

SPATIO-TEMPORAL VARIATIONS OF GROUNDWATER QUALITY OF WARRI, DELTA STATE, NIGERIA.

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ABSTRACT: The study aims to assess the spatio-temporal variations of groundwaters quality parameters in Warri. Groundwater quality has deteriorated as a result of natural factors (flooding and seawater intrusion into the coastal aquifer) and anthropogenic activities resulting from industries and poor management of solid wastes and waste water. To meet the water needs, assessment of the current groundwater quality was needed. To achieve this objective, 50 groundwater samples were collected during dry and wet seasons and analysed for 26 physico-chemical and bacteriological parameters (temperature, pH, electrical conductivity (EC), Total Dissolved Solids (TDS) and dissolved oxygen (DO), turbidity, total hardness (TH), total suspended solids (TSS), biochemical oxygen demand (BOD), chemical oxygen demand (COD), total coliform bacteria, sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), sulphate (SO_4), nitrate (NO_3), chloride (Cl^-), bicarbonate (HCO_3), ammonium (NH_4), phosphate (PO_4), iron (Fe), cadmium (Cd), chromium (Cr), copper (Cu), and lead (Pb). Using internationally accepted standard methods of testing water and compared to WHO permissible standards for safe drinking water. The water quality index (WQI) was also evaluated. The results showed that most of the groundwater parameters were not within the permissible limits set by the World Health Organization in both seasons and had higher concentrations during the rainy season. The geochemical data were interpreted using WQI for drinking water. The spatial distribution maps of Water Quality Index showed that the highest quality was found, during both seasons, in the south and the south eastern part of the study area, corresponding to the recharge zone, whereas the poor and very poor water quality was found in the outflow part of the aquifer in Warri metropolis.

KEYWORDS: spatial, temporal, water quality. Water quality index, groundwater.

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I. INTRODUCTION

Groundwater is the major source of water supply for domestic, industrial, and agricultural sectors of many countries all over the world as approximately one-third of the world's population uses groundwater for drinking (Nickson et al., 2005). Major cities and rural communities are already facing a situation of severe water quality degradation, mainly due to anthropogenic activities (agriculture, industry, urban development, and increasing exploitation of water resources) as a direct consequence of climate change and other natural factors. Most groundwater pollutants stem from land uses such as municipal/domestic (i.e. ranging from hydrocarbon contaminant plumes, solid waste, leachates, leakages, liquid waste, cesspools, septic tanks, saline water intrusion and interchange through wells and solid wastes from landfills), industrial (i.e. liquid wastes, tank and pipeline leakages, oil field stockpiles in industrial, construction and brines) and agricultural sources i.e. irrigation return flow which are sometimes saline (Todd and Mays, 2005). The situation is worsened by climate change, urbanization, industrialization, some geological formations, population boom and uncontrolled

anthropogenic activities at the surface (Causapé et al., 2004; Nwankwo and Ogagarue, 2011; Oliveira et al., 2012; Tyagi et al., 2013). Geochemical conditions also affect the quality of water in the aquifer (Huat et al., 2011; Orji and Egboka, 2015). The chemical composition of groundwater is regulated by various factors, which include atmospheric input (i.e., sea spray, aerosols, etc.), mineral weathering through rock-water interaction, anthropogenic activities, and biogeochemical processes (Akoteyon, et al., 2011). The weathering of minerals exerts an important control on groundwater chemistry (Kim et al., 2005; Kim et al., 2011). This process generally dominates the concentration of the major cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+) in groundwater (Kim et al., 2005; Kim et al., 2011). Natural factors like earthquakes, volcanoes, algal bloom, storms, flooding, sea level rise (salt water intrusion) and river flows also contribute to the contamination of groundwater. Ocheri et al. (2014), stated that groundwater quality in Nigeria is influenced and controlled by such factors as the geological conditions of the soil through which it flows, geochemical and physical processes of the environment, heavy metals, bacteriological pollution and climatic factors. All these may therefore result in temporary or permanent loss of this important resource. Pollution of groundwater is a major issue because aquifers and the contained groundwater are inherently susceptible and vulnerable (Thirumalaivasan et al., 2003). Crude oil exploration and hydrocarbons related activities are the dominant industries in Warri. These activities have put the soil and groundwater at greater risk of contamination that threatens human health and economic development (Sayyed and Wagh, 2011; Tiwari, 2011). The exploration, exploitation, and unscientific management of groundwater resources and anthropogenic activities especially from the petroleum industries in the study area have posed a serious threat of reduction not only in quantity but also deterioration in its quality as a result of the presence of different harmful contaminants (Basavaraja et al., 2011; Trevisan et al., 2000). The Furthermore, the transport of contaminants in the groundwater system is affected by different processes such as advection, dispersion, diffusion, adsorption and decay (Kim et al., 2011).

The use of contaminated water affects human health, economic development, and social prosperity (Milovanovic, 2007). The importance of good water quality in human health has recently attracted a great deal of interest (Tili-Zrelli et al., 2016). An understanding of the spatial variation and processes affecting water quality is essential in sustaining usable water supplies under changing climate and local environmental pressures. Temporal changes of recharged water composition, hydrologic and human factors, may cause periodic changes in groundwater quality (Vasanthavigar et al., 2010). The quality of alluvial groundwater in rural areas is sensitive to contaminants originating from agricultural chemicals, such as, fertilizers, pesticides, and lime (Kelly, 1997; Stigter et al., 1998). The use of nitrogen fertilizers frequently leads to extremely high nitrate concentrations in groundwaters and may cause serious health problems (Cey et al., 1999; Peterson et al., 2001). In such circumstances, the knowledge of temporal and spatial trends of water quality should help in the decision-making process, particularly in developing countries, where there are insufficient data (Massoud et al., 2003). Water resources are both scarce and unequally distributed through time and space, with a potential decrease, due to overexploitation, exploitation, salinization, and pollution (Tili-Zrelli et al., 2016). Agriculture uses approximately 80% of all water resources (DGRE, 2010). This paper highlights the spatial and temporal variations in groundwater quality in Warri and evaluates the suitability of groundwater for drinking purposes for basic human needs using the Water Quality Index (WQI).

II. STUDY AREA

Warri is situated at latitude $5^{\circ}54'00''\text{N}$ and $5^{\circ}35'00''\text{N}$ of the Equator and longitude $5^{\circ}42'00''\text{E}$ and $5^{\circ}54'00''\text{E}$ of the Greenwich Meridian, in the western end and coastal region of the Nigerian Niger Delta about some 40 kilometres away from the shores of the Atlantic Ocean in Delta State, in Southern Nigeria (Fig.1). The study area is situated on a low-lying plain generally below six metres above sea level, consisting mainly of unconsolidated sediments (Izeze and Konboye, 2018). The geological formation consists of more than 90% sands and about 10% shale/clays. The sands range in size from fine-to-medium and coarse-grained unconsolidated sands, with occasional intercalations of gravelly beds that are also poorly-sorted, sub-angular to well-rounded, and bear lignite streaks and wood fragments peat or lenses of plastic clay (Akpoborie et al., 2011; Fetter, 1999; Nwajide, 2006). This formation contains the most productive and hence most tapped aquifer in the Niger delta region due to the fact that it is shallow (Amangabara and Ejenma, 2012). The average annual of about 3000mm and occurs mostly due to the south-west monsoon wind (Adejuwon, 2012). Crude oil exploration and exploitation activities in the study area has subjected both groundwater and surface water serious threat of contamination. The near absence of government water schemes has compelled individuals to drill and own their personal boreholes to meet their water needs.

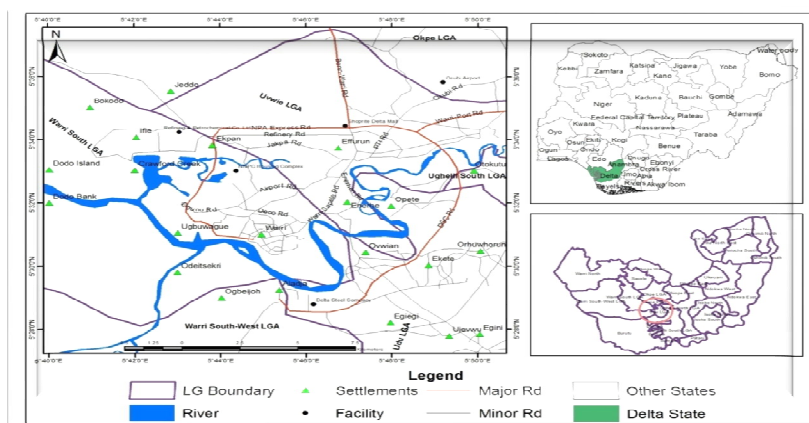


Fig. 1. Map of Warri and its environs [(Source: Google Maps, 2021; Agori, 2021)

III. SAMPLING LOCATIONS, SAMPLES COLLECTION AND ANALYSIS

From the satellite imagery of the study area, the built-up areas were digitized and gridded at 1km intervals. Existing boreholes at or close to the intersection of the gridlines were used as the sampling points to ensure adequate coverage and uniform spacing of sampling locations. Fifty (50) sampling locations were selected and established using hand-held GPS (GARMIN GPSMAP 76CSx model) and their UTM coordinates recorded. Depth of some boreholes were determined using plumb bulb, line and measuring tape. Water samples were collected during the dry season (December, 2019 – January, 2020) and the wet season (June, 2020 – August, 2020) from the 50 locations. The samples were analysed for twenty six (26) physico-chemical and bacteriological water quality parameters: temperature, pH, electrical conductivity (EC), turbidity, total hardness (TH), total suspended solids total dissolved solids (TDS), dissolved oxygen (DO), biochemical oxygen demand (BOD), chemical oxygen demand (COD), total coliform bacteria, sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), sulphate (SO_4), nitrate (NO_3), chloride (Cl^-), bicarbonate (HCO_3), ammonium (NH_4), phosphate (PO_4), iron (Fe), cadmium (Cd), chromium (Cr), copper (Cu), and lead (Pb) for each of the fifty (50) sampling locations in both the dry season and wet season. Temperature, pH, electrical conductivity (EC), dissolved oxygen (DO) and total dissolved oxygen (TDS) were measured in situ. Samples were kept in ice block chests, transported to the laboratory and stored in refrigerators at 4°C for their subsequent chemical analyses using the methods shown in Table 1.

Table: 1: Methods of analysis for different water quality parameters

S/N	Parameter	Methods
1	Turbidity	Nephelometric
2	Total Hardness	EDTA Titrimetric
3	Total suspended solid	Gravimetric after filtration
4	Biochemical Oxygen Demand (BOD)	Bottle incubation for 3-days at 27°C
5	Chemical Oxygen Demand (COD)	Open reflux
6	Total coliform bacteria-MPN	Total multiple tube fermentation
7	Sodium	Flame emission photometric
8	Potassium	EDTA Titration
9	Calcium	EDTA Titration
10	Magnesium	Calculation from TH and calcium
11	Sulphate	Nephelometry
12	Nitrate	UV Spectrophotometric
13	Chloride	Spectrophotometer
14	Bicarbonate	Calculation from pH and Alkalinity
15	Ammonium	Distillation titrimetric
16	Phosphate	Ascorbic acid spectrophotometric
17	Heavy metals (Fe, Cd, Cr, Cu, Pb)	Atomic Absorption Spectrophotometer (AAS)

Source: APHA, 2017.

The obtained results were applied to statistical study using Microsoft excel tool. Statistical summaries

of the parameters analysed for this study are presented in Table 2. The mean values were compared to WHO permissible limit for drinking and public health. The results of the concentration of water quality parameters obtained from both field and laboratory analysis of water samples were compared the WHO permissible limit for drinking and public health. The Water Quality Index (WQI) was evaluated using the weighted arithmetic method and data were made available in a format that is accessible via GIS. Kriging interpolation of the ArcGIS 10.6 software was used to generate different spatial distribution maps of various chemical constituents in the study area.

Table 2: Statistical summary of hydrochemical parameters of the study

Parameter (mg/l)	Dry season (n = 50)				Wet season (n = 50)			
	Range		Mean	SD	Range		Mean	SD
	min	Max			min	max		
Temperature (°C)	23.21	32.20	27.27	2.40	22.20	32.20	27.47	2.52
pH	4.20	6.70	5.41	0.62	3.40	5.90	4.49	0.54
EC ($\mu\text{S}/\text{cm}$)	40.00	532.00	162.74	127.37	46.00	678.00	186.68	149.96
Turbidity (NTU)	0.00	37.53	5.69	7.84	0.00	35.77	6.27	7.53
TH (mg/l)	3.72	336.29	51.03	91.94	3.72	336.29	55.53	90.38
TSS (mg/l)	0.00	42.47	6.88	9.18	0.00	46.92	11.17	10.39
T.D.S (mg/l)	22.00	298.00	91.16	71.36	26.00	380.00	104.52	83.96
DO (mg/l)	1.00	7.70	3.22	1.66	1.90	9.60	4.29	2.42
BOD (mg/l)	0.30	1.40	0.07	0.36	0.70	2.50	0.70	0.48
COD (mg/l)	1.10	8.90	4.36	1.89	0.30	9.20	3.92	2.49
Total Coli (CFU s/100ml)	0.00	35.00	11.13	11.58	0.00	36.54	11.58	11.19
Na (mg/l)	1.50	27.30	9.30	6.98	1.50	30.50	10.34	7.62
K (mg/l)	0.10	3.90	1.30	0.91	0.10	4.20	1.74	1.22
Ca (mg/l)	4.00	69.00	18.54	16.15	4.10	90.20	21.42	19.68
Mg (mg/l)	0.10	1.90	0.47	0.38	0.11	2.40	0.59	0.45
SO ₄ (mg/l)	0.12	5.92	1.00	1.14	0.14	8.08	1.20	1.51
NO ₃ (mg/l)	0.02	3.27	0.83	0.81	0.01	4.12	1.06	1.08
Cl (mg/l)	10.30	117.00	34.89	26.69	12.30	147.10	39.41	30.40
HCO ₃ (mg/l)	3.10	79.50	19.62	16.69	3.10	82.30	21.92	19.05
NH ₄ (mg/l)	0.00	0.09	0.01	0.02	0.00	0.06	0.02	0.02
PO ₄ (mg/l)	0.01	0.79	0.19	0.17	0.04	0.91	0.28	0.24
Fe (mg/l)	0.20	0.24	0.21	0.01	0.19	0.26	0.22	0.01
Cd (mg/l)	0.00	0.01	0.00	0.002	0.00	0.01	0.00	0.002
Cr (mg/l)	0.000	0.002	0.00	0.001	0.000	0.002	0.00	0.001
Cu (mg/l)	0.01	0.19	0.20	0.246	0.01	0.19	0.20	0.246
Pb (mg/l)	0.01	0.36	0.02	0.023	0.01	0.36	0.02	0.023

IV.COMPARISON OF WATER QUALITY RESULTS TO WHO PERMISSIBLE STANDARDS

The obtained mean values of measured concentrations of each water quality parameter in both dry and wet seasons were compared with the WHO permissible standard values.

V. WATER QUALITY INDEX (WQI)

Water Quality Index (WQI) is defined as a rating reflecting the composite influence of different water quality parameters (Ramkrisahniah et al., 2009). WQI was used to determine the suitability of the water samples for drinking purposes. The Water Quality Index is one of the most effective tools to communicate information on the quality of water to the concerned citizens and policymakers. It is an important parameter for the assessment and management of groundwater. By mapping the index, the areas of high and low water quality can easily be distinguished by scientists as well as by policymakers or the general public, for treatment before various uses (Saeedi et al., 2010). The weighted arithmetic method of evaluating WQI was adopted in this work using Equations 1- 4.

$$\text{Relative weight } (W_i) = \frac{w_i}{\sum_{i=1}^n w_i} \quad (1)$$

$$\text{Quality rating scale } (q_i) = \frac{c_i}{s_i} \times 100 \quad (2)$$

$$SI_i = W_i \times q_i \quad (3)$$

$$WQI = \sum SI_i \quad (4)$$

where;

w_i = weight of each parameter

n = number of parameters

c_i = concentration of each parameter in each water sample in mg/l

SI_i = sub – index of i th parameter

q_i = rating based on concentration of i th parameter

S_i = standard value

VI. RESULTS AND DISCUSSION

A. GROUNDWATER GEOCHEMISTRY

- Temperature:** The mean temperature values are within the ranges of 23.21°C to 32.2°C for dry season and 22.2°C to 32.2°C in the wet season. Temperature variations suggests a high temperature environment, with a low temperature variability. The lower temperatures during the dry season are probably as a result of the harmattan cold which causes water temperature to drop. The values for temperature exceeded WHO standard limits except for locations OGD, UGT, UBJ 2, OGB, WAP, OGU, FGC, OKL, UDR, OTO and OKE that have limits within the stipulated standards. The water temperature controls the rate of all chemical reactions. The spatial variation of temperature is a function of the recharged water and of the infiltration transfer time, which in turn both depend on porosity, lithology, and thickness of the unsaturated zone. Global warming and urbanization together with development of subsurface infrastructures (e.g. subways, shopping complexes, sewage systems, and Ground Source Heat Pump (GSHP systems) will likely cause a rapid increase in the temperature of relatively shallow groundwater reservoirs (subsurface thermal pollution). For the same sampling period, the spatial variation is marked by a decrease as the depth increases.
- pH:** pH is classed as one of the most important water quality parameters. Measurement of pH relates to the acidity or alkalinity of the water. A sample is considered to be acidic if the pH is below 7, while it is alkaline if the pH is higher than 7. Acidic water can lead to corrosion of metal pipes and plumbing system, while alkaline water shows disinfection in water. The normal drinking water pH permissible standard values range from 6.5 to 8.5. The pH values are in the range of 4.2 to 6.7 and 3.4 to 5.9 and the mean values are 5.41 and 4.49 in the dry and wet seasons respectively. The pH values of most of the water samples are not within the desirable limits set by the World Health Organization (WHO, 2004). The reduced rate of photosynthetic activity, the assimilation of carbon dioxide and bicarbonates are ultimately responsible for increase in pH, the low oxygen values coincided with high temperature during the dry season. The high precipitation in the study area attributed to the acidic conditions of groundwater in most of the sampling locations. pH levels are increased in the wet season due to high water levels as a result of dilution of alkaline substances (Sisodia and Moundiotiya, 2006). Application of chemical fertilizers, run off from agricultural field, leaching of industrial/domestic waste and sewage inflow and other anthropogenic sources are the possible point and non-point sources that cause the acidity of groundwater.
- Electrical Conductivity (EC):** The electrical conductivity values are in the range of 40 to 532 and 46 to 678 $\mu\text{S}/\text{cm}$ and the mean values are 162.74 and 186.68 $\mu\text{S}/\text{cm}$ for the groundwater samples in dry and wet seasons respectively. The EC values are within the permissible limit of 400 $\mu\text{S}/\text{cm}$ (WHO, 2011) in most of the groundwater sampling locations except at locations APR, UGT, JED, OSA, OGB, and EDJ in both seasons. Electrical conductivity of water relates to the total concentration of different dissolved solids and ions (ionizable ions) in the water. EC is a function of ions activities and the high values of EC may be due to high concentration of ionic constituents present in the water bodies (LENNTECH, 2016). EC is directly proportional to the total dissolved solids (Nair et al., 2006). Percolation of industrial wastes, agricultural activities, land use, and intrusion of sewage may also enhance the high EC values in the aforementioned sampling locations which affect the mineral contents and thus the electric conductivity of the water (Scatena, 2000).
- Turbidity:** Turbidity is the cloudiness of water caused by a variety of particles and is another key parameter in drinking water analysis. The turbidity values are within the ranges of 0 to 37.53 NTU for dry season and 0 to 35.77 NTU in the wet season with mean values at 5.69 and 6.27 NTU in the dry and wet seasons respectively. All turbidity values are below 5 nephelometric turbidity units (NTU), the standard recommended maximum turbidity limit set by WHO and NDWQS for drinking water except for stations ARB, JKR, SHA, EKP, EFM, JED, UBJ 2, OSM, WAP, EDHE, IGM, UDR, MAM, DST, OKE, MOF, FUP, SHP, ROP, ESR and ROR which were above the recommended limit. The turbidity levels for JKR, EFM, JED, PEM, ENE and UDR are low only in the wet season but are high in the dry season as a result of soil runoff. Lower turbidity values during the dry season are probably due to less groundwater recharge and infiltration. Higher levels of turbidity

are associated with disease causing bacteria.

- **Total Hardness (TH):** Minerals that cause hardness exist to some degree in every water supply. The total hardness values are found to be in the range of 3.72-336.29mg/l together with the mean values which are 51.03 and 55.53mg/l for the groundwater samples in dry and wet seasons respectively (Table 2). The total hardness values for all sampling stations are within the WHO permissible limit of 500mg/l. High value of TH is observed in stations OKU, UGT, EDJ, BOA, ORH, MAM, DST and MOF. TH was recorded comparatively highest in the wet season than in dry season. High rate of evaporation increases the concentration of total hardness in groundwater samples (Namdeo et al., 2013). Percolation of industrial wastes and domestic wastes, presence of calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions in water also enhanced the increase TH concentration in these locations.
- **Total Suspended Solids (TSS):** The total suspended solids (TSS) relatively measure the physical or visual observable dirtiness of a water resource. The total suspended solid values are found to be in the range of 0 to 42.47mg/l and 0 to 46.92mg/l with mean values at 6.88 and 11.17mg/l for the groundwater samples in dry and wet seasons respectively. There is no specified limit for this parameter (WHO, 2011). The low levels of TSS in borehole water are quite understandable, as groundwater was originally been filtered by nature and then extracted by filter aided mechanical pumps and because most sample collection points in these areas had filtration systems attached to the taps, thus removing all the suspended particles such as silt, clay, and other inorganic particles. The higher TSS value during the wet season could be due to the increased weathering intensity and groundwater recharge during wet season and the presences of petroleum refining and other petroleum related activities. Lower TSS during the dry season is as a result of water filtration.
- **Total dissolved solids (TDS):** The TDS values are found in the range of 22 to 298mg/l and 26 to 380mg/l with mean values at 91.16 and 104.52mg/l for the groundwater samples in the dry and wet seasons respectively. The TDS values are below the permissible limit of 500mg/l (WHO, 2011) in all of the groundwater sampling stations in dry and wet seasons except in locations BOA and MAM. TDS is the presence of all dissolved salts, that is, TDS are the inorganic matters and small amounts of organic matters which are present as solution in water. It is a function of the sum of ions in solution and the degree of dissolved substances such as metal ions in the water. A higher TDS means that there are more cations and anions in the water. The increased concentration of TDS in the wet season could be attributed to weathering intensity and the increased amount of groundwater recharge, the addition of solids from sewage, runoff water, and industrial effluents. Maximum value of TDS is found in location BOA in the dry season which could be due to the discharge from industries and untreated waste water (Viswanathan and Meenakshi, 2008). The increase in TDS is also as a result of runoff intrusion and soil disturbance within the sampling locations (Mkwate et al., 2017).
- **Dissolved oxygen (DO):** DO is one of the most important water quality parameters that gives direct and indirect information about the water, e.g. bacterial activity, photosynthesis, availability of nutrients, stratification etc., (Premlata, 2009). The values of DO are found in the range of 1-7.7mg/l and 1.9-9.6mg/l with mean values at 3.22 and 4.29mg/l in dry and wet season respectively (Table 2). The DO values are below the permissible limit of 6mg/l (WHO, 2011) in most of the sampling stations. The low dissolved oxygen levels in groundwater may be attributed to the effluents from industrial sources, septic tanks/soakaway pits and leachate from the unengineered waste dumps scattered within the study area. The nitrogen and phosphorus contained in them stimulate the growth of micro-organisms that consumes the dissolved oxygen of water (Sisodia and Moundiotiya, 2006). The difference in initial and final DO give the amount of oxygen consumed by the bacteria during test period. The concentration of DO values are inversely proportional to temperature. High dissolved oxygen concentrations occur during wet season as a result of aeration in the atmosphere through precipitation. The values are depleted during dry season because of high temperature which reduces the oxygen holding capacity of water and percolation of sewage or other wastes in the dry season and increased microbial activity (Kataria et al., 1996; Morrisette and Mavinic, 1978; Moss, 1972, Krishnamurthy, 1990; Sisodia and Moundiotiya, 2006).
- **Biochemical oxygen demand (BOD):** BOD is a measure of the amount of biologically oxidizable organic matter present in water. That is, it is a measure of organic material contamination in water. The values of BOD are found in the range of 0.3 to 1.4mg/l and 0.7 to 2.5 mg/l with mean values at 0.07 and 0.7mg/l for the groundwater samples in dry and wet season respectively. The BOD values are lower than the permissible limit of 10 mg/l (WHO, 2011) in all the groundwater sampling stations in the dry and wet seasons. The high BOD during the dry season could be due to the reduced groundwater recharge, presence of decomposable organic matter (clay), percolation of leachate from solid waste dump sites and organic pollution of water body (organic wastes and sewage) and chemical pollution from industrial wastes (Mishra et al., 2003). BOD value higher than 6mg/l means organic material contamination in water. High BOD registered during wet season may be due to high concentration of dissolved solids in water, high input of organic pollutants and increased biological activities while in dry season, reduced rate of flow and decrease in biological activities due to

elevated temperature lowers the BOD (Palharya et al., 1993; Shukla et al., 1993). The high BOD values could be due to acidification of water by elevated microbial degradation of organic debris and concentrated dissolved solids.

- **Chemical oxygen demand (COD):** The COD values are in the range of 1.1 to 8.9 mg/l and 0.3 to 9.2 mg/l in dry and wet season respectively (Table 2). The COD values are well below the permissible limit of 10 - 20mg/l (WHO, 2011) in all the groundwater sampling locations in dry and wet seasons. COD is representative of pollution by biodegradable and chemically degradable organic matter (Elangovan and Dharmendirakumar, 2013). It is also an indication of organic matter susceptible to oxidation by chemical oxidant which is typical of reduced organic as well as inorganic pollution in the groundwater (Bhanja and Mohanta, 2000).
- **Total Coliform:** The Total Coliform values are in the range of 0 to 35MPN/100L and 0 to 36.54MPN/100L with mean values at 11.13 and 11.58MPN/100L for the groundwater samples in dry and wet season respectively (Table 2). These values are higher than the WHO, 2011 recommended 10MPN/100L of water in all groundwater sampling locations in the dry and wet seasons with notable variational increase in concentrations levels in the wet season. This is representative of pollution by biodegradable and chemically degradable organic matter in the study area (Elangovan and Dharmendirakumar, 2013). These results are typical of reduced organic as well as inorganic pollution in the groundwater (Bhanja and Mohanta, 2000). The high amount of coliform during the wet season could be due to the fact that water availability favours the movement and reproduction of the organisms. Furthermore, the presence of coliform could be from collapsed septic tanks which occurs more in the wet season and movement of leachate from open dumpsites.
- **Sodium (Na):** It is a natural component of water. The mean values of sodium are observed at 9.3 and 10.34mg/l concentrations which were also in the range of 1.5 to 27.3mg/l and 1.5 to 30.5mg/l for the groundwater samples in the dry and wet seasons respectively (Table 2). High content of sodium in groundwater may be from the release of the soluble products during the weathering of rocks and minerals (Udayalaxmi et al., 2010). Higher values of Na, K, Mg and Ca in wet seasons could be attributed to the high dissolution of rock colouring the mineral of these metals. High level of Na leads to nausea, vomiting and stomach cramps. Distribution of Na is similar to that of DO, BOD and COD. Majority of the study area has the range of less than 15mg/l. Maximum ranges of more than 20mg/l is located as small patches in the low-lying areas and in the clay zones.
- **Potassium (K):** The K concentration mean values exist in the study area at 0.1 to 3.9mg/l and varies in ranges of 0.1mg/l to 4.2 mg/l and 1.3mg/l to 1.74 mg/l for groundwater samples in dry and wet season respectively. Potassium concentration is influenced by the cation exchange mechanism (Narain and Chauhan, 2000). The low values of potassium may be due to the absence of geochemical strata in the study area (Mahananda et al., 2010). Distribution of K shows similarity to that of Na, having most of its range in the study area less than 5mg/l. This range showed significant correlation with BOD in the wet seasons. Naturally, water has much lower concentrations of K as compared with Na. During weathering, K^+ tend to be either adsorbed or fixed in the soils or weathered products especially in the clay minerals. As a result, the concentration of K^+ in natural waters is relatively less. As opposed to the case of Na distribution, K also does not show any serious differential concentration.
- **Calcium (Ca):** The mean values of calcium are found to be at 4 and 69mg/l varying from 4.1 to 90.2mg/l in the dry periods and 18.54 to 21.42mg/l in the wet periods (Table 2). This range coincides with the range of K, with the maximum concentration as 90.2mg/l which can be related to oxidation of organic matter (Narain and Chauhan, 2000). The calcium values are within the stipulated standard by the WHO in all of the groundwater sampling locations in both seasons except for location APR. High content of calcium is recorded in few sampling stations in both dry and wet seasons and is likely caused by precipitate soaps, anionic surfactants and anionic emulsifiers.
- **Magnesium (Mg):** Magnesium is one of the most common minerals that make water hard. The obtained Mg concentration ranged between 0.1mg/l and 1.9mg/l in the dry season and 0.11mg/l to 2.4mg/l in the wet season respectively, with an average concentration of 0.47mg/l and 0.59mg/l in both dry and wet seasons respectively. High content of magnesium is recorded in a few sampling stations in both dry and wet seasons. The concentration of magnesium depends upon exchange equilibria and the presence of the ions like sodium. The higher concentrations of magnesium values recorded during wet season could be due to dissolution of the underground deposits of magnesium minerals of sedimentary rock (Azrina et al., 2011; Vasanthavigar et al., 2010). Generally, magnesium maintains equilibrium in most waters (Ishaku et al., 2011). In the study area, Mg content is less than Ca and most of the sampled areas show levels less than 5mg/l. Maximum content of above 10mg/l is recorded in clayey and in some low-lying areas.
- **Sulphate (SO_4):** Range of SO_4 concentration values are between 0.12mg/l to 5.92mg/l and 0.14mg/l to 8.08mg/l, with mean values of 1mg/l and 1.2mg/l for samples in the dry and wet seasons respectively. The sulphate values were observed to be lower in the wet season than in the dry season which may be due to dilution effect. Sulphate in water is due to dissolved Ca/Mg/Fe. The higher sulphate concentration during the

dry season could be attributed to the reduction in groundwater recharge resulting from low precipitation, higher temperature and evaporation during the dry season which, also reflects the dissolution of sulphides from interstratified peat within the geological formation. The elevated concentration of SO_4 may be also due to the fact that the Deltaic plain is a sequence of sands and silt with local intercalation of peat and sulphur-rich clays or high-level combustion of sulphur containing hydrocarbon fuels in the study area. The dissolution of sulphides such as pyrite from the interstratified material by percolating water also produces SO_4 ions in water. Gaseous emissions from increasing heavy traffic flow and petroleum activities also contribute significant amount of sulphur to groundwater. It could also be from the direct consequence of oxidation of sulphur containing compounds after rainwater has been charged to ground water resources.

- **Nitrate (NO_3):** The levels of nitrate are from 0.02 to 3.27mg/l and 0.01 to 4.12mg/l with average values at 0.83 and 1.06mg/l for the groundwater samples in dry and wet season respectively. Nitrate pollution is strongly associated with runoff from agricultural activities (fertilizer use), leakages from septic tanks, sewage, erosion of natural deposits. The percolation of domestic sewage, industrial wastes, dumping of garbage and leakage of septic tanks enhance the nitrate value (Jameel and Hussain, 2011). Also, the higher nitrate concentration during the dry season could be attributed to the reduction in groundwater recharge resulting from low precipitation, higher temperature and evaporation during the dry season. The high concentration levels of nitrate and chloride are due to organic pollution resulting from sewage mixing, higher animal waste, poor sewerage and solid waste disposal system, and increased temperature and evapo-transpiration of water, leaky sewers, large number of septic tanks and soak pits, and practice of sewage discharge through open surface drains (Haran, 2002; Majagi et al., 2008; Shanthi and Ramaswamy, 2002; Sivakumar et al., 2000).
- **Chloride (Cl):** Chloride parameter has values ranging from 10.3-117mg/l and 12.3-147.1mg/l, mean concentration values stand at 34.89 and 39.41mg/l in dry and wet seasons. The chloride values are within the standard requirement of 5mg/l (WHO, 2011) in both seasons. High content of chloride in groundwater at these locations may result from both natural and anthropogenic sources such as run-off containing salts, the use of inorganic fertilizers, landfill leachates, septic tank wastes, animal feeds, industrial effluents, irrigation drainage and salt water intrusion water additives used to control microbes and disinfect water (Bundela, et al., 2012). Soil porosity and permeability also has a key role in building up the chloride concentration in these stations (Chanda, 1999). The spatial distribution maps of chloride show that the lowest values are recorded both during the wet and the dry season in the southern and southeastern parts of the study area. These parts correspond to the natural recharge area (dilution effect) with an increasing trend of salinity values in the water flow direction. The high salinity levels are related to the infiltration of salty water from Crawford marshes and of salty soil leachate. Concentrations of chlorides show little seasonal variation and the slight decrease can be explained by the dilution caused by rainwater infiltration during the wet season, whereas evaporation contributes to ion concentration increase throughout the dry season.
- **Bicarbonate (HCO_3):** The analysed HCO_3 levels range from 3.1 to 82.3mg/l in the wet season and 3.1 to 79.5mg/l in the dry season, and similarly, with an average value of 19.62 to 21.92mg/l in the study area. The bicarbonate values are all within the WHO recommended limit of 125mg/l at the sampling stations in wet and dry seasons. This may be due to the action of dissolution of atmospheric CO_2 and CO_3 released from organic decomposition (Umapathy, 2011). The nature of rock type in the study area is another important factor that contributes to the presence of bicarbonate. The primary source of bicarbonate ions in groundwater is the dissolution of carbonate minerals in the study area. The decay of organic matter present in the soil releases carbon dioxide (CO_2). Water charged with CO_2 dissolves carbonate minerals, as it passes through soils and rocks to give bicarbonates.
- **Ammonium (NH_4):** Ammonia recorded a mean value of 0.01mg/l, Minof 0mg/l, Max of 0.09mg/l with standard deviation of 0.02mg/l in the dry season and a mean value of 0.02mg/l. Min of 0 mg/l, Max of 0.06mg/l with standard deviation of 0.02mg/l in the wet season. The permissible limit are values lesser than 1.5mg/l in both seasons, with NCAT, SHA, EKP, UCE, UBJ 2, OSM, OGU, FGC, AJA, WAG, OKL, WAP, ESL, IGM, MAM, MOF, ROP, ESR and PTR stations recording levels below detectable limits. The presence of high values of ammonium observed could be due to dissolved gases and degradation of organics, pollution from sewage attributed to areas of poor waste management, old boreholes and are usually localized. The average values of ammonia recorded highest in wet season compared to dry season, which could be due to acidification of water by elevated microbial degradation of organic debris and concentrated dissolved solids in wet period. Furthermore, NH_4 temporal variational increases during the seasons may be due to anthropogenic activities from surface run-off and agricultural activities (Nightingale and Simenstad, 2001).
- **Phosphate (PO_4):** The values of phosphate are found in the range of 0.01mg/l to 0.79 mg/l and 0.04mg/l to 0.91 mg/l for the groundwater samples in dry and wet seasons respectively (Figs 2a and 2b), and average values of 0.19 to 0.22mg/l in both seasons. The phosphate values exceed the permissible limit of 0.3mg/l (WHO, 2011) in sampling locations EFG, APR, EFM, OGD, UGT, UBJ 1, OSA, OGB, EDJ, EDHE, OKR, ESL, ORH, SHP and ROR in wet and dry seasons. The excess concentration of phosphate may be due to

percolation of domestic sewage and agricultural inputs in the study area. During the natural process of weathering, the soils/rocks gradually release the phosphorus as a phosphate ion which are soluble in water and mineralize phosphate compounds breakdown. Moreover, the phosphate levels recorded in this study are relatively high which could explain the presence of photosynthetic bacterial activity in the water.

- **Iron (Fe):** The Fe values are in the range of 0.2mg/l to 0.24mg/l and 0.19mg/l to 0.26mg/l with mean values of 0.21mg/l and 0.22mg/l for the groundwater samples in dry season and wet season respectively. Fe values are higher in the dry season probably due to reduced groundwater recharge. The Fe values were below the permissible limit of 0.3mg/l (WHO, 2011) in all the groundwater sampling stations for the dry and wet seasons. Iron occurs naturally in soil, sediments and groundwater, and can be found in many types of rocks. The presence of iron in ground water is attributed to the nature of the geological formation, from natural deposits, improper waste disposal sites, industrialization, natural water recharge, corrosion of iron containing metals which are part of distribution channel and water-soil/rock interaction. Surface water charged with atmospheric and biogenic CO₂ infiltrates into the subsurface and aggressively attack aluminosilicates including feldspar and micas present in the formation liberating cations such as iron, calcium, and magnesium into the water and leaving residues of clay minerals (Amangabara and Ejenma, 2012). These weather conditions resulting from long duration and intensive rainfall couple with high temperature accelerate weathering of the geologic formation in the area. The weathering processes release the iron element into waters, under oxygen-poor conditions, occurring mainly as binary iron. But under acidic and neutral, oxygen-rich conditions it becomes part of many organic and inorganic chelation complexes that are generally water soluble and the dissolved iron is mainly in the form of Fe(OH)²⁺ (aq) (Amangabara and Ejenma, 2012). Similarly, high values of iron recorded in the wet season could be due to acidification of water by elevated microbial degradation of organic debris and concentrated dissolved solids in wet period. The measure of deviation shows 0.01 for both seasons. This indicates that the source of contamination remains the same throughout the season.
- **Cadmium (Cd):** The Cd values are found to be in the range of 0.00 to 0.01mg/l and 0.00 to 0.01mg/l with mean values of 0.001mg/l and 0.003mg/l for the groundwater samples in dry and wet season respectively. Cd concentrations are higher in the wet season probably due to groundwater recharge. All locations are well below detection limits for this parameter except for 15 locations with OKU, APR, JKR, EKP, UCE, EFM, OGD, AJA, OKR, AGS, ENE, UDR, OTO and MAM having limits of <0.001mg/l in both seasons. The high Cd levels in these areas could be attributed to effluents containing heavy metals discharged by chemical and petroleum industries in and around those areas such as paints, pigments, plastic stabilizers, mining and smelting operations, and other industrial operations such as electro plating and fossil fuel, fertilizer, and sewage sludge disposal. Cd also occurs naturally in rocks and soils and may have entered the water when there is contact with soft groundwater or surface water. High concentration of Cd in the water sample might be due to corrosion of galvanized steel pipes used for piping of water distribution. These galvanized steel pipes are plated with zinc, which usually has 1% of Cd. Similarly, Cd can also come from fittings with cadmium soldering (El-Harouny, et al., 2008).
- **Chromium (Cr):** The Cr values are in the range of 0.00 to 0.002 mg/l and 0.00 to 0.002mg/l with mean values of 0.0001 and 0.0001mg/l for the groundwater samples in dry and wet season respectively. All measured locations are within the acceptable limit of 0.05mg/l. The concentration of Chromium and Copper in the study area could be attributed to the dumping of wood treated with chemicals made from salts of Arsenic, Chromium and Copper in mixed soluble formulation (as copper-chrome arsenate preservative) being used to prevent fungi and pest attack which provide a potential source of chemical spills and drainage from the treated wood within and around the refinery, which support the earlier findings of Ndiokwere, (2004). Similarly, the contamination of Cr might have also resulted from erosion of natural deposits within the surrounding areas, industrial and laboratory effluents around the study area could also be a source of Chromium, (Braide et al., 2004).
- **Copper (Cu):** Cu values are in the range of 0.01mg/l to 0.19mg/l and 0.01mg/l to 0.19mg/l with mean values of 0.2mg/l and 0.2mg/l for the groundwater samples in dry and wet season respectively. Furthermore, Cu levels recorded between 0.01mg/l minimum to 0.19mg/l maximum. Cu was not detected in OKU, APR, JKR, AJA, OKR, AGS, ENE, UDR, OTO and MAM study locations. Cu values do not show significant variation for both seasons. These values suggest industrial activities within the area which are responsible for the elevated levels of heavy metals in water.
- **Lead (Pb):** Seasonal comparison of lead shows that all locations where groundwater was sampled are well below the acceptable level. Values measured depict average limits of 0.01mg/l to 0.36mg/l in the dry season concentrations and 0.01 to 0.36mg/l in the wet season. The mean values are 0.02 and 0.02mg/l in the dry and wet seasons respectively. All measured locations are within the acceptable limit of 0.01mg/l. Pb in groundwater could have resulted from indiscriminate dumping of electronic wastes, oil, batteries and oil exploration and processing activities. Lead enrichment in these areas could have resulted from NNPC refinery

and petrochemical wastes in the northwestern part of the study area and from leachates associated with unregulated dumpsites that have been traditionally used for waste disposal. Also, higher concentration of Pb may be due to the piping used for the water distribution system (Hanaa, et al., 2000) and also the surrounding soil which may have a higher amount of Pb, which may be leached into the water (Dissmeyer, 2000).

Heavy metals contamination in drinking water poses a threat to humans and is often the root cause various severe health issues such as cancer and organs (lungs, liver, kidney, bone, blood and other vital organs) damage. They can also bring about reduced mental and central nervous functions that can lead to learning difficulties, memory impairment and behavioural issues in the form of aggression and hyperactivity. They are slow poisons to man's health as their effect is not immediate.

Table 3 presents the descriptive statistics of each water quality parameter from each location compared to the WHO standard for both seasons in groundwater of the study area.

Table 3: Comparison of water quality parameters with WHO standards

Parameter (mg/l)	Dry Season		Wet Season		WHO Permissible Standards	Re-mark
	Mean Values	Std. deviation	Mean Values	Std. deviation		
Temp. ($^{\circ}\text{C}$)	27.27 \pm 0.340	2.40	27.47 \pm 0.356	0.622	25	AL
pH	5.41 \pm 0.088	0.62	4.49 \pm 0.077	1.061	6.5 – 8.5	BL
EC ($\mu\text{S}/\text{cm}$)	162.74 \pm 18.013	127.37	186.68 \pm 21.207	20.506	400	WL
Turbidity (NTU)	5.69 \pm 1.108	7.84	6.27 \pm 1.065	0.339	5	WL
TH (mg/l)	51.03 \pm 13.003	91.94	55.53 \pm 12.781	16.327	500	WL
TSS (mg/l)	6.88 \pm 1.280	9.18	11.17 \pm 1.469	8.726	No guideline	NL
TDS (mg/l)	91.16 \pm 10.092	71.36	104.52 \pm 11.874	11.314	500	WL
DO (mg/l)	3.22 \pm 0.234	1.66	4.29 \pm 0.342	1.556	6	AL
BOD ₅ (mg/l)	0.07 \pm 0.030	0.36	0.70 \pm 0.121	1.061	10	WL
COD (mg/l)	4.36 \pm 0.267	1.89	3.92 \pm 0.353	2.263	10 - 20	WL
Total Coli. (MPN/100l)	11.13 \pm 1.637	11.58	11.58 \pm 1.582	17.847	10	AL
Na (mg/l)	9.30 \pm 0.987	6.98	10.34 \pm 1.077	0.212	40	WL
K (mg/l)	1.30 \pm 0.129	0.91	1.74 \pm 0.173	0.000	20	WL
Ca (mg/l)	18.54 \pm 2.285	16.15	21.42 \pm 2.783	3.465	75 - 200	WL
Mg (mg/l)	0.47 \pm 0.054	0.38	0.59 \pm 0.064	0.014	30	AL
SO ₄ (mg/l)	1.00 \pm 0.161	1.14	1.20 \pm 0.213	0.099	250	WL
NO ₃ (mg/l)	0.83 \pm 0.114	0.81	1.06 \pm 0.152	0.106	50	WL
Cl (mg/l)	34.89 \pm 3.774	26.69	39.41 \pm 4.299	4.172	5	AL
HCO ₃ (mg/l)	19.62 \pm 2.360	16.69	21.92 \pm 2.694	2.758	125 – 350	WL
NH ₄ (mg/l)	0.01 \pm 0.002	0.02	0.02 \pm 0.002	0.006	< 1.5	WL
PO ₄ (mg/l)	0.19 \pm 0.024	0.17	0.28 \pm 0.034	0.106	0.3	WL
Fe (mg/l)	0.21 \pm 0.001	0.01	0.22 \pm 0.002	0.01	0.3	WL
Cd (mg/l)	0.0001 \pm 0.000	0.002	0.00 \pm 0.003	0.002	0.003	WL
Cr (mg/l)	0.00 \pm 0.000	0.001	0.00 \pm 0.000	0.001	0.05	WL
Cu (mg/l)	0.20 \pm 0.047	0.246	0.20 \pm 0.035	0.246	2	WL
Pb (mg/l)	0.02 \pm 0.077	0.023	0.02 \pm 0.088	0.023	0.01	AL

KEY: AL – Above Limit, WL – Within Limit, NL – No Limit, Perm. – Permissible, BL – Below Limit

B. COMPARISON OF GROUNDWATER QUALITY PARAMETERS IN WARRI WITH WHO DRINKING WATER STANDARDS

The results of the physico-chemical analyses and microbial composition of groundwater samples collected from the domestic water boreholes are summarized in Table 3. These values were compared to WHO permissible limit.

- **Temperature:** The mean temperature value is 27.27 \pm 2.4 $^{\circ}\text{C}$ and 27.47 \pm 2.52 $^{\circ}\text{C}$ in the dry and wet seasons respectively. While the WHO permissible limit for temperature is 25 $^{\circ}\text{C}$. All values for temperature are well

above permissible limit except for sample locations OGD, UGT, UBJ 2, OGB, WAP, OGU, FGC, OKL, UDR, OTO and OKE in both seasons. 16% of the sampled boreholes had their temperature values within WHO permissible limit and 84% were above the permissible limit in the dry season. While 20% of the sampled boreholes are within limit and 80% are above the WHO permissible in the wet season. Temperature changes could trigger changes in physical, chemical, and microbial processes in the subsurface environment, resulting in groundwater quality changes (Banks, 2008). Carbonate precipitation, silicate dissolution, and mobilization of cations (Na, NH_4 , K, Mg, and Ca), heavy metals and trace elements and dissolved organic carbon (DOC) as well as progression to strongly reductive conditions, such as sulphate reducing and methanogenic conditions, could be observed (Bonte et al., 2013b).

- pH:** The mean pH values are 5.41 ± 0.62 in the dry season and 4.49 ± 0.54 in the wet season and ranges from 4.2 to 6.7 and 3.4 to 5.9 in the dry and wet seasons respectively. All the boreholes had their pH values showing weak acidity and below the WHO permissible limit (6.5 to 8.5) for potable drinking water. This implies that the water in these boreholes were majorly acidic and not recommended for consumption without treatment. Of all the samples of groundwater analysed, 44% have values of pH above the average value of 4.95. This is characteristic of the acidity of the tested water. pH is most important in determining the corrosive nature of water. A sample is considered to be acidic if the pH is below 7, while it is alkaline if the pH is between 7 and 14. In the dry season, where the pH levels are relatively low, the state of other water quality parameters is affected. pH affects mucous membrane, causes bitter taste and corrosion. The lower the pH value the higher is the corrosive nature of water, pH is positively correlated with electrical conductance (Gupta et al., 2009). Acidic water can lead to corrosion of metal pipes and plumbing system, while alkaline water shows disinfection in water. The water quality depletes when metals become more soluble in the water making disease causing pathogens to thrive in the water. This results in indirect health problems to humans (Khan et al., 2013) and also affects the geological formation (Sojobi, 2016) of the soil. The higher pH values observed suggests that carbon dioxide, carbonate-bicarbonate equilibrium is affected more due to change in physicochemical condition (Karanth, 1987). The water could be treated with lime before use to bring pH level to the desired level. pH is changed due to different dissolved gases and solids.
- EC:** EC values range from 40 to 532 $\mu\text{S}/\text{cm}$ with mean concentration of $162.74 \pm 127.37 \mu\text{S}/\text{cm}$ in the dry season and ranges from 46 to 678 $\mu\text{S}/\text{cm}$ with mean value of $62.5 \pm 149.96 \mu\text{S}/\text{cm}$ in the wet season. Concentration limits for EC in all locations are well below the WHO recommendation of 400 $\mu\text{S}/\text{cm}$ apart from APR, UGT, JED, OSA, OGB and EDJ in both seasons. EC and turbidity in 22% of the boreholes are within limit while 78% were above limit in the dry season. Conductivity does not have direct impact on human health. It is determined for such purposes such as determination of mineralization rate (existence of minerals such as potassium, calcium, and sodium) and estimating the number of chemical reagents used to treat water (Cidu et al., 2011; Kavcar et al., 2009; Khan et al., 2013; Muhammad et al., 2011). High conductivity may lead to lowering the aesthetic value of the water by giving mineral taste to the water. High conductivity increases corrosive nature of water. It is critical to monitor the EC of water if it is to be used for industrial and agricultural activities. Water with high conductivity may cause corrosion of metal surface of equipment such as boiler. It is also applicable to home appliances such as water heater system and faucets. Food-plant and habitat-forming plant species are also eliminated by excessive conductivity (Jia et al., 2010; Katsoyiannis and Zouboulis, 2013). 69% of the boreholes had their BOD, COD and DO values well within permissible limits while only 31% had values of these parameters above the permissible limit in the dry season. In the wet season 72% were within limit and 28% were above limits.
- Turbidity:** Turbidity had mean values of $5.69 \pm 7.84 \text{NTU}$ in the dry season and $6.27 \pm 7.53 \text{NTU}$ in the wet season. Standard WHO limits for turbidity is 5NTU. Turbidity is related to the content of diseases causing organisms in water, which may come from soil runoff. All turbidity values are below the standard recommended maximum turbidity limit set by WHO for drinking water except for stations ARB, JKR, SHA, EKP, EFM, JED, UBJ 2, OSM, WAP, EDHE, IGM, UDR, MAM, DST, OKE, MOF, FUP, SHP, ROP, ESR and ROR which were above the recommended limit. The turbidity levels for JKR, EFM, JED, PEM, ENE and UDR are low only in the wet season but are high in the dry season as a result of soil runoff. Lower turbidity values during the dry season are probably due to less groundwater recharge and infiltration. Higher levels of turbidity are associated with disease causing bacteria and indicative of potential pollution and decreased water quality.
- Total Hardness:** Total Hardness (TH) have concentration ranges of 3.72mg/l to 336.29mg/l, with mean level at $51.03 \pm 91.94 \text{mg}/\text{l}$ in the dry season but 3.72mg/l to 336.29mg/l and average level of $55.53 \pm 90.38 \text{mg}/\text{l}$ in the wet season. The total hardness values for all sampling stations are within the WHO permissible limit of 500mg/l. High value of TH is observed in stations OKU, UGT, EDJ, BOA, ORH, MAM, DST and MOF. Poor lathering with soap; deterioration of the quality of clothes; scale forming.
- Total suspended solid (TSS):** The mean values TSS in the dry season and wet seasons are $6.88 \pm 9.18 \text{mg}/\text{l}$, $11.17 \pm 10.39 \text{mg}/\text{l}$ in the wet season. 50% of the groundwater samples analyzed have concentrations of TSS

below the mean value of 9.03mg/l. There is no specified limit for this parameter (WHO, 2011). This tells of the water samples being significantly clear of suspended organic and inorganic particles.

- **The Total dissolved solid (TDS):** The water samples have average values of 91.16±71.36mg/l in the dry season and 104.52±83.96mg/l in the wet season. All locations have values below the WHO recommended standards of 500mg/L in both seasons except in locations BOA and MAM. The amounts of total solids are influenced by organic materials. TDS concentration is affected by the presence of bicarbonates, carbonates, sulphates and chlorides of calcium (Subba Rao et al., 1998; Deepali et al., 2001). TDS causes gastrointestinal irritation (Jain et al., 2003). High value of TDS influences the taste, hardness, and corrosive property of the water (Haran, 2002; Joseph and Jaiprakash, 2000; Subhadra et al., 2003). The high concentrations of TDS are due to leaching of solid wastes from the ground surface as well as enhanced seepage from domestic sewages and some industrial activities within the study area. This suggests that the water is aesthetically unsatisfactory for drinking and bathing. Water containing high TDS concentration may cause laxative or constipation effects, undesirable taste, gastro-intestinal irritation, corrosion or incrustation (Ch, et al., 2016).
- **Dissolved Oxygen (DO):** The mean DO concentration values are 3.22±1.66mg/l in the dry season and 4.29±2.42mg/l in the wet season. In the dry season, locations JKR, OKR, ROP and ESR have concentration limits above the set limit of 6 (WHO, 2011), while in the wet season, locations EKP, UCE, EFM, OGD, UGT, JED, UBJ 1, UBJ 2, OSM, OSA, OGB, WAP, OGU, EDJ, EDHE, FGC, AJA, WAG, ESL, IGM, AGS, BOA, IYA, PEM, ORH, ENE, UDR, OTO, BDE, UPE, MAM, DST, OKE, MOF, FUP and ROR have levels within the standard limit. 18% of the water samples analysed were above the standard limit, suggestive of bacterial and pollutant presence (which could be either untreated or partially treated sewage, organic discharges and also anoxic discharges) in the water. The DO values are below the acceptable limit of 6mg/l (WHO, 2011) in most of the sampling stations. Increase in phytoplankton and microbial activity contribute to low DO values and consequently increase in BOD and COD. The low DO values don't give water the desired tastelessness. Oxygen is known to degrade metals through internal oxidation, therefore high DO values corrode water lines, boilers and heat exchangers.
- **Biochemical oxygen demand (BOD):** Biochemical oxygen demand has mean concentration values of 0.07±0.36MPN/100l in the dry season and 0.7±0.48MPN/100l in the wet season. Forty two (42) locations, OKU, ARB, NCAT, APR, SHA, EKP, UCE, EFM, UGT, JED, UBJ 1, UBJ 2, OSM, OSA, OGB, WAP, OGU, EDJ, AJA, WAG, OKL, OKR, MRQ, ESL, IGM, BOA, IYA, PEM, ORH, UDR, OTO, BDE, UPE, DST, OKE, MOF, FUP, SHP, ROP, ESR, ROR and PTR had concentration limits below the detection levels in the dry season, while in the wet season, all values were within the standard limits apart from a few others which were still below detection limits. Also, in the dry season, the concentration of BOD is completely within set limits. This is typical of water having a low degree of organic pollution. The BOD values are lower than the permissible limit of 10 mg/l (WHO, 2011) in all the groundwater sampling stations in the dry and wet seasons. Though lower than WHO permissible limit, the relatively high BOD values in some locations show that the overall groundwater quality in the study area is doubtful and it raised some concern especially in the dry season. High BOD decreases level of dissolved oxygen.
- **Chemical oxygen demand (COD):** Chemical oxygen demand values range from concentration levels of 1.1 to 9.2mg/l, and with a mean concentration level of 4.36±1.89mg/l in the dry season, while it ranged from 0.3 to 9.2mg/l with a mean value of 3.92±2.49mg/l in the wet season. The COD values are well below the permissible limit of 10 - 20mg/l (WHO, 2011) in all the groundwater sampling locations in dry and wet seasons. COD is representative of pollution by biodegradable and chemically degradable organic matter (Elangovan and Dharmendrakumar, 2013). It is also an indication of organic matter susceptible to oxidation by chemical oxidant which is typical of reduced organic as well as inorganic pollution in the groundwater (Bhanja and Mohanta, 2000). Both BOD and COD are key indicators of the environmental health of a surface water supply.
- **Total coliform:** The biological parameter measured is Total Coliform counts. The bacterial composition of the groundwater analysed had mean concentration of 11.13±11.58MPN/100l and 11.58±11.19 MPN/100l in the dry and wet seasons respectively while the WHO permissible standard is 10NMP/100l. The observed contaminations of groundwater by pathogens may be attributable to the existence of high-water table resulting from high rainfall, soil characteristics or the presence of faecal matter in the study area resulting from poor and failed septic tanks and as well as leachate from unengineered waste dumps which is common during higher recharge period of the year and the shallowness of the aquifers. The presence of coli form bacteria is indicative of faecal contamination. Bacteriologically, 54% of the boreholes had Total Coliform concentrations within the permissible limits with 46% above limit in both the dry and wet seasons. Results of the analyses of biological parameters for sampled domestic boreholes in dry season and wet season are given in Table 3. Domestic borehole systems can become contaminated with potentially harmful bacteria and other microorganisms. Total coliform includes organisms that can survive and grow in water. Hence, they are not used as an indicator of faecal pathogens, but they can be used to assess the cleanliness and integrity of distribution systems (USEPA,

2009). Total coliform bacteria (excluding *E. coli*) should be absent immediately after disinfection, and the presence of these organisms indicates inadequate treatment. The presence of total coliforms in distribution systems and stored water supplies can reveal re-growth (WHO, 2011). Its seasonal comparison states that this parameter is above the standard limit. The obtained values for the total coliform counts in the groundwater samples are significantly high (with an increased associated risk of water borne illnesses), which shows that up to 45 percent of shallow groundwater samples are hydraulically connected to on-site disposal systems and as such not fit for drinking.

- **Sodium:** Na has average limits of 9.3 ± 6.98 mg/l in the dry season and mean concentrations of 10.34 ± 7.62 mg/l in the wet season. These are well below WHO standard limit of 40 mg/l. Sodium concentration is one of the important parameters in the classification of irrigation water. Water containing a large proportion of sodium with carbonate as predominant anion are termed alkaline water and those with chloride or sulphate as predominant anion are termed as saline water and these affects plant growth (Todd, 2007). Majority of the study area has the range of less than 15 mg/l. Maximum ranges of more than 20 mg/l is located as small patches in the low-lying areas and in the clay zones.
- **Potassium:** Mean concentration values of K are 1.3 ± 0.91 mg/l in the dry season and 1.74 ± 1.22 mg/l in the wet season. The values of potassium are below the WHO permissible limit of 20 mg/l in all the sampling locations.
- **Calcium:** Ca concentration mean value is 18.54 ± 16.15 mg/l in the dry season and 21.42 ± 19.68 mg/l in the wet season. The WHO limit for Ca is 75 mg/l, values for all locations were less than 100 mg/l for both seasons. The presence of Ca^{+} in groundwater is a good indicator of its hardness. The calcium values are within the stipulated standard by the WHO in all of the groundwater sampling locations in both seasons except for location APR. The presence of calcium causes hardness of water and interferes in dyeing, textiles, paper industry etc.
- **Magnesium:** The Mg parameter had values from 0.1 to 1.9 mg/l, and a mean concentration of 0.47 ± 0.38 mg/l, and from 0.11 to 2.4 mg/l, and mean value of 0.59 ± 0.45 mg/l in the dry and wet seasons respectively. Values for all locations in the study area are well below the acceptable limit. High concentration of Mg may cause laxative effect particularly on new boreholes and other problems associated with calcium in water. Mg deficiency is associated with structural and functional changes. It is essential as an activator of many enzyme systems (Narain and Chauhan, 2000). However, 78% of the boreholes had their magnesium concentrations exceeding the limit during the wet season with only 14% within the standard limit in the dry season.
- **Sulphate (SO_4):** The obtained SO_4 concentration mean values are 1 ± 1.14 mg/l and 1.2 ± 1.51 mg/l in the dry and wet seasons respectively. SO_4 values for all of the samples are within the WHO maximum permissible limits of 250 mg/l. High limits of sulphate impart a bitter taste to water (Bhalerao and Khan, 2000). It may increase the acidity and toxicity of open-wells and borehole water resources. Sulphate in water affects taste, causes gastro-intestinal irritation and calcium sulphate scale. Its ingestion causes dehydration and laxative effects.
- **Nitrate (NO_3):** The NO_3 concentration mean value of 0.83 ± 0.81 mg/l in the dry season and 1.06 ± 1.08 mg/l in the wet season were recorded. The nitrate values are less than the WHO permissible limit of 50 mg/l all through the sampling stations. Nitrate in drinking water is highly deleterious to human health and it is recommended that nitrate in water for domestic use be less than 10 mg/l of water. Its effect on infants below the age of six months include shortness of breath and blue-baby syndrome. High nitrate and lead levels observed have been associated with agrochemicals and wastewater from farms and homes.
- **Chloride:** Chloride had average values of 34.89 ± 26.69 mg/l for the dry season and 39.41 ± 30.4 mg/l in the wet season. The values are within the standard requirement of 5 mg/l by WHO in both seasons. Excessive chloride in drinking water causes eye/nose irritation, stomach discomfort and increases the corrosive character of water.
- **Bicarbonate (HCO_3):** The HCO_3 mean concentration value stands at 19.62 ± 16.69 mg/l and 21.92 ± 19.05 mg/l in the dry and wet seasons respectively. All locations have values for this parameter <125 mg/l in both seasons which are within the WHO recommended limit of 125 mg/l. Carbonate causes product imbalance, unsatisfactory production and short product life. Nitrate and chloride concentration exceeding the permissible limits is an indicator of pollution. High incidence of nitrate can be attributed to be the major cause of water related diseases such as typhoid, cholera, diarrhea, jaundice and methemoglobinemia/blue baby syndrome in humans (Durfor and Baker, 1964; Hudak, 2000; WHO, 1985). Non wholesome water supply, poor sanitation and inefficient solid waste collection and disposal system worsen the situation of water contamination (Degaonkar, 2003). Furthermore, of the samples analysed 35% of them have concentration above the mean and 65% lesser than it. These concentrations are thus fairly acceptable and are representative of the level of hardness of the water. It is clear from Table 3 that the concentration of cations is lower in the order; $\text{Ca} < \text{Na} < \text{K} < \text{Mg}$.
- **Ammonium (NH_4):** Measured NH_4 levels indicate mean levels of 0.01 ± 0.02 mg/l in the dry season and 0.02 ± 0.02 mg/l in the wet season. Permissible WHO standard for NH_4 is below 1.5 mg/l. The values of sample

concentrations are less than 1.5mg/l in both seasons, with NCAT, SHA, EKP, UCE, UBJ 2, OSM, OGU, FGC, AJA, WAG, OKL, WAP, ESL, IGM, MAM, MOF, ROP, ESR and PTR stations recording levels below detectable limits. NH_4 causes corrosion of copper and zinc alloys by formation of complex ions.

- Phosphate (PO_4):** The analysed PO_4 concentration mean value of $0.19 \pm 0.17 \text{ mg/l}$ in the dry season and $0.28 \pm 0.24 \text{ mg/l}$ in the wet season were recorded. In the dry season, locations APR, EFM, UGT, UBJ 1, OSA, OGB, EDJ, OKR, ORH, SHP and ROR have values of PO_4 above the acceptable limits, and in the wet season, locations EFG, APR, EFM, OGD, UGT, UBJ 1, OSA, OGB, EDHE, OKR, ESL, ORH, SHP and ROR have concentration limits above recommended standards. The phosphate values exceed the permissible limit of 0.3 mg/l (WHO, 2011) in sampling locations EFG, APR, EFM, OGD, UGT, UBJ 1, OSA, OGB, EDJ, EDHE, OKR, ESL, ORH, SHP and ROR in wet and dry seasons. Persistence of high concentrations of phosphate in groundwater body can reduce its recreational use and also inhibit its use, stimulate microbial growth, rancidity and mould growth (Oluyemi et al., 2010). 75% of the boreholes had their PO_4 values within permissible limit in both seasons.
- Iron:** The iron content of the study location suggests mean concentration value of $0.21 \pm 0.01 \text{ mg/l}$ in the dry season and $0.22 \pm 0.01 \text{ mg/l}$ in the wet season. The iron levels in both seasons, show concentration levels well below WHO standard limit of 0.3 mg/l for drinking water. Also, iron was discovered to show increased concentration levels in all study locations for the wet season over the dry, except in SHA and FUP areas. This is suggestive of the action of seepage and corrosion infiltrating the groundwater in the study area. Thus, indicating toxicity, and its consumption would cause costly damages and other issues. Iron in water gives it a reddish-brown colour and increase turbidity (Mkwate et al., 2017). Presence of Iron in drinking water in large quantity is responsible for hemochromatosis, impart objectionable taste and colour (WHO, 2008; Rowe, et al., 1995). Iron will cause staining of laundry, dishes, utensils and even glassware. Iron can affect the flavours and colour of food and water. It may react with tannins in coffee, tea and some alcoholic beverages to produce a black sludge which affects both taste and appearance (Agunwamba, 2000; Al-Layla et al., 1978). This study further supports the report of high Iron concentrations in groundwater in Nigeria (WHO, 2008).
- Cadmium:** The mean value of cadmium is $0.00 \pm 0.002 \text{ mg/l}$ in the dry season, and $0.00 \pm 0.002 \text{ mg/l}$ in the wet season. All locations are well above detection limits for this parameter except for 21 locations with IYA and ESR having limits of $<0.001 \text{ mg/l}$ in both seasons. The Cd values are all within the permissible limit of 0.003 mg/l in all the sampling locations in dry and wet seasons except for stations JED, UBJ 1 and UBJ 2 which were observed to be more than the WHO standard limit in both seasons. The groundwater in these areas may not be safe for drinking purpose especially without treatment because of heavy metal contamination (Chamon et al., 2005). Excess Cadmium in drinking water quality can lead to severe gastro-intestinal upset (WHO, 1984) and also renal or kidney problems (Schmoll, et al., 2006). Cadmium in water causes carcinogenic ailments (Dahunsi et al., 2014; Khan et al., 2013), vomiting and diarrhea and lower levels for longer period can cause kidney impairment (USEPA, 1993; Mkwate et al., 2017).
- Chromium:** the mean concentration of $0.00 \pm 0.001 \text{ mg/l}$ in the dry season and $0.00 \pm 0.001 \text{ mg/l}$ in the wet season were recorded. All measured locations are within the acceptable limit of 0.05 mg/l . The Cr values did not exceed the permissible limit of 0.05 mg/l (WHO, 2011) in all the groundwater sampling stations in dry and wet seasons except for stations JED, UBJ 1 and UBJ 2 which showed increased concentrations more than the required limit. Though, Chromium was found to be within the standard limit of WHO (2006) for drinking water quality, high concentration of Chromium could cause digestive tract cancer in man, or increase the risk of lung cancer in man (Todd and Mays, 2005).
- Copper:** The mean Cu concentration value was $0.2 \pm 0.246 \text{ mg/l}$ in the dry season and $0.2 \pm 0.246 \text{ mg/l}$ in the wet season. The Cu values are lower than the permissible limit of 2 mg/l (WHO, 2011) in all the groundwater sampling stations in dry and wet seasons except for stations JED, UBJ 2, OSM and EDHE which were in excess concentrations of 2 mg/l . Copper in water affects both its quality and safety. Presence of Copper in excess in drinking water is responsible for nausea (Araya, et al. 2010). A high level of copper in water gives it a metallic or unpleasant bitter taste. Consumption of high level of copper can cause nausea, vomiting, diarrhea, gastric (stomach) complaints and headache. Cu was not detected in ARB, NCAT, OGD, EDHE, IGM, AGS, OKE, UGT, OSA, OKL, OKR and MRQ study locations.
- Lead:** The mean values are $0.02 \pm 0.023 \text{ mg/l}$ and $0.02 \pm 0.023 \text{ mg/l}$ for the dry and wet seasons. The Pb values were all below the permissible limit of 0.01 mg/l (Table 3) in all the groundwater sampling stations in dry and wet seasons. Locations SHP and ROR showed increased Pb content in the dry season while, locations UDR and ROP revealed reduced Pb concentration in the wet season. High concentrations cause kidney damage, brain damage, miscarriage in pregnant woman, convulsion and neurological damage in children and damage to the male reproductive organ (Khan et al., 2013; Owamah, 2019; USEPA, 1993). High Pb levels are generally indicative of potential pollution and decreased water quality. Cadmium and Pb, which have no known beneficial effects, may become toxic to plants and animals if their concentrations exceed certain values (Adriano, 1996).

From the foregoing, it could be inferred that, the groundwater quality in Warri and its environs is contaminated more in the wet season than in the dry season and the reason for this, are as highlighted in Section 6.2 above. The level of detected heavy metals in groundwater quality in the study area further confirm the findings of (Tengrui, et al., 2007) who reported that, these metals are brought into groundwater system by human activities such as industrial, landfill among others.

C. WATER QUALITY INDEX (WQI)

The result of the calculated WQI for the study area is presented in Table 4 and Table 5, for dry and wet seasons respectively. The spatial distribution of Water Quality Index (Figs 2a and b) shows the highest quality (12.5% and 40% of groundwater samples fell into excellent to good quality water during both seasons). These two categories characterize the southern and the southeastern part of the aquifer, corresponding to the recharge zone. The water samples within poor quality, very poor quality, and unsuitable for drinking purposes contributed 35.5%, 5%, and 7.5% of groundwater samples, respectively in the wet season with no remarkable difference in the dry season. were found in the central and northern part of the aquifer.

D. WATER QUALITY INDEX (WQI)

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Table 4: Water Quality Index (WQI) Calculation (dry season)

Water Quality Parameters	QUALITY RATING (qi)									Parameter Index (Si) = qi * Wi									WQI	Type of Water									
	pH	TDS	Cl	SO ₄	HCO ₃	NO ₃	Ca	Mg	Na	pH	TDS	Cl	SO ₄	HCO ₃	NO ₃	Ca	Mg	Na											
WHO Standard Values (Si)	7.5	500	250	100	100	50	75	0.2	200	qi = (ci/si)*100																			
Relative Weight (Wi)	0.122	0.148	0.155	0.132	0.164	0.076	0.092	0.076	0.076																				
SAMPLE LOCATION CODE	MEASURED VALUES (Ci)									pH	TDS	Cl	SO ₄	HCO ₃	NO ₃	Ca	Mg	Na	pH	TDS	Cl	SO ₄	HCO ₃	NO ₃	Ca	Mg	Na		
OKU	6.92	112.00	2.67	0.13	2.92	0.32	3.21	0.67	1.74	92.27	22.40	1.07	0.13	2.92	0.64	4.28	335.00	0.87	11.26	3.32	0.17	0.02	0.48	0.05	0.39	25.46	0.07	41.20	Good
FFG	3.89	150.00	25.58	1.12	0.01	0.72	6.75	3.14	1.77	51.87	30.00	10.23	1.12	0.01	1.44	9.00	1570.00	0.89	6.33	4.44	1.59	0.15	0.00	0.11	0.83	119.32	0.07	132.83	Unfit for Drinking
ARB	6.84	10.11	18.78	8.36	3.12	10.34	13.94	14.33	4.36	91.20	2.02	7.51	8.36	3.12	20.68	18.59	7165.00	2.18	11.13	0.30	1.16	1.10	0.51	1.57	1.71	544.54	0.17	562.19	Unfit for Drinking
NCAT	5.74	10.07	8.17	7.89	1.94	10.16	13.16	8.42	4.73	76.53	2.01	3.27	7.89	1.94	20.32	17.55	4210.00	2.37	9.34	0.30	0.51	1.04	0.32	1.54	1.61	319.96	0.18	334.80	Unfit for Drinking
APR	7.05	32.00	26.41	31.57	3.16	2.13	4.99	1.32	0.45	94.00	6.40	10.56	31.57	3.16	4.26	6.65	660.00	0.23	11.47	0.95	1.64	4.17	0.52	0.32	0.61	50.16	0.02	69.85	Poor
JOR	6.00	227.00	12.01	8.44	35.00	2.38	1.18	0.09	0.08	80.00	45.40	4.80	8.44	35.00	4.76	1.57	45.00	0.04	9.76	6.72	0.74	1.11	5.74	0.36	0.14	3.42	0.00	28.01	Good
SHA	5.90	152.00	7.90	0.13	0.18	0.00	3.50	1.92	14.56	78.67	30.40	3.16	0.13	0.18	0.00	4.67	960.00	7.28	9.60	4.50	0.49	0.02	0.03	0.00	0.43	72.96	0.55	88.58	Poor
EXP	4.48	52.00	20.02	0.18	0.10	0.07	2.23	0.97	4.92	59.73	10.40	8.01	0.18	0.10	0.14	2.97	485.00	2.46	7.29	1.54	1.24	0.02	0.02	0.01	0.27	36.86	0.19	47.44	Good
UCE	5.72	84.75	6.06	0.14	3.55	0.48	1.04	1.24	1.99	76.27	16.95	2.42	0.14	3.55	0.97	1.38	620.00	1.00	9.30	2.51	0.38	0.02	0.58	0.07	0.13	47.12	0.08	60.19	Poor
EFM	6.40	306.00	25.03	14.94	32.00	1.98	1.61	0.12	0.09	85.33	61.20	10.01	14.94	32.00	3.96	2.15	60.00	0.05	10.41	9.06	1.55	1.97	5.25	0.30	0.20	4.56	0.00	33.30	Good
OGD	6.20	254.00	14.80	0.01	19.85	0.01	2.04	4.20	1.24	82.67	50.80	5.92	0.01	19.85	0.01	2.73	2100.00	0.62	10.09	7.52	0.92	0.00	3.26	0.00	0.25	159.60	0.05	181.68	Unfit for Drinking
UGT	6.10	17.00	6.50	1.65	7.32	0.75	4.85	3.31	2.79	81.33	3.40	2.60	1.65	7.32	1.50	6.47	1655.00	1.40	9.92	0.50	0.40	0.22	1.20	0.11	0.59	125.78	0.11	138.84	Unfit for Drinking
JED	6.40	79.60	4.50	2.52	3.00	12.46	2.13	0.14	0.05	85.33	15.92	1.80	2.52	3.00	24.92	2.84	70.00	0.03	10.41	2.36	0.28	0.33	0.49	1.89	0.26	5.32	0.00	21.35	Excellent
UBJ1	6.40	76.60	51.97	4.00	42.79	0.00	2.33	1.25	3.52	85.33	15.32	20.79	4.00	42.79	0.00	3.11	625.00	1.76	10.41	2.27	3.22	0.53	7.02	0.00	0.29	47.50	0.13	71.37	Poor
UBJ2	4.10	63.78	4.50	2.52	18.00	12.49	2.13	0.14	0.05	54.67	12.76	1.80	2.52	18.00	24.98	2.84	70.00	0.03	6.67	1.89	0.28	0.33	2.95	1.90	0.26	5.32	0.00	19.60	Excellent
OSM	7.44	228.54	127.91	15.86	0.31	1.32	0.89	1.70	19.98	99.20	45.71	51.16	15.86	0.31	2.64	1.19	850.00	9.99	12.10	6.76	7.93	2.09	0.05	0.20	0.11	64.60	0.76	94.61	Very Poor
OSA	6.72	36.99	14.81	0.91	0.31	0.30	0.24	0.32	2.56	89.60	7.40	5.92	0.91	0.31	0.60	0.32	160.00	1.28	10.93	1.09	0.92	0.12	0.05	0.05	0.03	12.16	0.10	25.45	Excellent
OGB	7.00	14.90	1.70	0.00	4.56	0.02	1.42	0.12	1.63	93.33	2.98	0.68	0.00	4.56	0.03	1.90	60.00	0.82	11.39	0.44	0.11	0.00	0.75	0.00	0.17	4.56	0.06	17.48	Excellent
WAP	7.20	25.90	2.10	0.01	23.48	0.02	2.64	15.00	1.66	96.00	5.18	0.84	0.01	23.48	0.03	3.52	7500.00	0.83	11.71	0.77	0.13	0.00	3.85	0.00	0.32	570.00	0.06	586.85	Unfit for Drinking
OGU	5.90	171.10	16.10	0.06	0.08	0.01	3.20	2.13	13.76	78.67	34.22	6.44	0.06	0.08	0.01	4.27	1065.00	6.88	9.60	5.06	1.00	0.01	0.01	0.00	0.39	80.94	0.52	97.54	Very Poor
EDJ	7.00	15.00	1.40	0.01	20.02	0.00	2.11	0.56	0.34	93.33	3.00	0.56	0.01	20.02	0.00	2.81	280.00	0.17	11.39	0.44	0.09	0.00	3.28	0.00	0.26	21.28	0.01	36.75	Good
EDHE	7.60	122.00	6.51	2.66	18.00	10.72	2.40	0.43	0.06	101.33	24.40	2.60	2.66	18.00	21.44	3.20	215.00	0.03	12.36	3.61	0.40	0.35	2.95	1.63	0.29	16.34	0.00	37.95	Good
FGC	6.20	22.20	2.60	0.00	8.21	0.01	0.84	3.03	1.19	82.67	4.44	1.04	0.00	8.21	0.01	1.12	1515.00	0.60	10.09	0.66	0.16	0.00	1.35	0.00	0.10	115.14	0.05	127.54	Unfit for Drinking
AJA	6.00	87.00	4.60	0.09	5.00	0.00	1.58	9.31	1.20	80.00	17.40	1.84	0.09	5.00	0.00	2.11	4655.00	0.60	9.76	2.58	0.29	0.01	0.82	0.00	0.19	353.78	0.05	367.47	Unfit for Drinking
WAG	6.50	14.90	1.70	0.00	0.04	0.01	1.83	4.73	2.96	86.67	2.98	0.68	0.00	0.04	0.02	2.44	2365.00	1.48	10.57	0.44	0.11	0.00	0.01	0.00	0.22	179.74	0.11	191.21	Unfit for Drinking
OKL	5.40	146.00	10.90	0.25	24.53	0.02	2.00	1.21	4.67	72.00	29.20	4.36	0.25	24.53	0.04	2.67	605.00	2.34	8.78	4.32	0.68	0.03	4.02	0.00	0.25	45.98	0.18	64.24	Poor
OKR	5.00	112.00	10.80	0.00	0.09	0.00	0.97	0.44	4.23	66.67	22.40	4.32	0.00	0.09	0.00	1.29	220.00	2.12	8.13	3.32	0.67	0.00	0.01	0.00	0.12	16.72	0.16	29.13	Good
NRQ	5.30	79.00	6.40	0.00	19.01	1.00	1.92	1.62	0.37	70.67	15.80	2.56	0.00	19.01	2.00	2.56	810.00	0.19	8.62	2.34	0.40	0.00	3.12	0.15	0.24	61.56	0.01	76.44	Very Poor
ESL	4.47	239.45	15.18	1.75	0.00	30.00	8.00	4.00	0.23	59.60	47.89	6.07	1.75	0.00	60.00	10.67	2000.00	0.12	7.27	7.09	0.94	0.23	0.00	4.56	0.98	152.00	0.01	173.08	Unfit for Drinking
IGN	7.40	294.70	104.00	45.78	7.70	31.24	14.90	9.89	10.95	98.67	58.94	41.60	45.78	7.70	62.48	19.87	4945.00	5.48	12.04	8.72	6.45	6.04	1.26	4.75	1.83	375.82	0.42	417.33	Unfit for Drinking
AGS	6.70	289.00	11.50	0.32	6.54	0.01	2.11	0.15	1.57	89.33	50.00	4.60	0.32	6.54	0.01	2.81	75.00	0.79	10.90	7.40	0.71	0.04	1.07	0.00	0.26	5.70	0.06	26.15	Good
BOA	6.60	598.00	4.21	0.14	3.84	0.47	2.25	1.86	1.68	88.00	119.60	1.68	0.14	3.84	0.94	3.00	930.00	0.84	10.74	17.70	0.26	0.02	0.63	0.07	0.28	70.68	0.06	100.44	Unfit for Drinking
IYA	5.40	192.00	9.20	0.25	0.18	0.00	1.07	2.22	11.25	72.00	38.40	3.68	0.25	0.18	0.00	1.43	1110.00	5.63	8.78	5.68	0.57	0.03	0.03	0.00	0.13	84.36	0.43	100.02	Unfit for Drinking
PEM	6.20	58.00	5.50	0.01	2.90	0.00	1.34	2.31	4.32	82.67	11.60	2.20	0.01	2.90	0.00	1.79	1155.00	2.16	10.09	1.72	0.34	0.00	0.48	0.00	0.16	87.78	0.16	100.73	Unfit for Drinking
ORH	7.20	328.00	1.71	0.12	1.69	0.24	4.23	0.83	0.83	96.00	65.60	0.68	0.12	1.69	0.48	5.64	415.00	0.42	11.71	9.71	0.11	0.02	0.28	0.04	0.52	31.54	0.03	53.95	Poor
ENE	4.38	36.57	2.83	2.98	0.00	0.33	8.00	4.00	1.82	58.40	7.31	1.13	2.98	0.00	0.66	10.67	2000.00	0.91	7.12	1.08	0.18	0.39	0.00	0.05	0.98	152.00	0.07	161.88	Unfit for Drinking
UDR	6.30	154.50	9.60	0.20	0.15	0.00	2.06	0.94	2.45	84.00	30.90	3.84	0.20	0.15	0.00	2.75	470.00	1.23	10.25	4.57	0.60	0.03	0.02	0.00	0.25	35.72	0.09	51.53	Poor
OTO	6.10	15.10	1.40																										

Table 5: WQI calculation for wet season

Water Quality Parameters	pH	TDS	Cl	SO ₄	HCO ₃	NO ₃	Ca	Mg	Na	QUALITY RATING (qi)										Parameter Index (Si) = qi * Wi										WQI	Type of Water						
WHO Standard Values (Si)	7.5	500	250	100	100	50	75	0.2	200	qi = (ci/si)*100																											
Relative Weight (Wi)	0.122	0.148	0.155	0.132	0.164	0.076	0.092	0.076	0.076																												
SAMPLE LOCATION CODE	MEASURED VALUES (Ci)									pH	TDS	Cl	SO ₄	HCO ₃	NO ₃	Ca	Mg	Na	pH	TDS	Cl	SO ₄	HCO ₃	NO ₃	Ca	Mg	Na										
OKU	7.02	130.00	4.76	0.26	7.72	0.24	1.52	1.09	0.54	93.60	26.00	1.90	0.26	7.72	0.48	2.03	545.00	0.27	11.42	3.85	0.30	0.03	1.27	0.04	0.19	41.42	0.02	58.53						Poor			
EFG	4.49	160.22	29.85	0.73	0.41	0.64	5.06	1.38	0.51	59.87	32.04	11.94	0.73	0.41	1.28	6.75	690.00	0.26	7.30	4.74	1.85	0.10	0.07	0.10	0.62	52.44	0.02	67.24						Poor			
ARB	7.34	21.33	20.78	5.91	7.92	9.85	6.97	6.83	2.08	97.87	4.27	8.31	5.91	7.92	19.70	9.29	3415.00	1.04	11.94	0.63	1.29	0.78	1.30	1.50	0.85	259.54	0.08	277.91						Unfit for Drinking			
NCAT	6.34	28.07	19.92	5.44	2.34	9.67	6.19	6.66	2.45	84.53	5.61	7.97	5.44	2.34	19.34	8.25	3330.00	1.23	10.31	0.83	1.24	0.72	0.38	1.47	0.76	253.08	0.09	268.88						Unfit for Drinking			
APR	6.95	42.50	38.16	29.21	3.56	2.05	3.30	0.44	1.83	92.67	8.50	15.26	29.21	3.56	4.10	4.40	220.00	0.92	11.31	1.26	2.37	3.86	0.58	0.31	0.40	16.72	0.07	36.87						Good			
JKR	6.06	239.56	10.10	5.99	39.80	2.30	0.51	0.09	2.20	80.80	47.91	4.04	5.99	39.80	4.60	0.68	45.00	1.10	9.86	7.09	0.63	0.79	6.53	0.35	0.06	3.42	0.08	28.81						Good			
SHA	6.00	167.45	5.09	0.62	0.58	0.00	1.81	0.56	9.52	80.00	33.49	2.04	0.62	0.58	0.00	2.41	280.00	4.76	9.76	4.96	0.32	0.08	0.10	0.00	0.22	21.28	0.36	37.07						Good			
EKP	4.78	70.00	31.77	0.12	0.50	0.05	0.54	0.79	2.64	63.73	14.00	12.71	0.12	0.50	0.10	0.72	395.00	1.32	7.78	2.07	1.97	0.02	0.08	0.01	0.07	30.02	0.10	42.11						Good			
UCE	5.92	74.57	8.55	0.12	8.35	0.40	0.65	0.52	1.22	78.93	14.91	3.42	0.12	8.35	0.80	0.87	260.00	0.61	9.63	2.21	0.53	0.02	1.37	0.06	0.08	19.76	0.05	33.70						Good			
EFM	6.70	306.56	23.30	12.49	36.80	1.90	0.08	1.88	2.19	89.33	61.31	9.32	12.49	36.80	3.80	0.11	940.00	1.10	10.90	9.07	1.44	1.65	6.04	0.29	0.01	71.44	0.08	100.92						Unfit for Drinking			
OGD	5.70	236.00	16.08	0.01	24.65	0.01	0.35	2.44	1.04	76.00	47.20	6.43	0.01	24.65	0.01	0.47	1220.00	0.52	9.27	6.99	1.00	0.00	4.04	0.00	0.04	92.72	0.04	114.10						Unfit for Drinking			
UGT	6.20	29.60	8.05	1.26	7.72	0.67	3.16	1.55	0.51	82.67	5.92	3.22	1.26	7.72	1.34	4.21	775.00	0.26	10.09	0.88	0.50	0.17	1.27	0.10	0.39	58.90	0.02	72.30						Poor			
JED	7.00	81.10	6.09	0.07	3.40	11.97	0.44	1.32	2.23	93.33	16.22	2.44	0.07	3.40	23.94	0.59	660.00	1.12	11.39	2.40	0.38	0.01	0.56	1.82	0.05	50.16	0.08	66.85						Poor			
UBJ 1	6.90	92.09	63.72	3.61	47.59	0.01	0.64	0.51	1.24	92.00	18.42	25.49	3.61	47.59	0.02	0.85	255.00	0.62	11.22	2.73	3.95	0.48	7.80	0.00	0.08	19.38	0.05	45.69						Good			
UBJ 2	4.70	73.87	6.50	0.07	22.80	12.00	4.84	1.62	2.23	62.67	14.77	2.60	0.07	22.80	24.00	6.45	810.00	1.12	7.65	2.19	0.40	0.01	3.74	1.82	0.59	61.56	0.08	78.05						Very Poor			
OSM	4.20	241.06	125.19	13.41	0.71	1.24	0.80	0.06	14.94	56.00	48.21	50.08	13.41	0.71	2.48	1.07	30.00	7.47	6.83	7.14	7.76	1.77	0.12	0.19	0.10	2.28	0.57	26.75						Good			
OSA	7.12	48.54	16.17	0.52	0.71	0.03	6.73	0.44	0.28	94.93	9.71	6.47	0.52	0.71	0.06	8.97	220.00	0.14	11.58	1.44	1.00	0.07	0.12	0.00	0.83	16.72	0.01	31.77						Good			
OGB	7.10	27.54	0.32	0.00	9.36	0.01	0.27	0.64	0.65	94.67	5.51	0.13	0.00	9.36	0.02	0.36	320.00	0.33	11.55	0.82	0.02	0.00	1.54	0.00	0.03	24.32	0.02	38.30						Good			
WAP	7.20	25.00	0.03	0.01	28.28	0.02	0.95	7.50	0.62	96.00	5.00	0.01	0.01	28.28	0.03	1.27	3750.00	0.31	11.71	0.74	0.00	0.00	4.64	0.00	0.12	285.00	0.02	302.24						Unfit for Drinking			
OGU	6.30	153.50	18.01	0.33	4.88	0.02	1.51	0.37	8.72	84.00	30.70	7.20	0.33	4.88	0.04	2.01	185.00	4.36	10.25	4.54	1.12	0.04	0.80	0.00	0.19	14.06	0.33	31.33						Good			
EDJ	7.30	33.00	3.04	0.01	24.82	0.01	0.42	0.20	1.94	97.33	6.60	1.22	0.01	24.82	0.02	0.56	100.00	0.97	11.87	0.98	0.19	0.00	4.07	0.00	0.05	7.60	0.07	24.84						Excellent			
EDHE	7.80	136.60	8.15	2.27	22.80	10.27	0.71	0.27	2.22	104.00	27.32	3.26	2.27	22.80	20.54	0.95	135.00	1.11	12.69	4.04	0.51	0.30	3.74	1.56	0.09	10.26	0.08	33.27						Good			
FGC	5.90	37.00	4.06	0.39	13.01	0.01	0.85	1.36	1.09	78.67	7.40	1.62	0.39	13.01	0.01	1.13	680.00	0.55	9.60	1.10	0.25	0.05	2.13	0.00	0.10	51.68	0.04	64.96						Poor			
AJA	5.60	100.50	6.40	0.09	5.40	0.01	5.39	7.55	1.08	74.67	20.10	2.56	0.09	5.40	0.02	7.19	3775.00	0.54	9.11	2.97	0.40	0.01	0.89	0.00	0.66	286.90	0.04	300.98						Unfit for Drinking			
WAG	7.10	29.80	3.07	0.00	5.44	0.04	0.14	2.97	0.68	94.67	5.96	1.23	0.00	5.44	0.08	0.19	1485.00	0.34	11.55	0.88	0.19	0.00	0.89	0.01	0.02	112.86	0.03	126.42						Unfit for Drinking			
OKL	5.90	128.00	14.09	0.14	29.33	0.02	0.31	0.55	2.39	78.67	25.60	5.64	0.14	29.33	0.04	0.41	275.00	1.20	9.60	3.79	0.87	0.02	4.81	0.00	0.04	20.90	0.09	40.12						Good			
OKR	5.40	129.50	12.08	0.00	4.89	0.00	0.72	1.32	1.95	72.00	25.90	4.83	0.00	4.89	0.00	0.96	660.00	0.98	8.78	3.83	0.75	0.00	0.80	0.00	0.09	50.16	0.07	64.49						Poor			
MRQ	5.40	88.00	8.04	0.00	23.81	0.51	1.23	0.56	1.91	72.00	17.60	3.22	0.00	23.81	1.02	1.64	280.00	0.96	8.78	2.60	0.50	0.00	3.90	0.08	0.15	21.28	0.07	37.37						Good			
ESL	4.77	257.35	17.18	1.61	0.01	29.51	1.03	2.24	2.05	63.60	51.47	6.87	1.61	0.01	59.02	1.37	1120.00	1.03	7.76	7.62	1.07	0.21	0.00	4.49	0.13	85.12	0.08	106.47						Unfit for Drinking			
ICM	6.90	304.70	106.11	43.33	12.50	29.28	13.21	8.13	5.91	92.00	60.94	42.44	43.33	12.50	58.56	17.61	4065.00	2.96	11.22	9.02	6.58	5.72	2.05	4.45	1.62	308.94	0.22	349.83						Unfit for Drinking			
AGS	6.30	232.41	13.05	0.07	11.34	0.01	0.42	0.14	0.71	84.00	46.48	5.22	0.07	11.34	0.01	0.56	70.00	0.36	10.25	6.88	0.81	0.01	1.86	0.00	0.03	5.32	0.03	25.20						Good			
BOA	6.60	581.60	6.12	0.13	8.64	0.23	0.35	0.10	1.53	88.00	116.32	2.45	0.13	8.64	0.46	0.47	50.00	0.77	10.74	17.22	0.38	0.02	1.42	0.03	0.04	3.80	0.06	33.70						Good			
IYA	6.00	185.50	11.02	0.14	0.58	0.00	0.62	0.46	6.21	80.00	37.10	4.41	0.14	0.58	0.00	0.83	230.00	3.11	9.76	5.49	0.68	0.02	0.10	0.00	0.08	17.48	0.24	33.84						Good			
PEM	6.80	76.00	7.05	0.01	3.30	0.00	0.35	0.55	2.04	90.67	15.20	2.82	0.01	3.30	0.00	0.47	275.00	1.02	11.06	2.25	0.44	0.00	0.54	0.00	0.04	20.90	0.08	35.31						Good			
ORH	7.70	335.40	2.17	0.27	2.09	0.16	2.54	0.39	1.48	102.67	67.08	0.87	0.27	2.09	0.32	3.39	195.00	0.74	12.53	9.93	0.13	0.04	0.34	0.02	0.31	14.82	0.06	38.18						Good			
ENE	4.88	37.07	4.38	2.59	0.01	0.23	1.03	2.24	0.46	65.07	7.41	1.75	2.59	0.01	0.46	1.37	11																				

Table 6: Number/percentage of boreholes within each WQI index range

Water quality index range	Type of water quality	No/Percentage of boreholes during dry season within each range	No/Percentage of boreholes during wet season within each range
0 – 25	Excellent	17 (34%)	16 (32%)
26 – 50	Good	22 (44%)	20 (40%)
51 – 75	Poor	5 (10%)	6 (12%)
76 – 100	Very poor	5 (10%)	7 (14%)
> 100	Unsuitable	1 (2%)	1 (2%)
Total		50 (100%)	50 (100%)

The WQI distribution maps in the study area for both dry and wet seasons are presented in Fig.2a and Fig 2b.

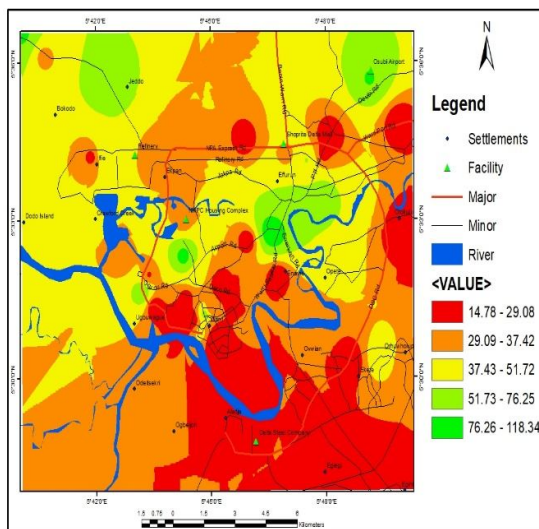


Fig.2a: Map showing water quality index distribution in the dry season

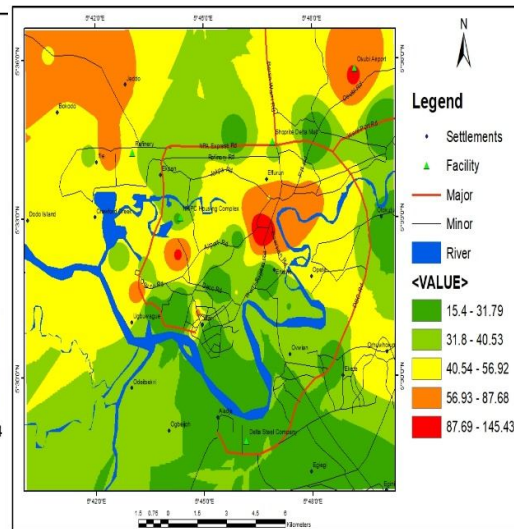


Fig. 2b: Map showing water quality index distribution in the wet season

From the results of WQI classification, only 34% were placed as Excellent, 44% were Good, 10% were Poor, 10% were Very poor and 2% were unsuitable for drinking purposes in the dry season, while in the wet season only 32% were placed as Excellent, 40% were Good, 12% were Poor, 14% were Very poor and 2% were unsuitable for drinking as stated earlier in Table 6. Though the concentration of water quality parameters were higher in the wet season, the WQI was better in the wet season. This could be attributed to dilution and some of the pollutants that would have infiltrated and percolated into groundwater are being transported into surrounding rivers and creeks. Also, WQI is based on chemical parameters only as biological assessments are not included in WQI evaluation. From the rating, domestic boreholes in Warri are moderately suitable for drinking but will require treatment. On the whole, the studied locations significantly indicate contamination from pollution sources, however, this influence is only for a few locations as most locations suggests otherwise. Thus, the groundwater condition of Warri and its environs are not adversely overwhelmed. Figs. 2a and 2b present the WQI zoning map using IDW model. From the groundwater quality parameters compared to the WHO standard and results from the evaluated WQI, it is recommended that for optimal water quality for domestic use, the water from the boreholes should be treated at least by chlorination. This is to ensure that the water from these locations don't impact the health of the consumers negatively. Water qualities that are poor and very poor cannot be used for drinking without any treatment and conventional disinfection, whereas water "unsuitable for drinking purposes" could only be used for aquaculture, irrigation, and industrial purposes and characterizes the outflow part of the aquifer (Jindal and Sharma, 2011).

VII. CONCLUSIONS

The objective of this study is to assess the seasonal variation in the physicochemical characteristics of water supply wells in Warri metropolis. WQI was applied to investigate the seasonal changes and the factors influencing groundwater hydrochemistry and hence its suitability for domestic purposes. The investigation results suggest the following:

- The highest quality was found during both the dry and wet season, in the southern and southeastern part of the aquifer, corresponding to the recharge zone where 12.5% and 40% of groundwater samples fell into excellent to good categories, respectively. Toward the flow direction, groundwaters become poor to very poor and need treatment before consumption.
- Most of the groundwater samples fell in doubtful to unsuitable categories, characterizing the eastern part of the aquifer and the outflow part, around the Crawford creek.
- the seasonal changes of groundwater quality of the study area are mainly related to dilution in the wet season, evaporation throughout the dry season, and agricultural activities.
- Spatial distribution of groundwater quality parameters varied through the study area. Occurrence of high values of some parameters was linked to both anthropogenic and natural sources, mainly based on the agricultural and domestic activities, seawater intrusion.

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