Hydrogeochemical Evaluation of Shallow and Deep-Groundwater Quality in Apata-NNPC: A petrochemical products storage facility hosting area in Ibadan, South West Nigeria

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ABSTRACT

In most developing countries like Nigeria, groundwater constitutes major source of water because it is less vulnerable to contamination. This assured safety could be easily compromised in a populated environment where dispensing of petroleum-products is common activity. This study is aimed at evaluating quality of groundwater in Apata-NNPC area of Ibadan, southwestern Nigeria.

In-situ measurement of physico-chemical parameters such as pH, Temperature and TDS were carried-out on twenty randomly collected Groundwater samples from hand-dug wells and boreholes across the study area. Electrical Conductivity was derived for samples. Atomic Absorption Spectrometer, Flame Photometer, Colorimetric and Titrimetric methods were used to analyse the concentration of ions in the samples. In-situ measurements revealed temperature ranged from 26.70 to 33.00ºC, pH ranged from 7.00 to 8.30, TDS ranged from 40 to 310ppm and EC ranged from 59.70 to 462.69µS/cm. The major ionic concentrations (in mg/L) ranged from 1.18 - 47.74 for Ca^{2+}, 1.42 - 59.32 for K^+, 1.5 - 34.85 for Mg2$^+$, 9.84 - 55.23 for Na^+, 54.9 – 305 for HCO_3^-, 25.2 – 136.8 for Cl^-, 0.07 - 2.81 for SO_4^{2-}, 0.01 - 0.76 for PO_4^{3-} and 0.02 - 4.45 for NO_3^-. The relative abundance of cations was in order of $K^+ > Na^+ > Ca^{2+} > Mg^{2+}$ and anions were in order $HCO_3^- >$ Cl- $> NO_3^- > SO_4^{2-} > PO_4^{3-}$. Contamination indices of trace/heavy elements such as Revelle index (RI) and Heavy Metal Evaluation Index (HEI) revealed unaffected to slightly affected contaminations and low heavy metals in the study area. Irrigation parameters such as Sodium Adsorption Ratio (SAR) showed good water quality. Gibbs plot revealed that 60% of the groundwater plotted in the rock –water interaction and 40% in the evaporation precipitation dominance. This observation suggests that dissolution of silicate minerals and anthropogenic sources controls the ground water chemistry in the study area.

This observation suggests dissolution of silicate minerals and anthropogenic sources controls the ground water chemistry, water is fairly good in terms of portability and fairly suitable for irrigation. Also, industrial activities showed limited impact on water quality except in few areas which are close to the depot.

Keywords: Groundwater qualities, Colorimetric and Titrimetric, rock-water interaction, Petroleum products, Contamination indices, Irrigation parameter

INTRODUCTION

Since the beginning of time and the existence of the universe, water has been an inevitable resource for all living things on earth. 70% of the earth's surface is covered with water present in oceans, streams, rivers, lakes and so on. Groundwater an important decentralized source of drinking, is the water that occurs in the subsurface below the water table where the cavities and pore spaces are fully saturated with water (Yunhu et al., 2021). Groundwater pollution which can also be described as water contamination, occurs when contaminants released to the ground make their way down into groundwater (Olusola et al., 2017). Industrial wastewaters are continually being discharged indiscriminately into surface waters resulting in impairment of general water quality (Ajayi and Olatunji, 2022).

Nigeria is a country where the increase in urbanization and industrialization has led to the sharp increase in petroleum product use for generation of energy. To ensure the security of petroleum product supply at low cost to the domestic market, the Nigerian National Petroleum Corporation (NNPC) was established. The Nigerian National Petroleum Corporation has about 20 oil depots facilities and more than 5,000km long pipelines for the storage of petrochemical products and transportation to the users (Adewuyi et al., 2012). Owamah 2013, studied the crude oils in Nigeria and it was revealed to contain a relatively high concentration of some heavy metals like lead, zinc, iron and copper. Petroleum products that are refined show higher toxicity compared to crude oil this is because metal speciation is altered and new metals are added during the refining processes to the matrix (Uzoekwe and Oghosanine, 2011).

Various cancer types such as breast cancer, colon cancer, cervical cancer have been found to increase in areas where exposure to oil industry pollutants is prevalent (Williams et al., 2020). Neurological diseases, kidney diseases and respiratory diseases in humans have also been attributed to toxicity from oil pollution (Ndubuisi and Asia, 2007). Oke, 2019 carried out research on the groundwater pollution around NNPC Depot Atlas Clove, Lagos State, the study revealed that pH values within the study area were not within the permissible limit by WHO. EC, TDS and BOD (Biochemical Oxygen demand) recorded very high values; the study revealed poor water quality in the study area.

The surface water in the vicinity of the NNPC oil depot, Apata have been assessed for some heavy metals and total petroleum hydrocarbons (Olayinka et al, 2020), a high concentration of lead was recorded in all the water samples (Oyeleke and Okparaocha, 2016), they were judged to be of poor quality and considered a potential threat to the people living in the area. A need for constant monitoring and checks to ensure public safety was also recommended.

In view of the foregoing therefore, the present study makes an effort to conduct a concise hydrogeochemical evaluation of the groundwater sources in NNPC oil depot Apata and its environs in Ibadan, Nigeria; in order to have a look into the groundwater chemistry, adjudge its portability and assess level of any anthropogenic impact the industrial activities might be posing on the groundwater sources.

Study Area

NNPC-Apata is in the South western part of Nigeria within the basement complex region. It is situated within longitude 7^{o}23’00’’N to 7^{o}25’00’’N and latitude 3^{o}47’00’’E to 3^{o}50’00’’E. In terms of accessibility, the metropolis is well connected with minor and major roads such as the Ibadan-Abeokuta express way, foot paths were also available to compliment the well pronounced road network (Fig. 1). The study area has a mean monthly temperature of 27^{o}C and the mean total rainfall is 1420.06mm, falling within approximately

109 days. There are two peaks of rainfall, June and September and the relative humidity is 74.55% (Egbinola and Amobichukwu 2013). The study area is drained by two major streams, Ogunpa Streams and Ona Streams these are complemented by streamlets (Fig. 2). An example is the streamlet flowing out from the depot.

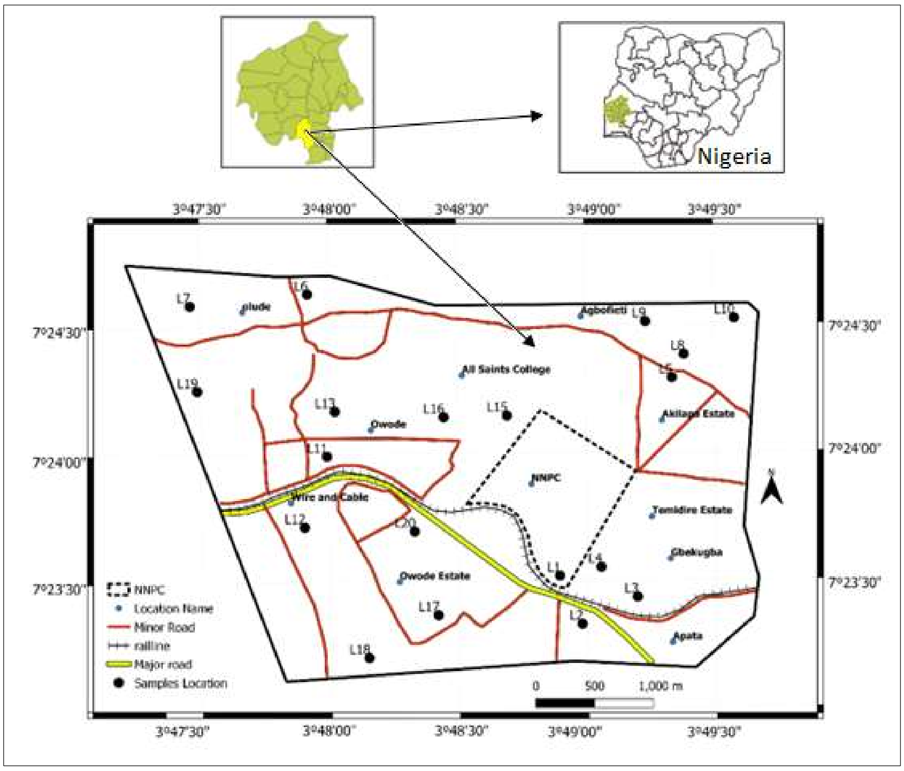


Figure 1: Location and accessibility map of the study area

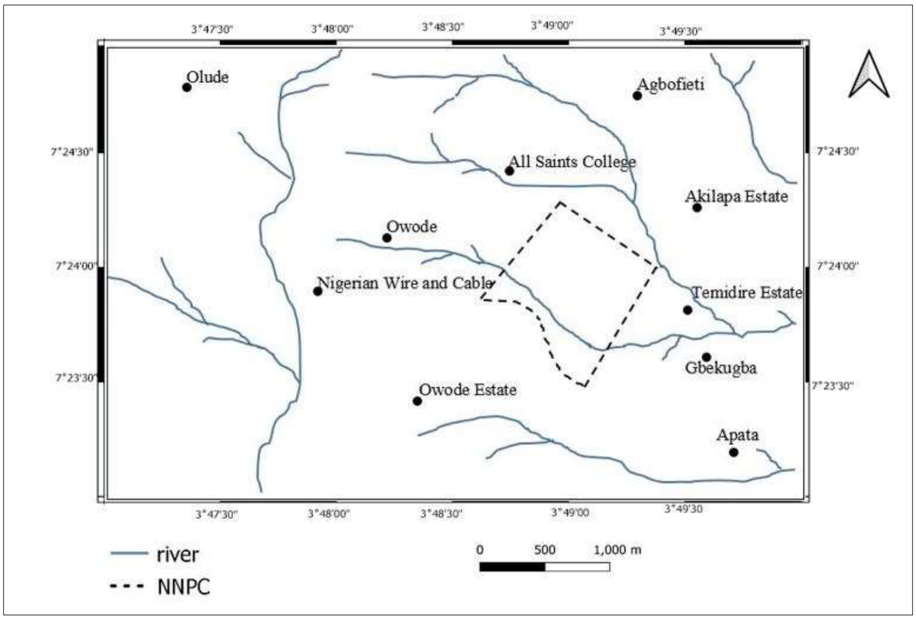


Figure 2: Drainage map of the study area

Geology of the Study Area

The study area lies in the Southwestern part of Nigeria, underlain by lithological units of the crystalline basement complex. This area is underlain by crystalline metamorphic rocks that are mainly quartzite, banded gneiss, augen gneiss, migmatite, garnet and amphibole schist (Bolarinwa, 2017). Basically, two crystalline rock types outcrops in the study area (granite gneiss and quartzite). Granite gneisses were seen along stream channels. Quartzite which is the dominant rock type was seen in various locations as well as in an active quarry (Fig. 3).

Figure 3: Outcrop of quartzite at Longitude 7°24’38.6” N and Latitude 3°47’35.53” in the study area

METHODOLOGY

The field work for this research entailed the collection of water samples. A total of twenty (20) samples were collected randomly from ground water sources in residential homes, schools and industries in accordance with APHA (2005). The samples were collected in new colourless plastic (50ml and 100ml) bottles. The 100ml bottles were used in collecting water samples for anions analysis. The 50ml bottles water samples were acidified with three drops of nitric acid (HNO_3), this was meant to preserve the samples before hydrogeochemical analysis was carried out. Physicochemical parameters such as pH, Temperature and Total Dissolved Solid (TDS) were measured on site using the pH multi-meter and the TDS multimeter. Electrical Conductivity (EC) was derived.

The samples were then arranged in a refrigerant container for easy transportation to the laboratory within forty-eight (48) hours of collection. The Atomic Absorption Spectrometer Model 205AAS was used to analyse Ca^{2+}, Mg^{2+}, Pb, Zn, Cd, Cu, Mn, Co, Cr, Ni and Fe. The flame photometer model FP 640 was used to determine the concentration of Na^{+} and K^{+} in water samples. Chloride was measured titrimetrically using silver nitrate titration method, potassium and chromate served as indicator. Bicarbonate was also measured using titration method. Phosphate, nitrate and sulfate were determined by colorimetric method.

RESULTS

Field Physico-Chemical Parameters

The pH is the negative of base 10 logarithm of concentration of hydrogen ions found in solution. Generally, the pH of pure water at room temperature (25° C) is 7 (Ajayi and Olatunji, 2022). The pH obtained from the study area ranges from 7 (neutral) to 8.30 (slightly alkaline). The present investigation reveals that the temperature of the water varies from a minimum of 26.70°C to a maximum of 33.0°C. Total Dissolved Solids (TDS) represents the total concentration of dissolved substances in water. The TDS values ranged from 40 to 310.00ppm and varied considerably between the samples (Cv> 50%) with an average of 120.00ppm. The Electrical Conductivity (EC) values ranged from 59.70 to 462.69µS/cm with mean value of 179.10 µS/cm (Table 1).

The physicochemical parameters such as TDS and EC varied greatly in the hand-dug well samples compared with borehole samples (Fig. 4). This could be as result of anthropogenic activities associated with the use of the wells. It was observed that the physical parameters (EC and TDS) also varied greatly in samples taken from the southeastern part compared to the northwestern part (Fig. 5). The observation was the parameters values were high in the southeastern part, while the northeastern end was lower. Wilson and Wang, 2013 attributed a high value of TDS in water samples to fossil fuel activities. The high values recorded in the southeastern part of the study area could be as a result of its proximity to the oil depot.

Based on the classification of salinity (Table 2**)**, the level of salinity of all the samples falls within non-saline category because a high concentration of dissolved solids alone is actually not a health hazard (Mor et al., 2007). A high concentration of TDS can produce hard water, and it is an indicator of iron, manganese, sulfate which are harmful contaminants that can be present in the water.

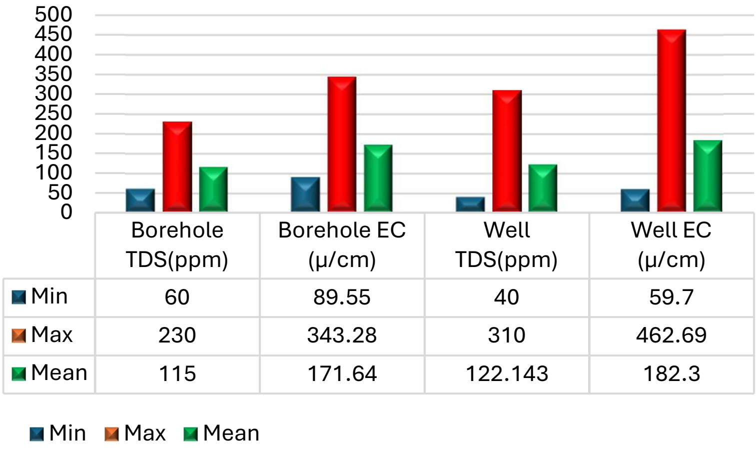


Figure 4: Bar Charts showing Summary of In-situ Parameter from Study Area

Table 1: Summary of In-situ Physico-Chemical Parameters (Number of samples=20)

Parameters	Min	Max	Mean	Standard deviation	Coefficient of variation
Temperature (^{0}C)	27	33	30.06	1.34	4.46
pH	7	8.3	7.7	0.34	4.48
EC (µS/cm)	60	462.7	179.1	117.72	65.73
TDS (ppm)	40	310	120	78.87	65.72

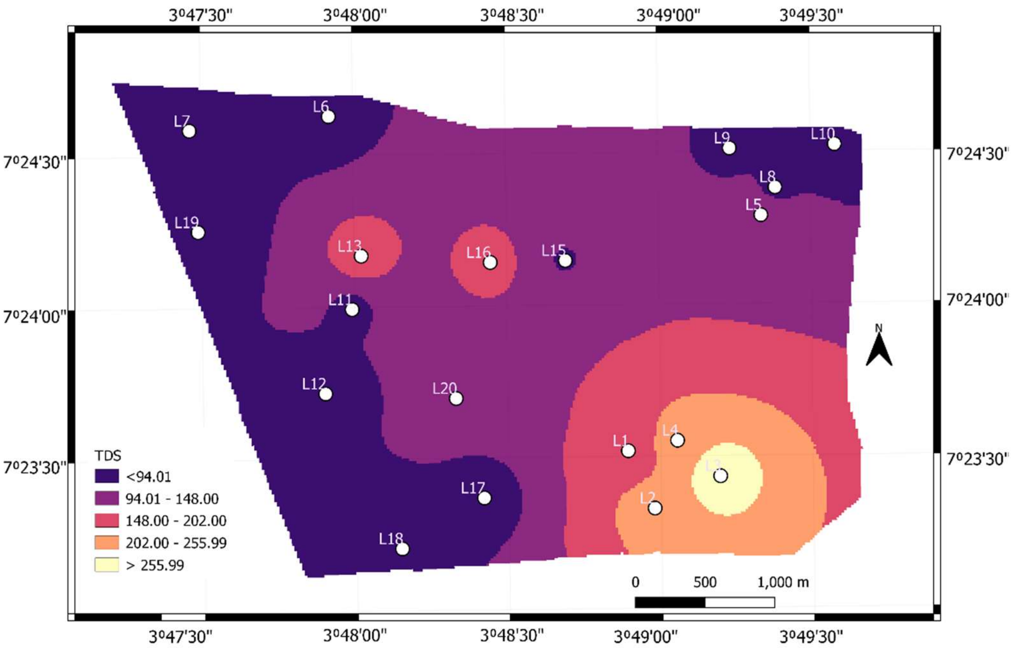


Figure 5: Spatial distribution of EC within the study area

Table 2: Classification of water samples based on TDS concentration (Jibrin et al., 2015)

Water category	TDS	Samples	Comment
Non-saline	<500-1000	20	Good
Moderately saline	>2000	-	Poor

Major Cations

The orders of abundance in the cations concentration is K^{+}>Na^{+}>Ca^{2+}>Mg^{2+}.

Potassium: Potassium concentration varied across the samples studied. The values ranged from 1.42 to 59.32mg/l with average value of 8.69mg/l. Generally, the values of potassium concentration in most of the samples were within the permissible limit by WHO, 2011. However, three locations

L03, L09 and L17 had extremely high values which were above the permissible limit by WHO, 2011 (fig. 5). These high values are not attributed to the geology of the study area because quartzite, the predominant rock in the area, do not weather easily. The high concentration recorded in the study can be related to anthropogenic activities and the personal hygiene of people in the study area. The spatial distribution map of potassium shows high concentration in the northeastern and southwestern part of the study area (Fig. 6). A high concentration of potassium in groundwater can result in kidney diseases, artery diseases and muscle weakness.

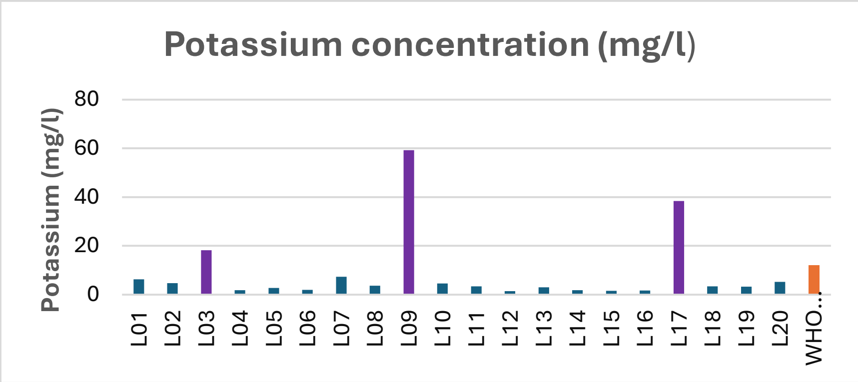


Figure 5: Comparison of potassium concentration in groundwater with WHO guideline of drinking water.

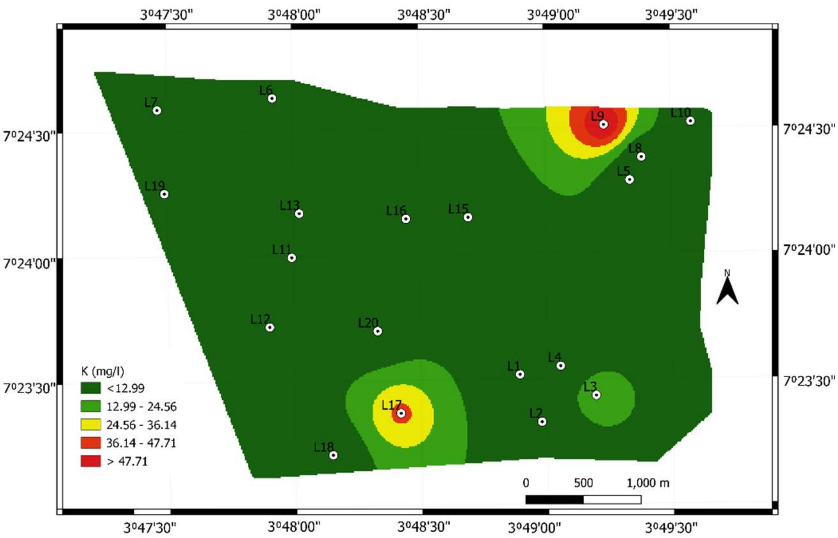


Figure 6: Spatial distribution of potassium within the study area

Sodium: The concentration of sodium in the water samples range from 9.84 -55.23 mg/l with an average of 29.81mg/l. The WHO (2011) maximum concentration for sodium in drinking water is 300mg/l and the NSDWQ (2007) concentration of sodium is 200mg/l (fig. 7). The sodium concentration of the studied water tends to be appropriate. High concentrations of sodium in drinking water could be detrimental to hypertensive individuals (Taluker et al., 2017). The spatial distribution map of sodium showed high values around the depot and could be related to the activities within the depot (Fig. 8).

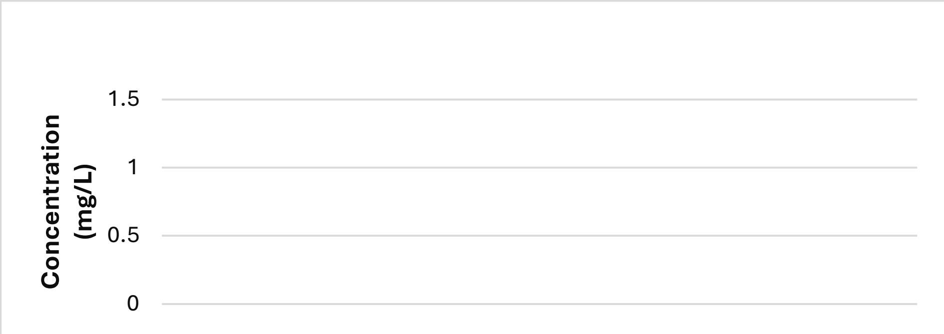


Figure 7: Comparison of the maximum concentration of Sodium, Magnesium and Calcium in groundwater with WHO guideline and NSDWQ guidelines of drinking water.

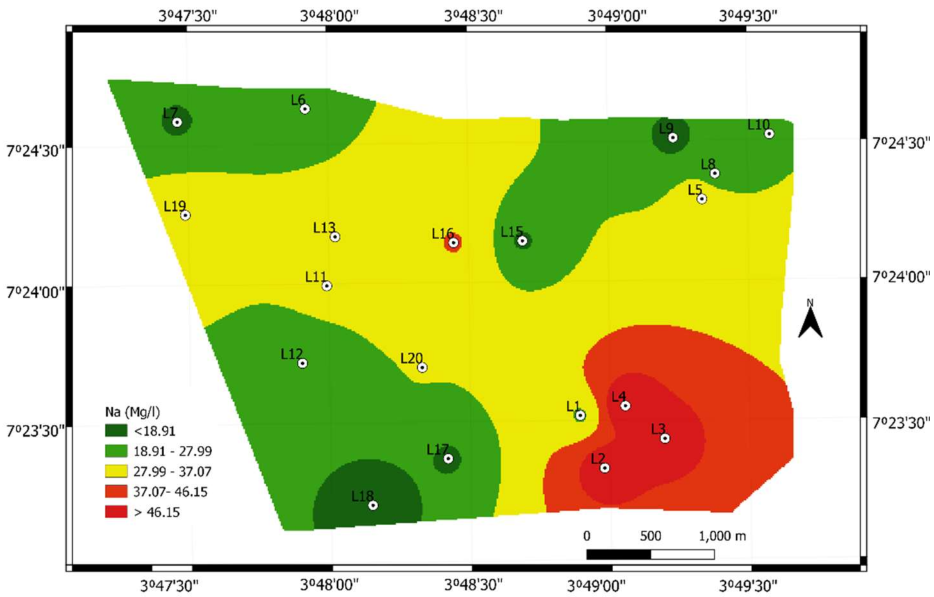


Figure 8: A distribution map of sodium within the study area

Calcium concentration: The concentration of calcium (mg/l) ranged between 1.18-47.74mg/l with an average of 19.14 mg/l in the study area. The values of Ca concentration in the groundwater resources fell within the recommended limit for drinking water by World Health Organization (2011) and the Nigerian Standard Drinking Water Quality, NSDWQ (2007) (Fig. 7). Calcium is very essential in human diet and is not harmful to the health. However, medical reports have state that a high concentration of calcium can lead to headache, spasm, asthma and other health problems (Power et. al., 2000). High values were also recorded in the southeastern areas close to the depot (Fig. 9).

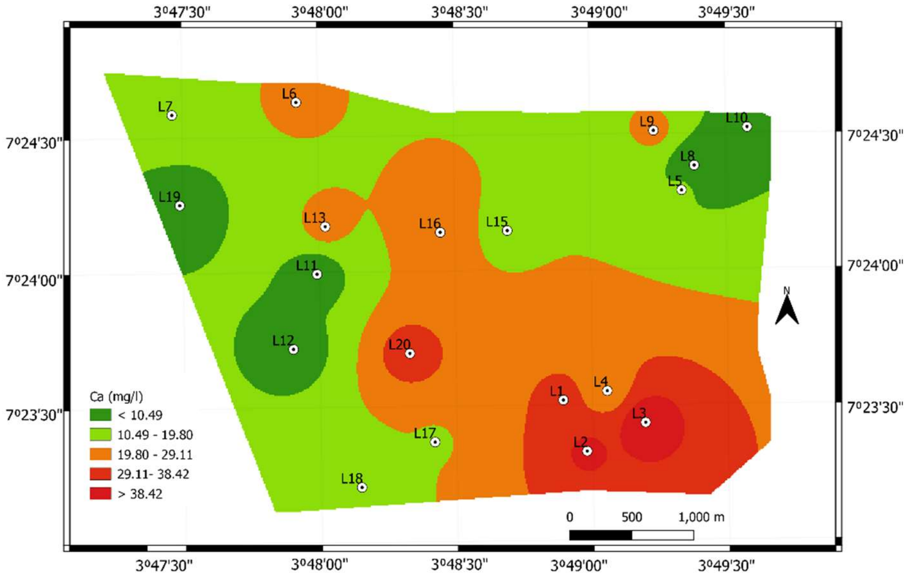


Figure 9: A distribution map of calcium within the study area

Magnesium concentration: The concentration of magnesium (mg/l) ranged between 1.5 - 34.85mg/l with an average of 12.38mg/l in the study area. The values of magnesium concentration in the groundwater resources fell within the recommended limit for drinking water by World Health Organization 2011 (fig. 7) and is therefore considered fit for drinking. Magnesium deficiency can lead to hypertension, coronary heart diseases and diabetes (Swaminathan,2003). High values were also recorded in the southeastern areas close to the depot this can also be attributed to the activities of the petroleum depot (Fig. 10).

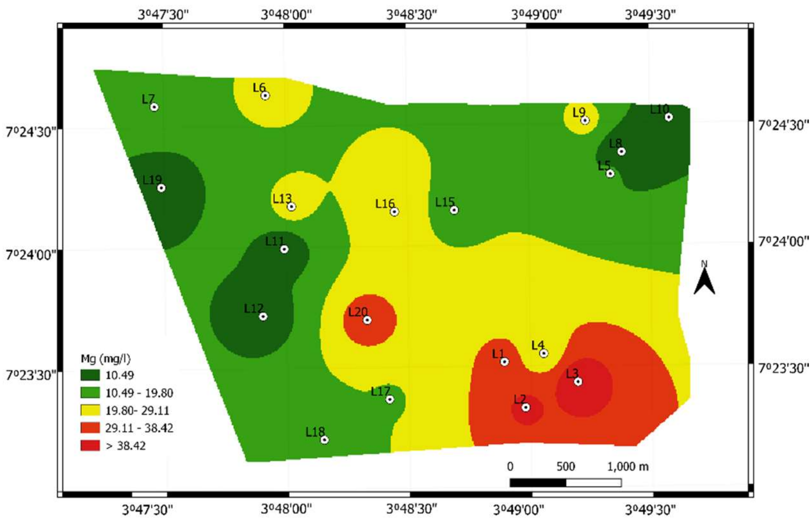


Figure 10: A distribution map of calcium within the study area

Results of Major Anions

The orders of abundance of anions concentration are $HCO_3^- > Cl^- > NO_3^- > SO_4^{2-} > PO_4^{3-}$.

Chloride: The concentration of chloride in the study area ranged from 25.2 to 136.8mg/l with an average of 62.83mg/l. The concentration of chloride within the study area fell below the WHO 2011 standard for drinking water which is 250mg/l. The NSDWQ 2007 has no limit for chloride. The concentration, however, is above the NSDWQ, 2017 standard for drinking water which is 100mg/l. The concentration of chloride in the study area can be attributed to anthropogenic sources where L02, LO3 and L04 which are very close to the depot had the highest concentration (Fig. 11). Hyperchloremia, a disorder in which a person has too much chloride in their blood can cause a range of symptoms; these include diarrhoea, vomiting, fatigue and dehydration (Balingit, 2024).

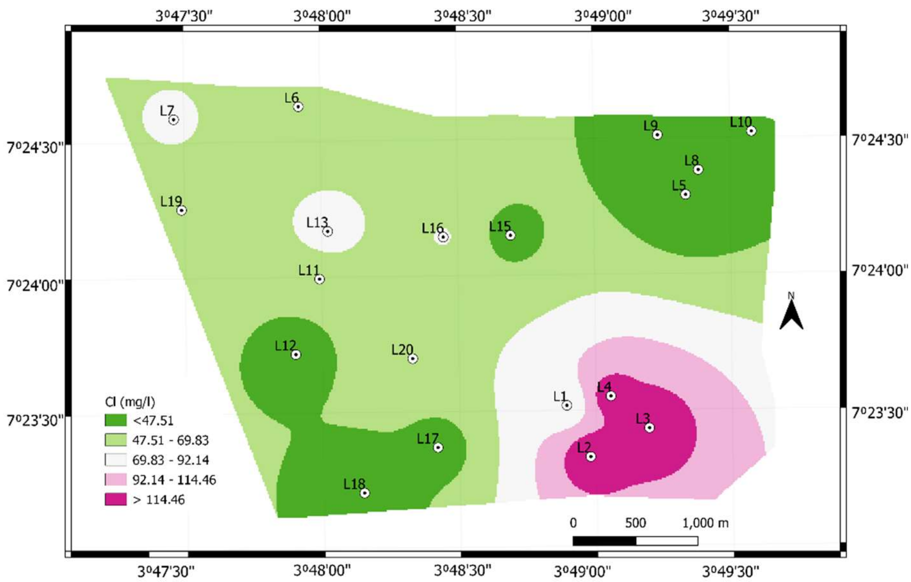


Figure 11: Spatial distribution of Chloride within the study area

Sulfates: Sulfates concentration in the study area ranged from 0.07 to 2.81mg/l with an average of 1.559mg/l. Sulfates concentrations fell below the guideline value recommended by WHO 2011 and NSDWQ 2007. The spatial distribution map shows the values of sulfate within the study area (Fig. 12).

Nitrates: Nitrates concentration in the study ranged from 0.02 to 4.45mg/l with an average of 1.408mg/l. Nitrates concentrations fell below the guideline value recommended by WHO 2011 and NSDWQ 2007. Fig. 13 shows the spatial distribution of nitrate in the study area.

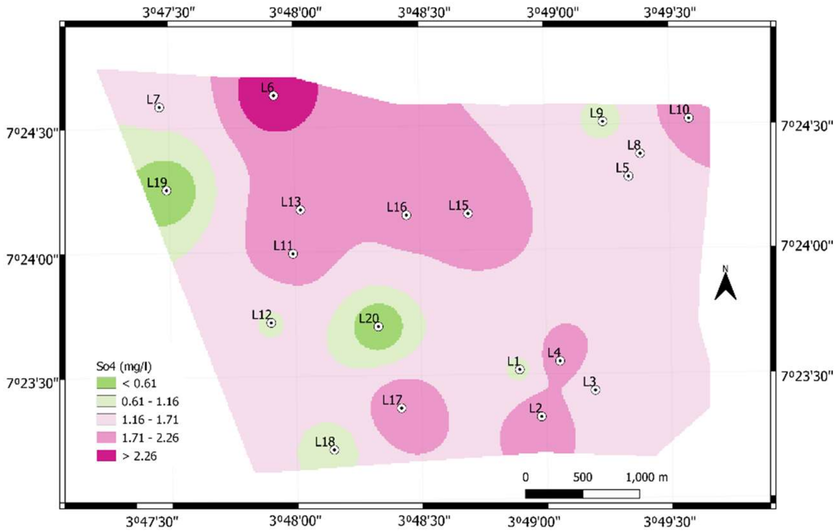


Figure 12: Spatial distribution of sulfates within the study area

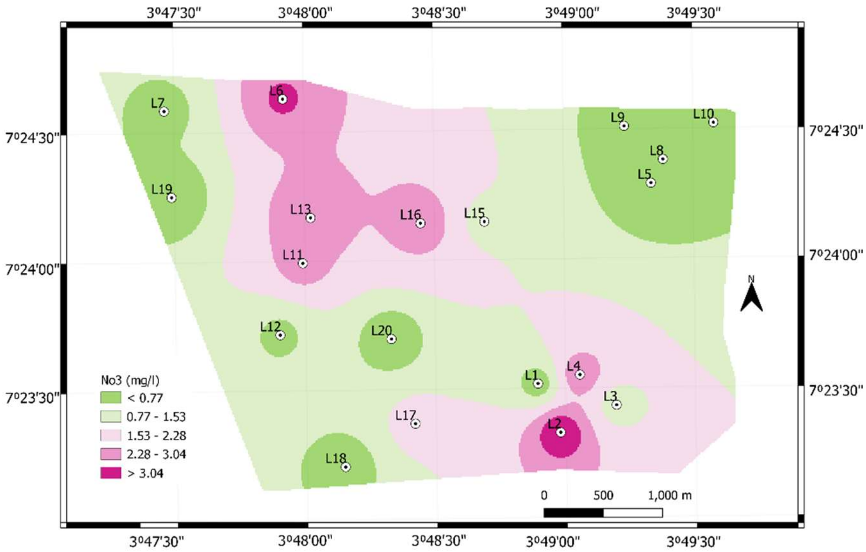


Figure 13: Spatial distribution of nitrates within the study area

Bicarbonates: The concentration of bicarbonates in the study area ranged from 54.9 to 305mg/l with an average of 155.85mg/l. The concentration of bicarbonates within the study area fell below the WHO 2011 standard for drinking water which is 550mg/l. The concentration of bicarbonates in the study area can be attributed to anthropogenic sources. A high concentration of bicarbonates can result in acidosis while a low concentration of bicarbonates can result in alkalosis in the body (Sabatini and Kurtzman, 2008). High values were recorded in areas close to the depot (Fig. 14).

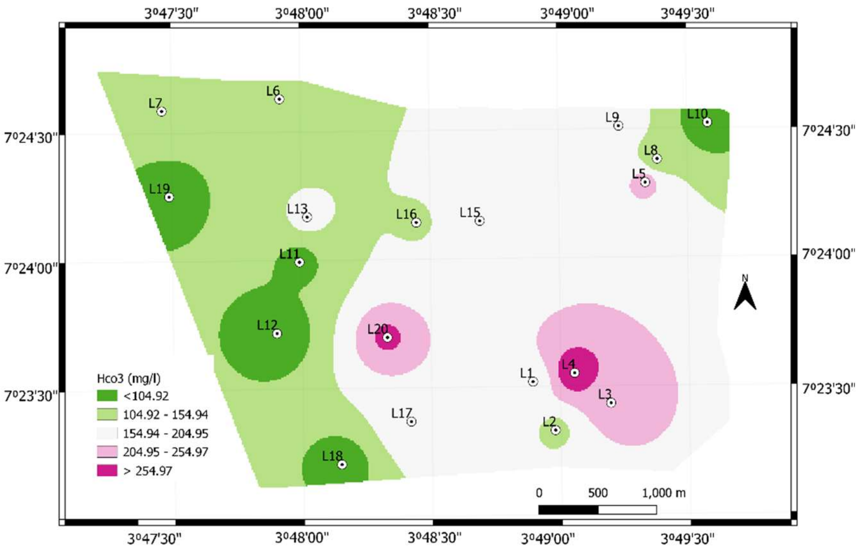


Figure 14: Spatial distribution of bicarbonates within the study area

Phosphate: The concentration of phosphate in the study area ranged from 0.08 to 0.76mg/l with an average value of 0.168mg/l. Although, there is no recommended standard for phosphate according to WHO (2011) and NSDWQ (2007), the recommended WHO (2008) standard is 0.5mg/l, the value of concentration within the study area were higher than this standard. The high concentration can be attributed to anthropogenic sources. Extremely high concentration of phosphate can result to digestive problems (Fadiran et al., 2008). A spatial distribution of phosphate is shown in Fig. 15.

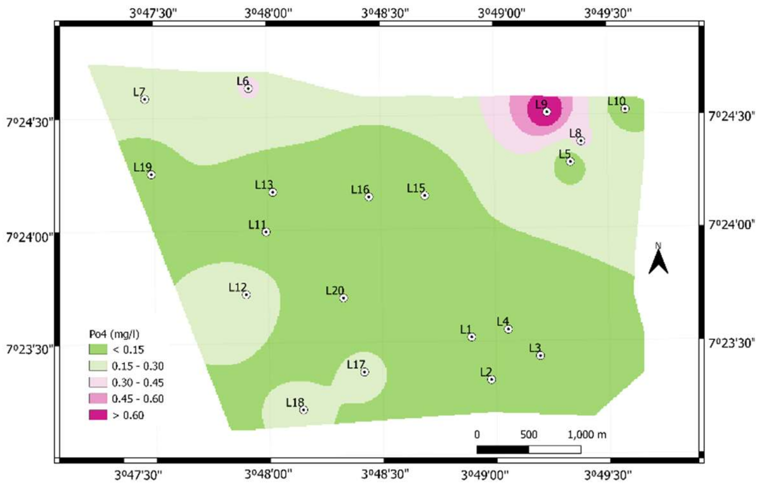


Figure 15: Spatial distribution of phosphate within the study area

Results of Trace metals

Trace metals in the study area were mostly below detectable limits (BDL) to low and high in concentrations. The concentration of trace metals (Mn, Fe, Cu, Zn, Co, Cr, Cd, Pb and Ni) in the analyzed samples ranged as follows; BDL to 0.2mg/l with an average of 0.037mg/l in manganese, BDL to 0.57mg/l with an average of 0.061mg/l in iron, copper ranged from BDL to 0.057 mg/l with an average of 0.006mg/l. zinc ranged from 0.01to 0.83mg/l with an average of 0.109mg/l, cobalt ranged from BDL to 0.001mg/l with an average of 0.0002mg/l. Chromium ranged from BDL to 0.003mg/l with an average of 0.0004mg/l. Cadmium ranged from BDL to 0.015mg/l with an average of 0.00125mg/l. Lead ranged BDL to 0.002mg/l with an average of 0.0003mg/l. Nickel ranged from BDL to 0.003mg/l with an average of 0.0006mg/l.

The concentration of manganese, copper, zinc, chromium, lead and nickel in the samples analyzed fell below the guideline value recommended by WHO, 2011 and NSDWQ, 2007 standard for drinking water. However, the concentration of iron within the study area rises far above the WHO (2011) and NSDWQ (2007) drinking water standard. The high concentration of iron can be attributed to anthropogenic sources probably emanating from some courtyard tin and iron fabricating workshop observed in the area. High levels of iron in drinking water can lead to unhealthy skin and hemochromatosis which can cause damage to the liver (Sharaa and El-Turki, 2017). Fig. 16 (a-i) show the spatial distribution of trace metals

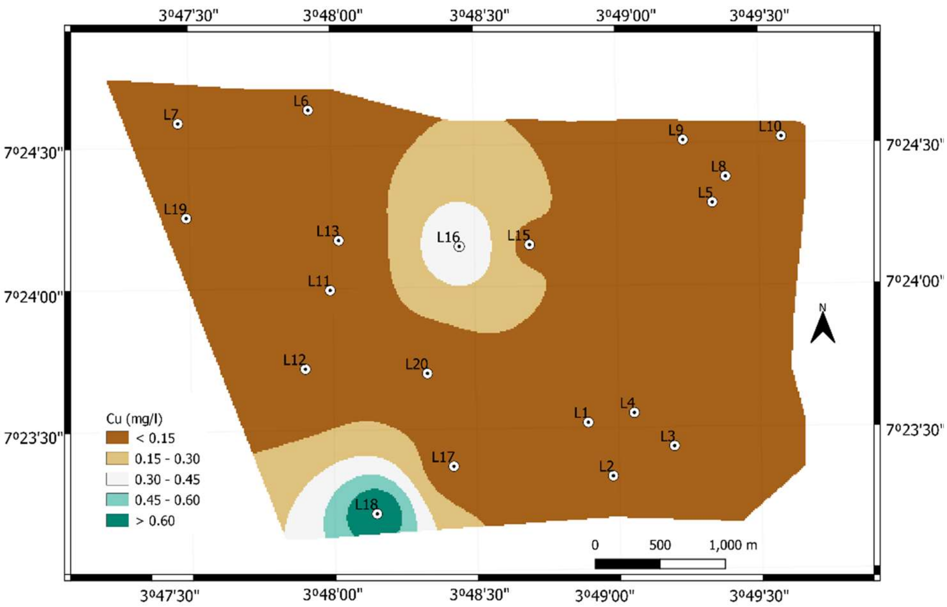


Figure 16 (a): Spatial distribution of copper within the study area

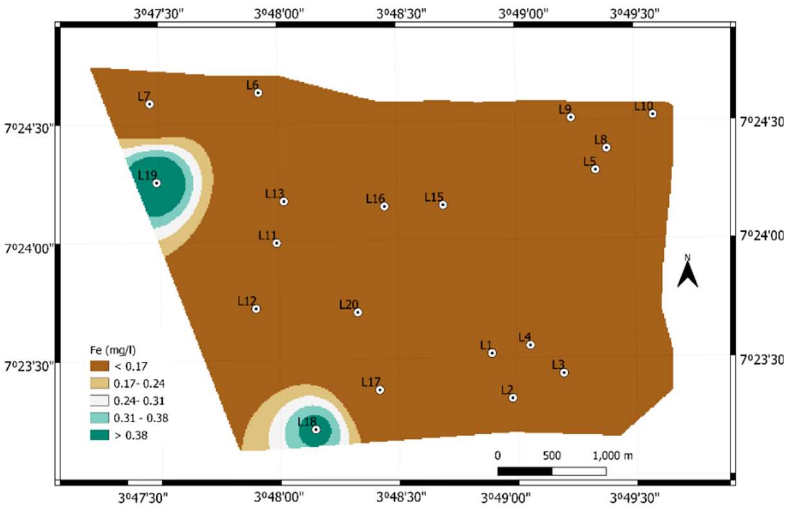


Figure 16(b): Spatial distribution of iron within the study area

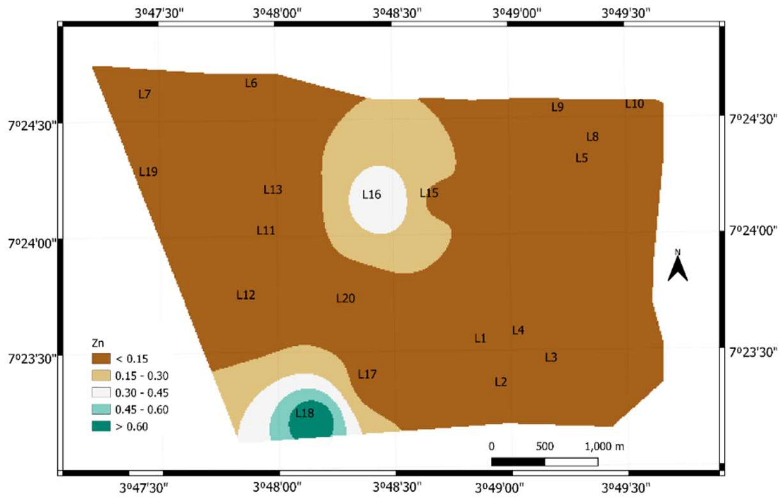


Figure 16(c): Spatial distribution of zinc within the study area

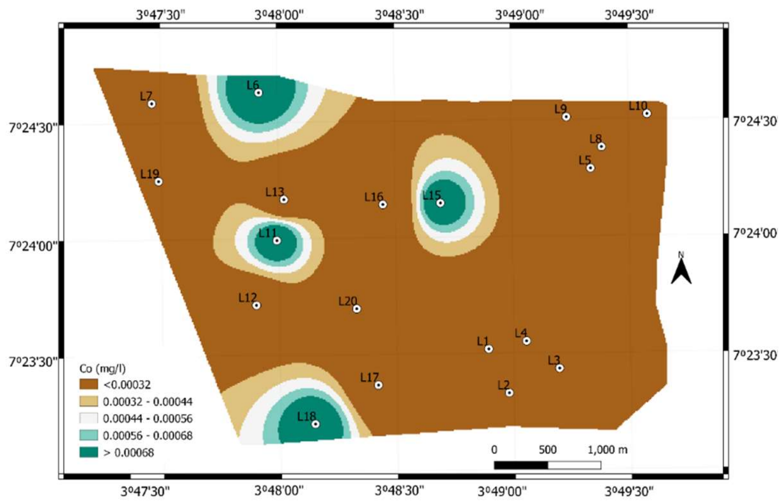


Figure 16(d): Spatial distribution of cobalt within the study area

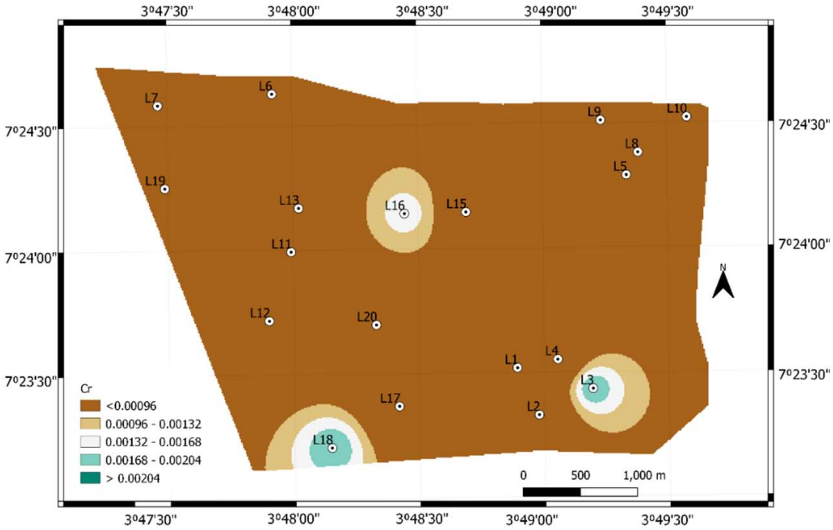


Figure 16(e): Spatial distribution of chromium within the study area

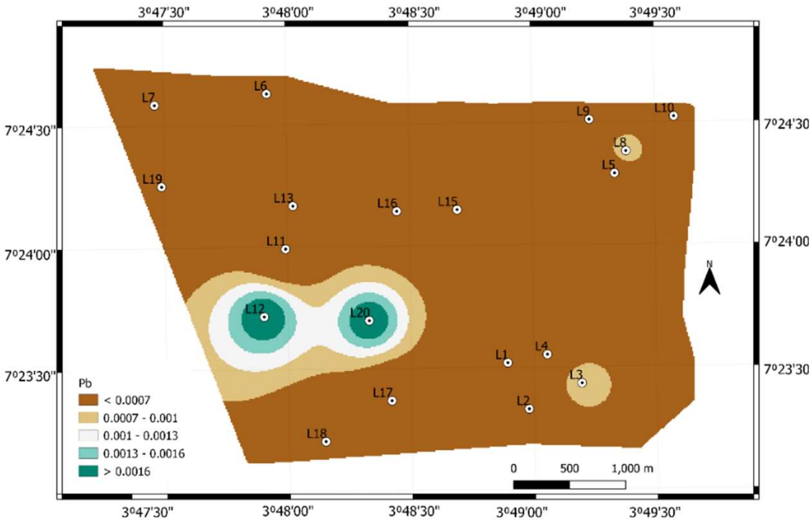


Figure 16(f): Spatial distribution of lead within the study area

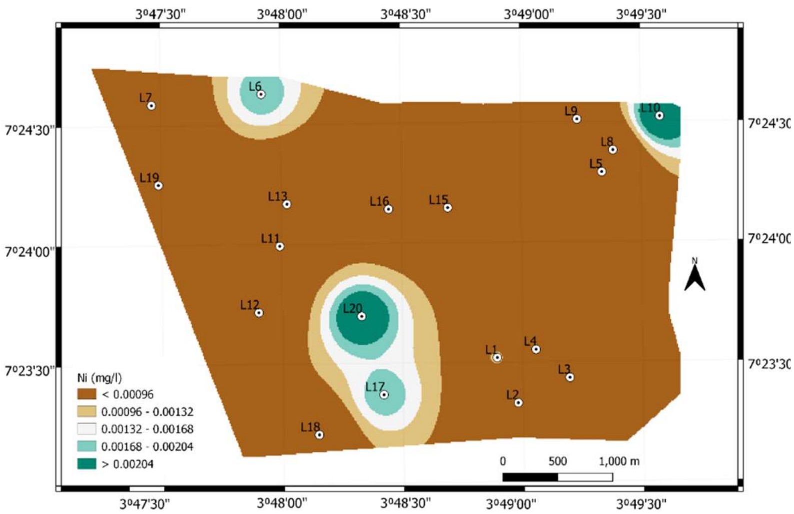


Figure 16(g): Spatial distribution of nickel within the study area

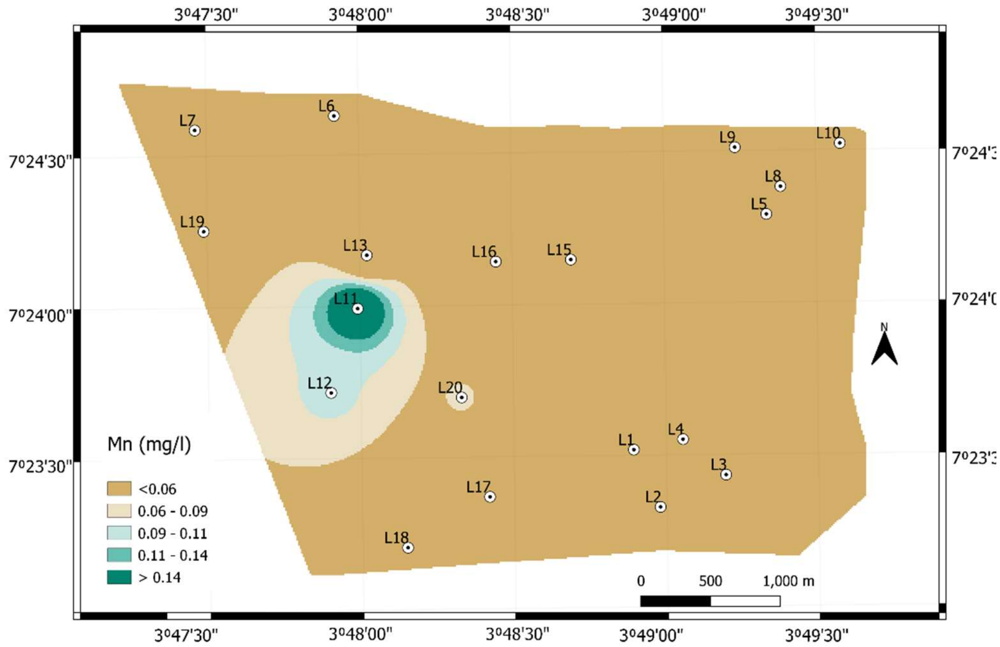


Figure 16(h): Spatial distribution of manganese within the study area

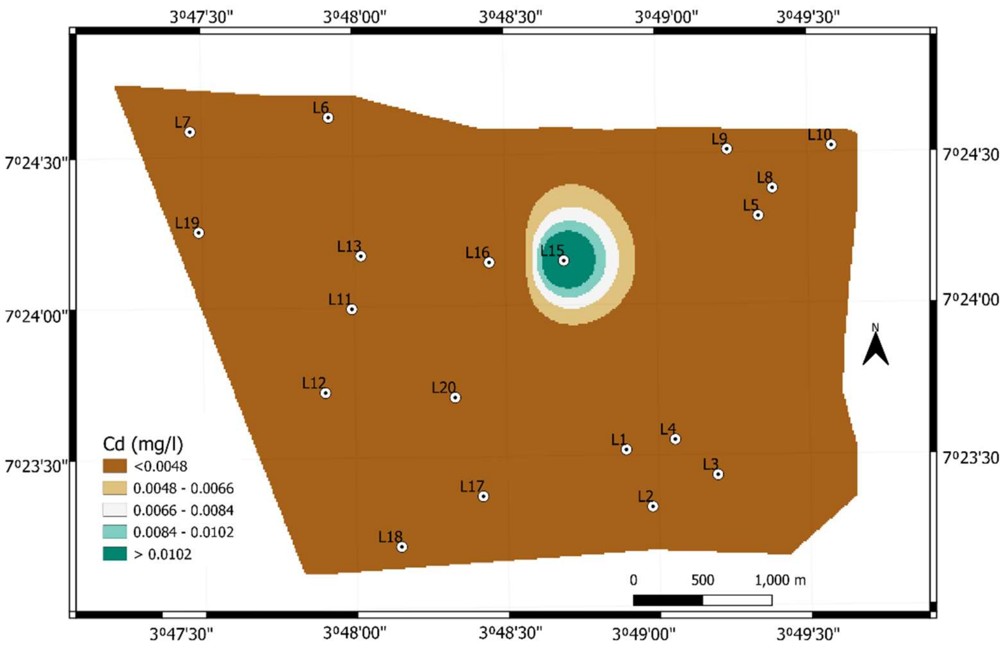


Figure 16 (i): Spatial distribution of cadmium within the study area

Water Contamination Assessment (Contamination Indices)

Water contamination happens when foreign substances are mixed with water. It is referred to as pollution when these contaminants are harmful to human health.

The suitability of water for drinking, agriculture and other purposes defines its quality. Various contamination indexes checks were conducted and for calculations within this section, WHO (2011) water guidelines were used for the estimations (Table 3).

Table 3: Comparison of Samples with Drinking Water Guidelines (n= 20) (BDL – Below Detection Limit)

Parameters	Range of parameters in the study area	WHO 2011		NSDWQ	Health Implication
		Permissible	Maximum	2007	
pH	7.4 – 8.3	6.5	8.5	6.5 – 8.5	Pipe corrosion, impaired taste
EC	59.70 – 462.69	900	1250	1000	Salty taste
TDS	40 - 310	< 600	1000	500	Salty taste, pipe scaling
Ca	1.18 – 47.74	100	500	75	Furring of kettles, waste soap
Mg	1.5 – 34.85	60	170	-	-
Na	9.84 – 55.23	200	300	200	High blood pressure
K	1.42 – 59.32	-	-	-	-
HCO_3	54.9 - 305	550	1000	100	-
Cl	25.2 – 136.8	250	-	100	Salty taste
SO_4	0.07 – 2.81	250	-	100	Laxative effects
NO_3	0.02 – 4.45	50	50	50	Methemoglobinemia (blue-baby syndrome)
Fe	BDL – 0.56	0.3	-	0.3	-
Cu	BDL – 0.06	1	2	1	Gastrointestinal, liver or kidney damage.
Pb	BDL – 0.002	0.01	-	0.01	Impaired mental development
Zn	0.01 – 0.83	3	5	3	-
Cd	BDL – 0.015	0.003	-	0.003	Toxic to the kidney
Co	BDL – 0.001		-	-	
Cr	BDL – 0.003	0.05	-	0.05	
Mn	BDL – 0.211	0.1	0.4	0.2	Causes of undesirable taste in beverages
Ni	BDL – 0.003	0.07	-	0.02	Possible carcinogenic

Revelle index

The contamination of groundwater quality in the study area was determined with the use of Revelle Index. Revelle Index (RI) is widely known as a criterion of groundwater quality assessment (Tziritis et al., 2008). Its calculation is based on the ionic ratio in meq/l (Revelle, 1946);

$$\mathrm{RI} = \frac{Cl-}{HCO3-}$$

Revelle index <0.5 indicates unaffected by salinity, 0.5 to 6.6 signifies slightly affected water salinity while >6.6 is an indicator of strong contamination. The samples ranged from 0.116 to 0.94939 with average of 0.447. Revelle Index assumes that there is contamination of chlorine in water, when the concentration of chlorine is higher than bicarbonate, which implies that it is of poor quality. Estimation showed (Table 4) that 75% of samples fell on unaffected; 25% of the samples were slightly unaffected and they can be considered to be of good quality for drinking.

Table 4: Classification of Revelle index (RI) (n= 20)

Parameters	**Range**	**Water class**	**Percentages (%)**	**Samples**
Revelle index (RI)	< 0.5	Unaffected	**75%**	1,4,5,6,8,9,11,12,13, 14,15,16,17,18,20
	0.5 -6.6	Slightly unaffected	**25%**	2,3,7,10,19
	>6.6	Strongly affected	**-**	**-**

Heavy Metal Evaluation Index (HEI)

Heavy Metal Evaluation Index (HEI) approach has been used for the evaluation which shows the composite influence of individual parameters on the overall quality of water (Tamasi and Cini, 2004). The HEI represents the sum of the ratio between the analyzed parameters and their equivalent national standard values (Chon et al., 1997) as given below:

$$\text{HEI} = \sum_{i=1}^{n} \frac{Hc}{Hmac}$$

Where: Hc: Concentration of sample Hmac: Maximum allowable concentration

The water quality index is classified into three categories which include: low heavy metals (HEI <400), moderate to high heavy metals (400 <HEI <800) and high heavy metals (HEI> 800). The results of heavy metal evaluation index ranged from 0.00 to 35.0, as shown in Table 5 all samples (100%) fell within low heavy metal contamination. This explains that the water is of low risk for drinking.

Table 5: Heavy Metal Evaluation Index (HEI) (n = 20)

Parameters	**Range**	**Water class**	**Percentages (%)**	**samples**
Heavy Metal Evaluation Index (HEI)	**< 400**	Low heavy metals	100	All samples
	400 -800	Moderate heavy metals	**-**	
	>800	High heavy metals	**-**	

n = Number of samples

Irrigation Water Quality Evaluation

Evaluation of the water for groundwater source in the vicinity of the study area was carried out to determine their suitability for irrigation purposes. The criterion for suitability of groundwater for irrigation is entirely different from drinking purposes. Water that is suitable for drinking may not be suitable for irrigation.

Percentage Sodium (%Na)

Sodium level in irrigation water can be expressed in %Na. When there are high sodium concentrations in water for irrigation, the sodium is absorbed by clay particles, thereby dispersing magnesium and calcium ions. This exchange process of sodium in water for Ca^{2+} and Mg^{2+} in soil reduces the permeability and eventually results in soil with poor internal draining.

The % Na is computed with respect to relative proportion of cations present in water as (Wilcox 1955);

$$Na\% = \frac{\mathrm{Na} +}{Ca + Mg + K + Na} \times 100\ Meq/l$$

The computed Na% for the study area ranged from 13.57 to 79.96% with an average of 40.31%, 10% of the samples were classified as excellent, 50% of samples fell in the good category, 25% fell in the permissible category and 15% of the samples were within the doubtful category (Table 6); this means that over 80% of the studied water samples are good for irrigation purposes.

Table 6: Classification of sodium percentage in the study area (n = 20)

Parameters	Ranges	Water class	Samples	Percentages
%Na (Wilcox,1955)	<20	Excellent	9,17	10
	20-40	Good	1,2,3,6,7,13,14,15,18, 20	50
	40-60	Permissible	4,5,10,12,16,	25
	60-80	Doubtful	11,19,8	15
	>80	Unsuitable	-	-

Sodium Adsorption Ratio (SAR)

Sodium in water for irrigation affects the permeability and also the infiltration. Excess salinity reduces the osmotic activity of plants (Subramani et al., 2005). The SAR is computed using the following equation:

$$SAR = \frac{Na+}{\sqrt{\frac{Ca2 + \; + \; \mathrm{Mg}2 +}{2}}}$$

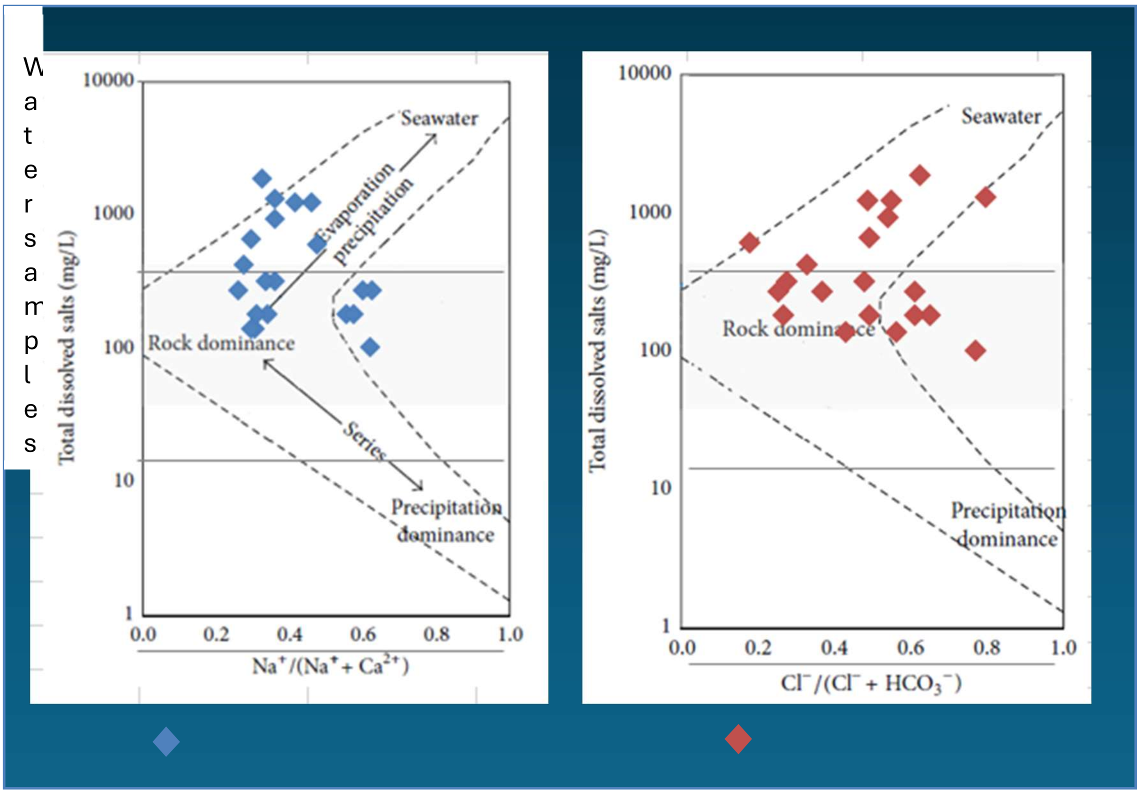
100% of the samples fell within the excellent class (Table 7), which means they are all good for irrigation.

Table 7: Classification of Sodium Absorption Ratio of samples in the study area (in percentage) (n = 20)

Parameters	**Ranges**	**Water class**	**Sample numbers**	**Percentages**
SAR (Richard,1954)	0-10	Excellent	1-20	100
	10-18	Good	-	-
	18-26	Permissible	-	-
	>26	Doubtful	-	-

Gibbs diagram

Groundwater and aquifer matrix reactions have a significant impact on water chemistry, and it can be used as a means to identify the origin of groundwater solutes (Subramani et al. 2005). Different processes like rock weathering evaporation and ion exchange can affect the chemistry of the groundwater system. Gibbs plots were used to identify the roles of hydrochemical processes such as precipitation, rock water interaction and evaporation on water resources chemistry in the study area. Gibbs (1970) suggested TDS versus Na / Na+ Ca" for cations and TDS versus C-(CI+HCO) for anions to illustrate the natural mechanism controlling groundwater chemistry, including the rainfall dominance, rock weathering dominance, and evaporation, precipitation dominance. Gibbs plot (figure 17) revealed that 60% of the groundwater plotted in the rock –water interaction and 40% in the evaporation precipitation dominance. This observation suggests that dissolution of silicate minerals and anthropogenic sources controls the ground water chemistry in the study area.



Piper Diagram

Groundwater samples hydrochemical facie was evaluated by means of calculating percentage milli-equivalents of the major ions (Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^+, Cl^- and SO_4^{2-}) separately in terms of the cations and anions and plotting them on a tri-linear diagram (piper diagram). The Piper (1944) diagram is very useful in classification of water on the basis of its chemical character and determining relationships between different dissolved constituents. The piper diagram indicated that majority of the samples 65% were mixed Ca-Mg-HCO3 type, 30% of the sample were Na-HCO_3 type, 5% of the samples were Na-Cl type. The triangular cationic field showed that 40% of the samples fell into the non-dominant type, 60% of the samples fell into the Na+K type. However, in the anionic triangle 100% of the samples fell in the HCO3 + C03 type (Fig. 18).

The Ca-HCO3 type is likely caused by rainfall recharge associated with low EC. The Ca-Mg-HCO3 water type is generally fresh recharge waters derived from rainfall and its interaction with the aquifer matrix, however the mixed Cations-Cl, Na-Cl and Ca-Cl types suggest anthropogenic sources (Freeze and Cherry 1979). Therefore, it is evident that the dissolved load of groundwater in the study area is contributed by diverse sources/processes, such as geogenic sources and anthropogenic factors.

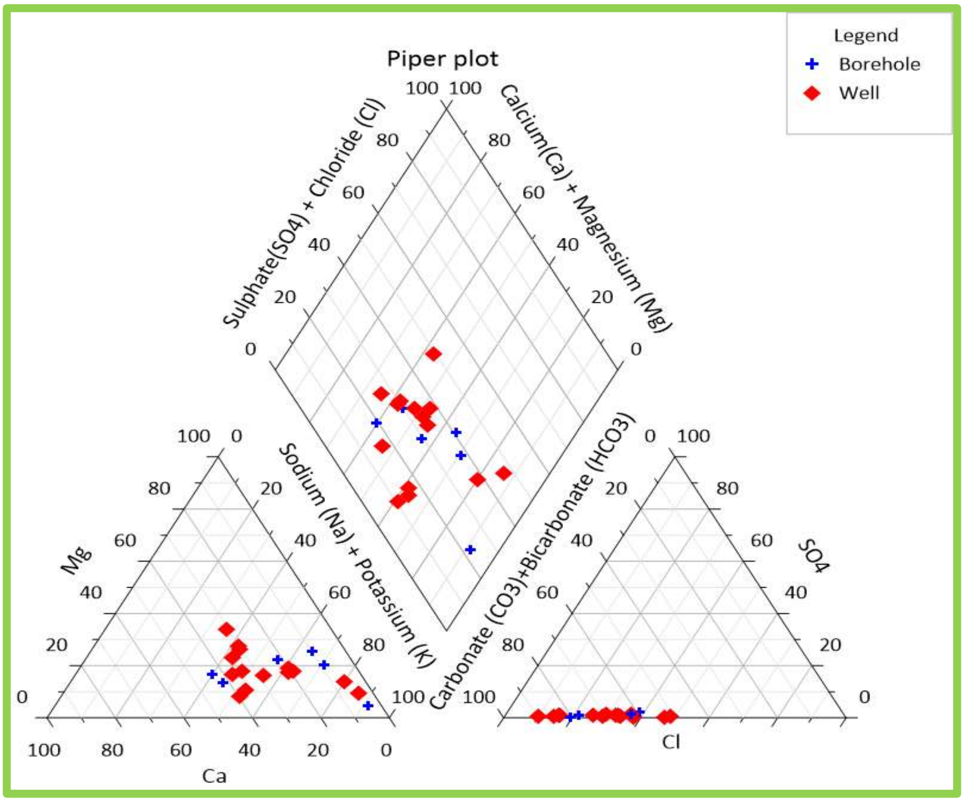


Figure 18: Piper diagram showing hydrochemical facies of water in the study area

CONCLUSION

In conclusion, at the end of this research it was observed that some parts of the areas studied were high in concentration of ions like chloride, phosphate, potassium, and iron; all these were below permissible limits by NSDWQ and WHO. Generally, it was observed that areas closer to the petroleum depot had higher ion concentrations compared to the surrounding areas, although, these ion concentrations were within the permissible limits by WHO and NSDWQ standard, it can be said that the depot has an impact on the surrounding areas' groundwater in a very minimal way. Contamination indices revealed that the water in the area was good in terms of potability and fairly suitable for irrigation purposes. It can therefore be summarized that the quality of water in the study area has low mineralization and some influence of anthropogenic contamination.

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