

Geochemical assessment of groundwater contamination with special emphasizes on fluoride, a case study from Midyan Basin, northwestern Saudi Arabia

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Abstract Water samples for chemical analyses were collected in January 2012. A total of 72 samples of groundwater were collected from 72 boreholes in the Midyan Basin, northwestern Saudi Arabia. Samples were collected in polyethylene bottles and preserved and the used analytical techniques were in accordance with the standard methods from American public health association. Geochemical analyses of the groundwater samples from Midyan Basin reveal the concentration of fluoride (F) between 0.98 and 2.1 mg/l. Other parameters, e.g. pH, EC, TDS, HCO_3 , SO_4 , NO_3 , Cl, K, Na, Mg, and Ca have been found in a variable proportion. Among them, the concentration of EC, HCO_3 , K, Na and Mg is higher than the permissible limits. According to thermodynamical considerations, most of the analysed samples are graded under-saturated with respect to calcite and fluoride, while saturation has been observed in some samples. The under-saturation could probably be attributed to low concentration of calcite and fluoride in the studied wells. Fluoride concentration shows weak positive correlation with EC, TDS, Na, Cl, and SO_4 . Factors controlling the concentration of fluoride (F) in the studied samples are the area climate, water chemistry and the presence of accessory minerals in the rocks through which groundwater is circulating, besides the anthropogenic activities in the area.

Keywords Geochemical analysis · Groundwater samples · Midyan Basin · Saudi Arabia

Introduction

Groundwater is the only reliable water resource for domestic, agriculture and industrial uses in the arid country like Saudi Arabia. Rapidly depleting groundwater aquifers as a consequence of high population growth and rapid industrialization are threatening the quality of water resources in Saudi Arabia. To evaluate the suitability of groundwater for different purposes, understanding about the chemical composition of these important resources is necessary. It is possible to investigate changes in groundwater quality due to rock–water interaction (weathering) or due to anthropogenic activities (Teotia and Teotia 1988; Batayneh et al. 2008, 2012a, b). The groundwater chemistry is subject to continuous modifications in any given hydrogeological environment, and its ionic content depends on the accompanying aquifer material; hence, it is imperative to study and understand the different hydrogeochemical characteristics of aquifers in different seasons and geological terrains. The appraisal of water chemistry attains significance, more so for a contaminated aquifer, so as to facilitate understanding the process of pollution and ability of the groundwater to assimilate extraneous elements. The chemical contaminants more commonly follow the preferred paths in any aquatic medium during dispersion and get absorbed relegating the genetic signatures of the host solution; hence, it is crucial to assess aquifer geometry, its mineral make up, and hydrodynamics apart from hydrochemistry for comprehensive exploration of a polluted watershed (Singh et al. 2007).

Occurrence of fluorine in groundwater has drawn worldwide attention due to its considerable impact on human physiology. Fluorine occurs mainly as free fluoride ion in natural waters, though their complexes in the shapes of Al, Be, B, and Si can also be encountered under specific

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conditions (Johnson et al. 1992). Fluoride is a common contaminant of drinking water. Concentration of fluoride in drinking water plays a key role in regulating body's physiological activities, where consumption of water with fluoride concentrations above or below certain permissible limit causes various kinds of poor dental hygiene, dental fluorosis, and also skeletal fluorosis (Chadha and Tamta 1999). The main source of fluoride for human body is usually drinking water covering about 75–90 % of daily intake need (Stallard and Edmond 1987). Traditionally, fluorosis has been connected with higher intake of fluoride through drinking water. According to the World Health Organization (1984), permissible limit for fluoride in drinking water is 1–1.5 mg/l; whereas, the United State public health service has set a range of allowable concentrations for fluoride in drinking water for a region depending on its climatic conditions because the amount of water consumed and consequently the amount of fluoride ingested is being influenced primarily by the air temperature (Subba Rao 2002). Ingestion of water with fluoride concentrations above 1.5 mg/l results in dental fluorosis characterized initially by opaque white patches, staining, mottling and pitting (Johnson et al. 1992). Skeletal fluorosis may occur when fluoride concentrations in drinking water exceed 4–8 mg/l, leading to increase in bone density, calcification of ligaments, rheumatic or arthritic pain in joints and muscles along with stiffness and rigidity of the joints, bending of the vertebral column and so on. This disease may be present in individuals at subclinical, chronic or acute levels of manifestation (World Health Organisation 2004). Besides the environmental concern of fluorine in natural waters, the deduction of the ultimate source of fluoride and establishing the mode of dissolution together with transport in natural waters and natural sinks of the fluoride ion are issues which needs to be addressed (Abu-Rukah and Alsokhny 2004). Keeping aside the anthropogenic activities as a potential sources of fluorine (such as burning of coal, extraction of aluminium, steel industries and phosphate fertilizers), the natural phenomenon, such as leaching through rocks and soils enrichment, can also contribute to a certain extent. Fluorite (CaF_2) is the only principle mineral of fluorine, mostly present as accessory mineral in granitic and occasionally in alkaline rocks (e.g., syenite and nepheline syenites). Minerals like apatite, amphiboles and micas, which are ubiquitous in igneous and metamorphic rocks, contain fair amounts of fluorine in their structure. Sedimentary horizons also have apatite as accessory mineral and fluorite as a cementing material in some sandstone. All these minerals are, therefore, natural contributors of fluorine to fluids interacting with them, such as ground, surface and thermal waters. Although, the geochemistry of fluorite solubility in natural water is known (Ellis and Mahon 1964; Pickering 1985).

Much has to be done to quantitatively evaluate the level of fluorine in groundwater, especially in terms of mineral-fluid equilibrium. Abu-Rukah and AISokhny (2004) reported a geochemical assessment of groundwater contamination in North Jordan and a concentration of 0.009–0.055 mg/l has been estimated for the fluoride. High concentration of fluorine (1.5 mg/l) has been reported in the groundwater of Nayagarh district (Orissa/India) and its relation with fluorine rich hot spring (more than 10 mg/l) have been investigated by Kundu et al. (2001) and Johnson et al. (1992). Apambire et al. (1997) studied the geochemistry of groundwater in the upper part of Ghana/India and ascribed the fluoride contamination qualitatively to the presence of coarse-grained hornblende granites and syenite in the area. They have further suggested that dissolution of fluoride and anion exchange in micaceous minerals and their clay alteration products are causes of fluoride enrichment. Hydrochemical processes controlling the occurrence of fluoride in groundwater include solution precipitation, adsorption–desorption processes, dispersion of chemical formation complex and abundance of fluorine in source rocks (Clark 1981). The present work focuses on chemical characterization of the groundwater bodies in Midyan Basin (northwestern Saudi Arabia), with special emphasis on fluoride contaminations and their possible sources.

Study area description

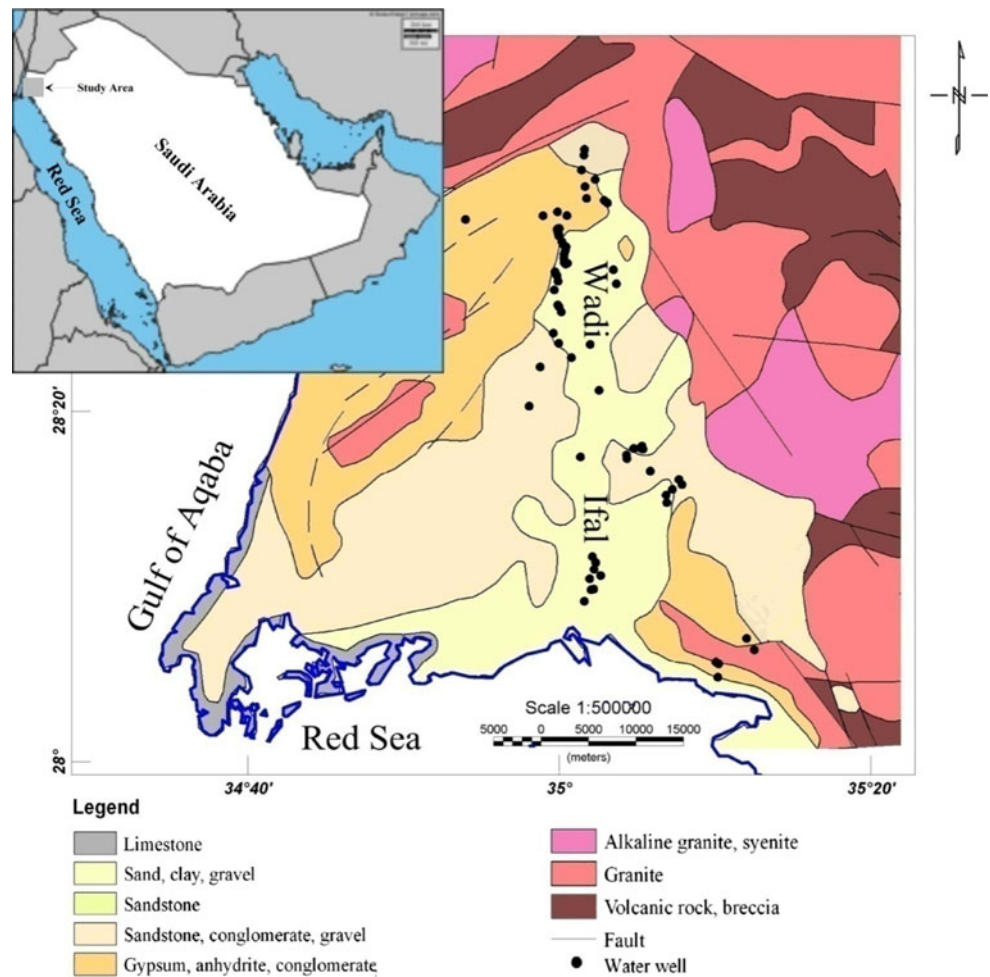
Location

The Midyan Basin is located in the west of Tabuk province, northwestern Saudi Arabia. This triangle shape basin is accessible by modern highway linking Tabuk city with the Gulf of Aqaba and Red Sea to the west. It is bounded to the north, east and northeast by mountains of the Proterozoic basement rocks, to the west by the Proterozoic basement and sedimentary rocks, and to the south by the Red Sea (Fig. 1). This basin is situated between latitude 28°00' and 28°40'N and longitude 34°40'–35°20'E, which covers an area of about 1,500 km² with a population of about 5,000 (Central Department of Statistics and Information 2012, personal communication).

Climate and general land use

Climate of the region is characterized by hot dry summer with temperatures in the excess of 47 °C and cold winter with an annual average precipitation of 60 mm (Batayneh et al. 2012a, b). Rainfall generally occurs during the winter months; however, some of the years pass without any

Fig. 1 Study area sampling, locations, and geological map of the Midyan Basin (geology modified after Wyn Hughes et al. 1999)



rainfall at all, while others receive heavy rainfall of short duration causing ephemeral flooding. (Saudi Presidency of Meteorology and Environment 2012, personal communication). The surface elevation ranges between 0 and 300 m above mean sea level. The dominant industries in the area are machine brick, ceramic, and asphalt manufacturing. Other main activities in this area are breeding sheep's/goats and agriculture crop production. The main crops produced in the area are clover, fruits and vegetables, which are mainly cultivated in the northern, central and eastern parts of the study area.

Geological setup

Other than few research reports, detailed geological/geophysical characteristics of northwestern Saudi Arabia remain to be documented. A preliminary geological Observations and related mapping (1:250,000 scale) for the Midyan Basin has been reported by Clark (1981). Following this, Wyn Hughes et al. (1999) have revealed that most parts of this basin are occupied by the plain of Wadi Ifal (Fig. 1).

According to the available information, the oldest sedimentary rocks in the basin are the Late Cretaceous Adaffa Formation (fluvatile in origin), which unconformably overlay the Proterozoic basement. The basement is made of ultramafic, metavolcanics, metasedimentary rocks and granitic plutons, which in turn are intruded by a variety of dikes swarms (including basaltic, rhyolitic and doleritic). The Adaffa Formation is then unconformably overlain by the Early Miocene Burqan Formation from Tayran Group (deep marine in origin), which in turn is overlain by the poorly exposed middle Miocene Mansiyah and middle to upper Miocene Ghawwas formations. The Mansiyah and Ghawwas formations are made of marine evaporates and shallow to marginal marine sediments, respectively. The youngest rocks in the basin are the alluvial sands and gravels of the Late Pliocene Lisan Formation. The upper Cretaceous rocks have been linked to pre-rift environment, the Miocene to syn-rift and the Pliocene-Pleistocene to post-rift. A generalized chronostratigraphic succession of the Midyan Basin (Wyn Hughes et al. 1999) is given in Fig. 2.

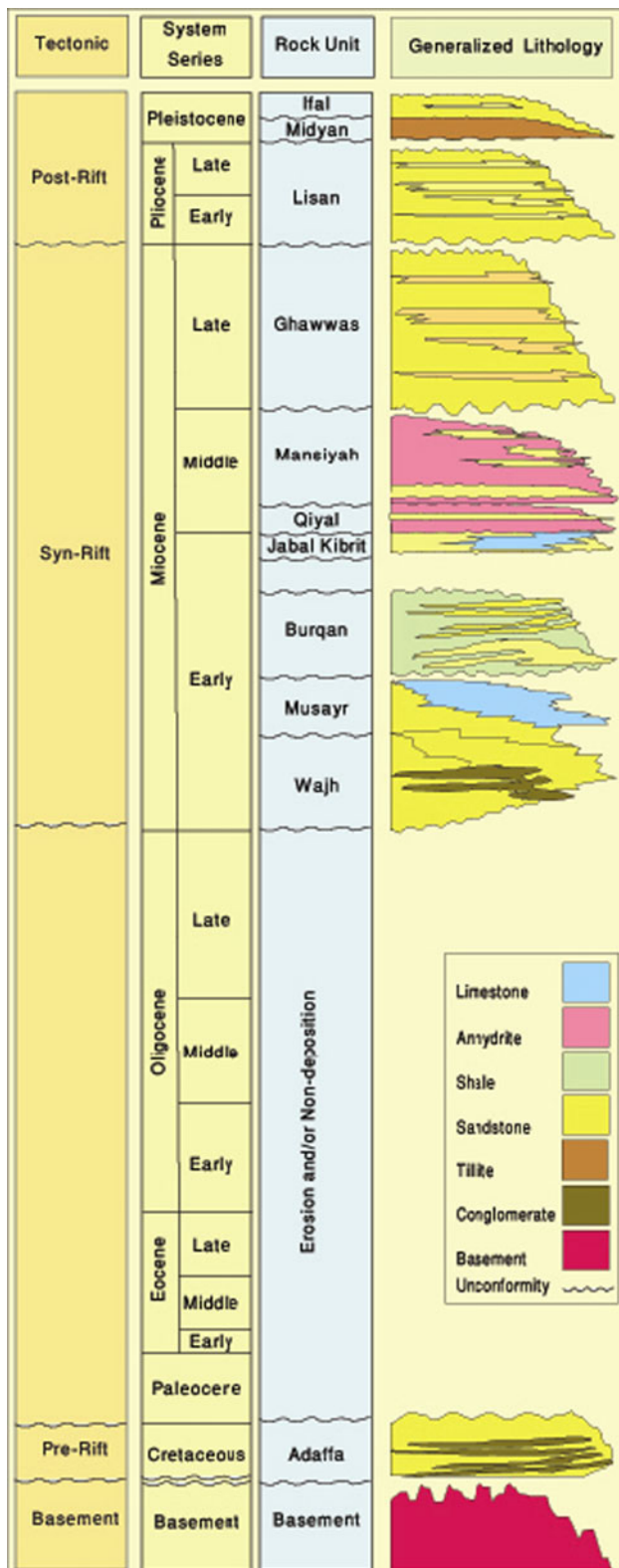


Fig. 2 Generalized chronostratigraphic succession for the Midyan region (modified after Wyn Hughes and Johnson 2005)

Hydrogeology

The Lisan Formation that was deposited during the opening of the Gulf of Aqaba during the Late Pliocene represents a shallow alluvial aquifer system in the basin (Bokhari 1981; Meng and Maynard 2001; Dey et al. 2012; Batayneh et al. 2012a). This formation is made of poorly consolidated fluvial sandstones and conglomerates. The recharge to this aquifer is taking place either along the elevated areas in the north, east and west, or from local surface water infiltrations. The drainage system in the basin is generally radial in nature to the centre of the basin.

The aquifer depth in the study area is <60 m with shallow groundwater table. The presence of joints and fractures mainly in the elevated western, northern and western parts of the basin makes the aquifer in the central and southern parts of the main Wadi Ifal more vulnerable to ion concentrations as a result of weathering and leaching.

Materials and methods

Water samples for chemical analyses were collected in January 2012. A total of 72 samples of groundwater were collected from 72 boreholes in the Midyan Basin, north-western Saudi Arabia (Fig. 1). Samples were collected in polyethylene bottles of one-liter capacity. Prior to their filling with sampled water, these bottles were rinsed to minimize the chance of any contamination. The samples preservation and the used analytical techniques were in accordance with the standard methods from American Public Health Association (APHA 1995). Unstable parameters such as hydrogen ion concentration (pH), total dissolved solids (TDS) and electrical conductivity (EC) were determined at the sampling sites with the help of a pH-meter, a portable EC-meter and a TDS-meter (Hanna Instruments, Michigan, USA). The Sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), and calcium (Ca^{2+}) ions were determined by atomic absorption spectrophotometer (AAS). Bicarbonate (HCO_3^-) and chloride (Cl^-) were analyzed by volumetric methods. Sulfate (SO_4^{2-}) was estimated by the colorimetric and turbidimetric methods. Silicon dioxide (SiO_2) was calorimetrically analyzed by ammonium molybdate method. Nitrate (NO_3^-) was measured by ionic chromatography.

Fluoride analyses in the collected groundwater samples were performed using pH Ion-meter (Metrohm model-781) in conjunction with the fluoride selective Solid-State Membrane Electrode (Metrohm ISE 6.0502.150) and

Reference Electrode (Ag/AgCl RE). Since the determination of fluoride at low levels demands very sensitive methods, the ion selective electrodes (ISEs) have been used for this purpose by replacing expensive and time-consuming chromatographic methods. As compared to other methods, the ISEs are easy to use and are thus suitable for continuous monitoring. In addition, they are cost-effective, sufficiently sensitive, selective and accurate.

Collected rock samples processed and analysed for determination of fluoride. After placing 500 mg of rock samples (powder form) in dry and clean Teflon digestion beaker, 2 ml of HNO₃ and 6 ml HCl were added. Samples were then digested on hot plate in a temperature between 120 and 150 °C for approximately 40 min. However, the resulted digest remained unclear, so a filtering process was applied using Whatman filter paper No. 42. The filtered digest was then transferred to a 50 ml plastic volumetric flask and filled it up to the mark with deionised water. Then for the further analysis, pH/Ion-meter in conjunction with a combination fluoride electrode Solid-state Membrane Electrode (Metrohm ISE 6.0502.150) and reference electrode (Ag/AgCl RE), Herisau Metrohm Company, Model 781, Switzerland was used.

For present study, analytical-reagent grade chemicals are used without further purification, while de-ionized distilled water has been used throughout the experiments. Fluoride stock solution (10 µg/ml) was prepared from sodium fluoride and stored in polyethylene container. Total ionic strength adjustment buffer (TISAB) solution has been prepared, which contains 58 g of sodium chloride, 57 ml of glacial acetic acid, 4 g of 1,2-cyclohexanediamine (*N, N, N'*), *N'*-tetraacetic acid (CDTA) and approximately 150 ml of 6 mol L⁻¹ NaOH in a volume of 1,000 ml (pH 5.0–5.5). The TISAB solution regulates the ionic strength of samples and the standard solutions. CDTA forms stable complexes with polyvalent metal cations (e.g., Al³⁺, Fe³⁺ and Si⁴⁺), which are more stable than metal-fluoride complexes (AlF₃, FeF₃, etc.) in solution. The *N'*-tetraacetic acid preferentially reacts with the polyvalent cations present in water by freeing the fluoride ion. The electrode is selective

for the fluoride ion over other common anions by several orders of magnitude. Metal concentration was measured by atomic spectrophotometer.

Results and discussion

General chemistry

Table 1 shows the minimum, maximum, mean and other statistical summary for various elements in the studied samples and their related statistical variations. The pH values obtained from analytical procedures indicate an alkaline nature of the studied water samples, where the maximum value of 9.63 and a minimum value of 7.38 have been recorded, giving an average value of 7.80. Higher electric conductivity (EC) values (i.e., between 1,106 and 14,290 µS/cm) have been observed in the study area, whereas the HCO₃ values ranged between 37.0 and 366 mg/l. Almost all locations, however, show higher than the permissible values of 22–26 mg/l. As a dominant constituents, the concentration of anion is in the order SO₄ > Cl > HCO₃. In case of cations, the observed range of Na has been placed between 172.5 and 4,637 mg/l, which shows some locations exceed the permissible limit (200 mg/l) (GCC Standardization Organization (GSO) GSO5/2008). The concentration of K has been found in a range between 8.50 and 182 mg/l, indicating that all analysed samples are above the permissible limits (3.7–5.2 mg/l) (Abu-Rukah and Alsokhny 2004). Higher concentration of Mg has been observed in the analysed samples, i.e., between 18.80 and 899.3 mg/l.

The fluoride concentration ranges between 0.98 and 2.10 mg/l. However, many locations show higher values compared to GCC Standardization Organization (GSO) GSO5/(2008) (1.5 mg/l). Fluoride in the surface water generally originates from weathering and subsequent leaching of fluoride bearing rocks and soils. Factors that control the concentration of fluoride in study area groundwater are the climate of the area, chemistry of water

Table 1 Statistical summary of the studied groundwater samples from Midyan Basin

| | pH | EC (µS/cm) | mg/l | | | | | | | | | |
|----------------|-------|------------|-------|------------------|----------------|------------------|-----------------|-------------------------------|-----------------|------------------------------|-------------------------------|----------------|
| | | | TDS | Ca ²⁺ | K ⁺ | Mg ²⁺ | Na ⁺ | HCO ₃ ⁻ | Cl ⁻ | NO ₃ ⁻ | SO ₄ ²⁻ | F ⁻ |
| Min. | 7.38 | 1,106 | 545 | 144 | 8.50 | 18 | 172 | 37 | 248 | 3.00 | 240 | 0.98 |
| Max. | 9.63 | 14,290 | 7,027 | 1,869 | 182 | 899 | 4,637 | 366 | 4,686 | 63 | 9,500 | 2.10 |
| Mean | 7.82 | 3,613 | 1,769 | 519 | 28 | 129 | 1,009 | 214 | 901 | 37 | 2,478 | 1.71 |
| Range | 2.25 | 13,184 | 6,482 | 1,724 | 173 | 880 | 4,465 | 329 | 4,438 | 60 | 9,260 | 1.12 |
| Std. deviation | 0.31 | 2,628 | 1,288 | 1,724 | 29 | 115 | 1,052 | 62 | 777 | 17 | 1,966 | 0.31 |
| Skewness | 2.87 | 1.79 | 1.80 | 2.14 | 3.35 | 4.55 | 1.62 | -0.59 | 2.49 | -0.02 | 1.34 | -0.81 |
| Kurtosis | 15.86 | 3.73 | 3.79 | 5.74 | 12 | 28 | 1.88 | 1.51 | 8.06 | -1.05 | 1.52 | -0.43 |

Table 2 Rock samples analysis

| Rock sample no. | Rock type | Ion concentration mg/kg | | | | | | | Dominant ions | | | | |
|-----------------|--------------------------|-------------------------|----------------|----------------|------------------|-----------------|-------------------------------|-----------------|-------------------------------|------------------------------|---|--|--|
| | | Ca ²⁺ | F ⁻ | K ⁺ | Mg ²⁺ | Na ⁺ | HCO ₃ ⁻ | Cl ⁻ | SO ₄ ²⁻ | NO ₃ ⁻ | | | |
| 1 | Sandstone, shale, halite | 16,495 | 350 | 8,500 | 32,950 | 23,750 | 11,034 | 33,810 | 71,300 | 8,934 | Na ⁺ , SO ₄ ²⁻ , Cl ⁻ , Ca ²⁺ , Mg ⁺ | | |
| 2 | Sandstone, shale, halite | 19,000 | 440 | 8,470 | 19,750 | 31,500 | 8,641 | 35,262 | 62,500 | 4,378 | Na ⁺ , SO ₄ ²⁻ , Cl ⁻ , Ca ²⁺ , Mg ⁺ | | |
| 3 | Anhydrite, gypsum | 98,000 | 380 | 1,760 | 5,625 | 1,200 | 9,603 | 7,557 | 64,900 | 1,164 | Ca ²⁺ , SO ₄ ²⁻ , HCO ₃ ⁻ | | |
| 4 | Anhydrite, gypsum | 97,500 | 520 | 600 | 19,000 | 1,450 | 14,250 | 12,276 | 54,010 | 1,769 | Ca ²⁺ , SO ₄ ²⁻ , HCO ₃ ⁻ | | |
| 5 | Mudstone | 46,000 | 490 | 2,700 | 16,900 | 8,000 | 13,413 | 24,061 | 48,880 | 1,863 | Ca ²⁺ , Mg ²⁺ , SO ₄ ²⁻ , Cl ⁻ , HCO ₃ ⁻ | | |
| 6 | Siltstone, clay, shale | 37,500 | 250 | 7,575 | 15,500 | 3,925 | 6,597 | 15,798 | 60,110 | 1,109 | Ca ²⁺ , SO ₄ ²⁻ , Cl ⁻ , Mg ⁺ | | |
| 7 | Siltstone, clay, shale | 74,166 | 370 | 775 | 11,050 | 5,620 | 9,350 | 16,618 | 55,250 | 2,096 | Ca ²⁺ , SO ₄ ²⁻ , Cl ⁻ , Mg ⁺ | | |

and the presence of accessory minerals in the rocks through which groundwater is circulating. Anthropogenic activities in the study area considered another source for fluoride. Industrial sources, production of glass, ceramics, electronics, steel and aluminium, processing pesticide and fertilisers and untreated waste water as well as the agricultural activities are all considered as important anthropogenic causes for fluoride in the study area. Agricultural and industrial development is placing huge demands on precious water supplies. There has been considerable over exploitation of the water resources and a large cone of depression has developed. As shown in Fig. 1 and listed in Table 2, fluoride bearing rocks in the study area include granite, syenite, shale, sandstone, and limestone. These rocks contain fluoride bearing minerals that could leach down to the groundwater upon weathering. The weathering prone minerals, which are well distributed in the rocks in significant concentrations, can be the main source of fluoride for the groundwater in the study area (Table 2).

The surface and subsequence geological strata's in the study area consist of marine mudstones, carbonates and evaporates. The youngest rocks are the alluvial sands, gravels and conglomerates. Under natural conditions, elements of geological formations are readily oxidized, transported by surface runoff and/or leached into the surrounding groundwater. To investigate the potential source of ions from the surrounding geologic materials, seven rock samples were collected from marine sedimentary outcrops and analyzed for major ionic contents. The results are shown in Table 3. Compared to other samples, sandstone, shale and halite samples (1 and 2, Table 2) have high total ion contents dominated by Na⁺, SO₄²⁻, Cl⁻, Ca²⁺, Mg²⁺ and HCO₃⁻. The ionic contents in anhydrite and gypsum samples (3 and 4, Table 2) are dominated by Ca²⁺, SO₄²⁻ and HCO₃⁻. Samples from mudstone, siltstone and shale (5, 6 and 7, Table 2) shows high ions content of Ca²⁺, Mg²⁺, SO₄²⁻, Cl⁻, and HCO₃⁻.

These characteristics of the studied samples suggest that weathering of the surface rock strata's is probably a major source of ions. However, it should be noted that the overall contribution of parent materials (rocks and soils) to major ion elements in the groundwater is different; suggesting some other contributing factors as well. Ions concentration in groundwater depends on many factors, including the size and depth of groundwater, and properties of parent material and soil, through which ions-bearing water percolates after rainfall. Ions input in the groundwater are also dependent on the nature of soils and rocks on the surface.

Hydro-facies interpretation

As reported in the literature, deposition and dissolution of fluoride in the groundwater are very much controlled by

Table 3 Correlation matrix for the studied groundwater samples from Midyan Basin

| | pH | EC | TDS | Ca | K | Mg | Na | HCO ₃ | Cl | NO ₃ | SO ₄ | F |
|------------------|----------|----------|----------|---------|--------|---------|----------|------------------|----------|-----------------|-----------------|--------|
| pH | 1 | | | | | | | | | | | |
| EC | -0.220* | 1 | | | | | | | | | | |
| TDS | -0.215* | 0.949** | 1 | | | | | | | | | |
| Ca | -0.268* | 0.47** | 0.595** | 1 | | | | | | | | |
| K | 0.005 | 0.193 | 0.251* | 0.217* | 1 | | | | | | | |
| Mg | -0.308** | 0.691** | 0.76** | 0.731** | 0.269* | 1 | | | | | | |
| Na | -0.126 | 0.942** | 0.933** | 0.294* | 0.186* | 0.551** | 1 | | | | | |
| HCO ₃ | -0.572** | 0.301* | 0.32** | 0.194 | 0.053 | 0.382** | 0.276* | 1 | | | | |
| Cl | -0.183 | 0.955** | 0.888** | 0.421** | 0.186 | 0.696** | 0.889** | 0.286* | 1 | | | |
| NO ₃ | -0.226* | -0.479** | -0.535** | -0.165 | -0.177 | -0.230* | -0.571** | 0.143 | -0.453** | 1 | | |
| SO ₄ | -0.202 | 0.883** | 0.974** | 0.661** | 0.273* | 0.755** | 0.882** | 0.294* | 0.782** | -0.526** | 1 | |
| F | -0.053 | 0.392** | 0.388** | 0.061 | -0.002 | 0.277* | 0.423** | 0.219* | 0.315** | -0.262* | 0.389** | 1 |
| SiO ₂ | -0.208* | 0.296* | 0.319** | 0.220* | 0.230* | 0.454** | 0.25* | 0.325** | 0.303** | -0.091 | 0.303** | 0.231* |

* Correlation is significant at 0.05 level (2-tailed)

** Correlation is significant at 0.01 level (2-tailed)

their chemical composition. Hence, major ion chemistry of the groundwater has been examined using (Batayneh et al. 2012b) a piper trilinear diagram to identify chemical alteration in the studied groundwater.

The trilinear diagram (Fig. 3) indicates a continuum mixing of Ca, Na, Cl, and SO₄ waters. The diagram also indicates a difference in concentration for the present ions in relative proportions. In fact, there is a visible increase in ionic strength, total dissolved solids and electric conductivity from potassium to sulfate end of the diagram. Figure 4 shows more information's on the variation of TDS with anions.

However, lack of variation can be observed in the cation proportions. Among major cations, the Na has been found as dominant constituent, representing an average of 51.62 %. Calcium and magnesium ions are observed as secondary important elements, representing average values of 37.63 and 8.49 %, respectively (Batayneh et al. 2012a). Potassium ion has a minor presence of about 2.26 %. Among the major anions, concentration of sulfate, chloride and bicarbonate lay in the range of 240–9,500, 248–4,686, 37–366 mg/l, respectively. The order of their abundance is SO₄ > Cl > HCO₃, contributing an average of 64.15, 25.69, and 8.44 % of the total anions, respectively (Fig. 5). The groundwater facies (Na–Ca–SO₄–Cl) in the study area are strongly influenced by ions input from surrounding marine sediments (siltstone, halite, gypsum, anhydrite, and mudstone), while the dissolution and evaporation processes played a significant role in regulating ion concentration in the groundwater. Concentration of Na and Cl could mainly be attributed to weathering of the marine origin halite sediments, while concentration of SO₄ and Ca ions comes mainly from the weathering of gypsum and anhydrites in the recharge areas. The anion concentration characterizes a range of composition from bicarbonate–sulfate–nitrate-rich solutions. These variations in chemical composition reflect the source of water affected significantly by dissolution of limestone, dolomite, gypsum or anhydrite.

Fluoride and calcite saturation index

One of the major sources of fluorine in aquatic systems is the weathering of fluorite (CaF₂). However, the presence of fluorapatite, mica, amphibole, clays and villianmite also contributes to the concentration of fluoride (Johnson et al. 1992; Piper 1994; Apambire et al. 1997). The soluble products of fluorite and calcite could naturally control the water composition, because calcium, fluoride, and carbonate activities are interdependent (Abu-Rukah and Alsokhny 2004). The saturation indexes of fluorite and calcite in the analysed water samples were calculated following the method of Stallard and Edmond (1987), as expressed below:

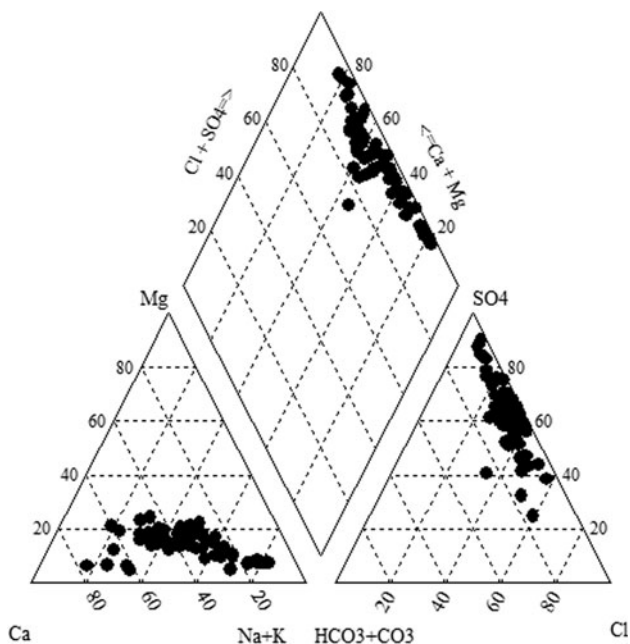


Fig. 3 Piper triangular diagram indicating water type in the study area (Batayneh et al. 2012b)

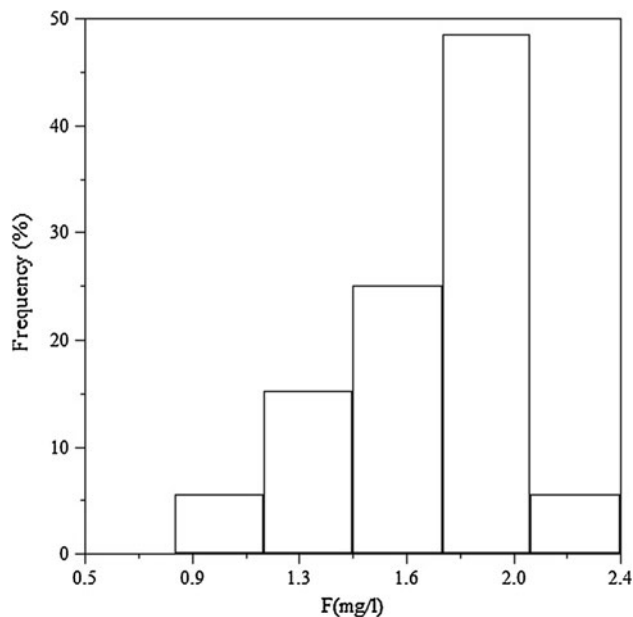


Fig. 5 Fluoride concentration (mg/l) in the studied groundwater samples

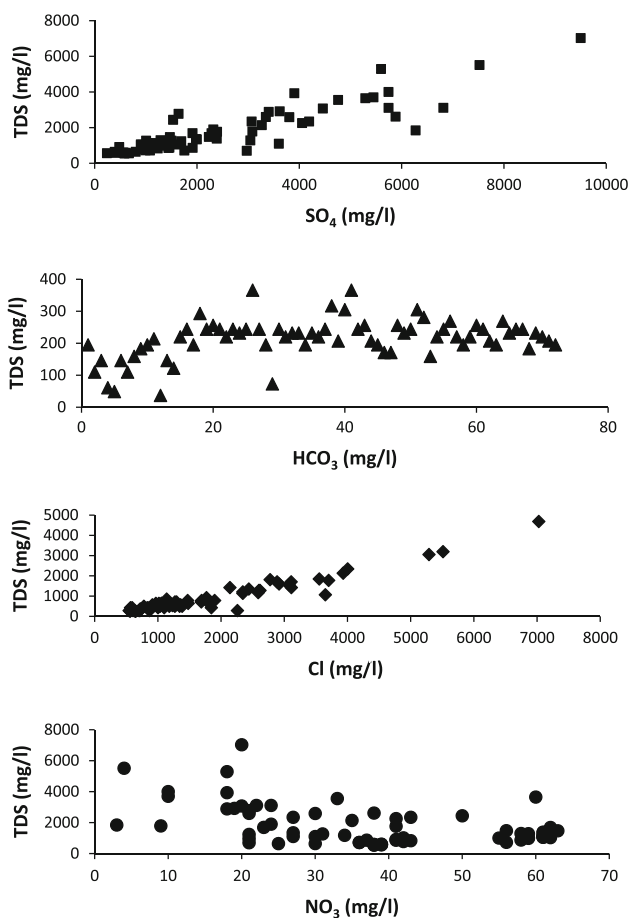


Fig. 4 Scatter diagrams of TDS versus anions

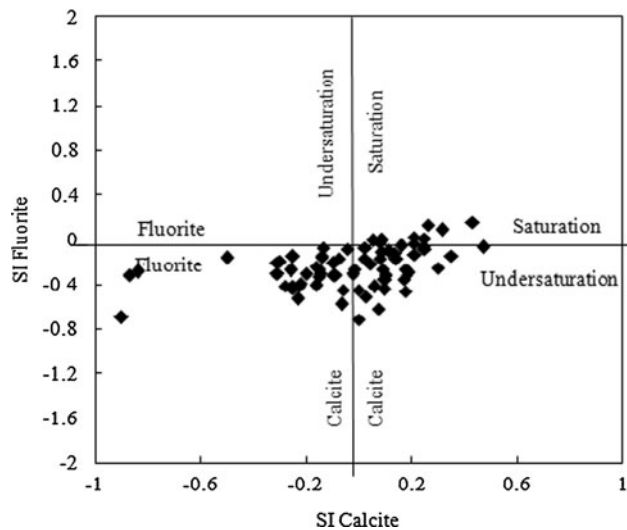


Fig. 6 Saturation indices for calcite and fluorite

$$\text{Fluorite: } SI_f = \log(a_{ca} \times a_f^2) - \log(IAP_{\text{fluorite}})$$

$$\text{Calcite: } SI_c = \log(a_{ca} \times a_{CO_3}) - \log(IAP_{\text{calcite}}),$$

where *a* is the activity (or mole concentration) term and IAP is the ion activity product. The log IAP values for fluorite and calcite (Calculated using SUPCRT 92, Jado et al. 1990) at 25–50 °C are 10.02–9.91 and 8.46–8.67, respectively. A plot of calcite saturation index (SIC) versus fluoride saturation index (Sif) is shown in Fig. 6, which clearly shows under-saturation for fluorite and calcite in

some samples and full saturation in others. Plots of fluoride versus Ca, K, Mg, Na, Cl, NO₃, SO₄ and HCO₃ are shown in Fig. 7. As concluded from Fig. 7, many wells in the study area show higher fluoride concentrations, exceeding the maximum permissible limit (1.5 mg/l) set by WHO (1984) and GCC Standardization Organization (GSO) GSO5/(2008). Fluoride concentration in wells 15, 19, 20, 24, 32, 34, 35, 36, 37, 42, 44, 45 and 54 exceeds the 2 mg/l level, which needs proper attention in terms of purification.

Correlation coefficient analysis (CA)

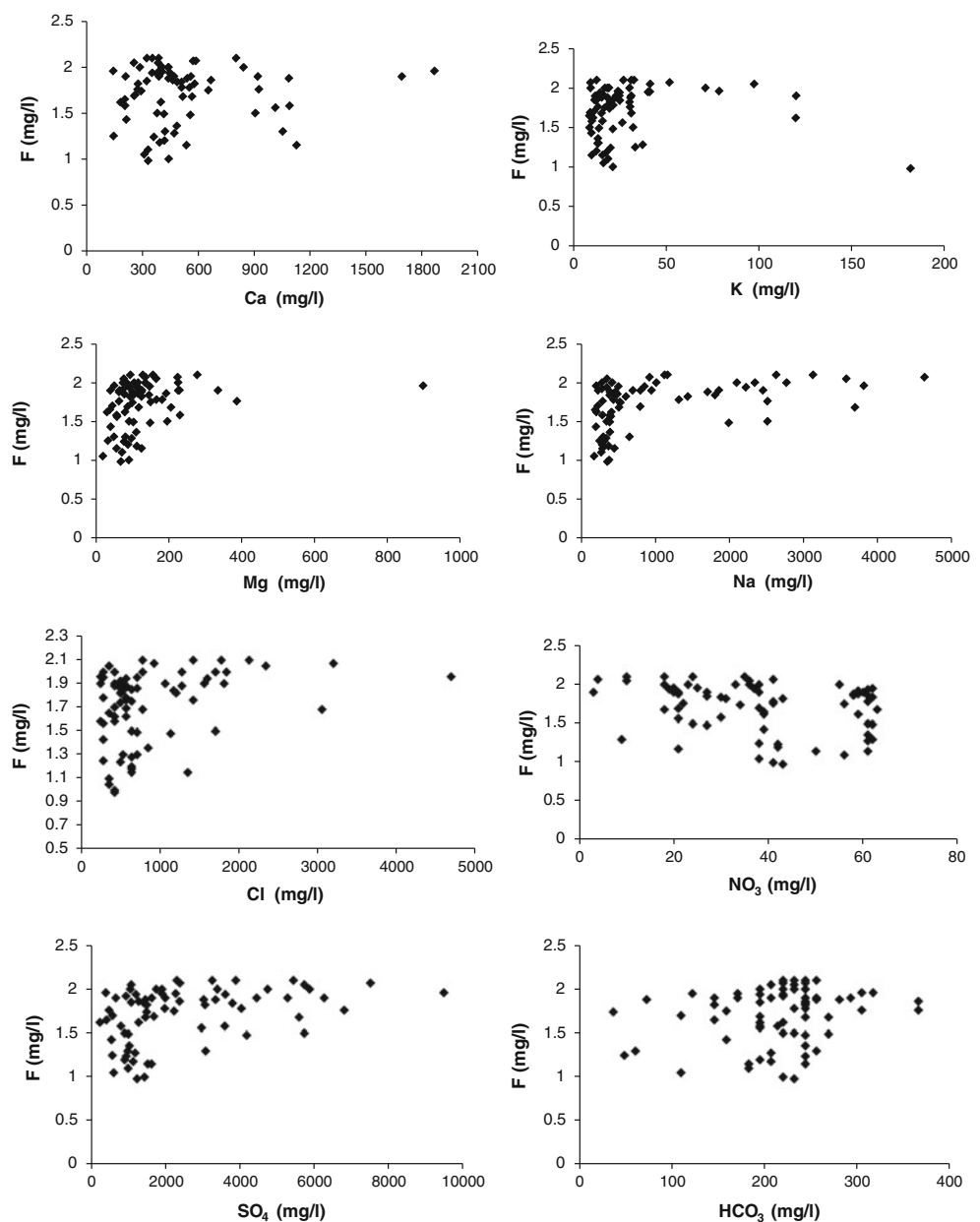
Pearson’s correlation coefficients for various elements are listed in Table 3. A finding is described as “statistically

significant” when the probability is <0.05 ($p < 0.05$) and as “highly statistically significant” when p is <0.01 ($p < 0.01$). If the probability value is >0.05 ($p > 0.05$), the coefficient of correlation is not significant.

Most of the chemical compound pairs exhibit positive relations (except for Ca, Mg, Na, HCO₃, Cl, NO₃, SO₄, F, with pH, and TDS, Ca, K, Mg, Na with NO₃). However, only few of these correlations are significant at 0.05 level (2-tailed), while majority of them are significant at 0.01 level (2-tailed). The parameters showing significantly higher positive correlation are Cl with EC, TDS and Na; TDS with EC; Na with TDS and EC; SO₄ with EC, TDS, Mg, Na and Cl.

Correlation of fluoride with other ions is not significant except for EC, TDS and SO₄. Fluoride shows low positive

Fig. 7 Plots of various parameters against fluoride



correlation with EC, TDS, Na, Cl, and SO_4 (Table 3), indicating dissolution of ions into the groundwater through ion exchange, weathering, oxidation–reduction reactions and anthropogenic activities (Subba Rao 2002).

The reason of the observed correlation for the various parameters is based on the geochemical behavior of the chemical species and/or the possible anthropogenic inputs to the water. Therefore, in this regard, the concentration of fluoride in the rocks, soils and groundwater is related to lithology and on the distance from the alteration areas, climate of the area, chemistry of water and the presence of accessory minerals of the rocks through which groundwater circulates. Also the leaching processes involved in the aquifers, weathering and subsequent leaching of fluoride bearing rocks and soils also can be considered.

Conclusions

Based on the above presented data in their related discussions, it can be concluded that:

1. An enhanced concentration of fluoride has been observed in the groundwater of Midyan Basin, which in most of the analysed samples exceeds the maximum permissible limits.
2. Chemistry of the studied groundwater samples shows more than the permissible limits to EC, HCO_3 , K and Mg.
3. Other than few of the studied water samples, most have been found undersaturated in terms of calcite and fluoride.
4. Correlation of fluoride with other chemical compounds is not significant except for EC, TDS and SO_4 .

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