

Research Article

Talal Alharbi*, Abdelbaset S. El-Sorogy

Groundwater quality and health risk assessment of nitrate and fluoride in Al Qaseem area, Saudi Arabia

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Abstract: Groundwater serves as the lifeline in arid regions, where aquifer overuse and climatic factors can substantially degrade its quality, posing significant challenges. The current study examines the drinking water quality in the Al Qaseem area and assesses the potential health risks from nitrate (NO_3^-) and fluoride (F^-) exposure to infants, children, and adults. This evaluation employs parameters such as the daily water intake, hazard quotient, and non-carcinogenic hazard index. Groundwater samples from 38 wells and boreholes were analyzed for major cations and anions. The water quality index and multivariate tools were utilized. The average concentrations of SO_4^{2-} , Cl^- , Ca^+ , Na^+ , Mg^{2+} , and K^+ exceeded acceptable limits. Among the 38 samples, 8 were unsuitable for drinking, with 5 categorized as very poor quality, 10 as poor, 14 as good, and 1 as excellent. Nitrate levels ranged from 1.30 to 108.00 mg/L, with a mean of 36.56 mg/L. Three wells exceeded World Health Organization (WHO) guidelines (50.00 mg/L). Fluoride ranged from 0.10 to 0.98 mg/L, with a mean of 0.71 mg/L and none surpassing WHO recommendations (1.5 mg/L). The HI values for adults, children, and infants were 0.993, 2.606, and 2.78, respectively. About 57.89% of the water samples exceeded the safety level of 1 for adults and 94.73% for both children and infants. Thus, the groundwater in the study area may pose non-carcinogenic health risks to infants, children, and adults when used as drinking water.

Keywords: nitrate, fluoride, hazard index, daily water intake, water quality index, Saudi Arabia

1 Introduction

Groundwater plays a crucial role in providing water for drinking and irrigation, particularly in arid and semiarid areas [1–4]. Contamination of groundwater poses substantial risks to human health and the environment, especially in cases where major cations and anions like nitrate and fluoride are present in high concentrations. Nitrate (NO_3^-) and fluoride (F^-) are among the most common contaminants found in groundwater worldwide, with sources ranging from agricultural runoff to industrial discharge and improper waste disposal [5–7]. Increasing the nitrate level in drinking water to more than 45 mg/L may lead to blue infant disorder. In adults, elevated nitrate levels have been associated with cancer risks, thyroid dysfunction, and hypertension [8,9]. However, fluoride concentrations exceeding 1.5 mg/L in drinking water can lead to dental and skeletal fluorosis, arthritis, infertility, and abortion [10–15].

Nitrate contamination in groundwater is often associated with agricultural activities, where nitrogen-based fertilizers and animal manure contribute to high nitrate levels in soil and water systems [16]. In regions with intensive farming practices, nitrate leaching from agricultural lands seeps into groundwater, leading to elevated nitrate concentrations in drinking water sources [17]. Similarly, fluoride contamination in groundwater is prevalent in areas with naturally occurring fluoride-rich geologic formations, where dissolution of fluoride-bearing minerals contributes to high fluoride concentrations in groundwater [18]. Anthropogenic activities such as industrial processes and mining can further worsen fluoride contamination in groundwater by releasing industrial effluents containing fluoride compounds. Understanding the dynamics of nitrate and fluoride contamination in groundwater is vital for implementing effective mitigation strategies and safeguarding public health. Monitoring programs, water quality assessments, and remediation efforts are crucial elements in managing groundwater contamination with major cations and anions, especially nitrate and fluoride. By pinpointing

* **Corresponding author: Talal Alharbi**, Geology and Geophysics Department, College of Science, King Saud University, Riyadh, 11451, Saudi Arabia, e-mail: tgalharbi@ksu.edu.sa

Abdelbaset S. El-Sorogy: Geology and Geophysics Department, College of Science, King Saud University, Riyadh, 11451, Saudi Arabia, e-mail: asmohamed@ksu.edu.sa

pollution sources, implementing pollution control measures, and advocating for sustainable land use practices, stakeholders can strive to reduce the impacts of nitrate and fluoride contamination on groundwater quality and human well-being [19].

In the last two decades, extensive research has been dedicated to studying the groundwater of central Saudi Arabia. This research has explored various aspects including water resources, suitability for drinking and agricultural purposes, as well as hydrochemical evaluations [20–27]. Some of these studies have uncovered elevated levels of TDS, Ca^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , and F^- , exceeding the allowable limits established by the World Health Organization (WHO) for drinking water [28]. However, studies addressing the health risks associated with these major ions remain limited. Consequently, this study has three main objectives: (1) to assess the groundwater quality in the Al Qaseem region by analyzing major cations and anions, (2) to determine the levels of nitrate and fluoride contamination and understand their distribution in the groundwater, and (3) to analyze the health risks associated with nitrate and fluoride ingestion for adults, children, and infants, using a method recommended by the United States Environmental Protection Agency.

2 Material and methods

2.1 Geological and hydrogeological setting

The Al Qaseem region, located in central Saudi Arabia, is a significant agricultural hub (Figure 1). The ground elevated from 600 to 750 m above mean sea level, with a gentle slope toward the east. It has a typical continental desert climate with an average annual rainfall of less than 150 mm [29]. Groundwater recharge rates are notably low because of the region's high evaporation rates, which can reach up to 3 cm per year [24].

The study area lies on the Arabian Shelf, which is composed of an unconformable sedimentary sequence that overlays the shield rocks to the west. The shelf rocks exhibit a slight eastward dip ($1\text{--}2^\circ$) and show a progressive decrease in age from west to east (Figure 1). Within the study area, Paleozoic and early Mesozoic sedimentary rocks predominate, including sandstone, limestone, shale, and gypsum [30]. In the study area, the Saq Formation has a thickness ranging from 350 to 750 m. It consists primarily of sandstones with some minor interbedded shale and siltstone layers, and it unconformably overlays the basement complex rocks. Apart from the Saq aquifer, the Tabuk, Khuff, and Neogene aquifers also serve as water sources, but they are separated from the Saq by the

Hanadir, Ra'an, and Qusaiba impermeable shales. Wells accessing the Saq Aquifer vary in depth, from less than 100 m in the unconfined outcrop area to over 1,200 m in the confined eastern sections.

2.2 Land-use pattern and urbanization

The focal region of Al Qaseem, pivotal to this study, exhibits a diverse combination of land use and land cover that mirrors its distinct geographical and socio-economic composition (Figure 1). Encompassing an expanse of 989 km², its agricultural areas signify the region's robust agricultural foundation and its pivotal role in food production. The residential sectors, spanning 918 km², shed light on the urban dynamics and residential spaces within the area. Extensive bare lands spanning 4,287 km² dominate the scenery, showcasing the region's natural and pristine environmental features. This diverse amalgamation of agricultural, urban, and natural landscapes underscores the multifaceted nature of Al Qaseem, rendering it a compelling subject for thorough examination and analysis.

2.3 Sampling and data analysis

In total, 38 water samples were gathered from irrigation and domestic wells that draw water from the Saq Aquifer. These wells are located between N25.8975–N26.7917 and E43.2247–E44.0179 (Figure 2). The researchers followed established protocols for collecting groundwater samples in the study area. They ensured accuracy by pumping the well 10 min before sample collection to guarantee that the water represented the aquifer conditions rather than stagnant well water. Approximately 1 L of water was collected from each groundwater well, a quantity deemed adequate for carrying out all essential analyses, and allowed for any re-testing that might be required as outlined in the APHA guidelines [31]. The samples were collected in pre-cleaned, high-density polyethylene bottles to prevent chemical interactions with the samples. Upon collection, the samples were promptly labeled, sealed, and placed in coolers with ice packs to maintain a temperature below 4°C, which is crucial to prevent chemical and biological reactions. Within 24 h of collection, the samples were transported to the laboratory to preserve their integrity.

Major cations (Mg^{2+} , Ca^{2+} , Na^+ , and K^+) were analyzed using atomic absorption spectrophotometry. HCO_3^- and Cl^- levels were determined through titration methods, while SO_4^{2-} concentrations were estimated using colorimetric techniques. NO_3^- levels were measured via ion chromatography

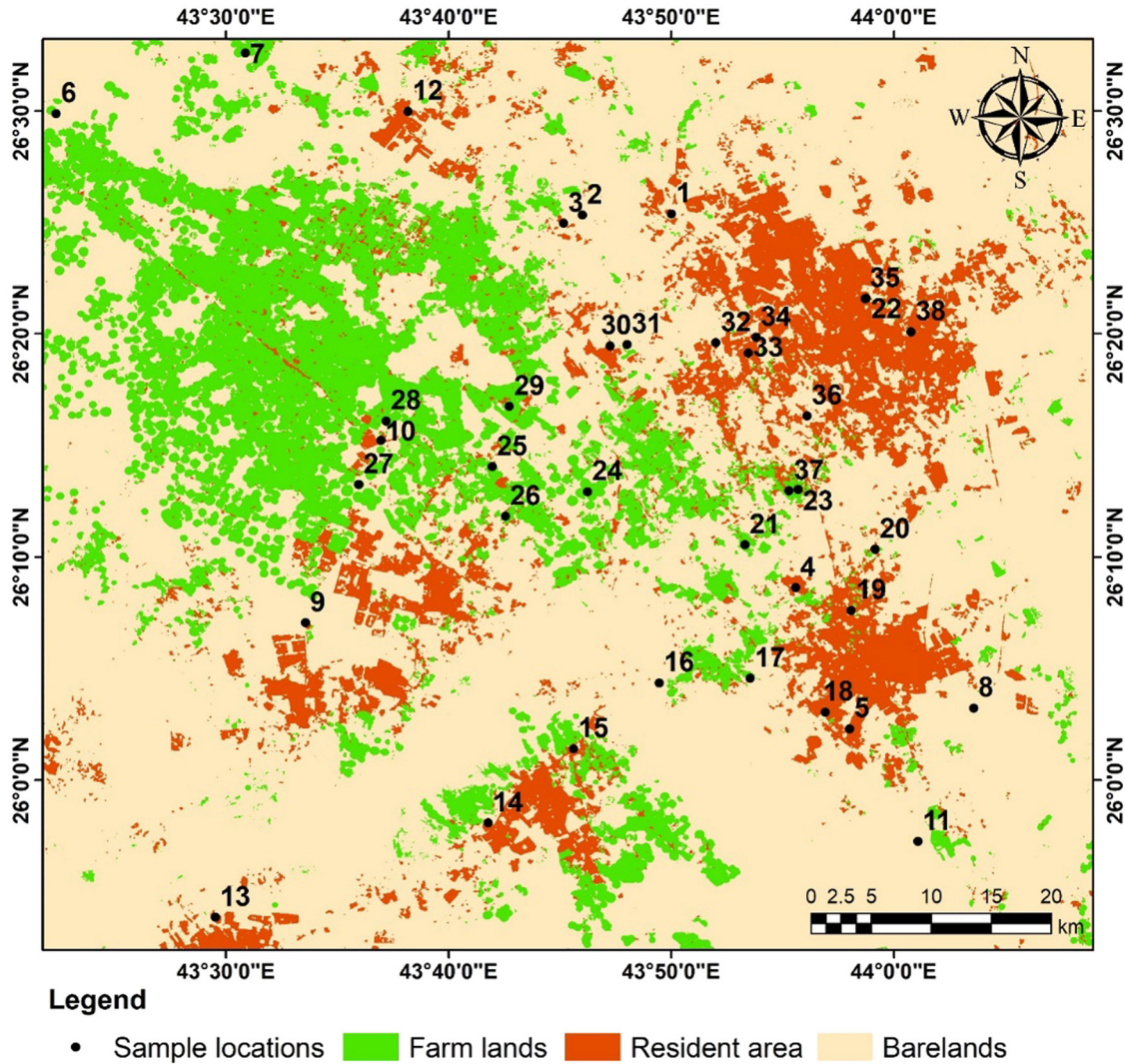


Figure 1: Land-use pattern of the Al Qaseem area using Landsat image.

(ELAN9000). The reliability of the results was confirmed by calculating the charge balance error for each sample. All samples showed a charge balance error of less than 5%, indicating that the results were within the acceptable range.

The following anion–cation balance equation is used to ensure data accuracy by eliminating samples with errors above $\pm 5\%$:

$$\% \text{Difference} = 100 \times \frac{\sum \text{Cations} - \sum \text{Anions}}{\sum \text{Cations} + \sum \text{Anions}}. \quad (1)$$

The water quality index (WQI) functions as a mathematical tool for evaluating the suitability of water for human consumption [32,33]. The equations used to compute the WQI are outlined as follows:

$$\text{WQI} = \sum \text{SI}_i, \quad (2)$$

$$\text{SI}_i = W_i \times q_i, \quad (3)$$

$$q_i = (C_i/S_i) \times 100, \quad (4)$$

$$W_i = w_i / \sum w_i. \quad (5)$$

The quality rating scale (q_i) for each parameter is determined by dividing the concentration of the parameter in each water sample by its corresponding standard [28], and then multiplying the result by 100. The calculated WQI values are categorized into five groups [25]: WQI < 50 (excellent water), WQI = 50–100.1 (good water), WQI = 100–200.1 (poor water), WQI = 200–300.1 (very poor water), and WQI > 300 (unsuitable for drinking purposes).

In this study, we assessed the potential health risks associated with the oral ingestion of NO_3^- and F^- for adults, children, and infants. The following formulas were employed to calculate the daily water intake (CDI), hazard quotient (HQ), and non-carcinogenic hazard index (HI) associated with drinking water [34,35]. The equations are as follows:

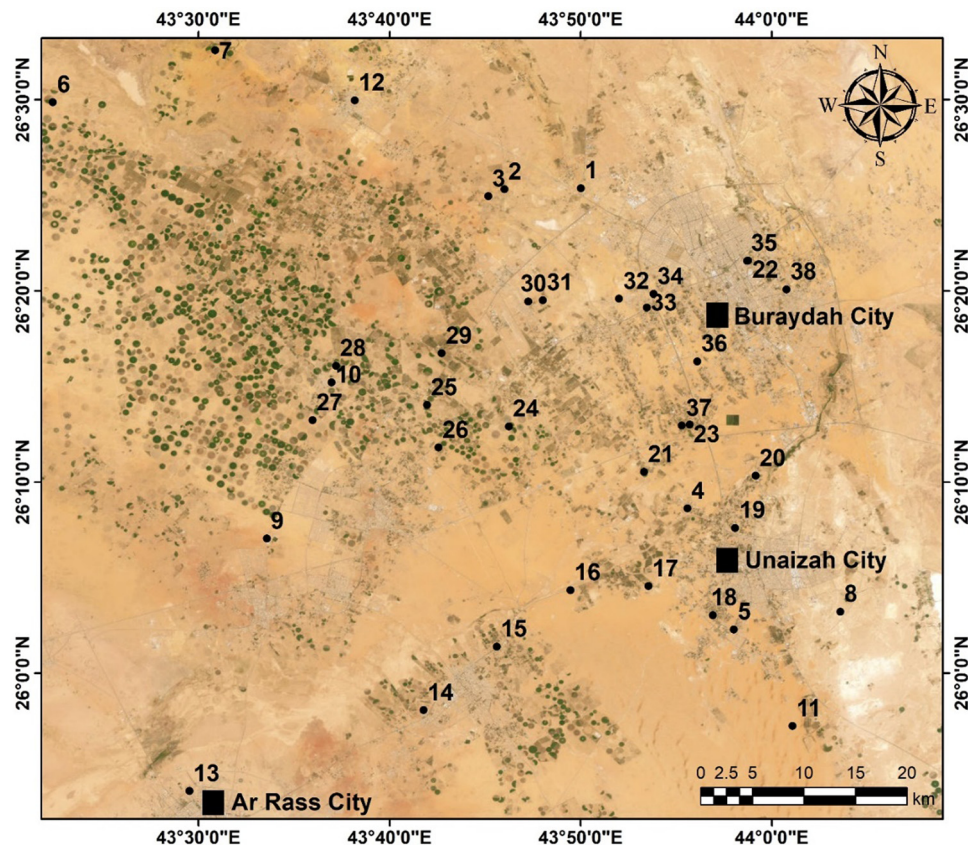


Figure 2: Locations of the groundwater samples in Al Qaseem area.

$$CDI = (C \times DI \times F \times ED)/(BW \times AT), \quad (6)$$

$$HQ = CDI/RfD, \quad (7)$$

$$HI = \Sigma(HQ \text{ fluoride} + HQ \text{ nitrate}). \quad (8)$$

Here, C represents the concentration of nitrate and fluoride in water (in mg/L); DI stands for the daily water consumption in liters; F denotes the frequency of days per year of exposure; ED signifies the duration of exposure in years; BW represents the weight of the specific age group in kilograms; AT indicates the average duration in days; and RfD refers to the reference dose ($NO_3^- = 1.6$ and $F^- = 0.06$ mg/kg/day) [36]. The parameter values utilized for health exposure assessment are detailed in Table 1.

3 Results and discussion

3.1 Hydrogeochemistry and groundwater quality

The coordinates of the wells from which groundwater samples were collected, along with the hydrogeochemical

dataset, are provided in Table S1. The pH ranged from 6.77 to 9.60, with an average of 7.26 (Table 2), indicating neutral to weakly basic waters [37]. Total dissolved solids (TDS) levels ranged from 534 to 5,664, averaging 1705.83 mg/L, indicating that 50% of the water samples exceeded the WHO's recommended limits (1,000 mg/L) [38]. Elevated TDS levels are often associated with extended groundwater residence times and significant water–rock interaction [3,39].

Table 1: Parameters applied for health exposure assessment through drinking water and HI classification

Risk exposure factors	Unit	Adults	Children	Infants
DI	L/d	2.0	1.5	0.8
F	d/year	365	365	365
ED	years	40	10	1.0
BW	kg	70	20	10
AT	d	14,600	3,650	365
$HI \leq 1$	No health risk to humans			
$HI > 1$	Higher level of hazard			

Table 2: Descriptive statistics of the investigated parameters

Parameter	Unit	Min.	Max.	Mean	Std. Dev.	MAC	Weight (w_i)	Relative weight (W_i)
pH	—	6.77	9.60	7.26	0.449	6.5–8.5	3	0.073
TDS	mg/L	534	5,664	1705.83	1491.31	1,000	4	0.098
EC	mg/L	920	11,560	3335.45	3121.27	500	3	0.073
Ca ²⁺	mg/l	61.30	1053.00	303.70	223.50	75	2	0.049
Na ⁺	mg/L	59.00	1816.00	418.37	570.88	200	2	0.049
Mg ²⁺	mg/L	12.00	133.00	35.27	26.78	30	2	0.049
K ⁺	mg/L	4.10	42.00	14.12	9.19	12	2	0.049
Cl ⁻	mg/L	78.10	3408.00	933.29	1124.75	250	3	0.073
HCO ₃ ⁻	mg/L	73.00	189.00	149.68	27.16	200	2	0.049
SO ₄ ²⁻	mg/L	112.00	1920.00	385.70	444.33	250	3	0.073
NO ₃ ⁻	mg/L	1.30	108.00	36.56	17.58	50	5	0.122
F ⁻	mg/L	0.10	0.98	0.71	0.311	1.5	5	0.122

Arranged in descending order, the mean concentrations of cations and anions (mg/L) were as follows: Cl⁻ (933.29), Na⁺ (418.37), SO₄²⁻ (385.70), Ca²⁺ (303.70), HCO₃⁻ (149.68), NO₃⁻ (36.56), Mg²⁺ (35.27), K⁺ (14.12), and F⁻ (0.71). According to WHO guidelines for drinkable water quality, the mean concentrations of SO₄²⁻, Cl⁻, Ca²⁺, Na⁺, Mg²⁺, and K⁺ exceeded the acceptable limits. However, in S5, S6, and S9, NO₃⁻ levels were elevated, with excess percentages of 7.89% for NO₃⁻, 31.58% for Mg²⁺, 42.11% for Na⁺, 47.36% for SO₄²⁻, 50% for K⁺, 76.32% for Cl⁻, and 92.11% for Ca²⁺. The heightened levels of these ions could stem from geochemical processes due to rainwater infiltration, rock–water interaction, and anthropogenic activities [40–42]. Elevated NO₃⁻ levels in the groundwater of some farms may be attributed to non-point sources such as the application of fertilizers, pesticides, and manure [43]. Electrical conductivity (EC) varied from 920 to 11,560, with an average of 3335.45 μ S/cm. The

elevated EC levels might be attributed to the increased levels of Ca²⁺ and Mg²⁺ [21].

TDS exhibit a positive correlation with EC, Ca²⁺, Na⁺, K⁺, and Cl⁻ (Table 3), indicating that the dissolution of carbonates and evaporites might play a role in the elevated concentrations of these ions in the groundwater [3,44,45]. However, a positive correlation was observed between Mg²⁺ and SO₄²⁻, as well as between F⁻ and Ca²⁺ and K⁺. On the other hand, NO₃⁻ and HCO₃⁻ show weak and negative correlations with other cations and anions, suggesting that these two anions have different sources in the study area. This indicates anthropogenic influences, particularly agricultural activities, due to the intensive use of chemical fertilizers [46].

Principal component analysis was employed to discern the potential origins of hydrogeochemical parameters in groundwater. Three principal components were derived,

Table 3: Correlation coefficient for the analyzed parameters

	pH	TDS	EC	Ca	Na	Mg	K	Cl	HCO ₃	SO ₄	NO ₃	F
pH	1											
TDS	-0.207	1										
EC	-0.225	0.998**	1									
Ca ²⁺	-0.230	0.786**	0.809**	1								
Na ⁺	-0.198	0.917**	0.914**	0.673**	1							
Mg ²⁺	-0.181	0.201	0.216	0.231	-0.009	1						
K ⁺	-0.312	0.500**	0.522**	0.600**	0.379*	0.515**	1					
Cl ⁻	-0.229	0.937**	0.943**	0.771**	0.976**	0.024	0.501**	1				
HCO ₃ ⁻	-0.379*	-0.536**	-0.523**	-0.327*	-0.635**	0.182	0.186	-0.569**	1			
SO ₄ ²⁻	-0.092	0.296	0.304	0.486**	0.211	0.535**	0.115	0.167	-0.198	1		
NO ₃ ⁻	0.322*	0.266	0.242	0.160	0.230	0.107	-0.078	0.201	-0.445**	0.154	1	
F ⁻	-0.347*	0.350*	0.410*	0.618**	0.309	0.347*	0.504**	0.424**	0.035	0.300	-0.151	1

* Correlation is significant at the 0.05 level (two-tailed).

**Correlation is significant at the 0.01 level (two-tailed).

Bold values represent positive correlation.

Table 4: Principal component loadings

Parameters	Component		
	PC1	PC2	PC3
pH	-0.261	-0.620	0.378
TDS	0.957	-0.138	-0.073
EC	0.969	-0.098	-0.077
Ca ²⁺	0.885	0.143	0.062
Na ⁺	0.904	-0.271	-0.221
Mg ²⁺	0.285	0.563	0.645
K ⁺	0.597	0.551	-0.047
Cl ⁻	0.945	-0.171	-0.254
HCO ₃ ⁻	0.503	0.757	-0.127
SO ₄ ²⁻	0.411	0.196	0.689
NO ₃ ⁻	0.245	-0.530	0.513
F ⁻	0.544	0.526	0.000
% of Variance	46.93	19.38	12.03
Cumulative %	46.93	66.31	78.34

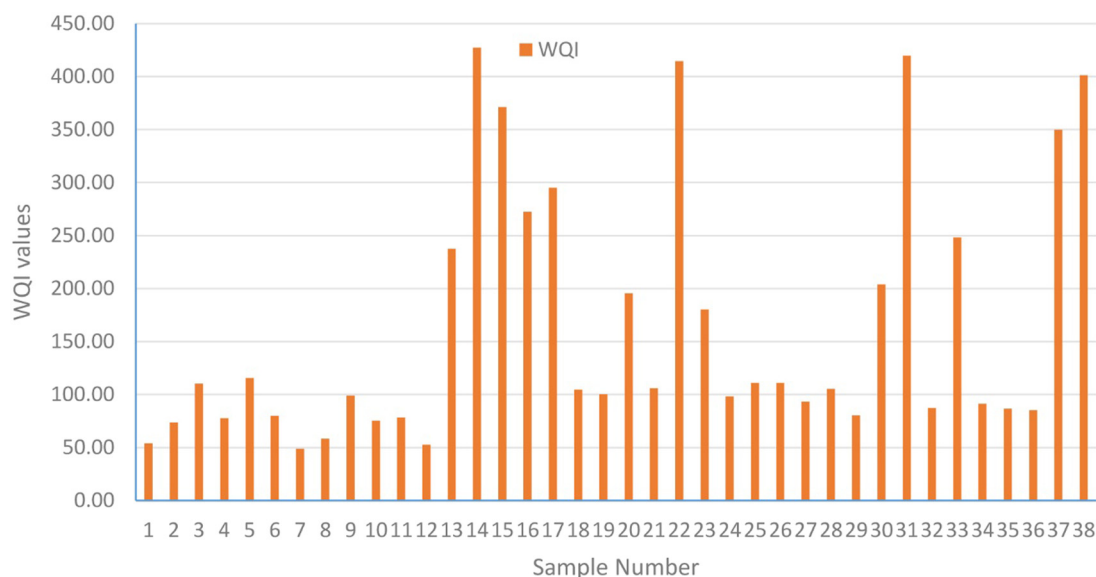
Bold values mean high loadings of the hydrogeochemical data.

collectively explaining 46.93, 19.38, and 12.03% of the total variance (Table 4). PC1 showed high loadings for TDS, EC, Ca²⁺, Na⁺, K⁺, Cl⁻, and F⁻, pointing to natural processes involving the dissolution and precipitation of silicates, gypsum, and carbonates [47,48]. Additionally, PC2 displayed elevated loadings of Mg²⁺, K⁺, and F⁻, suggesting influences from both human activities and natural sources [49]. PC3 demonstrated high loadings of Mg²⁺, SO₄²⁻, and NO₃⁻, indicating the distinct presence of these ions. The occurrence of Mg²⁺, K⁺, and F⁻ in multiple principal components suggests varied sources for these ions [7,50].

The WQI values varied between 48.63 and 426.98, averaging 166.81. According to the classification based on WQI, eight water samples were deemed unsuitable for drinking, five samples were categorized as very poor water quality, ten samples as poor quality, fourteen samples as good quality, and one sample as excellent quality (Table 5). Analysis of WQI values across sampling sites revealed hotspots

Table 5: Results and categories of the WQI applied in this study

S.No.	WQI	Classification	S.N.	WQI	Classification	S.N.	WQI	Classification	S.N.	WQI	Classification
1	54.09	Good	11	78.32	Good	21	106.02	Poor	31	419.49	Unsuitable
2	73.47	Good	12	52.62	Good	22	414.46	Unsuitable	32	87.07	Good
3	110.13	Poor	13	237.47	Very poor	23	179.94	Poor	33	248.31	Very poor
4	77.49	Good	14	426.98	Unsuitable	24	98.02	Good	34	91.18	Good
5	115.49	Poor	15	371.08	Unsuitable	25	110.89	Poor	35	86.44	Unsuitable
6	79.88	Good	16	272.48	Very poor	26	110.89	Poor	36	85.01	Unsuitable
7	48.63	Excellent	17	294.87	Very poor	27	93.14	Good	37	349.89	Unsuitable
8	58.38	Good	18	104.35	Poor	28	105.31	Poor	38	401.04	Unsuitable
9	99.08	Good	19	100.25	Poor	29	80.10	Good			
10	75.19	Good	20	195.42	Poor	30	203.74	Very poor			

**Figure 3:** Distribution of the WQI values per sample location in the study area.

in S14, S15, S22, S31, S37, and S38 (Figure 3). This phenomenon could be attributed to an increase in Ca^{2+} , Mg^{2+} , Na^+ , Cl^- , and SO_4^{2-} levels in these wells.

3.2 Health risk assessment

Fluoride and nitrate stand out as some of the most common and widely distributed contaminants discovered in various

groundwater reservoirs, presenting a notable environmental apprehension regarding water pollution. Elevated levels of NO_3^- in drinking water have been associated with a range of human health problems [50]. The release of F^- ions into groundwater is affected by the saturation levels of fluorite and calcite, along with the concentrations of Ca^{2+} , Na^+ , and HCO_3^- ions in the groundwater [51].

It has been observed that excessive fertilizer cannot be completely absorbed by plant roots. As a result, the surplus can be lost through denitrification, leaching, and

Table 6: CDI (mg/kg/day) of nitrate and fluoride for adults, children, and infants

S.No.	Well	CDI (NO_3^-)			CDI (F^-)		
		Adults	Children	Infants	Adults	Children	Infants
1	BU0294	0.037	0.0975	0.104	0.006	0.015	0.016
2	BU0295	0.334	0.8775	0.936	0.009	0.0225	0.024
3	BU0296	0.854	2.2425	2.392	0.009	0.0225	0.024
4	BU2003	0.917	2.4075	2.568	0.006	0.015	0.016
5	BU2004	3.086	8.100	8.640	0.006	0.015	0.016
6	BU9003	1.957	5.1375	5.480	0.014	0.0375	0.04
7	BU9007	0.540	1.4175	1.512	0.014	0.0375	0.04
8	BU9115	0.866	2.2725	2.424	0.006	0.015	0.016
9	BU9128	1.991	5.2275	5.576	0.006	0.015	0.016
10	BU9129	1.303	3.420	3.648	0.003	0.0075	0.008
11	BU9328	1.226	3.2175	3.432	0.006	0.015	0.016
12	BU9458	0.726	1.905	2.032	0.009	0.0225	0.024
13	Sq-1	1.029	2.700	2.88	0.027	0.0705	0.0752
14	Sq-2	1.343	3.525	3.760	0.025	0.066	0.0704
15	Sq-3	1.286	3.375	3.600	0.026	0.0675	0.072
16	Sq-4	1.171	3.075	3.280	0.028	0.0735	0.0784
17	Sq-5	1.143	3.000	3.200	0.026	0.069	0.0736
18	Sq-6	1.057	2.775	2.960	0.024	0.06375	0.068
19	Sq-7	0.800	2.100	2.240	0.027	0.06975	0.0744
20	Sq-8	1.000	2.625	2.800	0.027	0.072	0.0768
21	Sq-9	0.943	2.475	2.640	0.026	0.06825	0.0728
22	Sq-10	1.200	3.150	3.360	0.025	0.066	0.0704
23	Sq-11	1.086	2.850	3.040	0.026	0.069	0.0736
24	Sq-12	0.943	2.475	2.640	0.027	0.07125	0.076
25	Sq-13	1.029	2.700	2.880	0.025	0.0645	0.0688
26	Sq-14	1.029	2.700	2.880	0.027	0.06975	0.0744
27	Sq-15	0.686	1.800	1.920	0.025	0.06525	0.0696
28	Sq-16	0.971	2.550	2.720	0.026	0.06825	0.0728
29	Sq-17	0.600	1.575	1.680	0.025	0.0645	0.0688
30	Sq-18	1.143	3.000	3.200	0.027	0.07125	0.076
31	Sq-19	1.286	3.375	3.600	0.027	0.0705	0.0752
32	Sq-20	0.629	1.650	1.760	0.026	0.06825	0.0728
33	Sq-21	1.057	2.775	2.960	0.025	0.066	0.0704
34	Sq-22	0.714	1.875	2.000	0.026	0.0675	0.072
35	Sq-23	0.629	1.650	1.760	0.024	0.063	0.0672
36	Sq-24	0.629	1.650	1.760	0.025	0.066	0.0704
37	Sq-25	1.200	3.150	3.360	0.027	0.0705	0.0752
38	Sq-26	1.257	3.300	3.520	0.026	0.06825	0.0728
Min		0.037	0.098	0.104	0.003	0.008	0.008
Max.		3.086	8.100	8.640	0.028	0.074	0.078
Average		1.071	2.810	2.997	0.020	0.052	0.056

Table 7: HQ and HI for fluoride and nitrate in adults, children, and infants

S.No.	Well	HQ nitrates			HQ F ⁻			HI		
		Adults	Children	Infants	Adults	Children	Infants	Adults	Children	Infants
1	BU0294	0.02	0.06	0.065	0.10	0.25	0.27	0.12	0.31	0.33
2	BU0295	0.21	0.55	0.585	0.14	0.38	0.40	0.35	0.92	0.99
3	BU0296	0.53	1.40	1.495	0.14	0.38	0.40	0.68	1.78	1.90
4	BU2003	0.57	1.50	1.605	0.10	0.25	0.27	0.67	1.75	1.87
5	BU2004	1.93	5.06	5.40	0.10	0.25	0.27	2.02	5.31	5.67
6	BU9003	1.22	3.21	3.425	0.24	0.63	0.67	1.46	3.84	4.09
7	BU9007	0.34	0.89	0.945	0.24	0.63	0.67	0.58	1.51	1.61
8	BU9115	0.54	1.42	1.515	0.10	0.25	0.27	0.64	1.67	1.78
9	BU9128	1.24	3.27	3.485	0.10	0.25	0.27	1.34	3.52	3.75
10	BU9129	0.81	2.14	2.28	0.05	0.13	0.13	0.86	2.26	2.41
11	BU9328	0.77	2.01	2.145	0.10	0.25	0.27	0.86	2.26	2.41
12	BU9458	0.45	1.19	1.27	0.14	0.38	0.40	0.60	1.57	1.67
13	Sq-1	0.64	1.69	1.8	0.45	1.18	1.25	1.09	2.86	3.05
14	Sq-2	0.84	2.20	2.35	0.42	1.10	1.17	1.26	3.30	3.52
15	Sq-3	0.80	2.11	2.25	0.43	1.13	1.20	1.23	3.23	3.45
16	Sq-4	0.73	1.92	2.05	0.47	1.23	1.31	1.20	3.15	3.36
17	Sq-5	0.71	1.88	2.00	0.44	1.15	1.23	1.15	3.03	3.23
18	Sq-6	0.66	1.73	1.85	0.4	1.06	1.13	1.07	2.80	2.98
19	Sq-7	0.50	1.31	1.40	0.44	1.16	1.24	0.94	2.48	2.64
20	Sq-8	0.63	1.64	1.75	0.46	1.20	1.28	1.08	2.84	3.03
21	Sq-9	0.59	1.55	1.65	0.43	1.14	1.21	1.02	2.68	2.86
22	Sq-10	0.75	1.97	2.10	0.42	1.10	1.17	1.17	3.07	3.27
23	Sq-11	0.68	1.78	1.9	0.44	1.15	1.23	1.12	2.93	3.13
24	Sq-12	0.59	1.55	1.65	0.45	1.19	1.27	1.04	2.73	2.92
25	Sq-13	0.64	1.69	1.80	0.41	1.08	1.15	1.05	2.76	2.95
26	Sq-14	0.64	1.69	1.80	0.44	1.16	1.24	1.09	2.85	3.04
27	Sq-15	0.43	1.13	1.20	0.41	1.09	1.16	0.84	2.21	2.36
28	Sq-16	0.61	1.59	1.70	0.43	1.14	1.21	1.04	2.73	2.91
29	Sq-17	0.38	0.98	1.05	0.41	1.08	1.15	0.78	2.06	2.20
30	Sq-18	0.71	1.88	2.00	0.45	1.19	1.27	1.17	3.06	3.27
31	Sq-19	0.80	2.11	2.25	0.45	1.18	1.25	1.25	3.28	3.50
32	Sq-20	0.39	1.03	1.10	0.43	1.14	1.21	0.83	2.17	2.31
33	Sq-21	0.66	1.73	1.85	0.42	1.10	1.17	1.08	2.83	3.02
34	Sq-22	0.45	1.17	1.25	0.43	1.13	1.2	0.88	2.30	2.45
35	Sq-23	0.39	1.03	1.10	0.4	1.05	1.12	0.79	2.08	2.22
36	Sq-24	0.39	1.03	1.10	0.42	1.10	1.17	0.81	2.13	2.27
37	Sq-25	0.75	1.97	2.10	0.45	1.18	1.25	1.2	3.14	3.35
38	Sq-26	0.79	2.06	2.20	0.43	1.14	1.21	1.22	3.20	3.41
Min.		0.02	0.06	0.065	0.05	0.13	0.13	0.12	0.31	0.33
Max.		1.93	5.06	5.4	0.47	1.23	1.31	2.02	5.31	5.67
Aver.		0.668	1.756	1.873	0.333	0.874	0.930	0.993	2.606	2.78

volatilization, or it can remain in the soil [13,52,53]. Fluoride (F⁻) in groundwater can either occur naturally or be influenced by human activities [54]. The decomposition of fluoride-bearing minerals such as fluorite, amphiboles, apatite, and muscovite provides a natural source of F⁻ [13]. Additionally, anthropogenic sources of F⁻ in groundwater include phosphatic fertilizer plants, excessive groundwater extraction, brick manufacturing, coal combustion, and sewage discharge [55].

The CDI values of NO₃⁻ (mg/kg/day) differed among adults, children, and infants. For adults, the CDI ranged from 0.037 to 3.086 with an average of 1.071; for children, it ranged from 0.098 to 8.100 with an average of 2.810; and for infants, it ranged from 0.104 to 8.640 with an average of 2.997. The CDI values of fluoride (F⁻) for adults ranged from 0.003 to 0.028, with an average of 0.020. For children, the range was from 0.008 to 0.074, with an average of 0.052. For infants, the CDI values ranged from 0.008 to 0.078, with

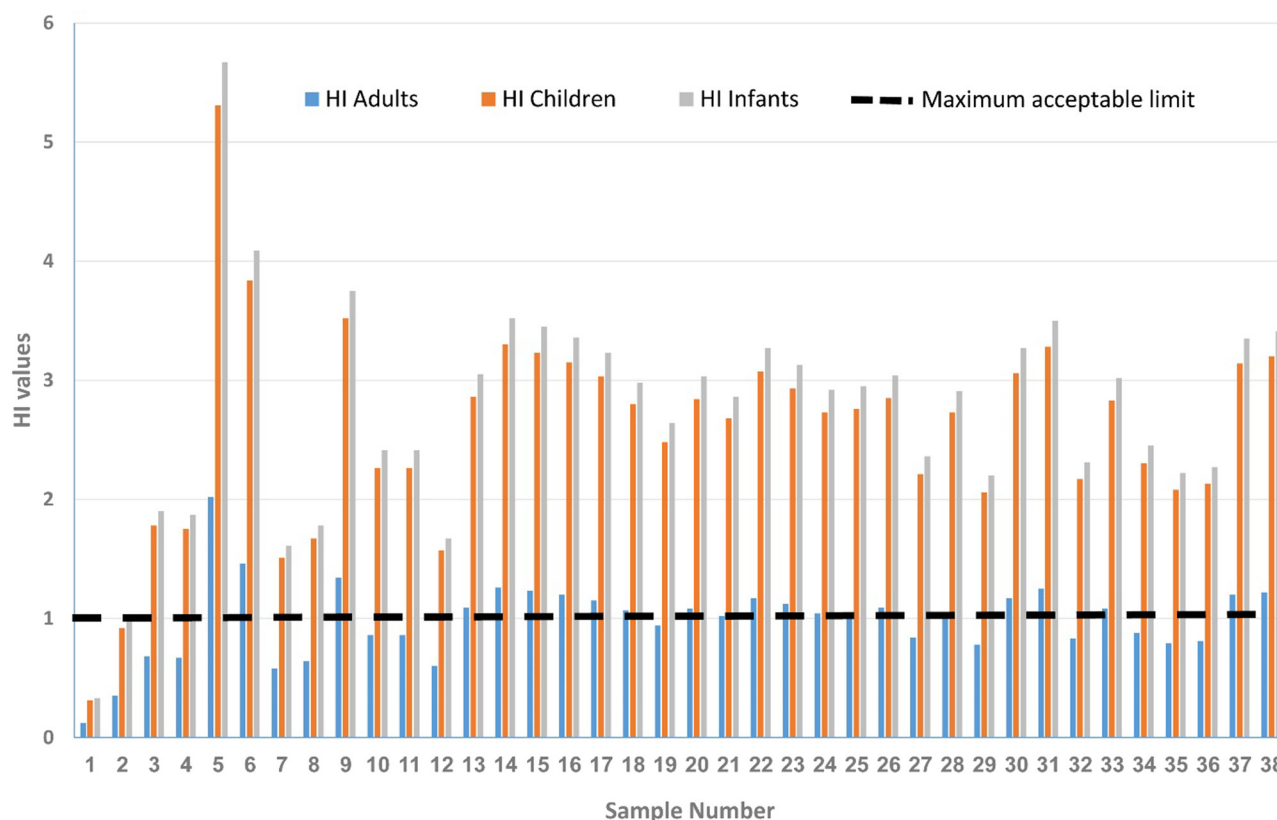


Figure 4: Non-carcinogenic risks induced by fluoride and nitrate in drinking water.

an average of 0.056 (Table 6). Moreover, the average HQ values for nitrate and fluoride were 0.668 and 0.333 for adults, 2.810 and 0.874 for children, and 1.873 and 0.930 for infants, respectively (Table 7).

The HI varied from 0.12 to 2.02 for adults, with an average of 0.993. For children, it ranged from 0.31 to 5.31, with an average of 2.606. For infants, the HI ranged from 0.33 to 5.67, with an average of 2.78 (Table 7 and Figure 4). Groundwater samples exceeded the safety threshold of 1, accounting for 57.89% (22 out of 38) for adults and 94.73% (36 out of 38) for both children and infants (Figure 4). The findings of the study indicate that the groundwater examined across various study areas, particularly in water samples 5, 6, 9, and 14–17 (from wells BU2004, BU9003, BU9128, Sq-2 to Sq-5, respectively), could potentially expose infants, children, and adults to non-cancerous health risks if used as drinking water. Furthermore, the results indicate that infants and children are more susceptible to non-carcinogenic health risks than adults, likely because of their lower body weights. Similar conclusions have been reported by researchers worldwide when assessing the health risks associated with nitrate and fluoride in groundwater. These studies include regions in China, Iran, India, Pakistan, and Saudi Arabia [4,15,34,50,51,56].

Nevertheless, to mitigate the elevated levels of NO_3^- and F^- in groundwater, three effective techniques can be employed: adsorption, electrocoagulation, and reverse osmosis. Adsorption is a straightforward and cost-effective method that involves using solid materials to capture F^- and NO_3^- ions from water [57]. Electrocoagulation is a quick and eco-friendly method where an electric current is applied to produce metal hydroxides, which precipitate F^- and NO_3^- ions from water [58]. Reverse osmosis is a highly effective and selective method that utilizes high pressure and a membrane to filter F^- and NO_3^- ions from water [59]. Recommendations include reducing the mentioned contaminants in the study area and exploring alternative sources of water, or mixing water from regions with lower concentrations of fluoride and nitrate.

The current study proposes several measures to improve groundwater quality and minimize potential health hazards, particularly in terms of drinking water consumption: (i) implementation of an effective water management strategy involving the mentioned techniques, (ii) ensuring proper landfill construction, and (iii) reducing the excessive use of fertilizers and pesticides in agricultural areas.

The protocol employed by the researchers in the current study for collecting groundwater samples demonstrates

a robust methodology aimed at ensuring the integrity and reliability of the findings. Nevertheless, it is important to acknowledge inherent limitations, including temporal variability and spatial coverage. Groundwater quality can vary over time due to seasonal changes and agricultural activities. Sampling at a single point in time may not capture these variations and might not represent the long-term average conditions of the groundwater.

This study could be limited by the spatial coverage of sampled wells and their distribution. Although the number of wells sampled is substantial, their uneven distribution means the results may not accurately represent the entire study area. Fieldwork can be challenging when collecting samples according to the researchers' preferences because some locations in the study area are inaccessible or belong to farming companies that do not allow researchers to collect from their groundwater wells. Addressing these limitations in future studies could involve conducting repeated samplings over different seasons and increasing the number of sampling locations.

4 Conclusions

The current work highlighted the water quality and non-carcinogenic hazards linked with nitrate and fluoride in groundwater sourced from the Al Qaseem region, Saudi Arabia. The findings indicated that numerous major cations and anions surpassed the guidelines set by the WHO. Out of the samples assessed, 8 were unsuitable for drinking, 5 displayed very poor water quality, 10 exhibited poor quality, 14 were of good quality, and 1 was deemed excellent. None of the fluoride samples exceeded the WHO's recommended drinking water limit of 1.5 mg/L, while three nitrate levels surpassed the WHO guideline of 50.00 mg/L. A significant proportion, 57.89%, of the water samples exceeded safety thresholds for adults, while 94.73% surpassed the thresholds for both children and infants, indicating potential health hazards. Consequently, groundwater in the study area may pose non-cancerous health risks to infants, children, and adults if utilized as drinking water. Urgent attention and remedial measures are essential to safeguard residents from the adverse effects of fluoride and nitrate in the study area.

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