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HYDROCHEMICAL STUDIES OF GROUNDWATER IN PARTS OF LAGOS, SOUTHWESTERN NIGERIA

Abstract: Groundwater samples were randomly collected from forty-five protected dug wells and thirteen boreholes in parts of Lagos, Southwestern Nigeria. Samples were analysed for pH, electrical conductivity and total dissolved solids in situ. Cations (calcium, magnesium, potassium and sodium) and anions (chloride, bicarbonate, sulphate and carbonates) were determined in the laboratory after standard procedure. The study is aimed at examining the extent of groundwater pollution and its possible sources using multivariate and graphical techniques. Rockware software was used to characterize groundwater composition while the sample locations were mapped with ArcMap 9.3 software. The results show high mean value in the groundwater characteristics of the protected dug wells compared to the boreholes. A significant relationship exists among EC/ TDS and major ions indicating the influence of sea water on the groundwater quality. The dominant cations and anions are in the order of: $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$; and $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-}$ respectively. Factor analysis extracted two major sources of pollution (sea water and industrial) responsible for the processes controlling groundwater quality in the area. The Piper plot revealed seven distinct water types including Ca-HCO₃, Ca-Cl, Mg-HCO₃, Na-SO₄, Mg-Cl, Na-HCO₃ and Na-Cl representing 44.8%, 25%, 15.5%, 5.2%, 3.4%, 3.4%, and 1.7% respectively. The paper recommended monitoring of groundwater abstraction and treatment of industrial effluent before being released into the subsurface to prevent salinization and quality deterioration in the study area.

Key words: groundwater chemistry, anthropogenic pollution, marine influences, Nigeria, Lagos

Introduction

Groundwater serves as a major source of drinking water globally (WWAP 2009). It was estimated that about 1,000 km³ of the world's aggregated groundwater is abstracted annually. Approximately 67% is used for irrigation, 22% for domestic, and 11% for industrial purposes (Siebert et al. 2010; AQUASTAT 2011). Naturally, groundwater is usually free from contamination but anthropogenic activities can impact significantly on the quality such that it will require interventions prior to usage (Yidana et al. 2012). Groundwater quality depends on several factors including lithology, chemical composition of the aquifers, climatic conditions prevailing during formation, quantity of water available in the aquifer and its rate of circulation (Todd and Mays 2005). The interaction between water and the host rock can influence of groundwater suitability and its chemistry. The degree to which rock/mineral weathering influences groundwater chemistry is a function of several factors such as residence time of groundwater in the host rock, the ambient temperature and pH, among others (Wen et al. 2005; Coetsiers and Walravens 2006; Banoeng-Yakubo et al. 2009; Shankar et al. 2011).

The concept of groundwater composition also known as hydrochemical facies is useful for the identification of the hydrochemical facies, water type, hydrochemical processes, chemical character of the water, their similarities and differences in any given aquifer system (Güler et al. 2002; Sadashivaiah et al. 2008). The Knowledge of the natural groundwater quality can provide important inferences of the natural water chemistry, recharge, mixing and discharge of groundwater (Todd and Mays 2005). Various methods have been developed for the visual understanding of hydrochemical data in order to show water classification, reveal the discernible patterns, trends, dissimilarities of water composition and quality the world over (Back 1965; Dalton and Upchurch 1978; Sadashivaiah et al. 2008). The simplest methods include plotting distribution diagrams, bar charts, pie charts, radial and Stiff diagrams. Although these are easy to construct, they are not convenient for graphical presentation of large numbers of analyses. Hence, other techniques used include Ternary, (Schoeller 1962), (Piper 1944) and (Durov 1948) diagrams.

In addition to these graphical techniques, multivariate statistical methods have also been employed for the analysis of groundwater composition. For instance, factor and cluster analyses have been widely used with

conventional graphical techniques to characterize hydrochemical systems adequately. Their uses have assisted in providing solutions to various environmental problems and also provided a better understanding of the groundwater flow regime (Meng and Maynard 2001; Güler et al. 2002; Thyne et al. 2004; Yidana et al. 2008a, 2008b). In order to ensure that the utilization of groundwater is sustained in the study area, adequate protection from pollution and monitoring of the quality must be ensured. Thus, the present study aimed at examining the extent of groundwater pollution and its possible sources using multivariate and Piper diagrams.

Study area

The study area is located approximately between latitudes $6^{\circ}23'30''\text{N}$ and $6^{\circ}34'15''\text{N}$ and longitudes $3^{\circ}28'0''\text{E}$ and $3^{\circ}38'45''\text{E}$. It is bounded on the East by Ibeju-Lekki, in the North by the Lagos Lagoon and in the South by the Atlantic Ocean and parts of the Lagos metropolis in the West (Fig. 1).



Fig. 1. Sampling locations

The climate is tropical, hot and wet. The area is characterized by coastal wetlands, sandy barrier islands, beaches, low-lying tidal flats and estuaries (Adepelumi et al. 2009). The average temperature is about 27°C with an annual average rainfall of about 1,532 mm (Adepelumi et al. 2009). The major seasons are wet and dry seasons. The wet season lasts for 8 months (April to November) and the dry season covers a period of 4 months (December to March) (Adepelumi et al. 2009). The dominant vegetation consists of tropical swamp forest (fresh water and mangrove swamp forests and dry lowland rain forest).

The area is drained by Lagos Lagoon (Emmanuel and Chukwu 2010). The geology is underlain by the Benin Formation and is made up of unconsolidated sands and gravels (Oteri and Atolagbe 2003). The groundwater flow direction shows a North to South direction with two small cones of depression in Apapa and Ikeja due to intense groundwater abstraction (Coode et al. 1997; Oteri and Atolagbe 2003). The hydrogeology is characterized by sand and clay from the underlying aquifer formation (Longe 2011). The major aquifer formations consist of coastal plain sand aquifer (CPS) and recent sediments (alluvium). CPS is categorized into four types namely the recent sediments/alluvium, the upper and lower CPS and the Abeokuta formation (Longe 2011). Groundwater occurrence in the CPS is essentially semi-confined to unconfined aquifers (Adelana et al. 2008). Variation in the thickness between the first and third CPS aquifer ranged between 200 m and 250 m respectively (Adelana et al. 2008); while the mean estimate of groundwater storage of the first CPS aquifer is about $2.87 \times 10^3 \text{ m}^3$. The water table ranged between 0.4–21 m with an annual fluctuation of less than 5 m (Asiwaju-Bello and Oladeji 2001). The upper coastal plain sand aquifer (UCPSA) is a water table aquifer with a relatively annual fluctuation below 5 m (Asiwaju-Bello and Oladeji 2001). The UCPSA is tapped by a hand dug well and is usually prone to pollution because it is near to the ground surface. Unlike the lower coastal plain sand aquifer (LCPSA), it is tapped by a borehole and is not vulnerable to pollution. The CPS aquifer is the most productive and exploited aquifer in Lagos state. More than 30% of groundwater supply in Lagos and its environs tap from this aquifer (Longe 2011).

Water supply in Lagos state is mainly through the mini water works across twenty-three towns with a total design capacity of about 53.2 million gallon per day (Mgd) while the micro water works covered about seventeen towns

across the state with a total design capacity of about 16.3Mgd (LWC 2012). Other sources include protected dug wells sunk by various households or private individuals who have the ability to construct one. According to LWC (2012) the mini and micro water works account for about 2,797.38Mgd and 1,208.77Mgd water supply respectively from the LCPSA (Longe 2011). The major settlements of the study area are located within Eti-Osa local government area (LGA). The major challenge is the rate of population growth, urbanization, sand mining/dredging, and ocean surge, among others. In addition, the LGA is also noted for high commercial and industrial establishments and tourist centres. These factors have resulted in increased waste generation with significant impact on the subsurface that serves as the major source of water supply in the area. Thus, for sustainable groundwater utilization in the area, the alarming rate of groundwater abstraction and waste generation into the subsurface must be curtailed.

Materials and method

Fifty-eight samples including 45 protected dug wells (PDW₁₋₄₅) and 13 boreholes (BH₄₆₋₅₈) were randomly selected for the hydrochemical analysis of groundwater composition in the study area. Samples were collected in clean 150ml polyethylene bottles and preserved in ice chests for onward delivery to the chemistry department, University of Lagos, Akoka. A pocket pH-102 meter (RoHS) was used to determine the pH. The pH meter was calibrated with a standard buffer solution prior to sampling. EC was measured in situ by EC DiST-3 meter (HANNA, HI 98303). TDS was measured using the TDS-3 meter, TDS/TEMP (HM Digital). The cations (Na⁺ K⁺, Ca²⁺ Mg²⁺) and anions (Cl⁻, HCO₃⁻, CO₃²⁻ and SO₄²⁻) were determined in the laboratory using standard methods as suggested by the American Public Health Association (APHA 1998).

Calcium was determined using 0.05 N EDTA titration, and chloride by a standard solution of 0.005 N AgNO₃ -argentometry titration using potassium chromate as an indicator. Bicarbonate and carbonates were determined by titration against standard H₂SO₄ solution (0.0392 N). Magnesium, potassium and sodium were determined by atomic absorption spectroscopy (AAS) (Hanna, HI 98180). Each metal was analysed at its specific wavelength. Sulphate was determined by direct reading using a spectrophotometer (HACH, DR/2000). Rockware (2006) software was

used for the graphical characterization of groundwater composition of the study area using a Piper diagram. The data were analysed using descriptive, bivariate and multivariate techniques using SPSS software 17.0 version. Co-ordinates of the sample locations were recorded by global positioning system (GPS) (Garmin map, 76CSX model) and thereafter were exported into ArcMap 9.3 software to produce map of the sampling locations.

A reliability test was conducted for the major ions. A reliability test is a method of identifying apparent inconsistencies in an analysis. Inconsistency only indicates that an analysis is unusual, not necessarily wrong (Hounslow 1995). The concentrations were computed using the charge balance error (CBE) formula (Appelo and Postma 2005) equation 1.

$$\frac{\Sigma \text{ cations} - \Sigma \text{ anions}}{\Sigma \text{ cations} + \Sigma \text{ anions}} \times 100\% \quad (1)$$

where the concentrations were expressed in meq/L. The calculated CBE shows that about 31% of the samples are less than or equal to $\pm 10.4\%$. The %CBE ranged between -61.7 and 77.1 with a mean value of 9.6.

Results and discussion

Groundwater characteristics

The descriptive statistics of the groundwater characteristics of the protected dug wells and boreholes are presented in Table 1.

The correlation analysis shows that a significant relationship exists among EC/ TDS and major ions in groundwater of the study area (Table 2). The strong positive correlations between TDS and Na^+ , Cl^- , Mg^{2+} , and SO_4^{2-} indicate the influence of sea water on the groundwater quality of the study area (Aiman and Mohamed 2010; Lu et al. 2011; Rao et al. 2012).

Factor analysis

The result of the factor analysis (FA) indicates two factors that can be used to explain the various processes controlling groundwater composition in the study area. The rotated factor matrix shows that the two factors extracted explain 82.54 % of the total variance (Table 3). According to Liu et al. (2003) factor loadings can be classified as strong, medium and weak corresponding

to values of >0.75 , $0.75 - 0.50$, <0.50 respectively. A factor loading of 0.75 was chosen as the parameter that influences that factor in this study (Kathy and Niranjali 2010). Factor I explains 68.62% of the total variance. It has a strong positive loading on Cl^- , Na^+ , EC, Mg^{2+} , TDS, Ca^{2+} , SO_4^{2-} and K^+ . The loading on pH, HCO_3^- and CO_3^- is very low. These parameters (Mg^{2+} , Cl^- , Na^+ , K^+ , and SO_4^{2-}) represent the dominant components of salinity (Lu et al., 2011). Factor II accounts for about 12.92% of the total variance which is characterized by medium positive loading of HCO_3^- and pH while carbonate is characterized by medium negative loading. The rest of the variables show weak loadings. The negative loading of CO_3^- and SO_4^{2-} on factor II confirms that the concentration of CO_3^- and SO_4^{2-} in the groundwater of the study area does not contribute significantly to HCO_3^- value. The application of FA to reduce the number of parameters needed to explain the groundwater data in this study is medium. Thus, 10 out of the examined parameters were needed to explain 82.54% of the variance in the data set across the two factors comprising 11 parameters. However, FA successfully identified the most significant sources/processes controlling the groundwater of the study area.

Table 1. Descriptive statistics of groundwater characteristics

Parameters Unit	pH	EC $\mu\text{S/cm}$	TDS mg/L^{-1}	Na^+ mg/L^{-1}	K^+ mg/L^{-1}	Ca^{2+} mg/L^{-1}	Mg^{2+} mg/L^{-1}	Cl^- mg/L^{-1}	HCO_3^- mg/L^{-1}	SO_4^{2-} mg/L^{-1}	CO_3^{2-} mg/L^{-1}
N	45	45	45	45	45	45	45	45	45	45	45
Minimum	3.40	40.00	30.00	0.60	0.20	12.00	0.00	6.00	0.00	2.00	0.00
Maximum	8.60	4040.00	2436.00	1080.10	52.30	1200.00	580.00	3400.00	621.60	1250.00	848.00
Mean	6.09	513.67	340.51	46.13	5.09	145.58	50.00	166.20	120.87	35.62	150.96
Std. Error	0.14	91.69	56.07	23.89	1.22	27.86	12.98	74.98	22.72	27.61	29.14

Parameters/ Unit	pH	EC $\mu\text{S/cm}$	TDS mg/L^{-1}	Na^+ mg/L^{-1}	K^+ mg/L^{-1}	Ca^{2+} mg/L^{-1}	Mg^{2+} mg/L^{-1}	Cl^- mg/L^{-1}	HCO_3^- mg/L^{-1}	SO_4^{2-} mg/L^{-1}	CO_3^{2-} mg/L^{-1}
N	13	13	13	13	13	13	13	13	13	13	13
Minimum	5.30	50.00	22.00	1.30	0.00	0.00	0.00	5.00	0.00	0.20	0.00
Maximum	7.10	403.00	301.00	31.00	12.30	88.00	42.00	31.00	149.10	45.00	398.20
Mean	6.01	155.39	106.49	13.33	3.91	23.60	9.98	18.27	38.74	13.80	78.42
Std. Error	0.14	32.74	24.80	3.37	1.01	9.46	4.51	2.24	9.69	4.89	41.90

UCPSA (Protected dug well)

LCPSA (Borehole)

UCPSA – upper coastal plain sand aquifer, LCPSA – lower coastal plain sand aquifer

Table 2. Relationship of groundwater parameters

Parameters	pH	EC	TDS	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	HCO ₃ ⁻	SO ₄ ²⁻	CO ₃ ⁻	
pH	Correlation	1										
	p-value											
EC	Correlation	0.095	1									
	p-value	0.479										
TDS	Correlation	0.09	.998**	1								
	p-value	0.502	.000									
Na ⁺	Correlation	0.104	.915**	.892**	1							
	p-value	0.437	.000	.000								
K ⁺	Correlation	0.145	.914**	.901**	.929**	1						
	p-value	0.277	.000	.000	.000							
Ca ²⁺	Correlation	0.053	.952**	.947**	.894**	.889**	1					
	p-value	0.695	.000	.000	.000	.000						
Mg ²⁺	Correlation	0.106	.933**	.920**	.944**	.890**	.886**	1				
	p-value	0.43	.000	.000	.000	.000	.000					
Cl ⁻	Correlation	0.085	.929**	.907**	.997**	.928**	.911**	.954**	1			
	p-value	0.527	.000	.000	.000	.000	.000	.000				
HCO ₃ ⁻	Correlation	0.236	.411**	.436**	0.2	.355**	.383**	.300*	0.214	1		
	p-value	0.075	0.001	0.001	0.133	0.006	0.003	0.022	0.107			
SO ₄ ²⁻	Correlation	0.082	.857**	.828**	.985**	.867**	.837**	.915**	.978**	0.084	1	
	p-value	0.542	.000	.000	.000	.000	.000	.000	.000	0.529		
CO ₃ ⁻	Correlation	-0.177	0.08	0.099	-0.049	-0.107	0.061	0.102	-0.025	-.268*	-0.022	1
	p-value	0.184	0.552	0.458	0.715	0.422	0.65	0.446	0.852	0.042	0.868	

** Correlation is significant at p> 0.01

* Correlation is significant at p> 0.05

Table 3. R-mode factor matrix of groundwater parameters

Parameters	Factor I	Factor II
pH	0.045	0.636
Electrical conductivity (μ /Scm)	0.971	0.108
Total dissolved solids(mg/L)	0.958	0.111
Sodium (mg/L)	0.974	0.061
Potassium (mg/L)	0.934	0.204
Calcium (mg/L)	0.948	0.088
Magnesium(mg/L)	0.968	0.037
Chloride (mg/L)	0.983	0.047
Bicarbonate (mg/L)	0.268	0.716
Sulfate (mg/L)	0.942	-0.022
Carbonate (mg/L)	0.093	-0.720
% of Variance	68.616	12.924
Cumulative % of Variance	68.616	81.540

Characterization of groundwater composition

The results of the dominant cation are in the order of $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$ while the anions indicate $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ (Table 4).

The characterization of the groundwater composition of the study area is presented in Figure 2. The result shows seven distinct hydrochemical water types including Ca- HCO_3 , Ca-Cl, Mg- HCO_3 , Na- SO_4 , Mg-Cl, Na- HCO_3 and Na-Cl. The Ca- HCO_3 is dominated by alkaline earths and weak acids (Karanth 1987). This water type occupies the diamond-shape section designated as II and accounts for 44.8% of groundwater in the study area. It comprised 44.4% and 46.1% of the contribution from PDW and boreholes respectively. Another water type in this section is Mg- HCO_3 representing 15.5% of groundwater and 20% of the contribution from PDW. Also included in this section is Na- HCO_3 water type representing 3.4% of the groundwater and 15.4% of the contribution from boreholes. The source

of these water types comprises either dolomite or calcite in the aquifer and is characterized by temporary hardness (Tay and Kortatsi 2007). The Na-SO₄ and Na-Cl water types have saline characteristics. These water types occupy the diamond-shape section designated as V and account for 5.2% and 1.7% respectively of groundwater in the area with contributions from the boreholes only. Their sources may originate from the sea or rain water (Tay and Kortatsi 2007). A minor water type, Ca-Cl water representing 25.1% of the groundwater is delineated in the diamond-shape field I. It comprised 28.9% and 15.4% of the contribution from PDW and boreholes respectively. The source aquifers contain gypsum or anhydrite that may have undergone dissolution and, therefore, are characterized by permanent hardness (Tay and Kortatsi 2007). The Mg-Cl water type occupies the section designated as III and forms 3.4% of groundwater with a 4.4 % contribution from PDW.

Table 4. Concentration of ions according to water type in the study area

Water type	Statistic	HCO ₃ ⁻ meq/l	SO ₄ ²⁻ Meq/l	Cl ⁻ meq/l	Ca ²⁺ meq/l	Mg ²⁺ meq/l	Na ⁺ meq/l	K ⁺ meq/l
Ca-HCO ₃ (n=26)	Min	0.41	0.00	0.17	0.10	0.06	0.03	0.00
	Max	13.90	0.35	4.00	15.73	3.45	1.66	0.13
	Mean	4.12	0.12	1.04	4.68	1.49	0.35	0.05
	Std. Error	0.60	0.02	0.21	0.77	0.20	0.07	0.01
Ca-Cl (n=15)	Min	0.00	0.02	0.14	1.19	0.00	0.06	0.00
	Max	10.00	26.10	96.18	60.05	47.86	47.12	1.34
	Mean	2.97	1.90	10.51	11.79	6.22	4.78	0.24
	Std. Error	0.78	1.73	6.20	3.80	3.07	3.06	0.09
Mg-HCO ₃ (n=9)	Min	3.30	0.10	0.90	1.50	2.10	0.20	0.10
	Max	13.60	0.40	5.00	5.70	2.10	0.20	0.10
	Mean	7.01	0.19	2.00	3.70	5.66	0.61	0.08
	Std. Error	1.17	0.03	0.43	0.44	0.78	0.14	0.01

Table 4. contd.

Water type	Statistic	HCO ₃ ⁻ meq/l	SO ₄ ²⁻ Meq/l	Cl ⁻ meq/l	Ca ²⁺ meq/l	Mg ²⁺ meq/l	Na ⁺ meq/l	K ⁺ meq/l
Na-SO ₄ (n=3)	Min	0.49	0.89	0.62	0.00	0.00	1.30	0.10
	Max	0.54	0.93	0.70	0.00	0.00	1.35	0.13
	Mean	0.51	0.91	0.66	0.00	0.00	1.32	0.12
	Std. Error	0.01	0.01	0.02	0.00	0.00	0.02	0.01
Mg-Cl (n=2)	Min	1.80	0.17	4.67	2.49	2.79	2.06	0.16
	Max	3.44	0.21	6.92	5.87	8.70	3.03	0.27
	Mean	2.62	0.19	5.80	4.18	5.75	2.55	0.22
	Std. Error	0.82	0.02	1.13	1.69	2.96	0.49	0.06
Na-HCO ₃ (n=2)	Min	0.79	0.11	0.31	0.32	0.19	0.35	0.05
	Max	2.44	0.24	0.48	1.10	0.82	1.14	0.31
	Mean	1.62	0.18	0.40	0.71	0.51	0.75	0.18
	Std. Error	0.83	0.07	0.09	0.39	0.32	0.40	0.13
Na-Cl (n=1)	Min	0.71	0.26	0.73	0.15	0.09	0.88	0.27
	Max	0.71	0.26	0.73	0.15	0.09	0.88	0.27
	Mean	0.71	0.26	0.73	0.15	0.09	0.88	0.27
	Std. Error							

Min – minimum, Max – maximum, Std – standard

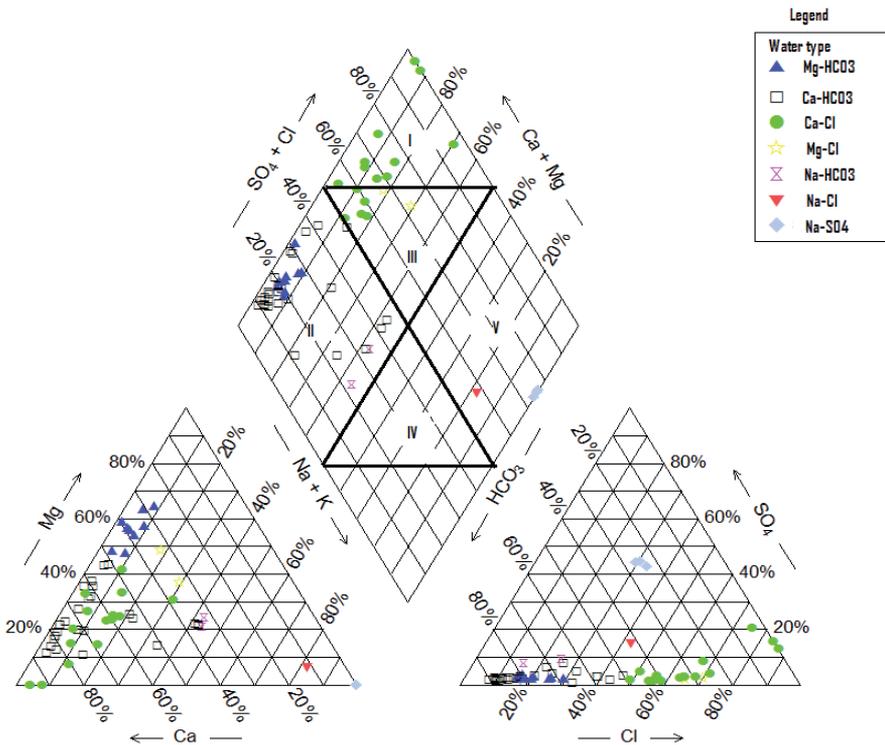


Fig. 2. Piper plot of groundwater composition

Conclusions

the study reveals a relatively higher mean value of the protected dug wells compared to the boreholes. A significant relationship exists at $p > 0.05$ level of significance among EC/ TDS and major ions indicating the influence of sea water on the groundwater quality in the study area. The dominant ions are in the order of $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$; $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-}$. Factor analysis indicates sea water and industrial wastes as the major sources of pollution responsible for the processes controlling groundwater quality in the area. The Piper plot characterized seven distinct water types including Ca-HCO₃, Ca-Cl, Mg-HCO₃, Na-SO₄, Mg-Cl, Na-HCO₃ and Na-Cl representing 44.8%, 25. %, 15.5%, 5.2%, 3.4%, 3.4%, and 1.7% respectively. The paper recommended monitoring of groundwater abstraction and treatment of industrial effluent before being released into the subsurface to prevent salinization and quality deterioration in the study area.

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