



Groundwater quality analysis in Hail region of northwest Saudi Arabia based on physicochemical investigation

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ABSTRACT

The acquired groundwater data from seventeen wells were hydrochemically analyzed for Sulfate, Chloride, Ammonia, Nitrate, Nitrite, pH, EC (Electrical Conductivity), TDS (Total Dissolved Solids), total hardness, and total alkalinity concentrations and then compared to the national and international standards. The results range as follows: *pH* (6.65–8.26), *EC* (382–1214 $\mu\text{S}\cdot\text{cm}^{-1}$), *Total hardness* (72–310 ppm), *TDS* (258–775 ppm), *Total alkalinity* (54–138 ppm), *Cl* (19–202 ppm), *Ammonia* (NH_3) (0.0 to 1.5 mg/liter), *Nitrate* (NO_3) (4.7 to 65.6 ppm), *Nitrite* (NO_2) (0.007 to 0.05 ppm), and *sulfate* (SO_4) (29–278 ppm). About 70.58 % of the study area's groundwater samples have TDS levels below 500 mg/l, which are considered safe for drinking. The EC of the groundwater found that 100 % of the samples fall within the allowed level. Based on these results, the groundwater quality is suitable for drinking and irrigation purposes in Hail region. Hence, this research shows that using GIS and chemical analysis of groundwater could be useful tools for the decision-making process of local and international authorities and water resources management.

1. Introduction

Analysis of groundwater quality is important as it is the main factor determining its suitability for drinking, domestic, agricultural, and industrial purposes (Subramani et al. 2005, Kouser et al., 2022, Badr et al., 2023, Alshehri and Abdelrahman, 2023, Alrowais et al., 2023, Iddrisu et al., 2023, Gao et al., 2023). Because groundwater can be used for a variety of reasons, both its quantity and quality are crucial. Physical and chemical characteristics that strongly affect the variance of a region's groundwater quality include geological formations and human activities (Kelley, 1940; Wilcox, 1948; Belkhiry et al., 2010; Alfaifi et al., 2020; Benjmel et al., 2022). The classification of water quality is significantly influenced by the chemical properties of groundwater. It was noted that the standards used to categorize water for one use based on concentration may not be appropriate for other uses, and better outcomes can be obtained by considering the combined chemistry of all ions rather than individual or paired ions (Handa, 1964, 1965; Hem, 1985; Ibrahim, 2018; Salem, 2021).

The chemical classification also sheds light on the interrelationships and concentration of several main cations and anions. Ions, dissolved gases, and single-celled creatures make up water. When these ions, dissolved gases, and hazardous organisms exceed a certain threshold, water is categorized as being unsafe for drinking and other domestic uses. This limit has been set for specific parameters based on how they behave when their concentration is above or below the WHO-recommended level (2004 and 2011; Table 1). The usefulness of

groundwater for use in agriculture and industry, as well as for human and animal sustenance, is determined by its quality. Since pure water is a poor conductor, the TDS parameter is frequently determined from the EC of the water. Water's capacity to conduct electricity is increased when impurities are dissolved in it. To classify the groundwater quality in the study area, TDS, pH, and EC were calculated.

Inorganic salts and trace amounts of organic materials that have been dissolved in water make up the TDS. It describes the quantity of dissociated minerals that are currently present in water. The concentration of each of its components determines how TDS affects the quality of the water. Significant hardness, taste, mineral deposition, and corrosion are typical characteristics of water that have been heavily mineralized (Basavarajappa and Manjunatha, 2015). A health-based guideline value has not been proposed, making it difficult to ascertain the negative impacts of TDS consumption on one's health. However, a recommended dosage of 1000 mg L⁻¹ has been established based on taste considerations. Water with exceptionally low TDS levels may not be suitable due to its bland, insipid flavor (Khan and Chohan, 2010). TDS may decrease the irrigated area's hydraulic conductivity, according to Jamrah (1999), and a TDS value above 480 mg L⁻¹ is of concern. Because different geological regions have varied mineral solubilities, the TDS in water greatly varies between them (WHO, 2011). The TDS concentrations and major ions are typically increased as a result of the groundwater being moved and staying along its flow path for an extended period. A high TDS value reflects the water's prolonged residence time. The main factor typically limiting or determining the use of groundwater for any purpose

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Table 1
Comparison of analytical results with international standards.

Parameter	Max	Min	Mean	WHO (2004)	WHO (2011)
pH	8.26	6.65	7.45	6.5–8.5	6.5–8.5
EC ($\mu\text{S cm}^{-1}$)	1214	382	1415.5	1500	300–750
TDS (mg L^{-1})	775	258	516.5	1500	755
SO ₄ (mg L^{-1})	278	29	153.5	250	
T.A (mg L^{-1})	138	54	96		200
Cl ⁻ (mg L^{-1})	202.35	19	110.675	600	250
T.H (mg L^{-1})	310	72	191		80–120
Ammonia	1.5	0.0	0.75		
Nitrate	65.6	4.7	35.15		
Nitrite	0.05	0.007	0.0285		

is its TDS concentration (Table 2a).

Based on the spatial distribution of hydrochemical groundwater constituents and their suitability for local residential uses and irrigation activities, the current investigation covers a large area of Hail region and seeks to evaluate the groundwater quality in the region using a GIS software package.

2. Materials and methods

2.1. Location and geology of study area

The Hail area lies in the northwest of Saudi Arabia (Fig. 1) and is distinguished by its diverse topography and geomorphology; the region is a part of the huge An-Nafud and the Arabian Shield. Geologically, the vast An-Nafud, which makes up a significant portion of the Hail region, is a sand-filled depression that extends over roughly 64,000 km² (Fig. 2). The limestone, sand, and steep wades that make up the Arabian Shield, which rises to hills, are distinctive. However, the dunes and sand sheets appear to be made of Paleozoic and Mesozoic sandstones (El-Ghanim et al., 2010). Hail's highest point is more than 1900 m above mean sea level in the province's far southwest corner, while the lowest point on the land is about 667 m. The region is made up of 55,270, 40,650, 18,380, and 1390 km² of plains, dunes, mountains, and arable land, respectively (Hereher et al., 2012).

Precambrian basement rocks, Paleozoic sedimentary formations, and Cenozoic unconsolidated deposits make up Hail geology (McGillivray and Husseini, 1992). As you move from southwest to northeast, the formations get younger and younger. Felsic igneous rocks make up the Precambrian basement rocks. The Saq Formation, Tabuk Formation, Jauf Formation, and Khuff Formation make up the Paleozoic era's sedimentary formation. The principal aquifer exposed in the research region is the Saq formation, which is composed of medium- to coarse-grained sandstone and ranges in age from the Cambrian to the Ordovician. The Tabuk formation, which consists of interbedded layers of sandstone, shale, and siltstone and is older than the Saq formation, varies in age from the Ordovician to the Silurian. The Devonian Jauf formation rocks conformably overlie it (Quartz sandstone, shale, and dolomite). The Permian Khuff Formation lies on top of the Jauf Formation (limestone and shale). The unconsolidated sediments from the Quaternary epoch serve as a representation of the Cenozoic era.

Table 2a
Groundwater classification based on TDS (Davis and DeWiest, 1966).

Davis and DeWiest (1966)		Freeze and Cherry (1977)	
TDS (mg L ⁻¹)	Classification	TDS (mg L ⁻¹)	Classification
< 500	Desirables for Drinking	< 1000	Freshwater type
500–1000	Permissible for drinking	1,000–10,000	Brackish water type
1000–3000	useful for irrigation	10,000–100,000	Saline water type
>3000	Unfit for drinking and irrigation	>100,000	Brine water type

The aeolian sand deposits, which are a part of the Nafud desert, cover the northern portion of the study region. The general flow direction is from west to east, and the piezometric levels range from 910 to 660 m. In the west, the hydraulic gradient is steeper, and it progressively flattens out as you move toward the east (Zaidi et al., 2014). In particular, in the area around the city of Hail, the groundwater levels are around 220 m below the surface and gradually get shallower (54 m) toward the central zone, having deeper water levels than the rest of the region (Fig. 4a). All of the wells that provided the water samples for analysis tap the Saq aquifer, and their depths range from 150 to 850 m.

2.2. Data collection

According to the operating method for groundwater sampling, samples were taken and kept (SESD, 2013). Groundwater quality data were collected in March 2023 from seventeen (17) boreholes to assess the quality of water underlying the study area. Samples were distributed to cover most of the study area. All water samples were gathered in polypropylene (PP) bottles that had been rinsed several times with sample water before collection and then stored at 04 °C in the ice box until subsequent laboratory analysis. Afterward, all water samples were transferred to the King Saud University laboratory for analysis. The samples were analyzed on the next day they were collected. The primary ions of the water samples that were obtained were identified. These groundwater samples had their ionic components Nitrate, Nitrite, and Cl⁻, minor elements, pH, electrical conductivity (EC), total dissolved solids (TDS), total alkalinity (TA), and total hardness (TH) measured (Table 1). Before taking water samples, groundwater that had become stagnant was flushed out of bore wells for around three minutes. Color, taste, odor, temperature, EC (measured with a conductivity meter), and pH are the physical parameters that are measured and recorded in the field (using pH meter).

2.3. Methodology

Fig. 3 shows the methodology of the current study, which includes groundwater sampling and analysis, comparing the obtained results with national and international standards, spatial distribution for sample locations, and different parameters using GIS.

3. Results and discussions

The results of the physicochemical characteristics of the groundwater have been obtained. Then, compared to the World Health Organization's (WHO, 2004 and 2011) as well as the Bureau of Indian Standards BIS (2012) recommended values for drinking water and irrigation activities (Table 1).

3.1. Groundwater quality

3.1.1. Total Dissolved Solids, TDS and pH, and Electrical Conductivity (EC)

The TDS content in the water has no health-based limit set by WHO, although beyond 1000 mg/l, the flavor of the water substantially changes. Very little TDS water has a bland flavor (Khan and Chohan, 2010). Geology has an impact on water's TDS since different minerals have varying degrees of solubility in water (WHO, 2011). The interaction of rocks with water and recharging from rainfall both affect TDS concentration. TDS typically establishes the overall quality of groundwater that can be used for a certain purpose. Poor sewage disposal practices, increased mineral dissolution leading to a smaller pH, or seawater intrusion could all contribute to a greater TDS content (Sarath Prasanth et al., 2012; Subba Rao, 2001; Ramesh et al., 2012). Based on the TDS value, the suitability of groundwater for different uses has been categorized, as indicated in Table 2a. According to Table 2a, all groundwater samples are within the levels that are acceptable for

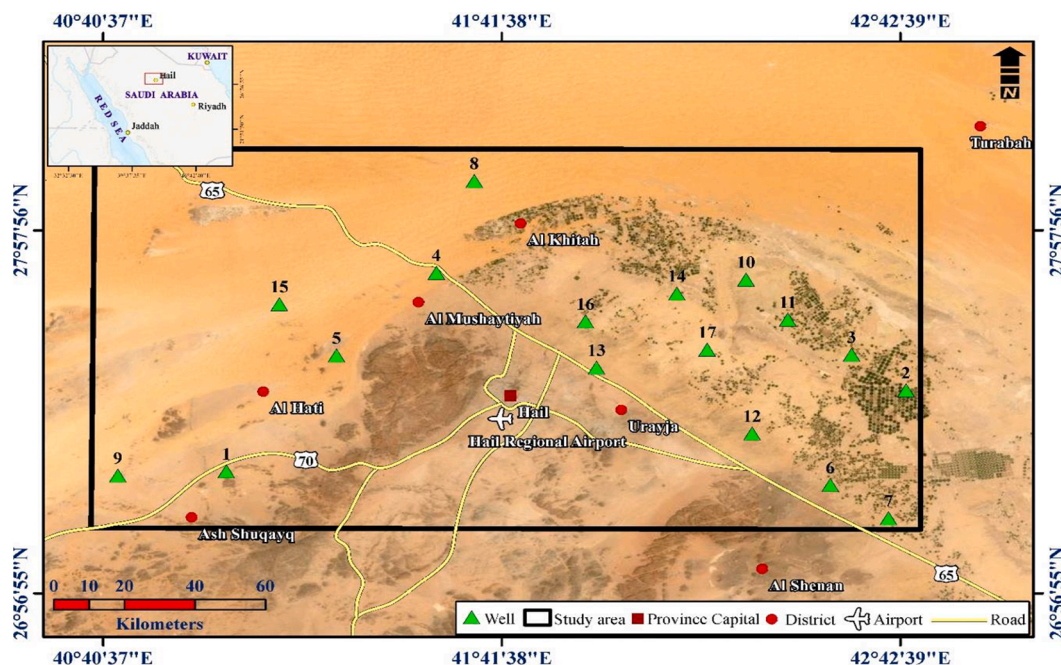


Fig. 1. Location map of the study area including the groundwater sampling wells.

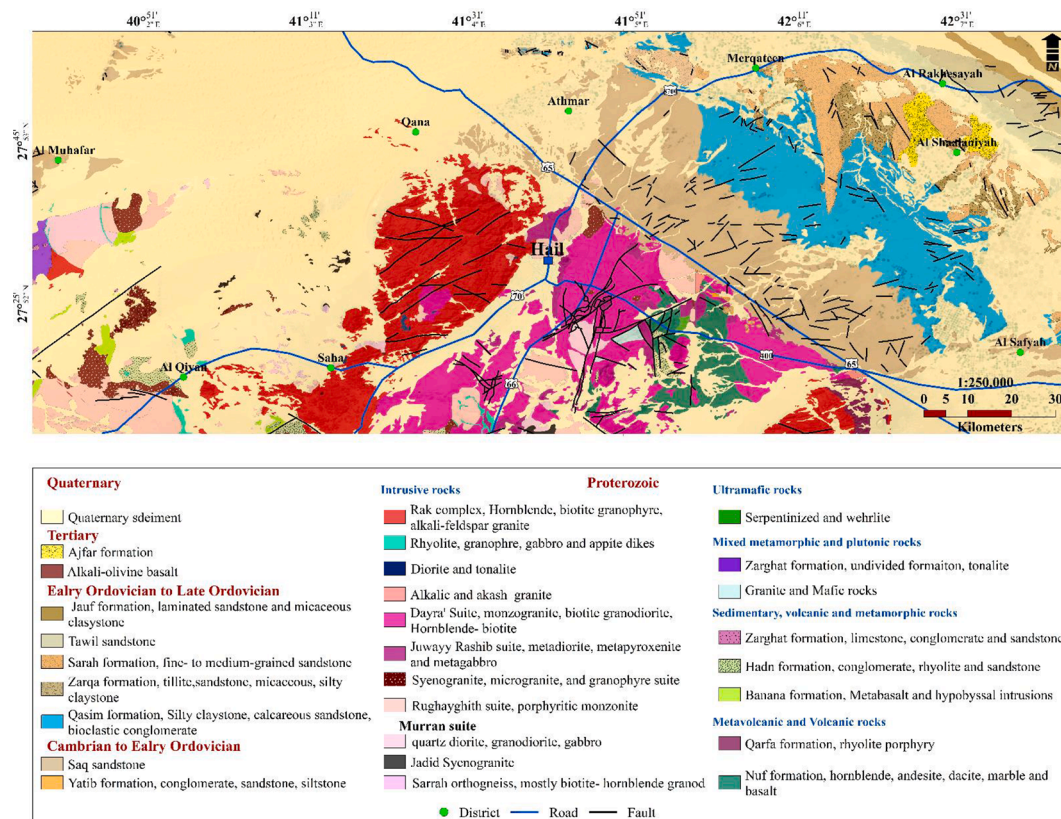


Fig. 2. Geological map of the study area.

drinking water, hence the groundwater that is produced by these wells is good for use in agriculture. In the collected groundwater samples, the TDS values in the current investigation range from 285 to 775 mg.L⁻¹ (Fig. 4b). All groundwater samples fall within the ranges that are safe for domestic drinking.

Besides, it is possible to assess how water interacts with rocks and

other objects by looking at its acidic and alkaline qualities (Hem, 1985). According to international standards and the Bureau of Indian Standards (BIS, 2012), the acceptable pH range for drinking water is 6.5–8.5. (WHO, 2004) (Table 1). Acidic water is defined as having a pH of 7 or lower, and alkaline water has a pH of 7 or higher. The collected groundwater samples in the area of study have a pH value between 6.65

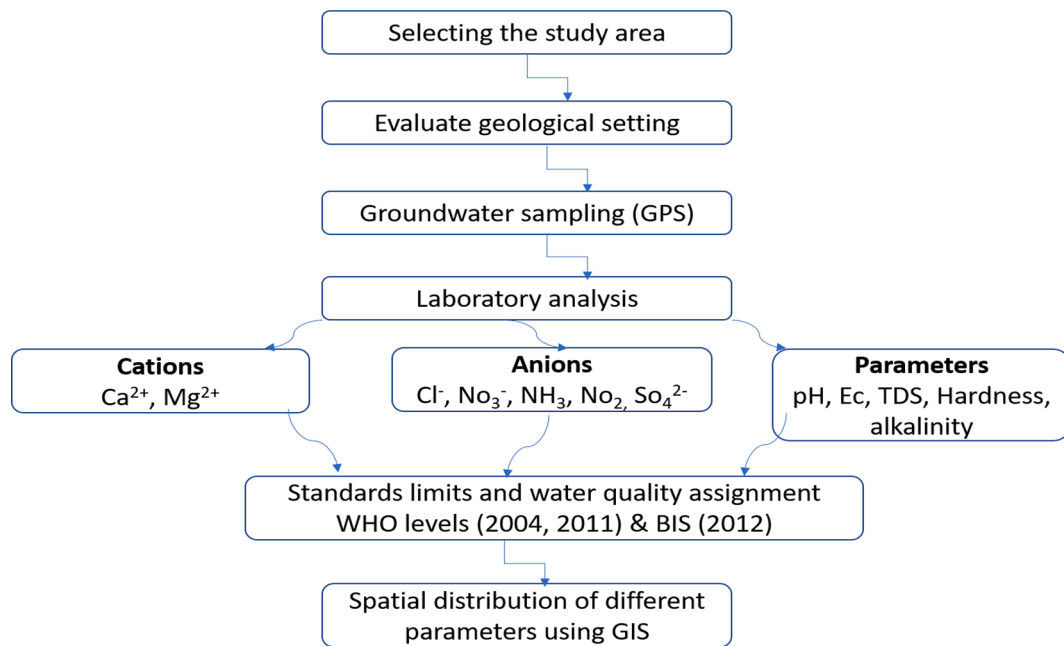


Fig. 3. Flowchart of research methodology in the current study.

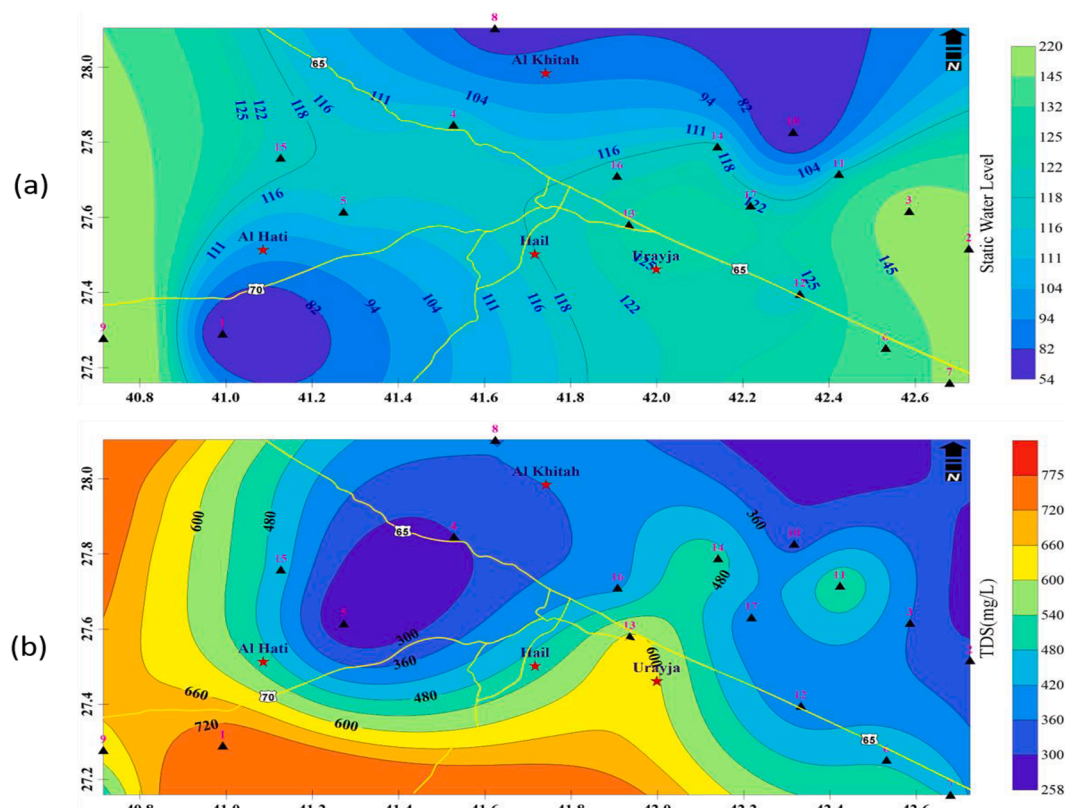


Fig. 4. A) the static water level in the study area, b) spatial distribution of tds in the study area.

and 8.25. This shows that the groundwater of the study area is mainly alkaline in nature.

Moreover, the geochemical processes of ion exchange, reverse exchange, evaporation, silicate weathering, rock-water interaction, sulfate reduction, and oxidation are primarily responsible for the EC variation in general (Ramesh, 2008). The study area's nutrient enrichment, evaporation rate, and arid climate could all be contributing factors to the

EC enrichment. High salinity and mineral content are linked to the higher electrical conductivity of water. Ions such as Cl^- and NO_3^- are present, which adds to the salinity of groundwater. According to WHO 2004 recommendations, $1500 \mu S \cdot cm^{-1}$ is the highest permitted value for EC (Table 2b). According to Manjunatha and Asode (2021), the EC can often be divided into the following four parts: C1: is Low ($0-249 \mu S \cdot cm^{-1}$), C2: is Medium ($250-749 \mu S \cdot cm^{-1}$), C3: is High ($750-2249$

Table 2b
Groundwater classification based on EC for drinking and irrigation purposes (Manjunatha and Asode, 2021).

Electrical conductivity ($\mu\text{S}\cdot\text{cm}^{-1}$) for drinking	Classification	Electrical conductivity ($\mu\text{S}\cdot\text{cm}^{-1}$) for irrigation	Suitability for irrigation
<1500	Permissible	Below 250	Entirely safe
1500–3000	Not permissible	250–750 (Moderately saline)	Safe under all conditions
>3000	Hazardous	750–2250 (medium to high salinity)	Safe only with permeable soil and moderate leaching
		2250–4000 (high salinity)	Unfair for irrigation
		4000–6000 (Very high salinity)	
		Above 6000 (Excessive salinity)	

$\mu\text{S}\cdot\text{cm}^{-1}$), and C4: is Very High (2250–5000 $\mu\text{S}\cdot\text{cm}^{-1}$). Based on the function of the amount of dissolved mineral matter in the water, electrical conductivity (EC) is determined. Drinking and irrigation waters are typically classified using the criterion EC (Srinivasamoorthy et al., 2014). In the current study, the EC value ranges from 382 to 1250 $\mu\text{S}\cdot\text{cm}^{-1}$ (Fig. 2b). According to this figure, all samples display values less than 1500 $\mu\text{S}\cdot\text{cm}^{-1}$ indicating freshwater. The figure shows that EC smaller values are noticed in the eastern and northwestern zones of the area.

3.2. Physicochemical parameters

Calculations of the spatial distribution of TDS concentrations and hydrochemical facies can be used to estimate relative groundwater flow

rates, identify areas of groundwater mixing, and discriminate between recharge and discharge zones. To depict the main ions' and hydrochemical facies' aerial distribution, contour maps were created.

3.2.1. Sulfate (SO_4^{2-})

The highest allowable limit of sulfate in groundwater is 400 mg/L, whereas the desired limit is 250 mg/L, according to WHO (2004). In the current investigation, the sulfate concentration ranges from 29 to 278 mg/L (Fig. 5b). Around well No. 1, in the southwest zone of the study area, higher sulfate values are detected. The presence of sulfide-bearing minerals, the dissolution of gypsum, the usage of sulfate-bearing fertilizers, and industrial wastes are all factors that contribute to the presence of sulfate in groundwater.

3.2.2. Total hardness

Due to the presence of CO_2 in the atmosphere and plant roots in the soil, precipitation that seeps into the ground is acidic. The groundwater becomes harder as a result of the low pH solution dissolving insoluble carbonates and contaminants such as sulfates, chlorides, and silicates. Higher hardness water should not be used for home or industrial uses (Sarith Prasanth et al., 2012; Gopinath et al., 2015; Tahlawi et al., 2016; Nag and Lahiri, 2012).

The carbonate hardness is primarily caused by the carbonate and bicarbonate salts of calcium and magnesium. Other than carbonate and bicarbonate salts, calcium and magnesium salts are responsible for non-carbonate hardness (such as calcium sulfate, CaSO_4 , or magnesium chloride, MgCl_2). The sum of the hardness of carbonates and non-carbonates is the total hardness, which varies in severity with alkalinity. The bulk of natural water contains bicarbonate ions, which are typically coupled with calcium, magnesium, and to a lesser extent, sodium and potassium (Shov, 2014).

The main factors for water hardness are calcium and magnesium.

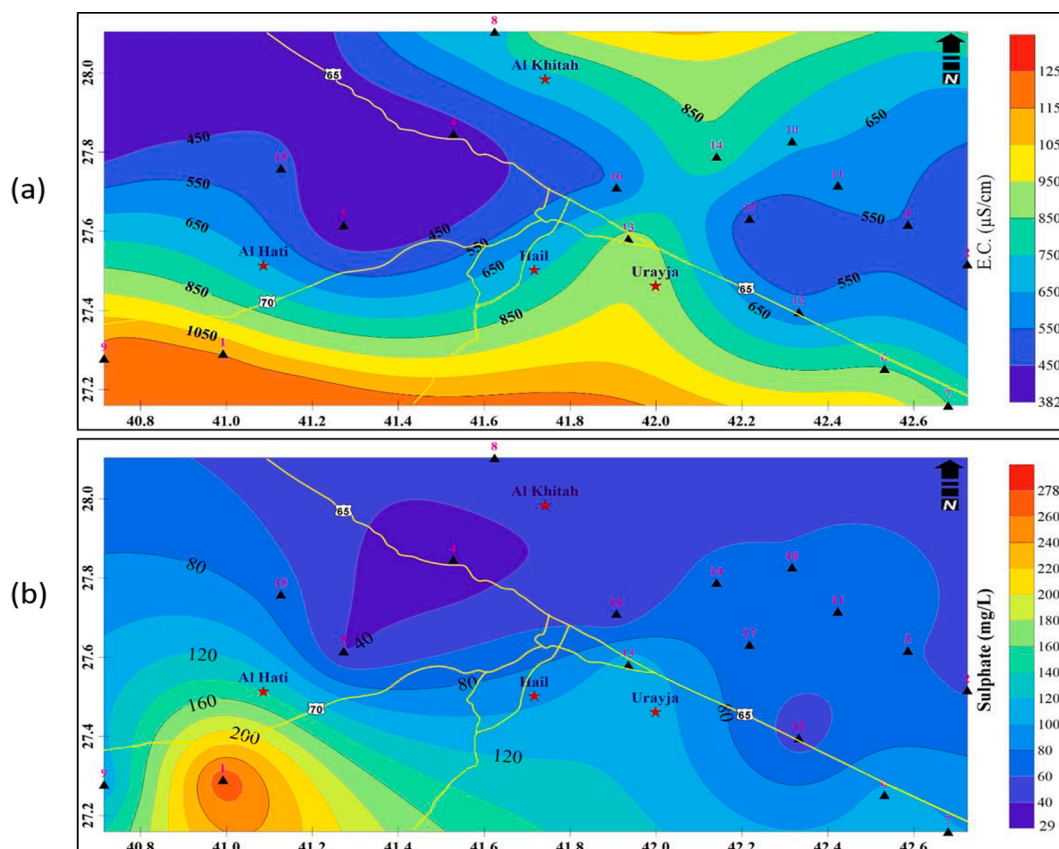


Fig. 5. A) spatial distribution of ec and b) distribution of Sulphate in the groundwater.

The hardness is often expressed as an equivalent concentration of dissolved calcite and describes the concentrations of particular metallic ions in water, particularly those of magnesium and calcium (CaCO₃). When detergent and the metallic ions in hard water interact, an insoluble deposit may result. If the water is hard, these kinds of metallic ions may also react with negatively charged ions to form a solid precipitate. Using the formula shown below, the total hardness of the water samples was calculated (Todd, 1980):

$$\text{Totalhardness} = 2.5Ca + 4.1M \tag{1}$$

where the amounts of calcium and magnesium are given in milligrams per liter.

In the area of interest, the total hardness of the water samples ranges from 72 to 430 mg/L (Fig. 6a). The classification of the water samples by Sawyer and McCarty (1967) was soft, moderately hard, hard, and very hard (Table 2c). The gathered water samples are exceedingly hard, as shown in this table.

3.2.3. Chloride (Cl⁻)

Chlorides were a frequent component of pure natural water. Cl⁻ was present in detectable concentrations between 19 and 202 mg/L (Fig. 6b). The percolation of irrigation return water or interconnection with higher, more salty strata may be to blame for the excessive levels of Cl⁻ in the investigated groundwater (Sharaf and Hussein, 1996; UN-ESCWA and BGR, 2013). When groundwater with high amounts of Cl⁻ is used for irrigation, the plants may become poisonous because the Cl⁻ is not absorbed by the soil and instead travels with the water in the soil, where it is absorbed by plants and stored in their leaves (Hussain et al., 2010).

3.2.4. Ammonia (NH₃)

When ammonia concentrations in water rise above the ppm limit, it

Table 2c

Classification of groundwater based on total hardness (mg/L) (after Sawyer and McCarty, 1967).

Total hardness (mg L ⁻¹)	Type of water	Remarks
< 75	Soft	Require little or no softening
75–150	Moderately hard	Require little or no softening
150–300	Hard	Require softening
> 300	Very hard	Require softening

becomes a poisonous toxin and a health risk. Unionized ammonia or the ammonium ion (NH₄⁺) are the two forms of ammonia in water. Usually, total ammonia or ammonia is stated as the figure, which is the total of both types. Ammonia can also come from organic debris, feces, or fertilizers, which are the main sources of pollution in homes, businesses, and agriculture. The pH level has a significant impact on how much of the two types are present in water relative to one another. When the pH is high, unionized ammonia, a poisonous form, predominates. When the pH is low, the ammonium ion, which is comparatively harmless, dominates.

When the pH is below 8.0, less than 10 % of the ammonia is typically in its hazardous form. As the pH rises, this ratio grows significantly. The temperature has an impact on the equilibrium between NH₃ and NH₄⁺. Warmer water contains more hazardous ammonia than colder water at any pH. Natural ammonia concentrations in groundwater are typically less than 0.2 mg/L. In layers with high concentrations of human compounds, iron, or wood, higher natural amounts (up to 3 mg/L) can be detected (Dieter et al., 1991). Ammonia concentrations in surface water can reach 12 mg/L. (WHO, 1986). The ammonia concentration in the study region ranges from 0.0 to 1.5 mg/liter (Fig. 7a). In general, it is less than 0.4 mg/liter, but well No. 4 has a unique circumstance that results in a high concentration that may be a common indicator of anthropogenic impacts, such as landfill leachate or agricultural activity

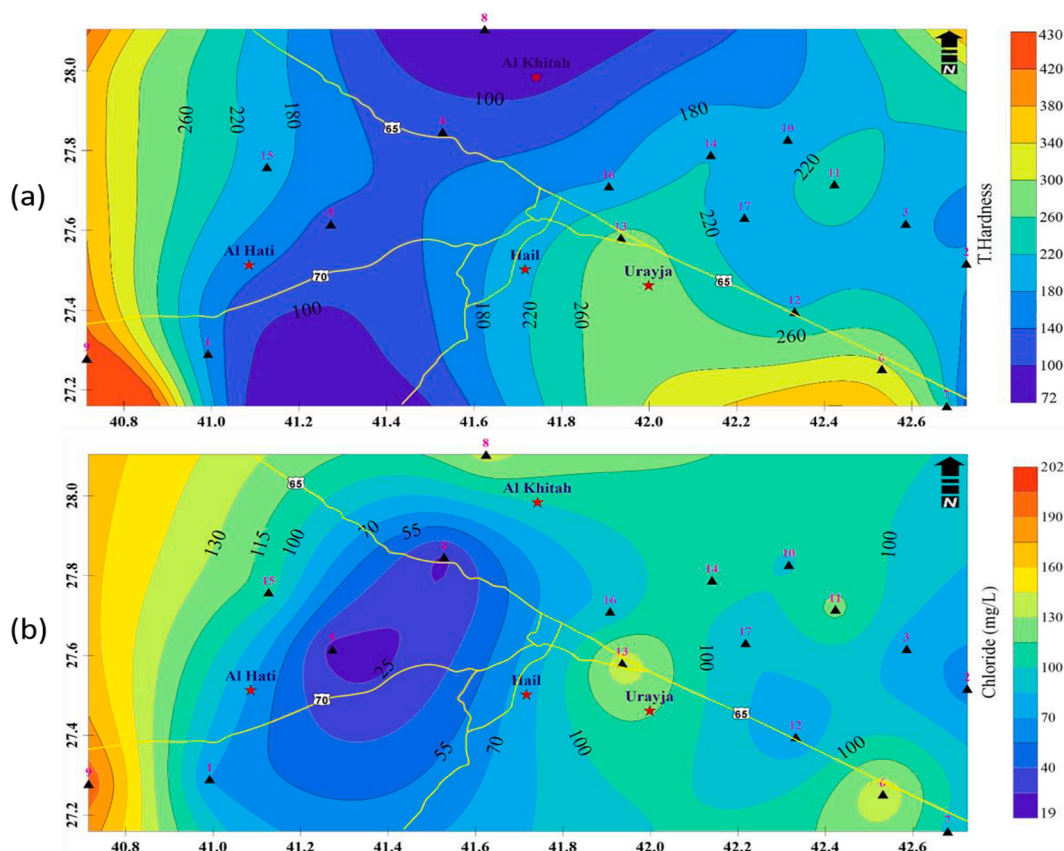


Fig. 6. A) Total Hardness (TH) distribution in groundwater samples, b) Cl⁻ concentrations in the groundwater samples.

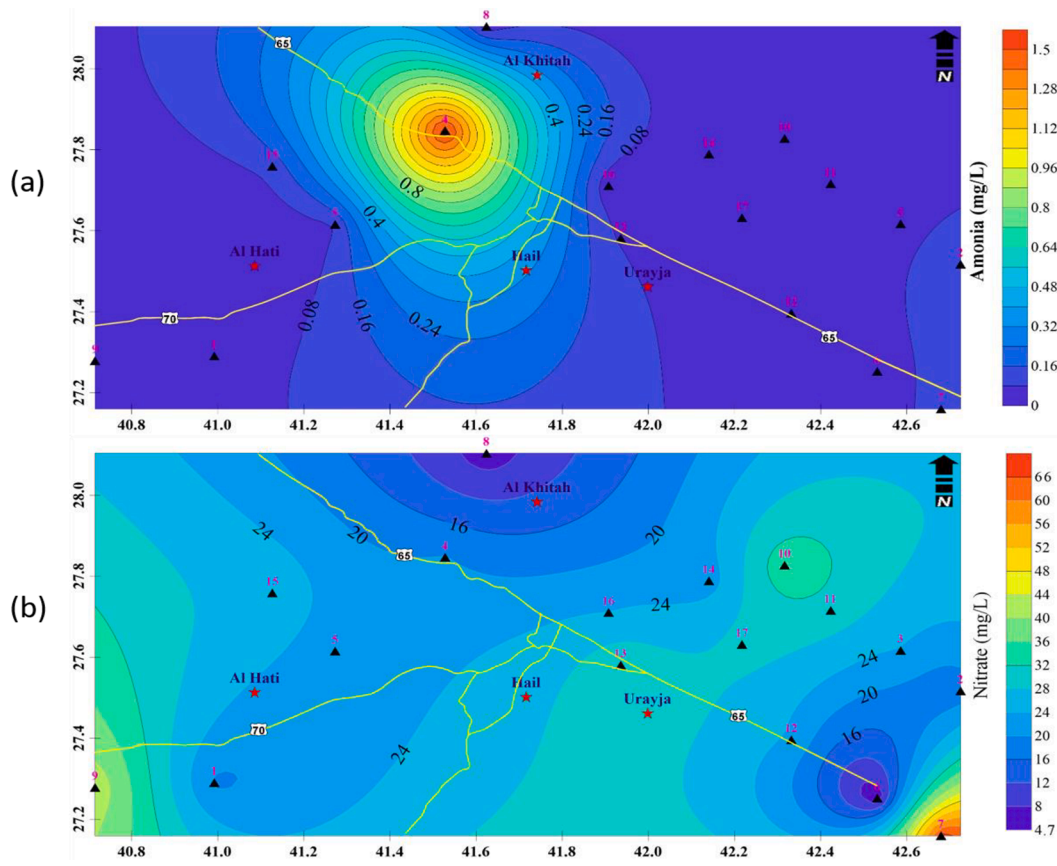


Fig. 7. A) ammonia concentrations in the groundwater, b) nitrate concentrations in the groundwater samples.

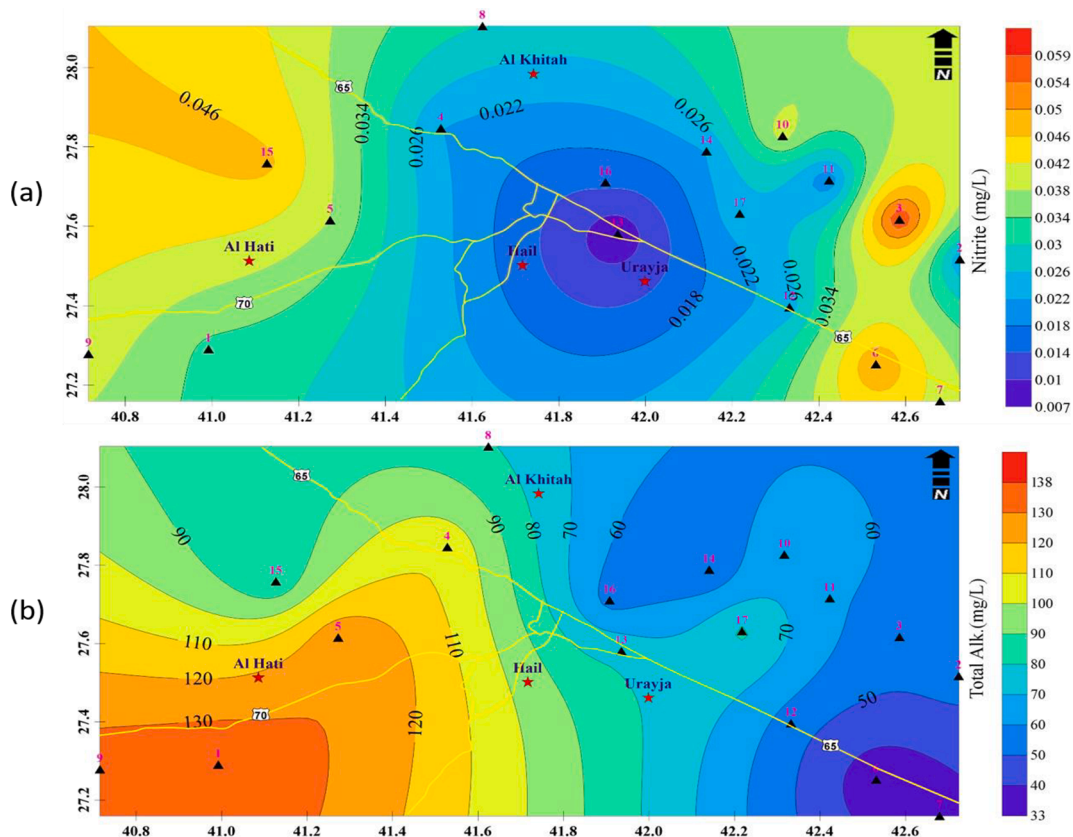


Fig. 8. A) spatial variations of nitrite concentrations in the groundwater samples, b) total alkalinity values of groundwater samples.

and/or due to the decay of natural organic material.

3.2.5. Nitrate (NO_3) and Nitrite (NO_2)

Under aerobic conditions, the natural nitrate concentration in groundwater is a few mg/L and is highly dependent on the soil type and geology (WHO, 2011). In industrial locations, rainfall nitrate concentrations of up to 5 mg/L have been recorded (van Duijvenboden and Matthijsen, 1989). Normal surface water nitrate concentrations range from 0 to 18 mg/L, although agricultural runoff can cause these levels to rise. In most nations, the amount of nitrate in drinking water that is made from surface water does not exceed 10 mg/L. However, owing to runoff, sewage effluent discharge, and industrial waste discharge, the concentrations are higher in some locations. Nitrite concentrations in drinking water are typically less than 0.1 mg/L. In the Netherlands, a high value of 0.21 mg/L was found in 1993. (RIVM, 1993). As the water travels to the system's edges, the concentration of nitrite could rise. Generally, nitrification in distribution systems has the potential to elevate nitrite levels by up to 3 mg/L. (AWWARF, 1995). Fertilizers and household trash that were transformed into nitrates in the soil are the main sources of nitrogen compounds (Kumar et al., 2009).

Away from the Hail urban area and in the farmland where farmers applied fertilizers for agricultural activities, both ions' concentrations rise. In the studied region, the nitrate concentration ranges from 0.14 to 25.08 ppm (Fig. 7b). In the northern and eastern zones, the value rises while falling in the southwest. The nitrite readings range from 0.015 to 0.136 ppm (Fig. 8a) where the minimum values are recorded in the central zone and increased away from the center.

3.2.6. Alkalinity

It is common to interpret the alkalinity of surface and groundwater in terms of the concentrations of the constituent's carbonate, bicarbonate, and hydroxide. Water's ability to neutralize acids increases with increasing alkalinity; on the other hand, its ability to do so decreases with decreasing alkalinity. The phenolphthalein and total alkalinity of the water were measured to identify various alkalinity types. Bicarbonate is connected to neutral water's overall alkalinity (Shov et al., 2014). In irrigation water, bicarbonate is a significant anion that is linked to calcium and, to a lesser extent, magnesium (Basavarajappa and Manjunatha, 2015). The WHO's recommended limits for all groundwater samples are met; the HCO_3^- the maximum permitted limit is 300 mg L^{-1} (WHO, 2011). Since it is the most prevalent anion in groundwater, silicates and weathering are the main causes of its dissolution in groundwater (Srinivasamoorthy et al., 2014).

All of the sampling wells recorded normal levels ranging from 33 to 138 mg.L^{-1} (Fig. 8b) that were within the WHO's 2011 total alkalinity limits (200 mg.L^{-1}). In the southwest of the Hail region, these values rise while falling in the east of Hail. The source of all the alkalinity in neutral water is bicarbonate (Shov et al., 2014). In irrigation water, bicarbonate is a significant anion concerning calcium and to a lesser extent magnesium (Basavarajappa and Manjunatha, 2015). Total alkalinity, a common anion in groundwater, dissolves primarily as a result of silicate breakdown and rock weathering (Srinivasamoorthy et al., 2014).

4. Conclusions

Groundwater samples from 17 wells in Hail area were collected, and their chemical and physical characteristics were examined and then compared to the World Health Organization's standard drinking water guidelines (SASO, 2000; WHO, 2008 and 2011). Based on the Hydrochemical analysis, groundwater contains acceptable concentrations of EC, total hardness, reasonable TDS, pH, Cl^- , and alkalinity values. Groundwater has been classified based on TDS values, to determine its suitability for drinking and irrigation uses. All groundwater samples in the area of interest are freshwater (Freeze and Cherry, 1977). About 70.58 % of the sample has TDS levels below 500 mg/l, which are safe for drinking. Moreover, the EC of the groundwater revealed that 100 % of

the samples fall within the permissible limit, though some samples are marginally well in quality by the World Health Organization (WHO) standard. Other factors influencing water quality are the type of rocks, the geological formation, and the weathering process occurring in the region. It can be concluded that the groundwater is valid for drinking and irrigation purposes. The outcome of this research work can be used by policy-makers, and local and regional authorities, to improve groundwater management and offer safe drinking water to all populations in arid and semi-arid areas.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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