 0.02 mg/L in Khana, while in Gokana, Cr and Pb ranged from <0.001 to 0.04 mg/L. The average Cr and Pb concentrations are 0.04 ± 0.03 mg/L and 0.009 ±0.008 mg/L in Khana area and 0.04 ± 0.02 mg/L and 0.025 ± 0.01 mg/L in Gokana area, respectively. The WHO and NSDWQ regulatory limit for Cr and Pb in potable groundwater are 0.05 mg/L and 0.01 mg/L. Based on these guidelines, the average Cr and Pb concentrations in groundwater samples from Khana area are within regulatory requirements. Only Lead exceeded WHO regulatory limit at Gokana area. Nickel was below the detectable limit of the measuring instrument at all sampled boreholes.

Cadmium concentration ranges from 0.001 to 0.006 mg/L with mean and SD of 0.003 ± 0.0015 mg/L in Khana, and from 0.002 to 0.005 mg/L with mean and SD of 0.003 ± 0.001 mg/L in Gokana area. Generally, WHO standard for Cadmium in potable drinking water is set at 0.003 mg/L. Apart from BH3, BH6 and BH10 in Khana, and BH14, BH16, BH17, BH20 and BH22 in Gokana which exceeded WHO limit, all other groundwater samples revealed Cadmium concentrations which are within the regulatory guideline for potable drinking water.

Copper concentration ranges from 0.06 to 0.66 mg/L with mean and SD of 0.34 ± 0.020 mg/L in Khana, and from 0.09 to 0.62 mg/L with mean and SD of 0.38 ± 0.17 mg/L in Gokana area. Generally, WHO standard for copper in potable drinking water is set at 1.0 mg/L. Hence, all the groundwater samples revealed copper concentrations which are within the safe limit for oral ingestion.

For the petroleum hydrocarbon compounds, Polycyclic Aromatic Hydrocarbons (PAH) ranged from <0.001 to 0.05 ug/L with mean and SD of 0.05 ± 0.03 ug/L in Khana, and from <0.001 to 0.09 ug/L with mean and SD of 0.06 ± 0.02 ug/L. These results are well within DPR (2002) limit of 0.15 ug/L for potable drinking water. Hence, based on PAH, all the groundwater samples are in good condition for oral ingestion.

Total Petroleum Hydrocarbons (TPH) ranged from 8.96 to 165 ug/L with mean and SD of 58.79 ± 49.21 ug/L in Khana, and from 2.93 to 104.53 ug/L with mean and SD of 38.63 ± 36.77 ug/L. In Khana, BH1, BH2, BH7, BH8 and BH10 all exceeded DPR (2002) limit of 50 ug/L;

while in Gokana, BH12, BH16, BH20 and BH21 all exceeded the DPR limit. Hence, based on TPH content, not all other boreholes had values within safety limit for oral consumption.

Table 3: Results of physicochemical, heavy metals and petroleum hydrocarbons in groundwater samples from Khana LGA, Rivers State

Parameter	Symbol	Unit	BH1	BH2	BH3	BH4	BH5	BH6	BH7	BH8	BH9	BH10	WHO (2012)	NSDWQ (2007)
pH	pH		6.54	6.22	5.43	6.61	5.89	5.76	6.32	6.15	5.71	6.35	6.5-8.5	6.5-8.5
Total Dissolved Solids	TDS	mg/L	165.00	134.00	87.00	96.00	65.00	198.00	75.00	29.00	439.00	65.00	500.00	500.00
Electrical Conductivity	EC	uS/cm	330.00	268.00	174.00	192.00	130.00	396.00	150.00	58.00	878.00	130.00	1000.00	1000.00
Sodium	Na	mg/L	8.33	5.32	2.65	9.55	4.54	10.70	7.30	10.86	2.78	3.43	200.00	200.00
Calcium	Ca	mg/L	6.50	8.34	7.55	6.20	6.98	8.40	9.80	7.54	5.98	9.55	75.00	75.00
Magnesium	Mg	mg/L	6.32	5.45	4.20	6.23	4.84	8.39	6.56	6.32	3.98	6.44	50.00	30.00
Potassium	K	mg/L	0.55	0.63	0.43	2.78	1.23	1.54	2.88	0.52	0.38	1.12	55.00	200.00
Sulphate	SO_4	mg/L	3.32	12.45	12.00	86.55	10.36	11.39	8.93	19.45	12.43	9.54	500.00	500.00
Nitrate	NO_3	mg/L	12.22	10.45	9.40	6.54	8.80	6.50	10.23	11.45	3.59	5.56	5.00	5.00
Chloride	Cl	mg/L	76.54	30.24	22.34	56.45	29.30	121.45	28.40	95.32	22.46	26.64	250.00	250.00
Bicarbonate	HCO_3	mg/L	1.34	8.50	9.43	11.38	21.09	32.54	12.78	22.54	21.63	23.21	600.00	600.00
Iron	Fe	mg/L	0.23	0.44	0.01	0.41	0.32	0.22	0.43	0.51	0.41	0.70	0.30	0.30
Zinc	Zn	mg/L	0.45	0.56	0.73	0.40	0.59	0.43	1.45	3.76	0.54	3.35	5.00	3.00
Manganese	Mn	mg/L	0.06	0.08	0.21	0.09	0.05	0.22	0.02	0.05	0.39	0.03	0.20	0.20
Chromium	Cr	mg/L	0.05	0.06	0.04		0.06	0.03	0.08		0.04	0.02	0.05	0.05
Lead	Pb	mg/L	0.001	0.007	0.003	0.010	0.009	0.002	0.020	0.007	0.020	0.020	0.01	0.01
Nickel	Ni	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	0.02
Cadmium	Cd	mg/L	0.002	0.003	0.004	0.002	0.003	0.005	0.002	0.003	0.001	0.006	0.003	0.003
Copper	Cu	mg/L	0.17	0.64	0.34	0.12	0.06	0.32	0.41	0.27	0.66	0.43	1.00	1.00
Polycyclic Aromatic Hydrocarbons	PAH	mg/L	<0.01	<0.01	<0.01	<0.01	0.05	<0.01	<0.01	0.04	0.03	0.09	0.15**	
Total Petroleum Hydrocarbons	TPH	mg/L	67.00	89.76	35.96	10.89	8.96	28.80	165.00	98.66	17.98	64.90	50.00**	

** **DPR (2002) target values**

Table 4: Results of physicochemical, heavy metals and petroleum hydrocarbons in groundwater samples from Gokana LGA, Rivers State

Parameter	Symbol	Unit	BH11	BH12	BH13	BH14	BH15	BH16	BH17	BH18	BH19	BH20	BH21	BH22	WHO (2012)	NSDWQ (2007)
pH	pH		6.20	6.43	5.43	6.25	6.67	5.80	6.17	6.65	5.82	5.98	6.24	5.82	6.5-8.5	6.5-8.5
Total Dissolved Solids	TDS	mg/L	420.34	334.8	164.38	83.55	34.54	294.00	224	513.5	67.78	652	340.00	183.70	500.00	500.00
Electrical Conductivity	EC	uS/cm	840.68	669.6	328.76	167.10	69.08	588.00	448	1027	135.56	1304	680.00	367.40	1000.00	1000.00
Sodium	Na	mg/L	8.50	8.76	6.66	5.98	2.54	7.30	8.54	6.67	3.90	4.98	3.67	4.30	200.00	200.00
Calcium	Ca	mg/L	7.80	9.43	8.33	7.49	6.44	9.62	10.65	9.60	4.66	11.50	6.43	7.55	75.00	75.00
Magnessium	Mg	mg/L	7.89	5.20	6.50	5.89	8.34	8.66	8.89	7.84	2.65	9.45	4.67	4.85	50.00	30.00
Potassium	K	mg/L	0.65	0.84	1.04	1.43	0.86	1.96	2.05	1.88	0.56	2.67	0.44	0.41	55.00	200.00
Sulphate	SO_4	mg/L	11.45	20.45	29.80	18.50	13.67	12.44	9.80	27.43	19.13	8.98	13.63	9.82	500.00	500.00
Nitrate	NO_3	mg/L	12.88	14.27	0.54	3.45	11.80	6.74	13.98	12.44	0.83	3.84	10.82	6.56	5.00	5.00
Chloride	Cl	mg/L	85.40	33.45	28.54	63.30	23.64	105.43	95.21	83.50	28.44	30.20	93.54	30.67	250.00	250.00
Bicarbonate	HCO_3	mg/L	12.30	9.45	8.54	12.44	23.67	29.88	13.58	28.54	18.23	14.58	19.81	8.55	600.00	600.00
Iron	Fe	mg/L	0.44	0.63	0.21	0.32	0.22	0.18	0.43	0.28	0.37	0.34	0.21	0.19	0.30	0.30
Zinc	Zn	mg/L	0.55	0.56	0.87	0.23	0.43	0.65	0.44	0.78	0.52	0.61	0.95	0.52	5.00	3.00
Manganese	Mn	mg/L	0.13	0.05	0.10	0.06	0.03	0.43	0.01	0.03	0.06	0.12	0.11	0.05	0.20	0.20
Chromium	Cr	mg/L	0.06	0.05	0.03	0.06	0.07	0.04	0.02	0.03	0.05	0.02	<0.01	<0.01	0.05	0.05
Lead	Pb	mg/L	0.030	0.010	0.030	0.040	0.020	0.020	<0.001	0.010	0.030	0.020	0.040	0.020	0.01	0.01
Nickel	Ni	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	0.02
Cadmium	Cd	mg/L	0.002	0.003	0.002	0.005	0.003	0.004	0.005	0.003	0.003	0.004	0.002	0.005	0.003	0.003
Copper	Cu	mg/L	0.32	0.52	0.11	0.09	0.34	0.62	0.48	0.33	0.38	0.58	0.46	0.31	1.00	1.00
Polycyclic Aromatic Hydrocarbons	PAH	mg/L	<0.01	0.05	<0.01	<0.01	0.06	<0.01	<0.01	0.09	0.07	<0.01	0.04	<0.01	0.15**	
Total Petroleum Hydrocarbons	TPH	mg/L	48.36	78.94	32.44	12.32	9.12	104.53	7.22	2.93	9.44	63.19	88.34	6.72	50.00**	

Results of Water Quality Index

The weight and relative weight assigned for each parameter utilized for evaluating groundwater quality index is presented in Table 6 along with WHO (2012) regulatory standards. Table 7 shows the water quality index (WQI) calculated along with the index interpretation. Figure 3 shows the spatial variation in water quality across Khana and Gokana local government areas.

Table 5: Statistical summary of groundwater quality analysis in the area

Parameter	Symbol	Unit	Khana L.G.A.				Gokana L.G.A.				WHO (2012)	NSDWQ (2007)
			Min	Max	Mean	S.D.	Min	Max	Mean	S.D.		
pH	pH		5.43	6.61	6.10	0.39	5.43	6.67	6.12	0.37	6.5-8.5	6.5-8.5
Total Dissolved Solids	TDS	mg/L	29.00	439.00	135.30	118.20	34.54	652.00	276.05	188.02	500.00	500.00
Electrical Conductivity	EC	uS/cm	58.00	878.00	270.60	236.40	69.08	1304.00	552.10	376.04	1000.00	1000.00
Sodium	Na	mg/L	2.65	10.86	6.55	3.22	2.54	8.76	5.98	2.10	200.00	200.00
Calcium	Ca	mg/L	5.98	9.80	7.68	1.33	4.66	11.50	8.29	1.96	75.00	75.00
Magnesium	Mg	mg/L	3.98	8.39	5.87	1.30	2.65	9.45	6.74	2.10	50.00	30.00
Potassium	K	mg/L	0.38	2.88	1.21	0.94	0.41	2.67	1.23	0.75	55.00	200.00
Sulphate	SO_4	mg/L	3.32	86.55	18.64	24.19	8.98	29.80	16.26	6.92	500.00	500.00
Nitrate	NO_3	mg/L	3.59	12.22	8.47	2.81	0.54	14.27	8.18	5.13	5.00	5.00
Chloride	Cl	mg/L	22.34	121.45	50.91	35.36	23.64	105.43	58.44	32.15	250.00	250.00
Bicarbonate	HCO_3	mg/L	1.34	32.54	16.44	9.25	8.54	29.88	16.63	7.46	600.00	600.00
Iron	Fe	mg/L	0.01	0.7	0.37	0.19	0.18	0.63	0.32	0.13	0.30	0.30
Zinc	Zn	mg/L	0.40	3.76	1.23	1.27	0.23	0.95	0.59	0.20	5.00	3.00
Manganese	Mn	mg/L	0.02	0.39	0.12	0.12	0.01	0.43	0.10	0.11	0.20	0.20
Chromium	Cr	mg/L	0.02	0.08	0.04	0.03	<0.01	0.07	0.04	0.02	0.05	0.05
Lead	Pb	mg/L	0.001	0.02	0.009	0.0075	0.01	0.04	0.025	0.01	0.01	0.01
Nickel	Ni	mg/L	<0.01	<0.01	-	-	<0.01	0.00	-	-	0.02	0.02
Cadmium	Cd	mg/L	0.001	0.006	0.003	0.0015	0.002	0.005	0.003	0.001	0.003	0.003
Copper	Cu	mg/L	0.06	0.66	0.34	0.20	0.09	0.62	0.38	0.17	1.00	1.00
Polycyclic Aromatic Hydrocarbons	PAH	ug/L	<0.01	0.09	0.05	0.03	<0.01	0.09	0.06	0.02	0.15**	
Total Petroleum Hydrocarbons	TPH	ug/L	8.96	165.00	58.79	49.21	2.93	104.53	38.63	36.77	50.00**	

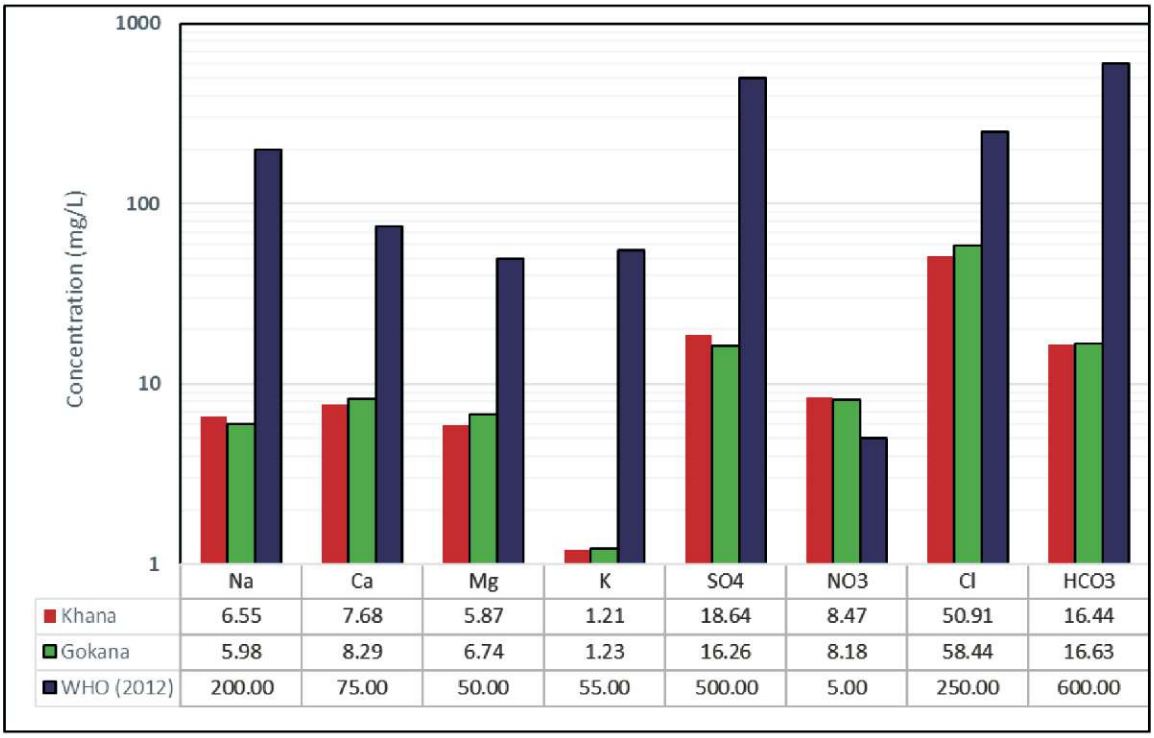

Fig. 2: Average concentration of physicochemical parameters in groundwater from the study area compared with WHO regulatory guidelines

Table 6: Weights assigned to the different WQI parameters

Parameter	Weight (wi)	Relative Weight (Wi)	Reference (WHO, 2012)
pH	3.00	0.07	6.5-8.5
TDS	4.00	0.09	500.00
NO_3	3.00	0.07	5.00
Fe	5.00	0.11	0.30
Zn	5.00	0.11	5.00
Mn	5.00	0.11	0.20
Cr	5.00	0.11	0.05
Pb	5.00	0.11	0.01
Cd	5.00	0.11	0.00
Cu	5.00	0.11	1.00
Sum	45	1	

Table 7: Results of WQI for groundwater across the study area

Community	Borehole	WQI	WQI Rating
Khana	BH1	53.66	Poor
	BH2	83.56	Very Poor
	BH3	63.80	Poor
	BH4	57.65	Poor
	BH5	69.55	Poor
	BH6	69.96	Poor
	BH7	93.21	Very Poor
	BH8	73.55	Poor
	BH9	98.23	Very Poor
	BH10	103.32	Unsuitable
Gokana	BH11	112.92	Unsuitable
	BH12	97.57	Very Poor
	BH13	72.71	Poor
	BH14	105.03	Unsuitable
	BH15	86.14	Very Poor
	BH16	104.55	Unsuitable
	BH17	74.25	Poor
	BH18	78.37	Very Poor
	BH19	85.82	Very Poor
	BH20	90.95	Very Poor
	BH21	99.38	Very Poor
	BH22	72.71	Poor

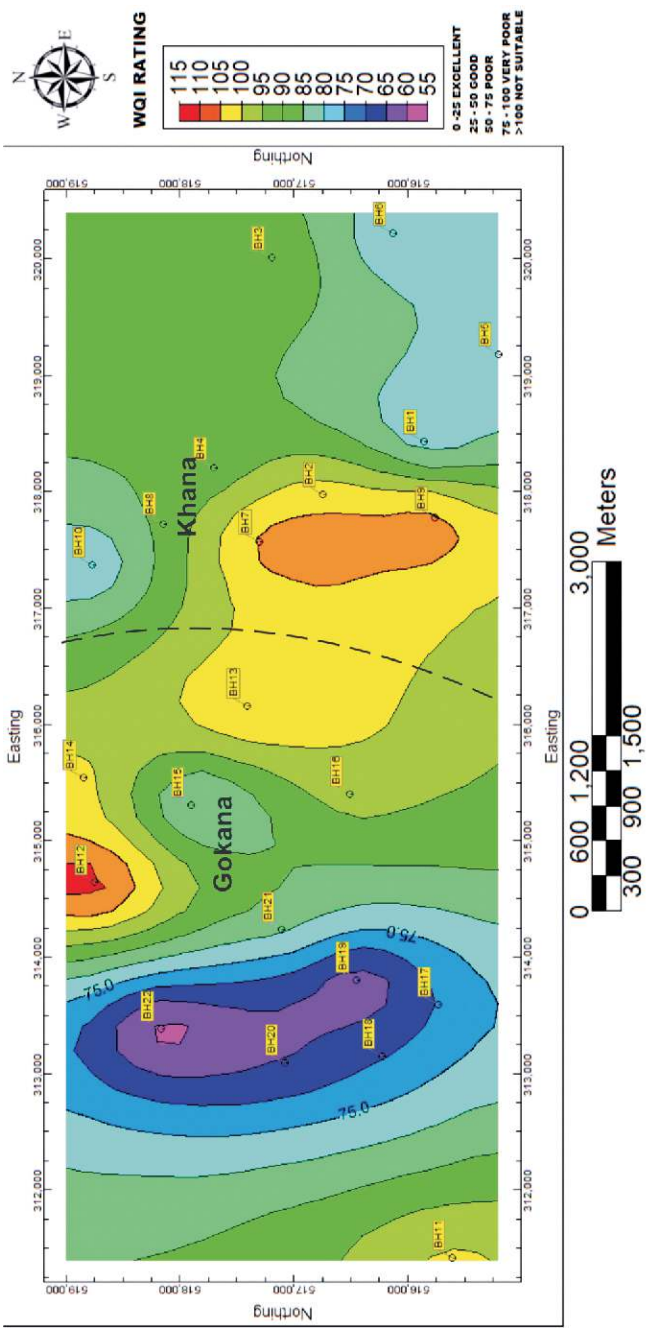

Fig. 3: Map showing variations in water quality within the study area

Groundwater Classification

Hydrogeochemical Facies and Classification

The concept of hydrochemical facies can be used to denote the diagnostic chemical character of water in hydrologic systems. The facies reflect the effect of complex hydrochemical chemical processes in the subsurface (SajilKumar, 2013) occurring between the minerals of lithologic formation and groundwater to investigate the spatial variability of groundwater chemistry in terms of hydrochemical evolution.

The chemical composition of groundwater is primarily dependent on the geology as well as on the geochemical processes which take place within the groundwater system. The Piper trilinear diagram (Piper, 1944) has been used for the purpose of characterizing the water types present in the area (Figure 4). Water types are often used in the characterization of waters as a diagnostic tool (Leybourne *et al.,* 1998; Pitkanen *et al.,* 2002). In addition, Piper diagram also permits the cation and anion compositions of many samples to be represented on a single graph in which major groupings or trends in the data can be discerned visually (Freeze and Cherry, 1979; Nwankwoala & Udom, 2011). Furthermore, it is used to assess the hydrogeochemical facies. Groundwater classification in the study area was achieved using Piper (1944), stiff (1951) and Durov diagrams.

Piper Tri-linear Diagram

Piper's tri-linear diagram (Piper, 1944) is most widely used to understand the hydrochemistry of any area. Piper's diagram is a major key to the identification and classification of rock-water interaction, solution kinetics, geology and sources of contamination in groundwater (Kaur *et al.,* 2019). From the Piper plot in Figure 4, all the groundwater samples fall under field I representing Ca^{2+}-Mg^{2+}-Cl−-SO_4^{2-} type water indicating an excess of alkaline earths than alkalies ($Ca^{+}+Mg^{2+}>Na^{+}+K^{+}$) and excess of stronger acidic anions than weaker acidic anions ($Cl^{-}+SO_4^{2-}>CO_3^{-}+HCO_3^{-}$) thus indicating permanent hardness (Ravikumar and Somashekar, 2017). Srivastava and Ramanathan, 2018 revealed that the presence of alkaline earth cation facies represents anthropogenic sources such as leaching of industrial effluent and fertilizers from agricultural fields into groundwater.

The diamond plot in Piper's diagram was further classified by Langguth (1966) into seven fields (A-G) (Figure 4). According to this classification, the groundwater samples were distinguished into two fields (C and E). Field C symbolizes normal earth alkali water type with prevailing sulphate and chloride. Field E symbolizes earth alkaline water with excessive alkalis concentration with prevailing sulphate or chloride.

Durov Diagram

Durov diagram is advantageous over the Piper diagram in revealing some geochemical processes that could affect groundwater genesis (Lloyd and Heathcoat, 1985). On the Durov plot which defines the hydrochemical processes involved along with the water type, most of the water samples plotted in Field 4 and (Figure 5). According to Lloyd and Heathcoat (1985) water classification scheme based on Durov plot, Field 4 is Ca and SO_4 dominant, frequently indicating recharge water in lava and gypsiferous deposits, otherwise, mixed water or water exhibiting simple dissolution may be indicated. Only BH15 plotted in the field of simple dissolution or mixing.

Stiff Diagram

Stiff (1951) diagram classifies groundwater quality on the basis on similarity in shape. Water of similar quality has a distinctive shape. The diagram is plots cations on the left and anions to the right-hand side. Three different water types were distinguished from the Stiff plots (Figs. 6a, 6b, 6c). Groundwater from BH1, BH6, BH8, BH11, BH14, BH16, BH17, BH18, BH18 and BH21 are Cl rich waters. Borehole BH2, BH3, BH4, BH5, BH7, BH9, BH10, BH12, BH13, BH19 and BH22 are Mg-Cl rich waters. Meanwhile BH15 and BH20 are Mg-Cl-SO_4 rich waters.

Summary and Conclusion

The water quality around the study area have been evaluated regarding the suitability of water for drinking purposes as well as the identification of the dominating sources of different water quality parameters. The study revealed that in the TDS and EC levels, apart from BH18 and BH20 in Gokana area, all other water samples had values within the stipulated regulatory guidelines of 500 mg/L and 1000 uS/cm. Cations such as Ca, Na, Mg, and K showed concentrations within WHO regulatory standards in all the samples analyzed. Generally, in order of decreasing concentration: Ca > Na > Mg > K in groundwater from the area. Anions such as SO_4, Cl and HCO_3 were within permissible standard except NO_3 that showed concentrations above the regulatory limit of 5.0mg/L in both Khana and Gokana LGAs. Thus, groundwater is in the study areas is unsafe for consumption based on the nitrate contents.

Iron (Fe) in Khana area showed concentration exceeding WHO (2012) and NSDWQ (2007) regulatory limits of 0.3mg/L in BH2, BH4, BH5, BH7, BH8, BH9 and BH10 while in Gokana area, BH11, BH12, BH14, BH17, BH19 and BH20 had Fe concentration exceeding the regulatory requirements. The result shows that Fe concentration in groundwater in the study area is significantly high to render the groundwater unsuitable for oral ingestion. Manganese concentration in samples from Khana showed concentrations above WHO standard in BH3, BH6 and BH9 while only BH16 exceeded the regulatory limit in Gokana area and then all other samples concentrations were within WHO regulatory limit for potable drinking water. Cupper (Cu) and Lead (Pb) concentration showed levels below permissible limits in all samples analyzed.

The WQI ranged from 53.55 to 103.32 in Khana area, denoting poor to very poor and unsuitable water quality for consumption. In Gokana area, WQI ranged from

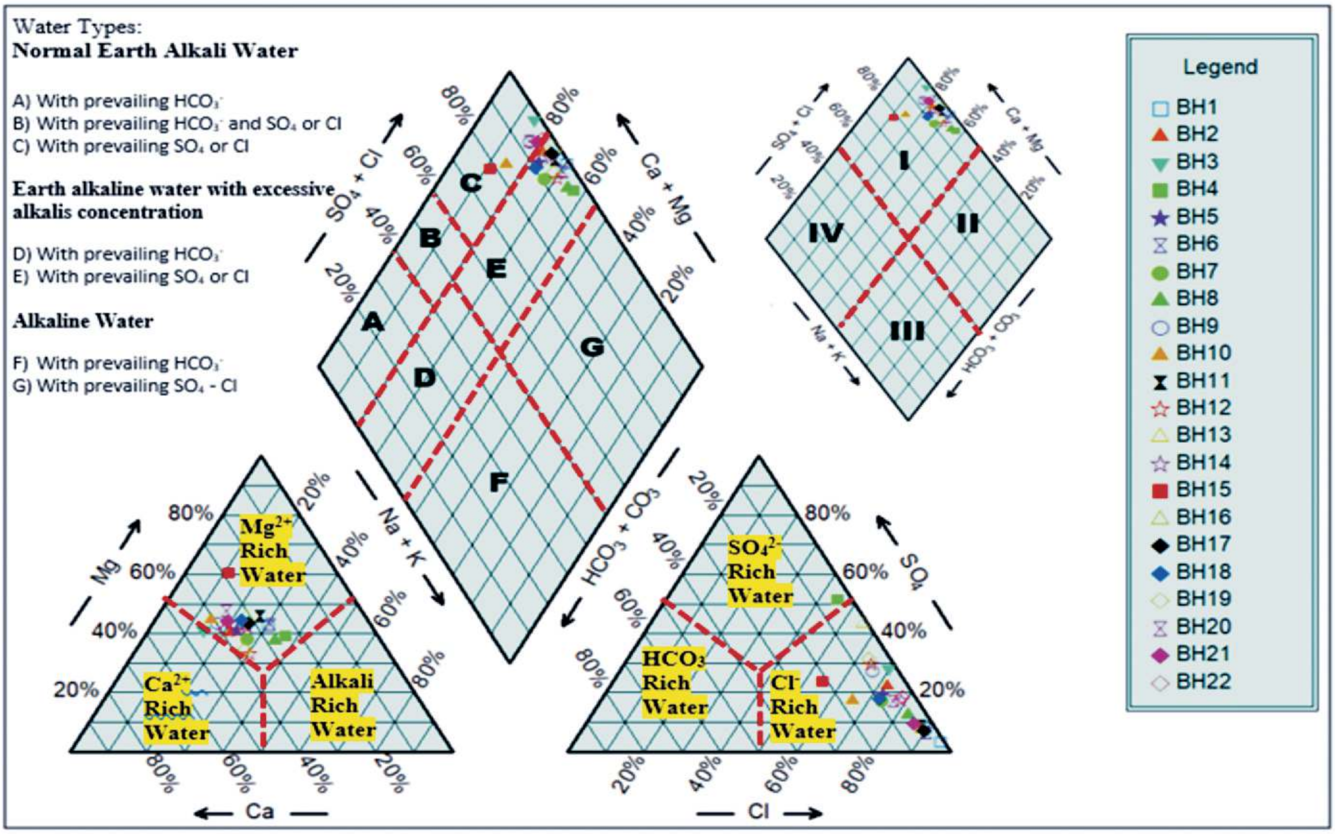

Fig. 4: Piper Trilinear Diagram showing groundwater facies in the study area

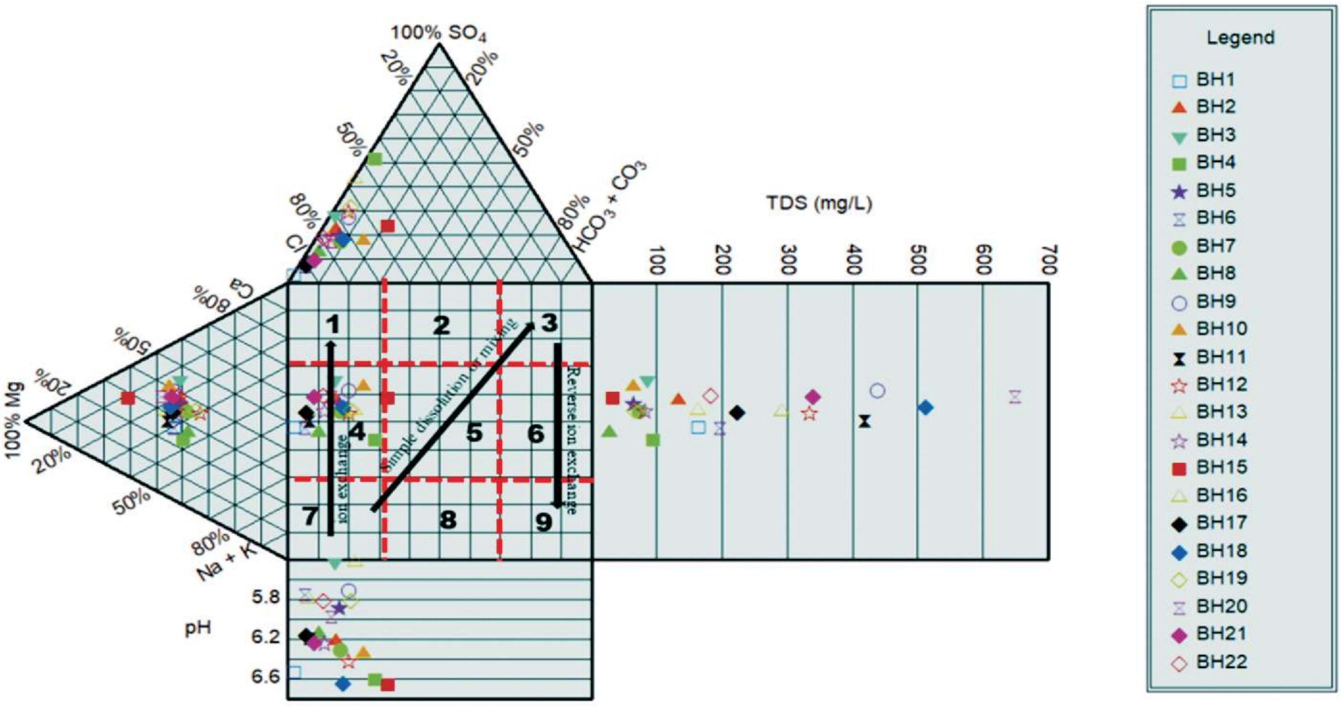

Fig. 5: Durov plot depicting hydrochemical processes acting on groundwater sources in the area

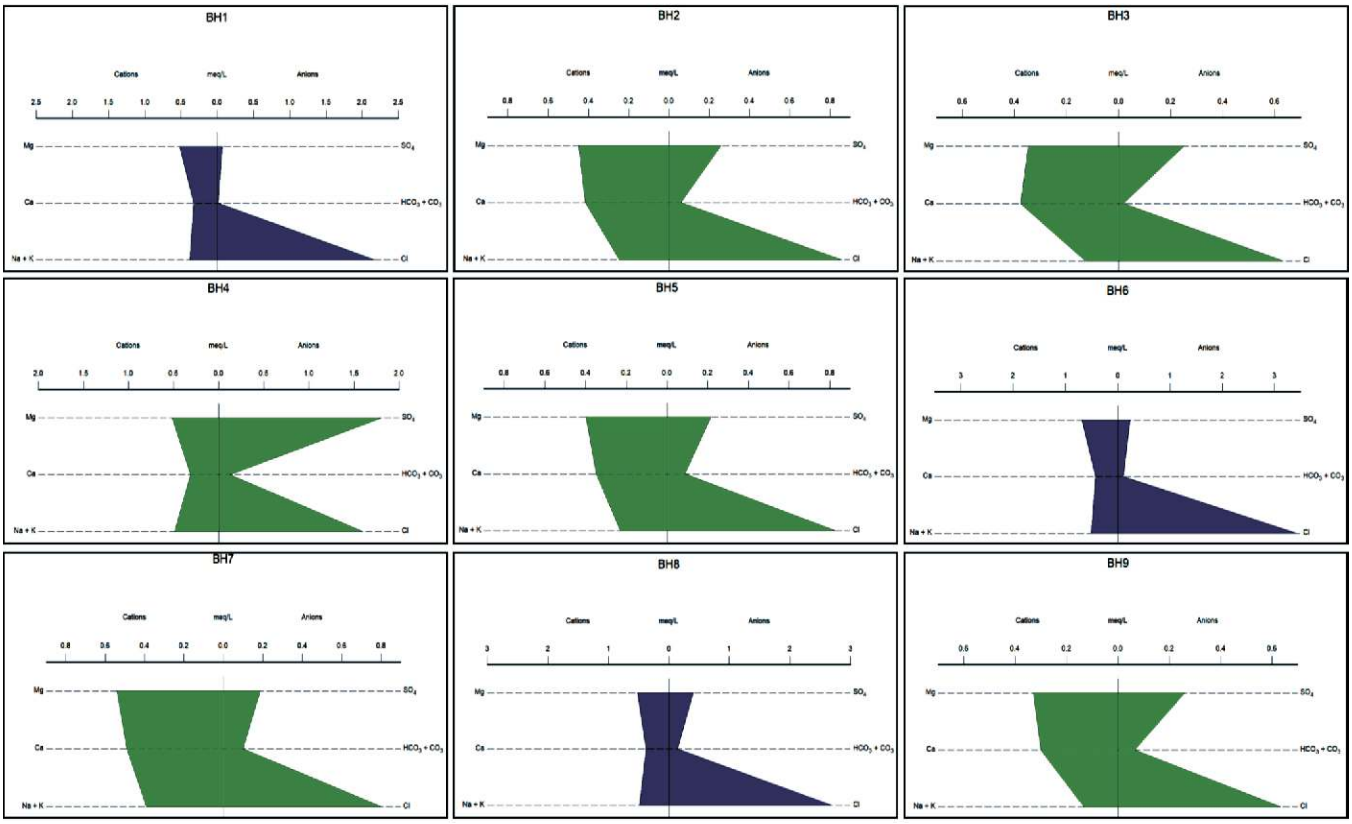

Fig. 6a: Stiff diagrams showing the various distinct shapes for the groundwater samples in the study area (BH1-BH9)

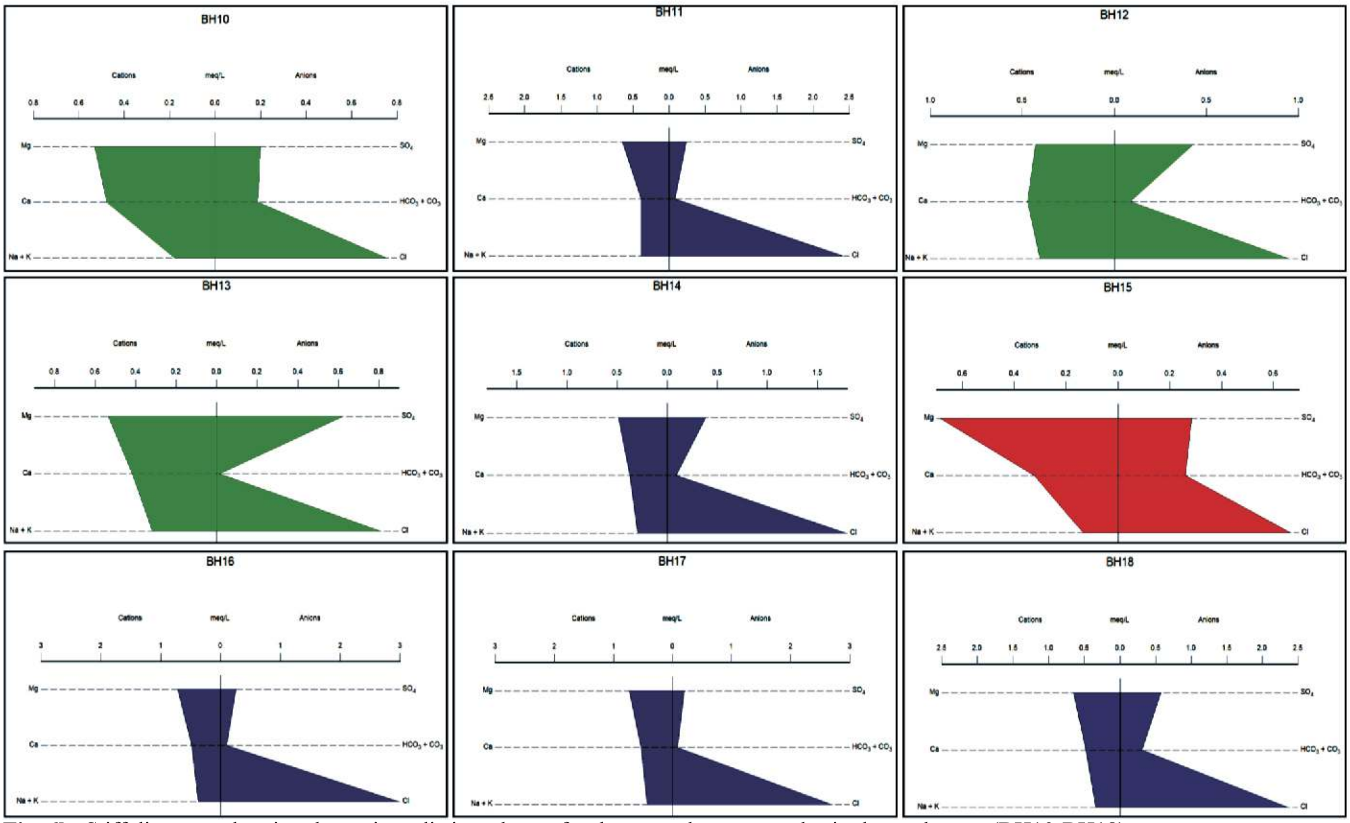

Fig. 6b: Stiff diagrams showing the various distinct shapes for the groundwater samples in the study area (BH10-BH18)

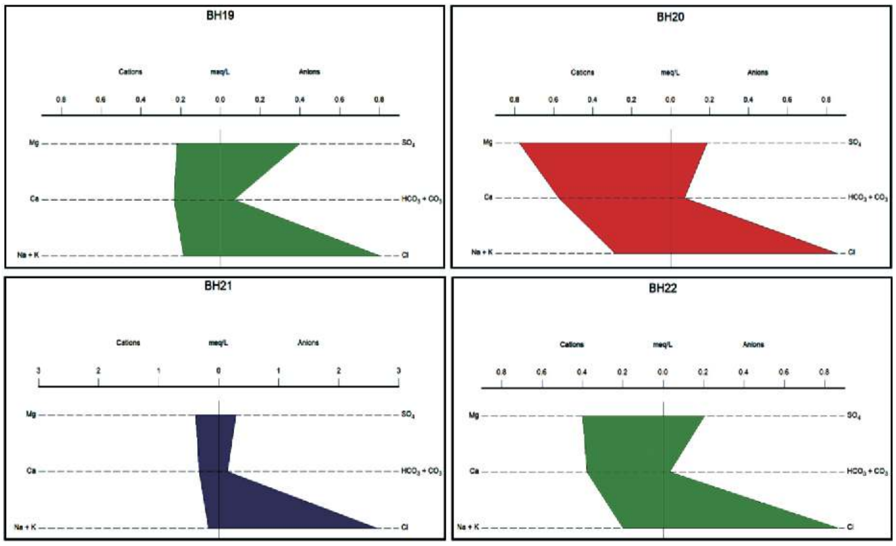

Fig. 6c: Stiff diagrams showing the various distinct shapes for the groundwater samples in the study area (BH19-BH22)

72.71 to 112.92, indicating poor to very poor and unsuitable water quality for consumption. The results from the WQI revealed that the groundwater in Khana and Gokana LGAs ranges from poor water quality to unsafe for drinking. This implies that groundwater in the study area is contaminated and thereby unsafe for drinking.

This study provides a qualitative measure of the water quality around the study locations which suggests the necessity of the remedial actions to the contaminated sources in order to keep the water safe and reliable for present and future consumption. The main innovative things of this study is that Water Quality Index (WQI) has been used which ultimately help us to understand the water quality in surrounding area. Moreover, it will be helpful in monitoring activities and for further water quality management to prevent the pollution. Based on the deteriorated quality of groundwater in the study area as revealed by this study, it is therefore recommended that residents install treatment plants in their groundwater pumping system before further usage for drinking and other purposes.

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