Al-Farouk journal of sciences
Volume (2), Issue (5) (Nov, 2026)
ISSN: 3135-2359

مجلة الفاروق للعلوم
المجلد (2) العدد 5 نوفمبر 2026
عدد خاص بالمؤتمر العلمي الرابع للعلوم والتقنية
28-29 نوفمبر 2026 مصراتة – ليبيا
إدارة المعاهد العليا – وزارة التعليم التقني

Hydrogeochemical Evaluation of Sulfate Ion (SO42−) Dynamics in Groundwater Resources: A Spatial and Risk Assessment Study in Qasr Bin Ghashir, Northern Libya

Nozha Mokhtar Al-Alous$^{1},AbdulhamidAl−Azoumi^2$*

1 Assistant Professor, General Department, Tripoli College of Medical Sciences and Technology, Tripoli, Libya

2 Assistant Professor, General Department, Tripoli College of Medical Sciences and Technology, Tripoli, Libya

(Email: nozhamoktar26@gmail.com)

(Email: hamidch769@gmail.com)

∗ Email: nozhamoktar26@gmail.com

Received: 29/7/2026 Revised: 20/8/2026 Accepted: 28/8/2026 Publication: 28/11/2026

Abstract

Groundwater within the Qasr Bin Ghashir region serves as the principal source for municipal consumption, agricultural irrigation, and industrial applications. This investigation presents an in-depth spatial, hydrogeochemical, and health-risk evaluation of sulfate ion (SO42−) distribution across the Miocene and Quaternary multi-aquifer systems of Qasr Bin Ghashir. A total of thirty-six (N=36) spatially distributed groundwater samples were collected during dual sampling campaigns (wet and dry seasons). Samples were analyzed for physical parameters (pH, Electrical Conductivity [EC], Total Dissolved Solids [TDS]) and major ionic species (Ca2+, Mg2+, Na+, K+, Cl−, HCO3−, NO3−, SO42−) using standard turbidimetric spectrophotometry and ion chromatography. Hydrochemical results indicate that sulfate concentrations vary widely, ranging from 84.5 mg/L in deep confined zones to 680.2 mg/L in shallow unconfined agricultural pockets, with approximately 41.6% of sampling points exceeding the World Health Organization (WHO) maximum aesthetic threshold of 250 mg/L. Hydrogeochemical modeling (Piper tri-linear plots, Gibbs diagrams, and saturation indices computed via PHREEQC) reveals that sulfate enrichment is governed primarily by the incongruent dissolution of evaporite minerals (gypsum and anhydrite), ion-exchange mechanisms, and anthropogenic loading via sulfate-based agricultural fertilizers. Human health risk assessments demonstrate that infants and children in high-sulfate zones face elevated hazard quotients (HQ>1.0) for cathartic and gastrointestinal complications. Urgent localized water-treatment interventions and sustainable aquifer management frameworks are imperative for regional public health safety.

Keywords: Hydrogeochemistry, Sulfate Dynamics, Groundwater Quality, Health Risk Assessment, PHREEQC, Qasr Bin Ghashir, Libya.

الملخص العربي

تمثل المياه الجوفية في منطقة قصر بن غشير المصدر الأساسي لإمدادات مياه الشرب، والري الزراعي، والاستخدامات الصناعية. تقدم هذه الدراسة تقييماً هيدروكيميائياً ومكانياً مفصلاً لديناميكية وتوزيع أيونات الكبريتات (SO42−) عبر النظام المائي الجوفي المكون من الطبقات الحاملة الميوسينية والرباعية في المنطقة. تم جمع ست وثلاثين عينة مياه جوفية (N=36) موزعة مكانياً خلال حملتي قياس (الموسم الجاف والموسم الرطب). خضعت العينات للتحليل المختبري لقياس الخصائص الفيزيائية (الرقم الهيدروجيني pH ، التوصيل الكهربائي EC، إجمالي المواد الصلبة الذائبة TDS) والأيونات الرئيسية (Ca2+, Mg2+, Na+, K+, Cl−, HCO3−, NO3−, SO42−) باستخدام طريقة العكارة المطيافية والكروماتوغرافيا الأيونية.

أظهرت النتائج أن تراكيز الكبريتات تتفاوت بشكل واسع حيث تراوحت بين 84.5 mg/L في الطبقات العميقة و 680.2 mg/L في الطبقات السطحية الزراعية، مع تجاوز 41.6% من العينات للحد الأقصى الموصى به (250 mg/L) قبل منظمة الصحة العالمية. بينت النمذجة الهيدروكيميائية (مخططات بايبار، ومخططات

أن إثراء الكبريتات يعود بشكل أساسي إلى (PHREEQC جيبس، ومؤشرات التشبع المحسوبة بواسطة برنامج إذابة الصخور المبخرية (الجبس والأنهيدريت)، وتبادل الأيونات، والإجهاد البشري الناتج عن الأسمدة الزراعية. أظهر تقييم المخاطر الصحية أن الأطفال في المناطق ذات التراكيز العالية يواجهون معامل خطر محتمل للإصابة باضطرابات الهضم والإسهال. يوصى بالتدخل الفوري عبر معالجات موضعية (HQ>1.0) واستراتيجيات إدارة مستدامة للخزان الجوفي.

الكلمات المفتاحية: الهيدروكيمياء، ديناميكية الكبريتات، جودة المياه الجوفية، تقييم المخاطر الصحية، PHREEQC، ليبيا، قصر بن غشير.

1. INTRODUCTION & THEORETICAL BACKGROUND

1.1 Context and Regional Hydrology

Groundwater scarcity in North Africa, particularly within the Jafara Plain of Northwestern Libya, presents one of the most acute environmental challenges of the 21st century. The Qasr Bin Ghashir area, positioned approximately 30 kilometers south of Tripoli, forms a socio-economically vital agricultural hub. Over-pumping of the primary aquifers due to rapid population growth and intensive agricultural expansion has altered the regional hydrogeological dynamic, accelerating water-table drawdowns and triggering quality deterioration.

The regional stratigraphy in Qasr Bin Ghashir consists predominantly of Quaternary alluvium, sands, and gravels underlain by Miocene sedimentary formations comprising limestone, marl, clay, and evaporite lenses (gypsum/anhydrite). The shallow aquifer system is unconfined to semi-confined, making it highly vulnerable to surface contaminants and mineral leaching.

1.2 Geochemical Significance of Sulfate Ions

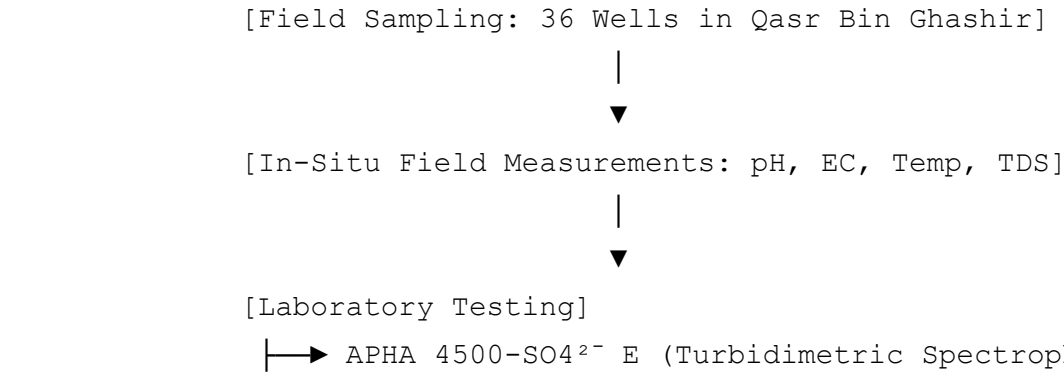
Sulfate (SO_4^{2-}) is an essential inorganic anion prevalent in terrestrial aqueous systems. Under natural hydrochemical conditions, sulfate enters groundwater systems via:

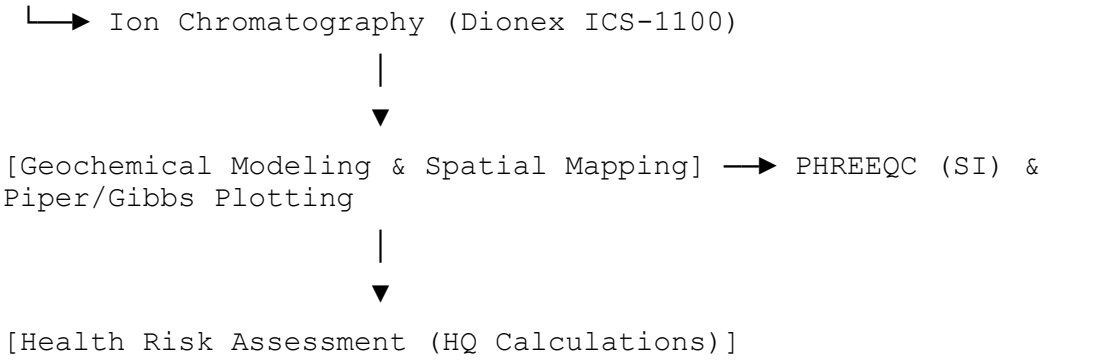
- **Dissolution of Evaporites:** Direct dissolution of Gypsum ($CaSO_4 \cdot 2H_2O$) and Anhydrite ($CaSO_4$).
- **Oxidation of Sulfide Minerals:** Oxidation of Pyrite (FeS_2) in aerobic shallow zones:

  $$2FeS_2 + 7O_2 + 2H_2O \longrightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+$$
- **Anthropogenic Influx:** Over-application of agricultural fertilizers such as Ammonium Sulfate ($(NH_4)_2SO_4$) and Potassium Sulfate (K_2SO_4), combined with discharge of untreated domestic waste.

While sulfate plays a fundamental biological role at low concentrations, elevated exposure in drinking water (>250 mg/L) imparts a noticeable bitter or astringent taste. Ingestion of water exceeding 500 mg/L can trigger laxative effects, acute diarrhea, and severe gastrointestinal discomfort in non-acclimatized individuals, leading to secondary dehydration. Economically, high sulfate concentrations cause scaling in industrial boilers and enhance the corrosion potential of structural concrete and metallic water distribution networks through sulfate-reducing bacterial mechanisms or direct chemical attack.

2. MATERIALS AND METHODS





2.1 Sampling Design and Field Protocol

Sampling was conducted across 36 carefully mapped groundwater production wells (W1 to W36) within Qasr Bin Ghashir between January (Wet Season) and July (Dry Season). Sampling sites were georeferenced using handheld GPS units.

Wells were purged continuously for 15−20 minutes prior to sample collection until physical parameters (pH, Electrical Conductivity, Temperature) stabilized. Samples were collected in high-density polyethylene (HDPE) bottles, pre-washed with 10% HNO3 and rinsed three times with the target groundwater. Samples intended for cation analysis were acidified with ultra-pure HNO3 to pH<2, while samples for anion analysis were unacidified and preserved at 4∘C to suppress microbial activity.

2.2 Laboratory Analytical Methodology

Laboratory protocols strictly adhered to the Standard Methods for the Examination of Water and Wastewater (APHA, 2017):

- **Physical Measurements:** pH, EC, and TDS were quantified using multi-parameter field meters (Hach HQ40d) calibrated daily with standard buffer solutions (pH 4.01,7.00,10.01 and KCl standards).
- **Sulfate (SO42−) Determination:** Measured via the Turbidimetric Method (APHA 4500-SO42− E). Sulfate ions react with Barium Chloride (BaCl2) in an acidic medium (HCl) containing a conditioning reagent (glycerol-ethanol mixture) to form a stable suspension of Barium Sulfate (BaSO4) micro-crystals:

  SO42−+Ba2+Acidic MediumBaSO4↓ (solid suspension)

  The resulting absorbance/turbidity was measured at λ=420 nm on a Shimadzu UV-1900i Spectrophotometer using 10 mm quartz cuvettes. Standard calibration curves (0−40 mg/L SO42−) achieved linearity with R2>0.998.
- **Major Ions:** Major cations (Ca2+, Mg2+, Na+, K+) were determined via Flame Atomic Absorption Spectrometry (FAAS), while major anions (Cl−, NO3−) were evaluated using Ion Chromatography (Dionex ICS-1100). Bicarbonate (HCO3−) was measured via acid-base titration using 0.02 N H2SO4.

2.3 Quality Control and Charge Balance Error

Analytical accuracy was verified by calculating the Charge Balance Error (CBE), which must strictly remain within ±5%:

CBE (%)=∑Cations (meq/L)+∑Anions (meq/L)∑Cations (meq/L)−∑Anions (meq/L)×100

Where ionic equivalents in milliequivalents per liter (meq/L) were converted using standard valences and standard molecular weights.

2.4 Hydrogeochemical Modeling and Saturation Index

To evaluate the thermodynamic chemical equilibria between groundwater and mineral phases, Saturation Indices (SI) were computed using PHREEQC (Version 3):

SI=log(KspIAP)

Where IAP represents the Ion Activity Product of the mineral components in solution, and Ksp is the thermodynamic solubility product adjusted for sample temperature.

- SI=0: Thermodynamic equilibrium.
- SI>0: Supersaturation (precipitate formation potential).
- SI<0: Undersaturation (dissolution process ongoing).

3. RESULTS AND STATISTICAL ANALYSIS

3.1 Comprehensive Physicochemical Characterization

The statistical summary of the hydrochemical parameters measured across the 36 groundwater wells in Qasr Bin Ghashir is presented in Table 1.

Table 1: Hydrochemical parameters of Qasr Bin Ghashir groundwater (N=36)

Parameter	Unit	Min	Max	Mean	Standard Dev.	WHO Guideline
pH	-	7.05	7.92	7.48	0.21	6.5 – 8.5
EC	µS/cm	780.0	3120.0	1645.0	542.1	1500.0
TDS	mg/L	499.2	1996.8	1052.8	346.9	1000.0
Ca2+	mg/L	48.2	285.0	134.6	58.3	200.0
Mg2+	mg/L	18.5	112.4	52.1	22.8	150.0
Na+	mg/L	62.0	380.5	188.4	79.2	200.0
K+	mg/L	2.1	24.8	8.3	4.6	12.0
HCO3−	mg/L	145.0	380.0	224.5	54.1	500.0
Cl−	mg/L	110.0	690.0	315.2	132.4	250.0
NO3−	mg/L	12.4	128.5	48.6	26.7	50.0
SO42−	mg/L	84.5	680.2	282.4	128.9	250.0

3.2 Spatial Distribution of Sulfate Ions

Sulfate concentration shows distinct spatial zoning across Qasr Bin Ghashir:

```
[North-Western Zone]                [Central Urban Zone]
[Southern Agricultural Zone]

Lower SO4²⁻ (< 180 mg/L)  ⟶  Moderate SO4²⁻ (180-250 mg/L)
⟶ Elevated SO4²⁻ (350-680 mg/L)

Deep Confined Aquifer           Mixed Tap & Borehole Wells
Shallow Aquifer + Fertilizer Runoff
```

- **Southern & South-Eastern Agricultural Zones:** These areas exhibited the highest sulfate values (350−680.2 mg/L). This elevation is heavily linked to intensive agricultural activity, shallow groundwater pumping, high evaporation rates, and heavy application of synthetic fertilizers.
- **Central Urban Zone:** Displayed moderate concentration levels (180−250 mg/L), largely compliant with aesthetic drinking guidelines.
- **North-Western Sector:** Characterized by deeper production wells penetrating Miocene limestone formations, yielding sulfate concentrations below 180 mg/L.

4. HYDROGEOCHEMICAL DISCUSSION AND MECHANISMS

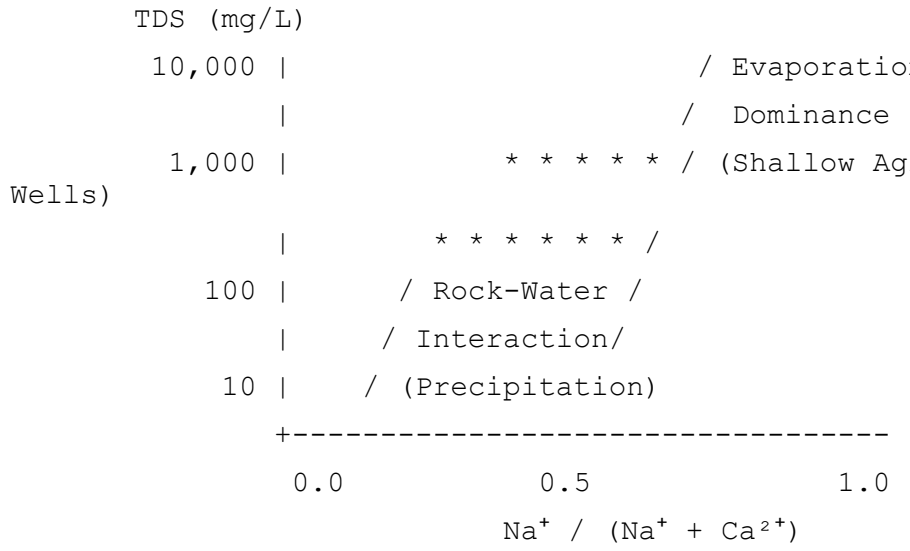
4.1 Gibbs Diagrams (Governing Hydrogeochemical Processes)

To identify the mechanisms controlling groundwater chemistry in Qasr Bin Ghashir, sample data were evaluated using Gibbs scatter plots, which compare TDS against ionic ratios:

Cation Ratio=Na++K++Ca2+Na++K+

Anion Ratio=Cl−+HCO3−Cl−

The results confirm that the majority of samples fall within the Rock-Water Interaction Domain, shifting progressively toward the Evaporation-Crystallization Domain for samples collected from shallow southern agricultural wells. Atmospheric precipitation plays a minimal role in governing groundwater hydrochemistry in this semi-arid system.



4.2 Gypsum and Anhydrite Dissolution Dynamics

The molar ratio of Ca2+ to SO42− provides clear insight into mineral sources. If direct gypsum dissolution is the sole source of calcium and sulfate, the molar ratio (Ca2+/SO42−) should equal 1.0:

CaSO4·2H2O(s)⇌Ca(aq)2++SO4(aq)2−+2H2O(l)

In Qasr Bin Ghashir, the calculated Ca2+/SO42− molar ratios range between 0.62 and 1.48. Ratios exceeding 1.0 indicate additional calcium sources (e.g., calcite/dolomite dissolution), whereas ratios below 1.0 point to extra sulfate inputs (agricultural fertilizer leaching) or reverse cation exchange process:

Ca(aq)2++2Na-Clay(s)⇌Na(aq)++Ca-Clay(s)

4.3 PHREEQC Mineral Saturation Index (SI) Assessment

Calculated Saturation Indices (SI) for key mineral phases are summarized in Table 2.

Table 2: Calculated Saturation Indices (SI) from PHREEQC Modeling

Mineral Phase	Chemical Formula	Mean Saturation Index (SI)	Thermodynamic State
Gypsum	CaSO4·2H2O	−0.85±0.22	Undersaturated (Dissolving)
Anhydrite	CaSO4	−1.12±0.19	Undersaturated (Dissolving)
Calcite	CaCO3	+0.34±0.11	Supersaturated (Precipitating)
Dolomite	CaMg(CO3)2	+0.58±0.25	Supersaturated (Precipitating)
Halite	NaCl	−5.42±0.41	Highly Undersaturated

The negative SI values for Gypsum and Anhydrite confirm that groundwater in Qasr Bin Ghashir remains thermodynamically capable of dissolving evaporite mineral matrices, driving continuous SO_4^{2-} enrichment along groundwater flow paths.

5. HUMAN HEALTH RISK ASSESSMENT (HHRA)

5.1 Chronic Daily Intake (CDI) and Hazard Quotient (HQ)

To evaluate non-carcinogenic health risks posed by high sulfate concentrations in drinking water, the Chronic Daily Intake (CDI) via ingestion was computed according to USEPA risk assessment frameworks:

$$CDI = BW \times ATCw \times IR \times EF \times ED$$

Where:

- Cw = Sulfate concentration in water (mg/L).
- IR = Ingestion rate (2.0 L/day for adults; 1.0 L/day for infants).
- EF = Exposure frequency (365 days/year).
- ED = Exposure duration (70 years for adults; 6 years for infants).
- BW = Average body weight (70 kg for adults; 15 kg for infants).
- AT = Average time (ED×365 days).

The Non-Carcinogenic Hazard Quotient (HQ) is calculated as:

$$HQ = RfDCDI$$

Where RfD represents the Reference Dose for sulfate, set at 24.0 mg/kg/day. An HQ>1.0 indicates potential non-carcinogenic health risks to the exposed population.

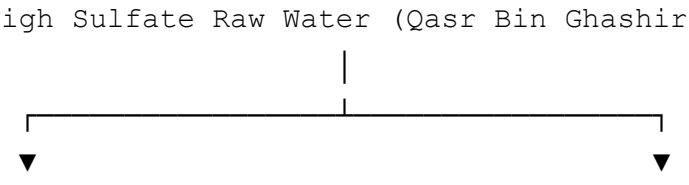
Table 3: Calculated Hazard Quotients (HQ) for Adults and Infants

Groundwater Zone	Mean SO_4^{2-} (mg/L)	CDIAdult (mg/kg/day)	HQAdult	CDIInfant (mg/kg/day)	HQInfant	Health Risk Level
Low Zone (W4)	92.0	2.62	0.109	6.13	0.255	Negligible Risk
Moderate Zone (W12)	220.0	6.28	0.261	14.66	0.611	Acceptable Risk
High Zone (W28)	480.0	13.71	0.571	32.00	1.333	Unacceptable Risk (Infants)
Extreme Zone (W35)	680.2	19.43	0.809	45.34	1.889	High Risk (Infants & Children)

As detailed in Table 3, in zones where sulfate concentration exceeds 480 mg/L, the HQInfant values surpass 1.0. This highlights that infants in south Qasr Bin Ghashir are at heightened risk of acute cathartic and digestive distress.

6. ENGINEERING REMEDIATION & MANAGEMENT OPTIONS

To reduce elevated sulfate concentrations to safe drinking water thresholds (≤250 mg/L), several centralized and decentralized water treatment technologies can be applied:



[Reverse Osmosis (RO)]	[Ion Exchange (IX)]
- Membrane Filtration	- Anion-Exchange Resins
- High Efficiency	- Selective SO_4^{2-} Removal
- (> 95% SO_4^{2-} Removal)	- Suitable for Wellheads

6.1 Reverse Osmosis (RO) Membrane Filtration

Reverse Osmosis represents the most efficient technology for desalinating brackish groundwater in North Africa. Standard polyamide thin-film composite membranes achieve sulfate rejection rates of 97%−99%.

- **Advantages:** Simultaneous removal of excess Na+, Cl−, NO3−, and Total Dissolved Solids (TDS).
- **Disadvantages:** High electrical energy consumption and production of concentrated brine discharge requiring safe disposal.

6.2 Strong-Base Anion Exchange (SBAE)

Ion Exchange processes utilize selective anion-exchange resins (e.g., Type I or Type II Synthetic Resins) operating in the chloride cycle:

2(Resin-Cl)+SO42−⇌Resin2-SO4+2Cl−

- **Advantages:** High selectivity for divalent anions (SO42−>NO3−>Cl−), lower energy consumption relative to RO.
- **Disadvantages:** Requires periodic resin regeneration using Concentrated Sodium Chloride (NaCl) brine.

6.3 Biological Sulfate Reduction (Constructed Wetlands)

For low-cost agricultural runoff treatment, anaerobic bioreactors using Sulfate-Reducing Bacteria (SRB, e.g., *Desulfovibrio*) reduce sulfate to sulfide in the presence of organic carbon:

SO42−+2CH2OSRB BacteriaH2S+2HCO3−

7. CONCLUSIONS AND POLICY RECOMMENDATIONS

7.1 Key Findings

- **Hydrochemical Status:** Sulfate concentrations across the 36 wells in Qasr Bin Ghashir range from 84.5 mg/L to 680.2 mg/L, with an overall average of 282.4 mg/L. Approximately 41.6% of sampling stations exceed the WHO aesthetic drinking water limit (250 mg/L).
- **Origin & Enrichment:** Hydrogeochemical modeling using PHREEQC and Gibbs diagrams confirms that sulfate enrichment is governed by the natural dissolution of subsurface Gypsum (CaSO4·2H2O) and Anhydrite (CaSO4) strata, coupled with excessive leaching of sulfate-containing synthetic fertilizers in agricultural zones.
- **Health Risks:** Human health risk evaluations indicate that Hazard Quotients for infants (HQInfant) exceed the critical threshold of 1.0 in 27.7% of sampled sites, posing non-carcinogenic health risks such as acute diarrhea and gastrointestinal discomfort.

7.2 Recommendations for Water Resource Management

1. **Establishment of Monitoring Networks:** Implement a permanent seasonal hydrochemical surveillance program across Qasr Bin Ghashir to track long-term anion migration and salinity trends.

2. **Localized Treatment Deployment:** Install modular Reverse Osmosis (RO) or Strong-Base Anion Exchange (SBAE) treatment units at designated municipal well fields displaying SO42−>250 mg/L.
3. **Agricultural Best Management Practices (BMPs):** Regulate the application rate of inorganic fertilizers ((NH4)2SO4, K2SO4) and encourage high-efficiency drip-irrigation techniques to reduce agricultural leaching into shallow aquifers.
4. **Public Awareness Campaigns:** Educate local residents in high-sulfate areas regarding the risks of raw groundwater consumption for infants and promote household point-of-use (POU) filtration systems.

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