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Hydrochemical Assessment of Groundwater from the Harrat Khyber Flood Basalts, Northwest Saudi Arabia

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Cite This: *ACS Omega* 2023, 8, 42186−42196

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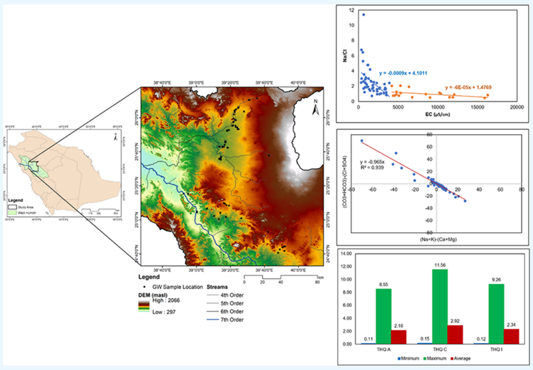
ABSTRACT: The present study was carried out in the Harrat Khyber region of the Madinah province in Western Saudi Arabia. The objective of the study was to determine the main factors affecting groundwater chemistry and assess the impact of groundwater quality on human health with respect to nitrate, fluoride, and heavy metals (arsenic, chromium, copper, nickel, selenium, and zinc). Hydrochemical data for 70 groundwater samples from dug wells and bore wells from Harrat Khyber were interpreted to achieve the research objective. The groundwater chemistry is influenced by ion-exchange and the evaporation process. A wide variation in the concentration of various major ions is observed primarily due to the varied nature of the aquifer system which includes the unconsolidated wadi deposits, weathered-fractured basaltic aquifer system, and subbasaltic sedimentary aquifer system. The total hazard quotient (THQ) with respect to NO_3 and F was determined. Although the F values are well within the limits of human consumption in water prescribed by WHO, the values of NO_3 exceed the allowable limits in 50% of the groundwater samples. The average THQ values are 2.16, 2.92, and 2.34 for adults, children, and infants, respectively, which makes the water unsafe for human consumption. Six heavy metals (arsenic, chromium, copper, nickel, selenium, and zinc) were used to calculate the heavy-metal contamination index (HCI). The average HCI value is 19.505. Overall HCI calculation shows that the groundwater is unpolluted with respect to heavy metals. The heavy metals in water are mainly of geogenic origin.



INTRODUCTION

Due to increased demand and limited supply, groundwater availability in terms of quantity and quality has grown to be a significant global issue. The problem has gotten significantly worse in the desert areas of the world due to harsh environmental conditions and increasing population pressure. Water supply is constrained, affecting both quantity and quality due to the lack of surface water, inadequate precipitation and groundwater recharge, excessive evaporation, and an over-reliance on groundwater for domestic and agricultural usage. Excessive groundwater pumping has also been linked with a deterioration in groundwater quality due to vertical leakage through aquitard in multilayer aquifer systems.[1] Since groundwater quality in arid and semiarid areas is intimately linked to socioeconomic development, it is imperative to assess it.[2−6] In order to determine the causes of groundwater quality decline and offer sustainable groundwater management alternatives, studies on groundwater quality assessments have emerged as a topic of interest for academics around the world.[7−11] Nitrate and fluoride pollution in groundwater is a global concern due to its adverse impact on human health.[12,13] Agriculture-related activities cause the inorganic compounds present in fertilizers to enter bodies of surface water and groundwater, increasing the nitrate content in the water, which then returns to the soil through irrigation.[14] Nitrates can harm human health by causing methemoglobinemia, thyroid problems, or cancer, as well as irreversible damage to the aquatic system.[15,16] Arid and semiarid regions globally have been associated with fluoride pollution.[17−20] Fluoride enters the human body mostly through drinking water.[21] Ingestion of fluoride at levels lower than 1.5 mg/L may aid to reduce the occurrence of dental caries and promote bone formation.[22] Fluoride concentrations exceeding 1.5 mg/L, on the other hand, create dental fluorosis or mottled enamel, while concentrations above 3.0 mg/L may cause skeletal fluorosis.[23]

Dawoud et al.[24] report that more than 80% of Saudi Arabia's water supply comes from nonrenewable (fossil) groundwater aquifers. The usage of this nonrenewable resource may be restricted due to declining groundwater quality, which might also worsen Saudi Arabia's already severe water stress.[25] As a

Received: June 9, 2023
Revised: October 17, 2023
Accepted: October 19, 2023
Published: November 2, 2023

https://doi.org/10.1021/acsomega.3c04008
ACS Omega 2023, 8, 42186−42196

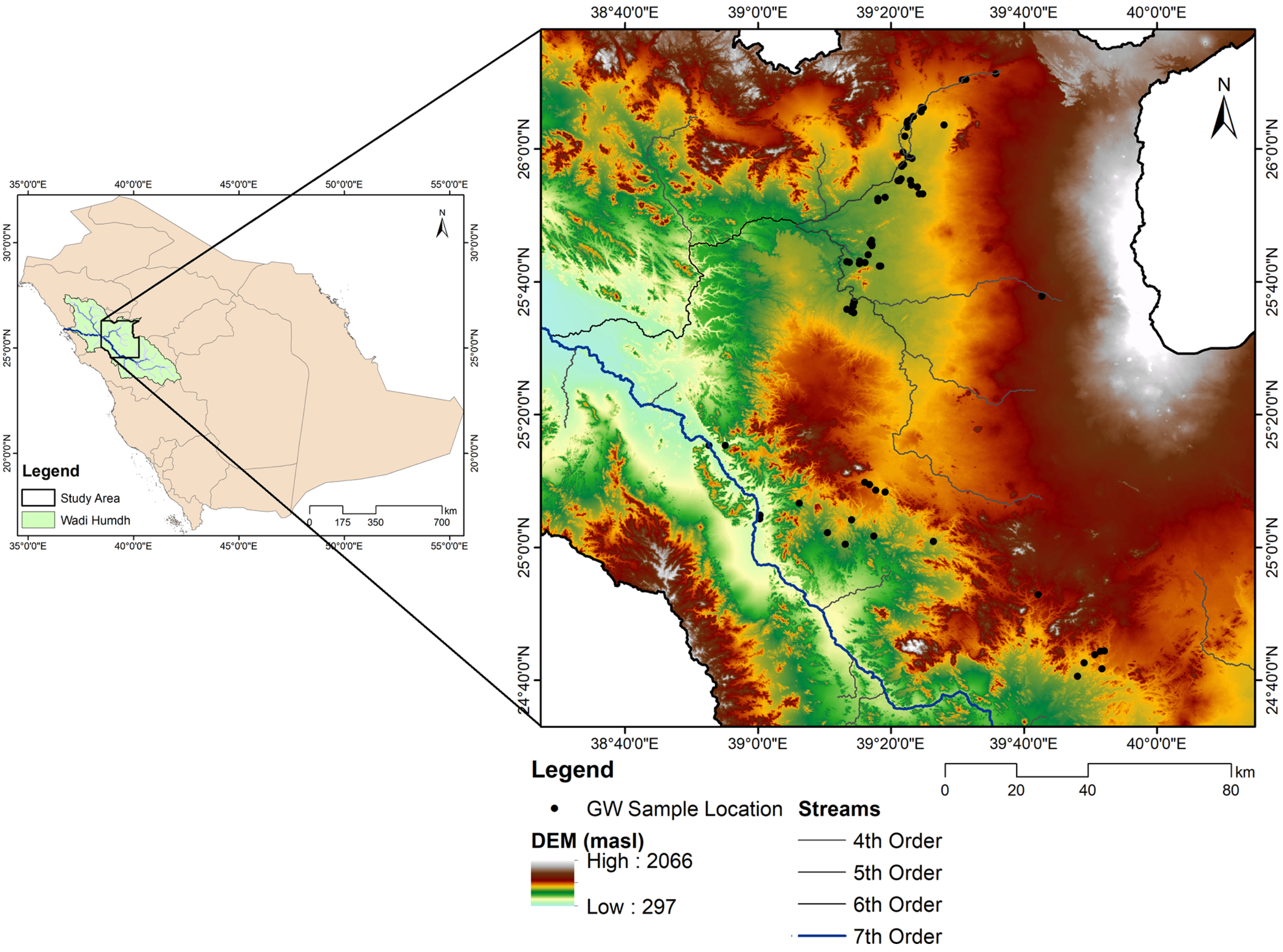


Figure 1. Map showing the location and geology of the study area. The boxed area in the inset map shows the study area.

result of agriculture, domestic sewage, and industrial effluent discharge, Saudi Arabia's shallow groundwater aquifers are getting contaminated.[26] Alabdula'aly et al.[27] carried out a detailed investigation about the status of nitrate pollution in Saudi Arabia. Their study showed that the concentration of NO_3 in groundwater varied between 1.1 and 884.0 mg/L. Most of the wells showing higher concentrations of NO_3 were used for agricultural and domestic purposes. Fluoride contamination in groundwater has also been reported from several regions of Saudi Arabia.[28−30] Several farms close to the cities of Al-Madinah and Khyber conduct significant agricultural activity. The increased biological oxygen demand and nitrate levels in the groundwater of Al-Madinah City were attributed to septic tanks and industrial waste disposal.[31] Groundwater contains excessive amounts of several inorganic contaminants, such as nitrate, chloride, arsenic, lead, zinc, and cadmium, as a result of the misuse of chemical fertilizers. People who are exposed to these pollutants may experience severe health issues.[32] Study conducted by Bamousa and El Maghraby[33] in the Madinah area has shown that 40% of the total analyzed samples had NO_3 concentration in excess of the limits prescribed by WHO and was related mostly to agricultural activities and sewage waste disposal.

Harrat Khyber area in Western Saudi Arabia has been a subject of investigation with respect to groundwater exploration[34,35] and groundwater quality studies with a focus on drinking water quality index.[36] However, no studies have been done on the variables impacting the chemistry of the groundwater in Harrat Khyber. Studies assessing the health dangers caused by dissolved ions such as fluoride and nitrate in groundwater are lacking. The region has also experienced the growth of numerous villages and residential areas, and the groundwater resources nearby are limited and insufficient for residential use and agricultural operations.[34]

The current study was carried out in the Harrat Khyber region of Western Saudi Arabia in order to comprehend the mechanisms influencing the groundwater chemistry of aquifers and to evaluate the risk that fluoride and nitrate contamination in groundwater poses to human health. Heavy-metal contamination index (HCI) was also calculated to determine the threat from dissolved heavy metals in groundwater.

■ STUDY AREA DESCRIPTION

The study area is a part of the Wadi Humdh basin and lies between latitudes 24.54°N and 26.31°N and longitudes 38.45°E and 40.25°E. Since the samples are located in a small part of Wadi Humdh, only that part of the area was selected, as a result of which some irregular boundaries are seen in Figure 1. The irregular boundaries are the limits of the Wadi Humdh watershed. The main characteristic of the area is the presence of quaternary flood basalts, which cover a large part of the area (Figure 2). These lava flows are a part of the

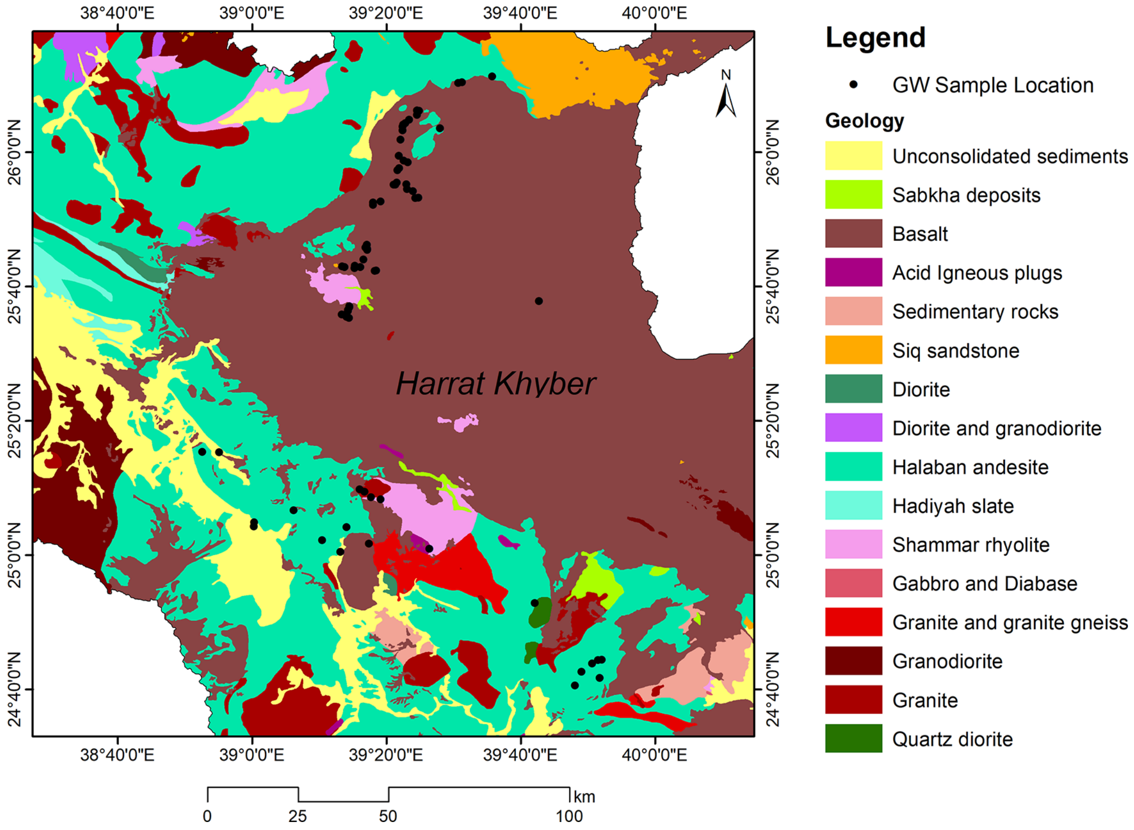


Figure 2. Geological map of the study area (modified from Pellaton 1981).

Harrat Khyber. It is an arid region with high temperatures throughout the year and annual rainfall of less than 53 mm. The elevation of the area varies from 297 to 2066 m amsl. The higher elevations are to the east and the streams flow from the southeast and northeast and join the mainstream of Wadi Humdh which then flows westward to join the Red Sea.

Geology of the Area. The geological map of the research region is shown in Figure 2. Quaternary basalts (Harrat Khyabar), one of the major Cenozoic volcanic fields in the western Arabian Cenozoic volcanic provinces,[37] cover a sizable portion of the study. According to Németh and Moufti,[38] the volcanic field is characterized by a variety of volcanic landforms, ranging from tiny, straightforward structures typical of monogenetic volcanoes, such as spatter cones, to more intricate structures clearly indicating long-lived eruptions. Harrat Khyber's white felsic rocks, which resemble tuff rings and domes with pyroclastic aprons, distinguish it from all other harrats in Saudi Arabia.[39] The 700−800 Ma Halaban andesite consists mainly of andesites and fine-grained diorite outcrops in the northwestern and southern parts of the area. The Precambrian granitic rocks outcrop at several places. The alkalic and peralkalic volcanic rocks of the Shammar Rhyolite are the youngest of the Precambrian rocks exposed in the area.[40] Outcrops of the Cambrian Siq sandstone are present in the northeastern part. The Quaternary unconsolidated deposits are present in the western part.

Hydrogeology of the Area. Harrat Khyber forms one of the largest plateau lava fields in Saudi Arabia, with a thickness of the lava flows reaching up to 90 m. The lava flows overlie the Khyber sandstone. In some places, the basaltic flows cover the ancient alluvial deposits. The sandstone and the subbasaltic alluvium form a confined aquifer system, whereas, as the basaltic flows, the overlying unconsolidated alluvium forms a semiconfined aquifer system.[41] Conglomerate, cobbles, and pebbles created by elements of metamorphic and basaltic origin make up the subbasaltic alluvium. The basalts serve as aquifers in places where crevices, joints, and fractures are present. Direct rainfall recharge is minimal in the area primarily due to the low rainfall and the impervious nature of the strata; however, the recharge can be of local significance where basalts have developed secondary porosity.

Owing to the low hydraulic conductivity and the heterogeneous nature of the basaltic aquifers, numerous dug wells are found in the area which might tap some potentially high conductivity zones owing to their large diameter. Sustainable yields are not possible for the underlying sandstones and the subbasaltic alluvium, but according to studies, they are the best source of reliable water supply in the area which can be accessed through borewells greater than 100 m in depth. The depth to water table in the wells ranges from 1.95 to 95 m below ground level. Transmissivity values between 163 and 1380 m^2/day and storativity values between values between 0.02 and 0.1 have been observed in the wells in the area.[42]

■ METHODOLOGY

For 70 groundwater samples from the Harrat Khyber area, values of main ion concentration and heavy metals, such as arsenic, chromium, copper, nickel, selenium, and zinc, were collected from Saudi Arabia's Ministry of Water and Electricity's unpublished publications.[43] While Mg^{2+} and Ca^{2+} were determined using the titration method with ethylenediaminetetraacetic acid, K^+ and Na^+ were measured using a flame photometer (Corning 400). Using acid titration, phenoldisulfonic acid, silver nitrate titration, and a turbidity technique, it was possible to determine the concentrations of HCO_3^-, NO_3^-, Cl^-, and SO_4^{2-}. Using ICP-MS, the heavy-metal concentrations were calculated.

The obtained values of the major ions were used to detect the main groundwater facies in the region using Piper plots. To identify the variables influencing groundwater chemistry, plots between the main ionic species in groundwater were generated. Additionally, various approaches were used to assess the groundwater quality for drinking, including the total hazard quotient (THQ) due to fluoride and nitrate and the HCI. The maps were generated using ArcGIS, whereas the various graphs have been plotted using Microsoft Excel.

■ RESULTS AND DISCUSSION

Major Ions. The groundwater contains major ions and heavy metals, and their concentration depends on the aquifer lithology, direction of groundwater flow, duration of rock-water interaction, and human activities.[44,45] The descriptive statistics of pH, EC, TDS, and major ions including nitrate and fluoride have been presented in Table 1. EC values of the analyzed samples range between 347 and 16,320 μS/cm. The mean EC value equals 3560.30 μS/cm. The TDS ranges between 225 and 10,590 mg/L with an average value of 2306.24 mg/L, whereas the pH ranges from 6.62 to 8.07. The water is mildly alkaline with an average value of 7.38. The groundwater moving through preferred pathways within the weathered-fractured basaltic aquifer system and the underlying subbasaltic alluvium and sedimentary formations have resulted in wide spatial variation in TDS and EC values in the samples. The cations in the decreasing order of abundance are Na (440.79 mg/L) Ca (173.85 mg/L), Mg (106.82 mg/L), and K (7.30 mg/L). The anions in the decreasing order of abundance include Cl (995.53 mg/L), SO_4 (613.12 mg/L), HCO_3 (179.82 mg/L), NO_3 (70.99 mg/L), and F (0.61 mg/L). All the major ions show very high variability in concentration. Groundwater pollution is a slow process and its rate and extent depend spatiotemporal variability of natural and anthropogenic causes.[46] The main pollutants, their possible sources, and the factors affecting the overall groundwater chemistry have been discussed in the following sections.

Table 1. Statistics of the Major Ion Concentration in the Groundwater Samples[a]

parameters	minimum	maximum	average	standard dev.
pH	6.62	8.07	7.38	0.38
EC (μs/cm)	347	16,320	3560.30	3633.36
TDS	225	10,590	2306.54	2361.24
Ca	11	983	173.85	200.49
Mg	7.1	808.8	106.82	143.97
Na	9.6	2243	440.79	467.73
K	0.2	32.7	7.30	7.48
Cl	5.5	4650	666.80	995.53
HCO_3	146	1025	379.63	179.82
SO_4	8	2560	581.92	613.12
NO_3	1	340	70.99	63.12
F	0.01	2.03	0.61	0.45

[a] Concentrations are expressed in mg/L.

Nitrate. The NO_3 measurements vary between 1.00 and 340.00 mg/L, with an average of 70.89 mg/L. Fifty percent of the samples ($n = 35$) exceed the limit of 50 mg/L prescribed by refs. 16,47 for drinking water. Agricultural activities resulting in nitrate contamination of groundwater in shallow aquifers have been well documented.[48−50] Although large-scale agricultural practice is not common in the region, groundwater samples show high values of NO_3. This may be due to the application of nitrogen-based fertilizers in individual farms. Figure 3 shows the images of some agricultural farms where the groundwater samples have been collected. The weathered and fractured nature of the aquifer must be responsible for the quick downward transfer of these ions to the groundwater. Fractured aquifers systems due to the presence of preferential pathways are often associated with high hydraulic conductivities which also makes them more vulnerable to pollution.[51]

Fluoride. The area's fluoride concentration ranges from 0.011 to 2.03 mg/L. The maximum allowed levels of 1.5 mg/L for drinking water as set by refs 16,47 are met by 66 samples, while the average F content in the region is 0.61 mg/L. High F concentrations in groundwater may be caused by the breakdown of minerals including amphiboles, biotite, and fluorapatite in the weathered-fractured basaltic aquifer system, which is predominantly composed of mafic rocks.[52] It is thought that small amounts of F are stored in the (OH) sites of hydrous minerals like amphibole, mica, and apatite at relatively shallow levels of the upper mantle where basaltic magmas are produced by partial melting of peridotites because the F anion has almost the same ionic radius (1.33 Å) as the (OH) anion.[53] The research area's fluoride levels are not of concern and are mostly caused by the weathering of fluoride-bearing minerals in basaltic rock.

Heavy Metals. The evaluated heavy metals and their summary statistics are shown in Table 2. The analyzed heavy metals included in this study are As, Cr, Cu, Ni, Se, and Zn. Cu, Ni, and Zn are well within the WHO recommended limits for drinking water for all the samples, whereas 5 samples exceed the WHO recommended values for As. A total number of 4 and 5 samples exceed the WHO recommended limits for Cr and Se, respectively. It appears that the concertation of dissolved heavy metals in water is mainly a result of rock—water interaction and not a cause of major concern for the area.

Evaporation Process. Examining the plot of Na/Cl versus EC (Figure 4) makes it easier to understand how the evaporation process affects the chemistry of groundwater. In an environment where evaporation is prevalent, the ratio of Na/Cl remains unchanged with increasing EC values.[54,55] The Na/Cl ratio shows a negative slope with a steeper gradient for EC values of less than 4000 μS/cm. This could be a result of the reverse ion exchange phenomenon where there is the removal of Na and addition of Ca to the groundwater system.[56,57] However, the Na/Cl values appear to remain constant at EC concentrations above 4000 μS/cm, suggesting that the evaporation process may be in control of the groundwater chemistry. The region's arid conditions can support an environment where evaporation dominates. The constant Na/Cl ratio with increasing salinity has been found in evaporation-dominant environments.[58] Evaporation-dominant environments are also associated with high fluoride concentration.[17]

Ion Exchange. The concentration of different dissolved ions in groundwater can be affected by geochemical processes such as ion exchange and reverse ion exchange.[57,59] Schoeller et al.[60] came up with chloroalkaline indices (CAIs) 1 and 2, which provide numerical data about the ion exchange process

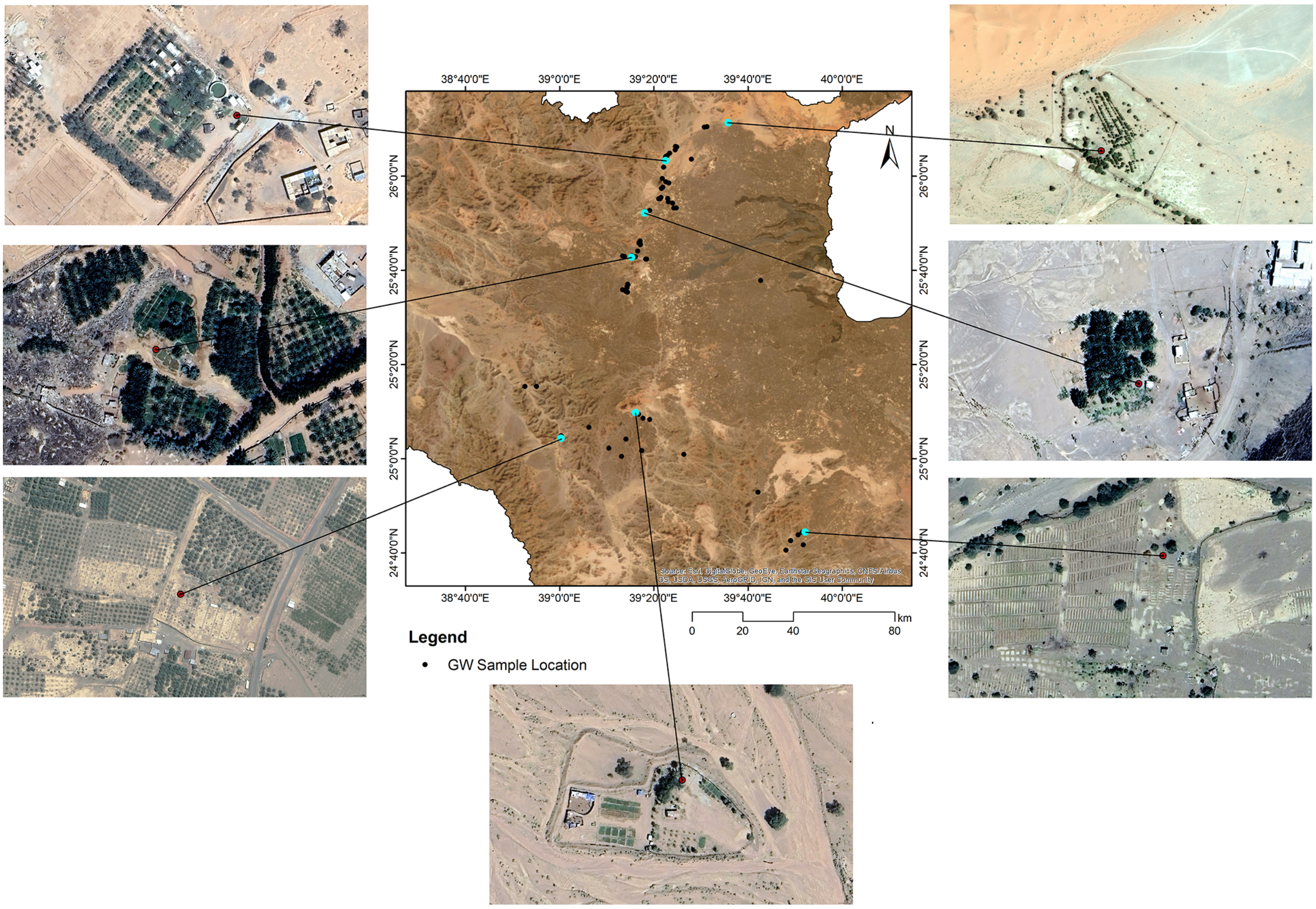


Figure 3. Image of some agricultural farms from where the groundwater samples have been collected.

Table 2. Statistics of the Heavy-Metal Concentration in the Groundwater Samples[a]

elements	minimum	maximum	average	standard dev.	WHO limits	samples exceeding WHO limits
arsenic	0.25	25.39	3.67	4.33	10	5
chromium	0.10	60.02	11.34	16.67	50	4
copper	0.13	7.64	1.53	1.67	2000	0
nickel	0.10	50.53	5.18	8.94	70	0
selenium	0.31	110.72	16.28	18.35	40	6
zinc	0.10	337.60	11.19	42.71	3000	0

[a] Concentrations are expressed in μg/L.

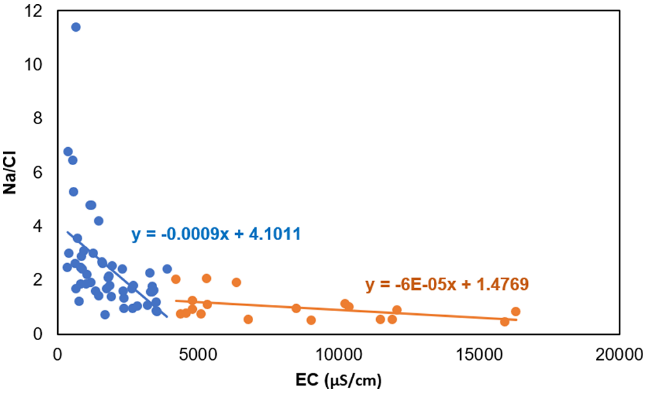


Figure 4. Plot between EC and Na/Cl to determine the influence of evaporation on groundwater samples.

between groundwater and the aquifer matrix. The following formulas can be used to calculate the indices:

$$\mathrm{CAI1} = [\mathrm{Cl} - (\mathrm{Na} + \mathrm{K})]/\mathrm{Cl} \qquad (1)$$

$$\mathrm{CAI2} = [\mathrm{Cl} - (\mathrm{Na} + \mathrm{K})]/(\mathrm{HCO_3} + \mathrm{Cl} + \mathrm{SO_4}) \qquad (2)$$

where all values are expressed in meq/L. A low concentration of Na and K relative to Cl will give a positive value for the indices.[61] The dominance of Cl over Na + K can be a result of reverse ion exchange whereby the Na and K present in groundwater have been replaced with Ca and Mg found in the aquifer matrix.[62] On the other hand, a negative value for the indices represents an excess of Na and K. The ion exchange process between the Na and K in the aquifer material and the Ca and Mg in water causes the Na and K concentration to increase relative to Ca and Mg.[63−65] Aoki et al.[53] samples from the current investigation show negative values of CAI 1 and

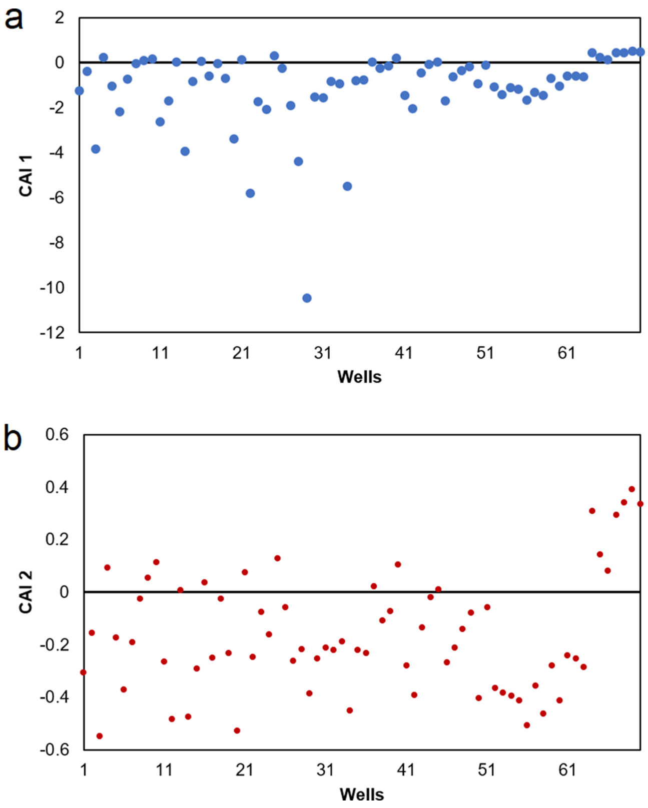


Figure 5. (a and b) CAI 1 and CAI 2 to determine ion exchange or reverse ion exchange as the main hydrochemical process.

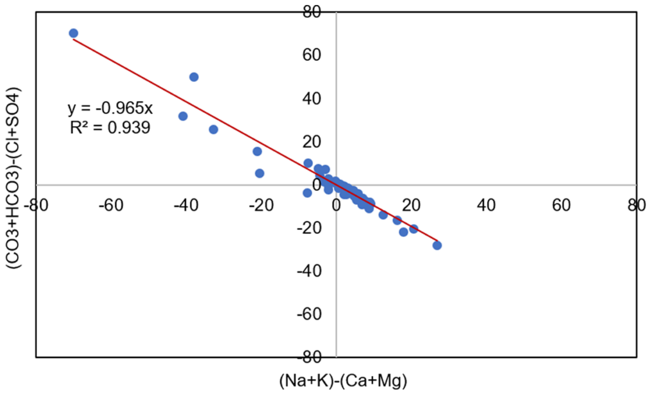


Figure 6. Plot between (Ca + Mg) − (SO_4 + HCO_3) and Na−Cl showing the relationship between major ions.

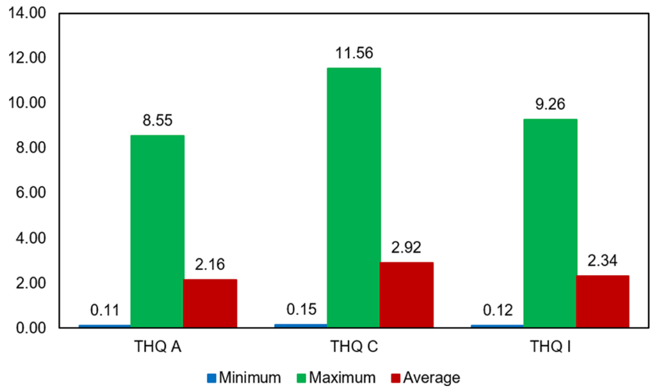


Figure 7. Graph showing the maximum, minimum, and average values of THQ for adults, children, and infants.

Table 4. HCI Calculation Was from the Analyzed Samples[a]

parameters	mean conc. (C_i)	S_i	A_{wi}	W_i (A_{wi} /$\sum A_{wi}$)	Q_i (C_i/S_i) × 100	M_i (W_i × q_i)
As	3.667	10	4	0.2	36.67	7.335
Cr	11.339	50	4	0.2	22.68	4.535
Cu	1.529	2000	3	0.15	0.08	0.011
Ni	5.176	70	4	0.2	7.39	1.479
Se	16.285	40	3	0.15	40.71	6.107
Zn	11.192	3000	2	0.1	0.37	0.037
$\sum A_{wi}$ = 20				HCI ($\sum M_i$) = 19.505		

[a] Si refers to the permissible value of the parameter as per WHO (2011) and A_{wi} refers to the assigned weight to each of the parameters.

Table 5. Classification of Groundwater Samples According to HCI Values

classification	range	number of samples	minimum	maximum	average
excellent	0–20	39	0.959	65.784	19.505
good	20–40	24			
marginal	40–60	6			
poor	60–80	1			
not suitable	>80	0			

CAI 2 (Figure 5a,b), indicating that ion exchange is the main hydrochemical mechanism operating in the area.

A plot of [Na−Cl] versus [(Ca + Mg) − (HCO_3 + SO_4)] was created to further demonstrate the existence of the ion exchange phenomenon (Figure 6). Rock–water interaction (absence of anthropogenic influences) results in a linear relationship with a slope of −1 and an intercept of 0. This

Table 3. Summary Statistics of HQ of Fluoride and Nitrate, Total HQ, and the Number of Samples Exceeding the Safe Limits of HQ in the Study Area[a]

	HQ (nitrate)			HQ (fluoride)			THQ		
N = 70	adult	children	infant	adult	children	infant	adult	children	infant
minimum	0.264	0.358	0.286	0.006	0.009	0.007	0.439	0.594	0.476
maximum	5.962	8.060	6.458	1.301	1.759	1.410	6.679	9.031	7.236
average	1.444	1.952	1.564	0.584	0.790	0.633	2.028	2.742	2.197
std. dev.	1.277	1.726	1.383	0.385	0.520	0.417	1.413	1.910	1.530
samples having HQ > 1									
N	41	52	54	4	7	4	56	59	57
%	58.57	74.29	77.14	5.71	10.00	5.71	80.00	84.29	81.43

[a] Std. Dev. stands for standard deviation.

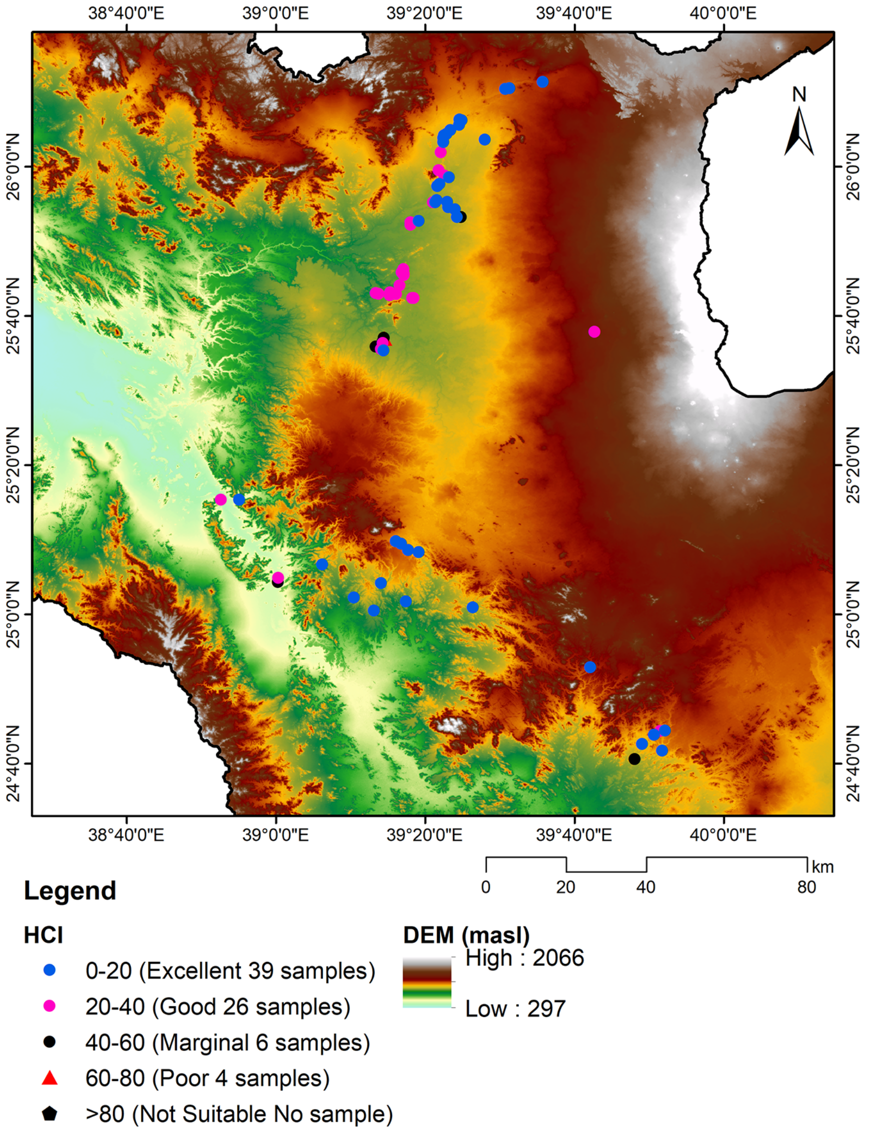


Figure 8. Arrangement of the individual groundwater samples in the study area based on HCI classes.

demonstrates that any excess Cl left after joining with Na is consumed by Ca + Mg following its bonding with HCO_3 + SO_4.[66,67] The addition of any of the dissolved ions through anthropogenic inputs will alter the linear relationship between the dissolved major ions. In the present study, the samples show a linear relationship with a slope of −0.965 and intercept of 0 indicating that Ca, Mg, Na, and K are all derived from geogenic factors and are related to each other via ion exchange phenomena.

Health Risk Assessment. Nitrate and fluoride contamination and the assessment of the associated health risks have been studied across many arid and semiarid regions of the globe such as China,[68] India,[69] Iran,[70] and Saudi Arabia.[71,72] Numerous important nutrients are needed for the human body to function properly, some of which can be supplied by drinking water. International agencies such as the WHO and quality and standards agencies of every country have determined a maximum permitted limit in drinking water in consideration of the harmful effects some of these substances can have on human health if consumed in excess. In the current study, 71% of the groundwater samples have fluoride concentrations over the maximum allowable limit of 1.5 mg/L and 50% have NO_3 concentrations beyond the maximum allowable limit of 50 mg/L in drinking water. Overconsumption of F and NO_3 can be the most harmful to human health of all of the major ions in groundwater. The United States Environmental Protection Agency[72] technique was used to determine the potential health risk and toxicity for various age groups of persons due to the continuous use of drinking water with high F and NO_3 levels.

When using water for domestic purposes, people may be exposed to a higher concentration of toxic elements in a number of ways, including (1) direct water consumption and (2) skin exposures through bathing and showering. Due to insufficient data to evaluate the latter pathway, the present analysis, however, only examined the exposure pathway of ingestion. Chronic daily intake (CDI) is estimated for a specific water sample as[73,74]:

$$\mathrm{CDI}_{\mathrm{oral}} = \frac{\mathrm{C*IR*EF*ED}}{\mathrm{BW*AT}} \qquad (3)$$

where $\mathrm{CDI}_{\mathrm{oral}}$ is the chronic daily intake expressed in mg/kg/day. C is the concentration of the specific ion in the examined water sample, expressed in mg/L. The ingestion rate (L/day), or IR, is defined by USEPA[75] as 2.5, 0.78, and 0.25 for adults, children, and infants, respectively. For all groups, it has been assumed that the exposure frequency, or EF, is 365 days annually. According to research,[73,76] the exposure duration (ED) for adults, children, and infants is 70, 6, and 0.5 years, respectively. Body weight (BW), which is expressed in kilograms, is given values of 65, 15, and 6 for adults, kids, and infants, respectively. AT is short for average exposure time. It has been calculated to be 25,550, 2190, and 182.5 for adults, children, and newborns, respectively. Since the AT is actually the product of EF and ED, it can be eliminated from the previous equation to get the following new equation:

$$\mathrm{CDI_{oral}} = \frac{C*\mathrm{IR}}{\mathrm{BW}} \tag{4}$$

Additionally, the hazard quotient (HQ)[77] is used to determine the possible noncarcinogenic risk associated with the consumption of any element, and the results are stated as:

$$\mathrm{HQ} = \frac{\mathrm{CDI_{oral}}}{\mathrm{RfD}} \tag{5}$$

$$\mathrm{THQ} = \sum_{i=1}^{n} \mathrm{HQ}_i \tag{6}$$

where THQ is the total hazard quotient (sum of HQ for F and NO_3 in the present research), RfD is the oral reference dose (mg/kg/day) for that ion, and HQ is the hazard quotient. According to USEPA,[78] the corresponding RfDs for F and NO_3 are 0.06 and 1.6 (mg/kg/day). The USEPA states that groundwater is safe to drink if CDIoral and HQoral concentrations are less than 1 mg/kg/day, but higher levels are hazardous to human health.

Fluoride in adults, children, and infants has an average HQ of 0.584, 0.790, and 0.633, respectively (Table 3). Children and infants typically face a greater health risk from fluoride exposure than adults. This is because CDI is inversely proportional to the average body weight. However, since the average F concentration (0.61 mg/L) in the study area is well within the maximum limits prescribed by WHO, it does not pose any health risk due to consumption. The HQ from NO_3 is 1.444, 1.952, and 1.564 for adults, children, and infants, respectively (Table 3). All values of HQ are above 1 for NO_3 and it poses a significant health risk. The THQ for adults, children, and infants is 2.028, 2.742, and 2.197 mg/kg/day, respectively (Table 3). All samples show THQ values of more than 1 and are considered unsafe for drinking. Due to the high HQ from NO_3, the THQ values are more than 1 for all the samples. In terms of THQ, all samples are unfit for drinking in the case of children, and all but one sample (95.24%) is not recommended for drinking in the case of adults and infants. Overall, it is not advised to consume groundwater samples without first treating them because prolonged exposure to them may result in noncarcinogenic health risks. Figure 7 shows the graph minimum, maximum, and average values of THQ for adults, kids, and infants, respectively.

Heavy-Metal Contamination Index. Rajkumar et al.[79] proposed a technique for determining the risk of heavy-metal pollution in drinking water that is comparable to the DWQI. There are 5 steps in the HCI calculation for a specific water sample. The analyzed heavy metals are first given a weight between 1 and 4 based on the threat they pose to human health (Table 4). The hazard weight was determined in this investigation using information from the New Jersey Department of Health's hazardous substance fact sheet (https://web.doh.state.nj.us/rtkhsfs/indexfs.aspx). A weight of 1 implies a minimal risk to human health, whereas a weight of 4 suggests a serious risk.

The following equation is used in the second step to assign relative weights to each of the parameters:

$$W_i = \frac{A_{wi}}{\sum_{i=1}^{n} A_{wi}} \tag{7}$$

where W_i is the ith parameter's relative weight, A_{wi} is the weight assigned to the ith parameter, and n is the total number of parameters. For each parameter of the sample being considered, the third stage entails calculating the quality rating scale (q_i):

$$q_i = \frac{C_i}{S_i}*100 \tag{8}$$

where S_i is the parameter's permitted limit in drinking water as determined by national or international standards and C_i is the concentration of the ith parameter in the examined sample.

The fourth step employs the equation below to derive the metal subindex of the ith parameter, MI_i

$$\mathrm{MI}_i = W_i*q_i \tag{9}$$

In the fifth phase, the HCI of a specific water sample is calculated by adding the MI_i values of all the parameters and is represented as

$$\mathrm{HCI} = \sum_{i=1}^{n} \mathrm{MI}_i \tag{10}$$

Based on the HCI values, the water quality can be classified into 5 different categories: 0–20 (excellent), 20–40 (good), 40–60 (marginal), 60–80 (poor), and >80 (not suitable). The six heavy metals used in the HCI computation in the current investigation were arsenic (As), chromium (Cr), copper (Cu), nickel (Ni), selenium (Se), and zinc (Zn). The HCI computation and the weights allocated to each parameter are displayed in Table 4. The HCI value ranges between 0.959 and 65.784, and the average value is 19.505 (Table 5). Thirty-nine samples fall within the excellent category, whereas 24 samples are in the good category. Six samples fall within the marginal category, whereas 1 sample falls in the poor category. There are no samples in the not suitable class. Figure 8 shows the classification of the groundwater samples based on their HCI values.

■ CONCLUSIONS

Groundwater quality investigation was carried out in the Harrat Khyber Region of Madina Province, and the major hydrochemical processes, health risk assessment using CDI and HQ, and HCI were determined for 70 groundwater samples. The following is a summary of the key findings:

- The ratio between the Na and Cl ions becomes constant at EC values more than 4000 S/cm, showing that samples with higher salinity are primarily impacted by the evaporation process. This is true considering the arid nature of the area.
- Ion exchange due to the release of Na and K from the aquifer matrix to replace Ca and Mg in groundwater affects groundwater chemistry, as seen by negative CAIs.

- Without any additional contributions from anthropogenic sources, the main ions are linked to one another through the ion exchange process.
- The average THQ values for adults, children, and infants are above 1, according to the health risk assessment for nitrate and fluoride, which exposes the population to a noncarcinogenic health concern. However, NO_3, which may be released as a result of agricultural activity nearby, poses the greatest threat to health. Fluoride levels in all samples are well under WHO recommended limits and are not cause for worry.

  The HCI values show that there is no danger from heavy-metal contamination in water because 90% of the samples fell into the excellent to good range.

■ ASSOCIATED CONTENT

Data Availability Statement

The study's corresponding author, F.K.Z. may provide the data backing up the study's conclusions upon request. Due to the fact that the data potentially threaten the privacy of research participants, they are not publicly available.

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Notes

The authors declare no competing financial interest.
Author has read, understood, and complied as applicable with the statement on "Ethical responsibilities of Authors" as found in the Instructions for Authors and is aware that with minor exceptions, no changes can be made to authorship once the paper is submitted.
All authors have read, understood, and have complied as applicable with the statement on "Ethical responsibilities of Authors" as found in the Instructions for Authors and are aware that with minor exceptions, no changes can be made to authorship once the paper is submitted.

■ ACKNOWLEDGMENTS

The authors extend their appreciation to the Deputyship for Research and Innovation, Ministry of Education, Saudi Arabia, for funding this research (IFKSURC-1-7306).

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