Source identification of nitrate in the upper aquifer system of the Wadi Shueib catchment area in Jordan based on stable isotope composition (Postprint)

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Abstract

Groundwater forms the main freshwater supply in arid and semi-arid areas, and contamination of this precious resource is complicated by the slow rate of recharge in these areas. Nitrate contamination of groundwater is a global water quality problem, as it entails threat to human health as well as aquatic ecosystems. Source identification of contamination is the cornerstone and a prerequisite for any effective management program of water quality. Stable isotope composition of the dissolved nitrate ($ $15N-NO3-and $ $18O-NO3-)hasbeenappliedtoidentifyNO3-sourcesandthemaintransformationprocessesintheupperaquifersyste H2O and $ $18O-H2O) in conjunction with the groundwater hydrochemistry were integrated to investigate the origin and evolution of the groundwater. Results revealed that groundwater in the study area is fresh and hard-very hard water, and mainly a Ca-Mg-Cl type. NO3-concentration was in the range of 7.0-74.0 mg/L with an average of 37.0 mg/L. Most of the samples showed concentration higher than the natural background concentration of NO3-(5.0-10.0 mg/L). The $ $2H-H2O and $ $18O-H2O values indicated that the groundwater is meteoric, and of Mediterranean origin, with a strong evaporation effect. The $ $15N-NO3-values ranged between 6.0‰ and 11.3‰ with an average of 8.7‰, and the $ $18O-NO3-values ranged between 1.6‰ and 5.9‰ with an average of 3.4‰. These values are in conformity with the stable isotope composition of nitrate derived the nitrification of wastewater/manure, and soil NH4. Nitrification and denitrification are the main transformation processes affecting nitrogen species. Statistical analysis revealed no significant differences in the $ $2H-H2O and $ $18O-H2O values, and $ $15N-NO3-and $ $18O-NO3-values for the three aquifers (A1/2, A4, and B2/A7), indicating that the groundwater of these aquifers has the same origin, and a common

source of pollution.

Full Text

Source Identification of Nitrate in the Upper Aquifer System of the Wadi Shueib Catchment Area in Jordan Based on Stable Isotope Composition

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Abstract

Groundwater forms the main freshwater supply in arid and semi-arid areas, and contamination of this precious resource is complicated by the slow rate of recharge in these regions. Nitrate contamination of groundwater is a global water quality problem that threatens both human health and aquatic ecosystems. Source identification of contamination is the cornerstone and prerequisite for any effective water quality management program. Stable isotope composition of dissolved nitrate (δ^{15}N-NO_3^- and δ^{18}O-NO_3^-) has been applied to identify nitrate sources and the main transformation processes in the upper aquifer system (A1/2, A4, and B2/A7 aquifers) in the Wadi Shueib catchment area, Jordan. Moreover, the stable isotope compositions of groundwater (δ^2H-H_2O and δ^{18}O-H_2O) in conjunction with groundwater hydrochemistry were integrated to investigate the origin and evolution of the groundwater.

Results revealed that groundwater in the study area is fresh and hard to very hard water, mainly of Ca-Mg-Cl type. NO_3^- concentration was in the range of 7.0–74.0 mg/L with an average of 37.0 mg/L. Most samples showed concentrations higher than the natural background concentration of NO_3^- (5.0-10.0 mg/L). The δ^2H-H_2O and δ^{18}O-H_2O values indicated that the groundwater is meteoric, of Mediterranean origin, with a strong evaporation effect. The δ^{15}N-NO_3^- values ranged between 6.0‰ and 11.3‰ with an average of 8.7‰, and the δ^{18}O-NO_3^- values ranged between 1.6‰ and 5.9‰ with an average of 3.4‰. These values are in conformity with the stable isotope composition of nitrate derived from the nitrification of wastewater/manure and soil NH_4^+. Nitrification and denitrification are the main transformation processes affecting nitrogen species. Statistical analysis revealed no significant differences in the δ^2H-H_2O and δ^{18}O-H_2O values, and δ^{15}N-NO_3^- values for the three aquifers

(A1/2, A4, and B2/A7), indicating that the groundwater of these aquifers has the same origin and a common source of pollution.

Keywords: δ^{15}N-NO_3^-; δ^{18}O-NO_3^-; nitrate sources; pollution; meteoric origin; aquifer; Jordan

1. Introduction

Similar to other arid and semi-arid areas, groundwater represents the main supply of freshwater in Jordan. However, it has been contaminated and depleted due to excessive pumping. The Sustainable Development Goals (SDGs) of the United Nations Development Program (UNDP) classified the sustainable management and protection of groundwater as a top priority (Megdal et al., 2017; Senarathne et al., 2019). Groundwater contamination by nitrate is a common environmental problem worldwide (Popescu et al., 2015; Soldatova et al., 2017; Machiwal et al., 2018). It is particularly challenging due to the slow rate of recharge, especially in arid and semi-arid areas where groundwater represents the main source of freshwater for domestic and agricultural uses (Re et al., 2017; Gutierrez et al., 2018). Natural background concentration of nitrate in groundwater is in the range of 5.0–10.0 mg/L as NO_3^- (Panno et al., 2006). Water contamination by nitrate has ecological effects such as eutrophication, oxygen depletion, and anoxia, as well as threats to human health, such as methemoglobinemia and stomach cancer (Kendall et al., 2007; Nixon, 2009; Kaushal et al., 2011; WHO, 2011; Jankowski et al., 2012; Chen et al., 2013; Lehmann et al., 2015; Yang et al., 2016). The maximum permissible limits in groundwater set by national and international organizations (such as WHO; 50.0 mg/L as NO_3^-) have been reported worldwide (e.g., Choi et al., 2000; Obeidat et al., 2007; Obeidat et al., 2012; Karroum et al., 2017; Re and Sacchi, 2017; Nejatijahromi et al., 2019; Tarawneh et al., 2019).

Elevated nitrate concentration in the Wadi Shueib of Jordan has been reported by several studies. Al-Kharabsheh and Al-Kharabsheh (2014) reported nitrate concentration in ten springs in the Wadi Shueib to be in the range of 27.0–104.0 mg/L. Grimmeisen et al. (2017) found nitrate concentration in the range of 23.0–86.0 mg/L in five springs emerging in the Wadi Shueib. Margane et al. (2010) reported nitrate concentration of more than 110.0 mg/L for some springs in the Wadi Shueib. Awawdeh et al. (2020) found nitrate concentration in the range of 21.0–66.0 mg/L in 11 springs and 3 wells in the Wadi Shueib. Nitrate in groundwater has been commonly linked to agricultural fertilizers (Wakida and Lerner, 2005). However, non-agricultural sources such as wastewater disposal and landfills are important sources of nitrate in groundwater (Gold et al., 1990; Jeon, 2001; Huang et al., 2013; Zhang et al., 2015; Kapelewska et al., 2019; Tiwari et al., 2019; Zendehbad et al., 2019; Obeidat et al., 2020; Yu et al., 2020).

Source identification of nitrate and transformation processes of nitrogen species in water is fundamental in any management program of water resources and

water pollution control (Johannsen et al., 2008; Hoefs, 2009; Popescu et al., 2015). Several approaches have been developed to trace water pollution, including solute transport modelling, statistical modelling, and chemical fingerprinting approaches (e.g., Mattern et al., 2009; Qin et al., 2013; Shalev et al., 2015; Levy et al., 2017; Aravinthasamy et al., 2019; Bodrud-Doza et al., 2019; Rashid et al., 2019; Guo et al., 2020; Huan et al., 2020; Jia et al., 2020; Lee et al., 2020; Nyam et al., 2020). In the context of the latter approach, nitrate sources can be investigated using the following methods (Zendehbad et al., 2019): the isotope composition of groundwater and dissolved nitrate, the chemistry and isotope composition of major and trace elements in groundwater, pollutants of known origins found in association with nitrate, and groundwater age.

Boron (B) isotopes have been used in conjunction with nitrogen isotopes to identify nitrate sources in groundwater, as these elements co-migrate in the aquifer, where B is unaffected by the redox reaction and biologic transformation that affect nitrogen compounds (Martinelli et al., 2018; Kruk et al., 2020). The δ^{11}B values can be used to distinguish manure from sewage sources of nitrate in groundwater (Biddau et al., 2019). Strontium (Sr) ratio ($^{87}Sr/^{86}Sr$) has also been utilized to better identify nitrate sources in groundwater, because its isotopic composition, as a result of water-rock interaction, is distinct from that of anthropogenic origin (Nigro et al., 2017). Integration of water chemistry with δ^{15}N-NO_3^-, δ^{18}O-NO_3^-, δ^{13}C of dissolved carbon, and δ^{18}O-SO_4^{2-} has been used to investigate denitrification processes and the factors that control them (Vitoria et al., 2008; Kaown et al., 2009). Moreover, groundwater age has been used as an indicator of direct migration of pollutants derived from the earth' s surface; tracers such as chlorofluorocarbon (CFC), tritium, and ^{14}C have also been utilized (Tesoriero et al., 2007; Koh et al., 2010; Jakobczyk-Karpierz et al., 2017). Meanwhile, a multi-isotopic approach in conjunction with groundwater hydrochemistry and statistical modelling such as principal component analysis have been applied to track nitrate and pollution sources in groundwater (Vitoria et al., 2008; Guo et al., 2020; Zhang and Wang, 2020).

In the last decades, nitrogen and oxygen isotopes of dissolved nitrate (δ^{15}N-NO_3^- and δ^{18}O-NO_3^-) have been successfully applied to tackle nitrate contamination of groundwater (Czekaj et al., 2016; Hu et al., 2019; Venkiteswaran et al., 2019; Zhao et al., 2019; Kruk et al., 2020; Li et al., 2020; Sui et al., 2020). Combining δ^{15}N-NO_3^- and δ^{18}O-NO_3^- results can help identify nitrate sources, mixing processes, and transformation processes of nitrate (Kendall et al., 2007; Xue et al., 2009; Thibodeau et al., 2013; Archana et al., 2018). Different sources of nitrate have distinct isotopic composition of δ^{15}N-NO_3^-: atmospheric nitrate, nitrate resulting from the nitrification of manure or sewage, nitrate in synthetic fertilizer, and natural soil organic matter are in the ranges from -13.0‰ to 13.0‰, 7.0‰ to more than 20.0‰, -3.0‰ to 3.0‰, and -3.0‰ to 5.0‰, respectively (Mayer et al., 2002; Lee et al., 2008; Xue et al., 2009; Gutierrez et al., 2018). On the other hand, δ^{18}O-NO_3^- values of atmospheric nitrate, nitrate in synthetic fertilizer, and nitrification-derived nitrate are in the ranges from 25.0‰ to more than 70.0‰, 17.0‰ to 25.0‰, and -15.0‰ to 15.0‰,

respectively (Durka et al., 1994; Mayer et al., 2002; Kendall et al., 2007; Xue et al., 2009). Moreover, the contributions of different sources can be estimated using isotope mass-balance mixing models, which are based on δ^{15}N-NO_3^- and δ^{18}O-NO_3^- values (Moore et al., 2006; Parnell et al., 2010; Zhang et al., 2015; Matiatos, 2016; Xia et al., 2017; Zhang et al., 2018).

The stable isotope composition of dissolved nitrate (δ^{15}N-NO_3^- and δ^{18}O-NO_3^-) is subject to modification by isotopic fractionation caused by physical, chemical, and biological processes, such as volatilization, assimilation, nitrification, and denitrification (Kaown et al., 2010). Nitrification is a two-step process of NH_4^+ oxidation to NO_3^- (Kendall et al., 2007; Gutierrez et al., 2018): the first step is called nitritation, where ammonia-oxidizing bacteria decompose organic nitrogen and ammonium under aerobic conditions into nitrite; the second step is called nitratation, where nitrite-oxidizing bacteria convert nitrite to nitrate. Nitrate originating from oxidation of animal waste/septic waste has a high δ^{15}N value due to volatilization of δ^{15}N-depleted ammonia, and subsequent oxidation of much of the residual waste material (Kendall et al., 2007). For animal waste with a δ^{15}N value of around 5.0‰, the δ^{15}N values are generally in the range of 10.0‰–20.0‰ when it is transformed to nitrate (Kreitler, 1979). Denitrification converts nitrate to N_2 gas; it is a significant transformation process, since it plays a vital role in attenuating nitrate concentrations. It occurs under the following conditions (Gutierrez et al., 2018): (1) oxygen concentration less than 1.0–2.0 mg/L (occurring in anaerobic pockets within an otherwise oxygenated sediment or water body); (2) presence of denitrifying bacteria, nitrate, and electron donor; (3) temperature of 25°C–35°C; (4) pH values of 5.5–8.0; and (5) trace nutrients.

In some situations, the isotopic composition of nitrate overlaps among different source materials and/or between source signatures and process signals (Chang et al., 2003). To overcome this drawback, the integration of hydrochemical tools with the isotope approach is very helpful (Widory et al., 2013). Research worldwide has shown that the combination of nitrate isotopes (δ^{15}N-NO_3^- and δ^{18}O-NO_3^-) with other tools such as hydrochemistry, statistical methods, and physical and chemical modeling provides useful insights about nitrate sources and transformation processes of nitrogen in the environment (Clague et al., 2015; Soldatova et al., 2017; Biddau et al., 2019). Conventional hydrochemical methods have been successfully used to characterize water type and evaluate the processes controlling water chemistry and degradation of aquifers (Abu-alnaeem et al., 2018; Tiwari et al., 2019). Schoeller indices (such as chloro-alkaline index, CAI) have been used to gain insights about ion exchange reactions between groundwater and the hosting aquifer material, as well as information about freshening or salinizing processes of groundwater (Stuyfzand, 2008; Abu-alnaeem et al., 2018; Tiwari et al., 2019).

The CAI can be determined using the following equation (Schoeller, 1967):

$$\mathrm{CAI} = \frac{\mathrm{Cl}^- - (\mathrm{Na}^+ + \mathrm{K}^+)}{\mathrm{Cl}^-}$$

where Cl^- is the chloride concentration (meq/L); Na^+ is the sodium concentration (meq/L); and K^+ is the potassium concentration (meq/L). CAI values can be negative or positive depending on whether the exchange of Na^+ and K^+ is from water with Mg^{2+} and Ca^{2+} in rock/soil or vice versa (Tiwari et al., 2019). There are two types of ion exchange processes (Ayadi et al., 2018): the first one is known as reverse ion exchange process, where Na^+ and K^+ are sequestered onto the aquifer material, and Ca^{2+} and Mg^{2+} are released into the water. The CAI values in this case are positive, and there is hardening of water (Zaidi et al., 2015). The second type is known as base ion exchange process, where Ca^{2+} and Mg^{2+} are sequestered onto the aquifer material and Na^+ and K^+ are released into the water. The CAI values in this case are negative, and there is softening of water (Argamasilla et al., 2017).

Tackling and understanding natural as well as anthropogenic processes/factors influencing groundwater quality and its evolution is crucial for the protection and sustainability of this priceless resource. This study aims to trace sources and transformation of nitrogen species in a three-aquifer system, which includes Na' ur aquifer (A1/2), Hummar aquifer (A4), and Amman/Wadi Wadi Es Sir aquifer (B2/A7) in the Wadi Shueib catchment area using hydrochemical methods and stable isotopes of groundwater (δ^2H and δ^{18}O) and dissolved nitrate (δ^{15}N-$NO_3{}^-$ and δ^{18}O-$NO_3{}^-$). The results of this study can help initiate prevention/remediation measures for groundwater contamination in the Wadi Shueib catchment area.

2.1 Study Area

The study area (31°53 01 –32°05 10 N, 35°37 32 –35°50 29 E) is located on the western slopes of the eastern highlands of the Jordan rift valley and covers an area of 200 km^2 [Figure 1: see original paper]. It has a rectangular shape, with the long axis oriented from northeast to southwest. Elevations range from 181 m below sea level (b.s.l.) in the southwest to 1136 m above sea level (a.s.l.) in the northeast. Several wadis are found in the catchment area, all draining from northeast to southwest toward the Jordan valley.

The study area is generally dominated by a Mediterranean climate, characterized by hot summers and cold winters. Due to the strong relief, climatic conditions vary considerably from the arid Jordan valley to the Mediterranean climate in the highlands in the northeast. Precipitation occurs periodically during the rainy season between October and May and is normally associated with frontal systems moving inland from the Mediterranean Sea (Margane et al., 2010). The average annual precipitation is highly variable over the basin and is influenced by topography (Riepl, 2013). Precipitation is 599 mm for Hummar station (953 m a.s.l.), located 3.5 km northeast of Fuheis City, and 175 mm for South Shuna

station (143 m b.s.l.), located on the eastern edge of South Shuna City. The annual average temperatures vary between 17.3°C at Salt station and 25.6°C at South Shuna station [Figure 1: see original paper].

The geology of the investigated area is dominated by sedimentary rocks of the Upper Cretaceous, consisting mainly of limestone, dolomite, and marls of the Ajloun (A) and Belqa (B) groups [Figure 2: see original paper]. These are underlain by sandstones of the Kurnub group of Lower Cretaceous age, outcropping on fault zones along the Wadi Shueib structure (Mikbel and Zacher, 1981). The Kurnub Sandstone consists mainly of cross-bedded massive bodies of porous varicolored quartz arenite and glauconitic sandstone. Particle size is coarse to medium sand fraction, usually loosely cemented (Kuntz, 2003). In the upper layers, carbonate cementation is evident and particle size becomes finer. The thickness of the Kurnub Sandstone is approximately 250 m (Powell, 1989).

The A and B groups are divided into a number of formations, ranging from A1 to A7 for the former, and from B1 to B5 for the latter (Masri, 1963). The A group consists of approximately 350–400 m thick interbedded limestones, marly limestones, and dolomitic limestones, whereas the B group mainly includes a sequence of limestones intercalated with thick-bedded chert but also includes chalk, marls, silicified limestones, and phosphatic horizons (Werz, 2006).

Na' ur formation (A1/2) of Cenomanian age overlies the Kurnub Sandstone formation, where two units are distinguished within this formation. First, a lower formation (A1) consists mainly of marls with a thickness of 37–80 m. Second, an upper formation (A2) consists mainly of limestone and marly limestone, with a thickness of 74–100 m. Fuheis formation (A3) of Cenomanian age overlies Na' ur formation and mainly consists of marl and interbedded limestone with a thickness of 69–75 m. Hummar formation (A4) of Cenomanian age consists of hard dense limestone and dolomitic limestone. Wadi Shueib formation (A5/6) of upper Turonian age is composed mainly of marly limestone and chalky marl. This formation has a thickness of 50–80 m and is divided into two sub-formations (Masri, 1963; MacDonald, 1965): A5, composed of thinly-bedded buff to grey limestone with thin marl intercalations; and A6, composed of white to grey crystalline massively bedded limestone. Wadi Es Sir formation (A7) of Turonian age consists of light grey, hard limestone with chert nodules. It has a thickness of 75–150 m.

The B group overlies the A group with a sequence of predominantly carbonates with abundant chert. It has been subdivided into five formations (B1–B5); only two of these are found in the study area, namely Wadi Um Ghudran formation (B1) and Amman Silicified Limestone formation (B2). The former is of Santonian age and is composed of well-bedded chalk and marl, with occasional beds of limestone with a thickness of 15 m (Ta' any, 1992); the latter is of Campanian age and consists of chert, marl, limestone, and some phosphatic bearing strata, with a total thickness of about 20 m. In some places, B1 is missing, and thus B2 directly overlies A7, forming a composite aquifer (B2/A7).

From a hydrogeological point of view, the aquifer systems are divided into two main aquifer systems (GTZ, 1977): the lower Cretaceous complex (Kurnub Sandstone) and the upper Cretaceous aquifer complex. This classification is based on lithology and hydrogeological conditions. The lower aquifer system, exposed west of Mahis Town, consists of varicolored sandstone with a thickness of 220–300 m; it is separated from the upper complex by a low permeability layer of 2$×10^{-8}$ m/s (Geyh et al., 1986). The upper aquifer system includes the A and B groups with an age ranging from upper Cretaceous to lower Tertiary. The A group represents the main aquifer system in the study area, where the aquifers are composed of limestone, dolomitic limestone, and marl. Three main formations of this group are considered aquifers: Na' ur formation (A1/2), Hummar formation (A4), and Wadi Es Sir formation (A7). On the other hand, Wadi Shueib and Fuheis formations are classified as aquitards. The whole aquifer is an unconfined system. There are 22 springs emerging from this aquifer system: five from A4, nine from A7, and eight from A1/2 (Al-Kharabsheh and Al-Kharabsheh, 2014). The Fuheis and Wadi Shueib formations are strongly vertically jointed and fractured, causing the whole upper aquifer system to be hydraulically interconnected through joints and fault zones (Werz, 2006). There are only two formations from the B group exposed in the study area: Wadi Um Ghudran formation (B1) and Amman formation (B2), where B1 is classified as aquitard and B2 as aquifer (Werz, 2006).

Because of insufficient wells in the study area, a groundwater level map cannot be constructed. However, Werz (2006) estimated the average depth of the groundwater as follows: 50 m for the Hummar aquifer (A4), 60 m for the Na' ur aquifer (A1/2), and 75 m for the Wadi Es Sir aquifer (A7). According to Zemann et al. (2015), the groundwater flow direction is toward the southwest. Direct recharge from precipitation was estimated at 21% (9.9$×10^{6}$ m^3) of the annual precipitation (WSPSP, 2004). The main hydraulic properties of the aquifer system are summarized in Table 1 (Margane et al., 2009). Water needs in the study area are covered by local groundwater (50%) and water imported from King Abdullah Canal (50%). The water supplied for domestic purposes is about 5.4$×10^{6}$ m^3/a. The basin is dominated by four main land covers [Figure 3: see original paper]: rainfed cropland (40.72%), built-up areas (17.80%), barren areas (15.10%), and sparse vegetation (14.73%). The study area hosts two wastewater treatment plants: Salt Wastewater Treatment Plant and Fuheis Wastewater Treatment Plant, which release their effluents into the main Wadi Shueib stream (Grimmeisen et al., 2017). Leaky sewers and cesspits are the main sources of contamination of the groundwater in the study area (Margane et al., 2010).

2.2 Experimental Design and Data Collection

Seventeen samples were collected from the upper aquifer system in the study area, representing 11 springs and 6 production wells [Figure 3: see original paper]. Seven samples were collected from the B2/A7 aquifer (six springs and

one production well), seven samples from the A4 aquifer (three springs and four production wells), and three samples from the A1/2 aquifer (two springs and one production well). The sampling campaign was conducted during the rainy season in January and February of 2018. The sampled wells are production wells used to supply the local community with freshwater. The sampled wells (samples 8, 13, 14, and 16) tapping the A4 aquifer have depths varying from 166 to 285 m. The sampled well (sample 6) tapping the A1/2 aquifer has a depth of 377 m, and that well (sample 7) tapping the B2/A7 aquifer has a depth of 283 m.

All water samples were field pre-filtered through 0.45 m Millipore filters into HDPE (high-density polyethylene) sample bottles with appropriate storage and preservation methods (e.g., refrigeration, freezing, acidification, and addition of chloroform). The methods described by APHA (1998) were followed during fieldwork and laboratory chemical analyses. Electrical conductivity (EC), temperature, and pH were measured in situ using portable meters. Prior to sample collection, well purging was performed for those wells that were not being pumped at the time of sampling. The goal was to ensure that the water sample truly represents the properties and conditions of the subsurface environment. Water was pumped from each well until the EC, temperature, and pH became constant. Spring samples, on the other hand, were collected at the mouth of springs.

Chemical analyses were carried out in the laboratories of Jordan University of Science and Technology and Yarmouk University, Jordan. The samples were analyzed for Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, $HCO_3{}^{-}$, $SO_4{}^{2-}$, $NO_3{}^{-}$, total hardness (TH), and total dissolved solids (TDS). Concentrations of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, and $SO_4{}^{2-}$ were analyzed using the Thermo Scientific Ion Chromatograph (Dionix ICS-1600, ThermoFisher Scientific, Waltham, USA). $HCO_3{}^{-}$ and $NO_3{}^{-}$ concentrations were determined by titration method and spectrophotometer, respectively. All samples were analyzed in triplicate with analytical uncertainty of less than 4%. We used the cations-anions balance to check the correctness of the analysis, where it was within $±$5%, calculated as follows:

$$\text{Error } (\%) = \frac{\text{Cations} - \text{Anions}}{\text{Cations} + \text{Anions}} \times 100\%$$

This value guarantees the reliability of the chemical analysis. TDS content (mg/L) was determined using a conductivity meter (HACH portable EC meter, HACH, Colorado, USA). TH value (mg/L) was calculated using the following equation:

$$\text{TH as } CaCO_3 = 2.5\text{Ca} + 4.1\text{Mg}$$

where $CaCO_3$, Ca, and Mg are the concentrations (mg/L) of $CaCO_3$, Ca^{2+}, and Mg^{2+}, respectively.

The importance of the saturation index (SI) is to determine dissolution or precipitation during water-rock interaction. The SI of a mineral can be calculated using the equation:

$$SI = \log\left(\frac{KIAP}{KSP}\right)$$

where SI is the saturation index; KIAP is the ionic activity product of the appropriate ion; and KSP is the solubility product of the mineral. If SI = 0, the water is in equilibrium. If SI > 0, the water is supersaturated with respect to that mineral, and the mineral is precipitated. If SI < 0, the water is undersaturated with respect to the mineral, and dissolution is taking place.

The saturation indices of the minerals calcite, dolomite, halite, and gypsum were calculated using the computer program PHREEQC (version 3.3.7.11094, USGS, USA) (Parkhurst and Appelo, 1999). The δ^{15}N-NO_3^-, δ^{18}O-NO_3^-, δ^{18}O-H_2O, and δ^2H-H_2O values were determined at the Environmental Isotope Laboratory, University of Waterloo, Canada, using the cadmium reduction method (Mcilvin and Altabet, 2005) to convert NO_3^- to N_2O and coupled with a Trace Gas-GVI IsoPrime-IRMS (TG-IRMS). The analytical precision of the laboratory analysis is $\pm$0.3 and $\pm$0.8 for δ^{15}N-NO_3^- and δ^{18}O-NO_3^-, respectively. The $^2H/^1H$ and $^{18}O/^{16}O$ ratios of the water samples were measured using a Los Gatos Research (LGR) Liquid Water Isotope Analyzer (LWIA), model T-LWIA-45-EP instrument (Los Gatos Research, Mountain View, California), with analytical precision of $\pm$0.2 and $\pm$0.8 for δ^2H-H_2O and δ^{18}O-H_2O, respectively.

The stable isotope ratio (δsample; ‰) was calculated as:

$$\delta_{sample} = \left(\frac{R_{sample}}{R_{standard}} - 1\right) \times 1000$$

where Rsample and Rstandard are the $^{15}N/^{14}N$, $^2H/^1H$, or $^{18}O/^{16}O$ ratios of the sample and international reference standard, respectively. Values of δ^{15}N were reported relative to N_2 in atmospheric air, and δ^{18}O and δ^2H values were reported relative to Vienna Standard Mean Ocean Water (VSMOW). Isotopic data of precipitation in Jordan were obtained from the Water Authority of Jordan (WAJ).

2.3 Statistical Analysis

Statistical analyses, including univariate and bivariate statistics and one-way analysis of variance (ANOVA), were performed using the software package SPSS 13 (version 21, SPSS Inc., Chicago, IL, USA). The one-way ANOVA test was used to test if there were significant differences in the isotope composition of groundwater (δ^2H-H_2O and δ^{18}O-H_2O values) and nitrate isotopes (δ^{15}N-NO_3^- and δ^{18}O-NO_3^- values) for the three aquifers (A1/2, A4, and B2/A7). The P-value ≤ 0.05 was used as the criterion for statistical difference.

3.1 Major Ion Chemistry

The univariate statistics of the hydrochemical parameters of groundwater samples representing the whole aquifer complex in the study area are shown in Table 2 . The following is a brief discussion of the major ion chemistry of individual aquifer units.

3.1.1 Na' ur Aquifer (A1/2)

Three water samples—one from production wells (sample 6) and two from springs (samples 1 and 2)—were collected from this aquifer. The groundwater pH value was slightly acidic, ranging between 6.6 and 6.7 with an average of 6.6. EC value was in the range of 617.0–821.0 µS/cm with an average of 743.0 µS/cm [Figure 4: see original paper]. Based on the classification of Davis and De Wiest (1967), we classified the groundwater as freshwater, where TDS content was in the range of 385.0–519.0 mg/L with an average of 466.0 mg/L. Based on Sawyer and McCarty classification (1968), we categorized the groundwater as very hard water, where TH value was in the range of 333.0–366.0 mg/L with an average of 344.0 mg/L as $CaCO_3$. Based on TDS and TH values, we described the groundwater of A1/2 aquifer as fresh-very hard water.

Mg^{2+} and Ca^{2+} concentrations ranged from 22.8 to 37.7 mg/L with an average of 28.3 mg/L, and from 71.8 to 109.0 mg/L with an average of 91.3 mg/L, respectively. Na^{+} and K^{+} concentrations ranged from 26.5 to 78.7 mg/L with an average of 53.4 mg/L, and from 1.3 to 6.0 mg/L with an average of 3.6 mg/L, respectively. HCO_3^{-} and SO_4^{2-} concentrations ranged from 160.0 to 176.0 mg/L with an average of 168.0 mg/L, and from 25.5 to 56.2 mg/L with an average of 44.2 mg/L, respectively. Cl^{-} concentration was in the range of 66.0–156.0 mg/L with an average of 107.0 mg/L. All of the above-mentioned parameters for all samples fell within the permissible limit set by the WHO (2011). NO_3^{-} concentration ranged from 18.5 to 65.0 mg/L with an average of 39.7 mg/L. All samples had NO_3^{-} concentration above the natural background of natural source of 5.0–10.0 mg/L (Panno et al., 2006). One sample (Sample 1) had NO_3^{-} concentration exceeding the permissible maximum limit of drinking water quality of 50.0 mg/L set by the WHO (2011). Potential sources of groundwater contamination in the study area are sewerage, solid waste, and slaughterhouses (Margane et al., 2010).

3.1.2 Hummar Aquifer (A4)

Seven water samples—four from production wells (samples 8, 13, 14, and 16) and three from springs (samples 4, 11, and 15)—were collected from this aquifer. In terms of pH value, the groundwater of this aquifer was similar to the groundwater of A1/2 aquifer; it was slightly acidic, where pH value ranged from 6.4 to 6.8 with an average of 6.6. EC value was in the range of 521.0–868.0 µS/cm with an average of 691.0 µS/cm. The groundwater is freshwater, where the TDS content was in the range of 323.0–541.0 mg/L with an average of 430.0 mg/L.

It is hard-very hard water with TH value ranging from 279.0–414.0 mg/L with an average of 341.0 mg/L.

Mg^{2+} and Ca^{2+} concentrations ranged from 12.0–40.0 mg/L with an average of 22.6 mg/L, and from 77.0 to 137.0 mg/L with an average of 99.4 mg/L, respectively. Na^{+} and K^{+} concentrations ranged from 24.0 to 78.0 mg/L with an average of 44.0 mg/L, and from 1.0 to 6.0 mg/L with an average of 2.0 mg/L, respectively. HCO_3^{-} and SO_4^{2-} concentrations ranged from 104.0–176.0 mg/L with an average of 154.0 mg/L, and from 24.0 to 118.0 mg/L with an average of 54.2 mg/L, respectively. Cl^{-} concentration was in the range of 42.0–148.0 mg/L with an average of 85.5 mg/L. All of the above-mentioned parameters for all samples fell within the permissible limit set by the WHO (2011). NO_3^{-} concentration ranged from 21.0 to 44.0 mg/L with an average of 32.2 mg/L. All samples had NO_3^{-} concentration above the natural background of natural source of 5.0–10.0 mg/L (Panno et al., 2006), and below the maximum permissible limit of drinking water quality set by the WHO (2011).

3.1.3 Amman Formation/Wadi Es Sir Aquifer (B2/A7)

Seven water samples—one from production well (sample 7) and six from springs (samples 3, 5, 9, 10, 12, and 17)—were collected from this aquifer. In terms of pH value, the groundwater of this aquifer was similar to the groundwater of A1/2 and A4 aquifers; it was slightly acidic, where pH value ranged from 6.4 to 7.1 with an average of 6.6. EC value was in the range of 498.0–892.0 µS/cm with an average of 660.0 µS/cm. The groundwater is freshwater, where the TDS content was in the range of 309.0–558.0 mg/L with an average of 410 mg/L. It is hard-very hard water with TH value ranging from 257.0 to 360.0 mg/L with an average of 303.0 mg/L.

Mg^{2+} and Ca^{2+} concentrations ranged from 15.0 to 32.0 mg/L with an average of 22.6 mg/L, and from 62.0 to 101.0 mg/L with an average of 84.0 mg/L, respectively. Na^{+} and K^{+} concentrations ranged from 22.0 to 81.0 mg/L with an average of 47.6 mg/L, and from 1.0 to 14.0 mg/L with an average of 5.8 mg/L, respectively. HCO_3^{-} and SO_4^{2-} concentrations ranged from 148.0 to 180.0 mg/L with an average of 157.7 mg/L, and from 22.0 to 93.0 mg/L with an average of 51.1 mg/L, respectively. Cl^{-} concentration was in the range of 33.0–134.0 mg/L with an average of 80.7 mg/L. All of the above-mentioned parameters for all samples fell within the permissible limit set by the WHO (2011). NO_3^{-} concentration ranged from 7.0 to 74.0 mg/L with an average of 41.2 mg/L. One sample (sample 7) had NO_3^{-} concentration within the natural background concentration of natural source of 5.0–10.0 mg/L (Panno et al., 2006), and two samples (samples 12 and 17) exhibited concentration above the maximum permissible limit of drinking water quality set by the WHO (2011).

3.2 Hydrochemical Facies and Processes

The distribution of major ions in groundwater in the Wadi Shueib catchment area showed the following patterns: (1) for the whole aquifer system, $Ca^{2+} > Na^{+} > Mg^{2+} > K^{+}$ and $HCO_3^{-} > Cl^{-} > SO_4^{2-} > NO_3^{-}$; (2) for the A1/2 aquifer, $Ca^{2+} > Na^{+} > Mg^{2+} > K^{+}$ and $Cl^{-} > HCO_3^{-} > SO_4^{2-} > NO_3^{-}$; and (3) for the A4 and B2/A7 aquifers, $Ca^{2+} > Na^{+} > Mg^{2+} > K^{+}$ and $HCO_3^{-} > Cl^{-} > SO_4^{2-} > NO_3^{-}$. Among the major ions, K^{+} had the highest variation (coefficient of variation (CV) = 109%), followed by SO_4^{2-} (CV = 57%), NO_3^{-} (CV = 47%), Na^{+} (CV = 46%), and Cl^{-} (CV = 43%). This may indicate multiple sources and hydrogeochemical and mixing processes controlling the spatial distribution of groundwater quality (Masoud, 2014).

Correlation coefficients are commonly used to find relationships between physiochemical parameters of groundwater and to demonstrate how well a parameter predicts the others (Islam et al., 2018; Bodrud-Doza et al., 2019). The bivariate statistics (Pearson correlation coefficient) of the physiochemical parameters of groundwater in the study area are presented in Table 3 . A very positive significant correlation was found among EC value and each concentration of Na^{+}, Cl^{-}, SO_4^{2-}, and K^{+}, indicating that the TDS value of the groundwater was mainly controlled by these ions. A moderate correlation was found between EC value and each concentration of NO_3^{-} and Ca^{2+}, which indicated that the more mineralized the groundwater, the higher the chance for nitrate contamination and accumulation. The significant positive correlations of K^{+} concentration with each concentration of Na^{+}, NO_3^{-}, and SO_4^{2-} indicated a common source of these ions in the groundwater, most likely domestic wastewater. A moderate negative correlation (-0.50) was found between Ca^{2+} and Mg^{2+} concentrations, indicating different sources of these ions. Potential sources of Mg^{2+} in groundwater are animal and domestic waste (Selvam et al., 2016), whereas the source of Ca^{2+} is calcite dissolution, which is the main mineral in the aquifers under consideration. The moderate correlation (0.50) between NO_3^{-} and Cl^{-} concentrations indicated a common source, most likely animal and human waste.

Piper diagram presentation of the major ions revealed that most samples are of mixed Ca-Mg-Cl type, and only three samples (sample 8 of A4 aquifer, and samples 7 and 9 of B2/A7 aquifer) are of Ca-HCO_3 type [Figure 5: see original paper]. Samples 7 and 8 were taken from two wells with depths of 283 and 285 m, respectively. The first type (Ca-Mg-Cl type) can be related to the fourth group of Geyh et al. (1986), which corresponded to fresh water mixed with saline water or fresh water that has passed through evaporites. However, this water tended to shift towards the second type (Ca-HCO_3 type), which indicated mixing between two end members: one fresh (Ca-HCO_3) water and another saline (Na-Cl) water (Panagopoulos et al., 2005). Ca-Mg-Cl water type can be interpreted as a mixture of high salinity water produced by surface contamination (e.g., domestic wastewater and septic effluents) with existing water followed by ion exchange reactions (Selvam et al., 2016). The Ca-HCO_3 water type can be considered as the natural background water in the study

area. Such water can evolve from the dissolution of carbonate rocks and can be influenced by rainfall infiltration or dissolution of atmospheric carbon dioxide (Ayadi et al., 2018; Ligavha-Mbelengwa and Gomo, 2020). Most samples plotted in the Ca-dominant zone in the cation facies, followed by the no dominant zone (no one cation-anion pair exceeded 50%). Moreover, most samples fell in the no dominant zone in the anion zone, with some samples falling in the HCO_3^- and Cl^- zones.

The relationships between dissolved ions have been extensively used to track salinity sources and evolution of groundwater (Thilakerathne et al., 2015; Senarathne et al., 2019; Tiwari et al., 2019). The ratio of HCO_3^- to ΣAnions for the groundwater samples in the study area ranged from 0.27 to 0.65 with an average of 0.41. These values indicated rock weathering, especially carbonate rocks (Halim et al., 2010; Bodrud-Doza et al., 2019).

The ratio between Na^+ and Cl^- concentrations has been used to identify sources of salinity, silicate weathering, seawater intrusion, halite dissolution, and ion exchange processes (Garcia et al., 2001; Rubasinghe et al., 2015). The Na^+/Cl^- ratio in the groundwater samples in the study area ranged from 0.60 to 1.00 with an average of 0.84. About 47% of the samples had Na^+/Cl^- ratio above the seawater ratio of 0.86 (Mercado, 1985), and close to 1.00, indicating contamination by domestic wastewater or water-rock interaction (Zhu et al., 2010; Abdalla, 2016). Plot of Na^+/Cl^- ratio vs. Cl^- can be used to identify sources of salinity in groundwater, where Na^+/Cl^- ratio should be equal to 1.00 if halite is the source of these ions, and other mechanisms such as salt water intrusion, ion exchange process, and rock-water interaction should be the sources if the Na^+/Cl^- ratio departs from 1.00 (Basins and Geo, 2004; Abu-alnaeem et al., 2018; Tiwari et al., 2019). The Na^+/Cl^- ratio of wastewater taken from Al-Salt wastewater treatment was about 1.03 (Al-Kharabsheh and Al-Kharabsheh, 2014). Except sample 7 (B2/A7 aquifer), which is of Ca-HCO_3 type, all other samples from the study area had a Na^+/Cl^- ratio below 1.00 [Figure 6: see original paper]. This may indicate mixing with more saline water (Ayadi et al., 2018) and reverse ion exchange process (Abu-alnaeem et al., 2018). Moreover, the HCO_3^-/Cl^- ratio can be used to indicate freshwater recharge (Ayadi et al., 2018). The HCO_3^-/Cl^- ratio of the groundwater samples used in the present study ranged from 0.63 to 3.19, with about 65% of the samples having a HCO_3^-/Cl^- ratio above 1.00, indicating freshwater recharge [Figure 6: see original paper]. Mixing processes, possibly with wastewater, led to a decrease in the HCO_3^-/Cl^- ratio less than 1.00.

The relationship between Cl^- and Ca^{2+}/Na^+ ratio [Figure 6: see original paper] showed that the Ca^{2+}/Na^+ ratio was greater than 1.00, indicating aquifer carbonate dissolution or depletion of Na^+ (Ayadi et al., 2018). The Ca^{2+}/HCO_3^- ratio can be used to evaluate carbonate dissolution. If calcite dissolution is dominant, the Ca^{2+}/HCO_3^- ratio should be close to 1.00, and if dolomite dissolution is dominant, the Ca^{2+}/HCO_3^- ratio should be close to 0.50 (Abu-alnaeem et al., 2018). Plot of Ca^{2+}/HCO_3^- ratio vs. Cl^- indicated that all samples from

the Wadi Shueib fell above the Ca^{2+}/HCO_3^- ratio of 1.00 [Figure 6: see original paper], indicating calcite dissolution. The excess in Ca^{2+} can be attributed to reverse ion exchange (Tiwari et al., 2019).

The SI-calcite of the groundwater samples ranged from -0.7 to -0.2 with an average of -0.4, and the SI-dolomite ranged from -1.8 to -0.8 with an average of -1.0 (Table 2). Moreover, the SI of gypsum and halite showed negative values, where it ranged from -2.3 to -1.3 with an average value of -1.9, and from -7.7 to -6.5 with an average of -7.0, respectively. These values indicate that the groundwater is unsaturated with respect to carbonate minerals, as well as evaporite minerals [Figure 7: see original paper], and dissolution of these minerals from the aquifer will lead to an increase in the TDS content of the groundwater in the study area.

The CAI values of the groundwater in the Wadi Shueib ranged from -0.1 to 0.4 with an average of 0.1 (Table 2; [Figure 8: see original paper]). Most samples had positive CAI values, indicating hardening of the groundwater (release of Ca^{2+} and Mg^{2+} ions into the water and sequestering of Na^+ and K^+ onto the aquifer material). This reaction is termed reverse ion exchange process (Abu-alnaeem et al., 2018; Tiwari et al., 2019). Three samples (samples 7, 12, and 17 of B2/A7 aquifer) had a negative CAI, indicating softening of the groundwater, and this reaction is termed base ion exchange process (Tiwari et al., 2019). However, the positive values of CAI clustered between 0.0 and 0.2, indicating a low level of this process. Moreover, cation exchange was confirmed by plotting $(Na^+ + K^+)$-Cl^- vs. $(Ca^{2+} + Mg^{2+})$-$(SO_4^{2-} + HCO_3^-)$ [Figure 8: see original paper].

The NO_3^-/Cl^- ratio can be used to discriminate nitrate pollution sources (Anornu et al., 2017). If groundwater is not affected by human activities, the NO_3^-/Cl^- ratio is in the range of 0.05-0.22. The NO_3^-/Cl^- ratio for the A1/2 aquifer ranged from about 0.10-0.37; for the A4 aquifer, it was in the range of 0.12-0.36; and for B2/A7, it was in the range of 0.12-0.37. These values indicated anthropogenic sources of NO_3^- in the three aquifers. The values of NO_3^-/Cl^- tended to decrease with increasing Cl^- concentration, approaching the NO_3^-/Cl^- ratio for wastewater which was about 0.42.

3.3 δ^2H and δ^{18}O Values of Groundwater

The stable isotope composition of water has been employed to investigate hydrological processes such as infiltration, evaporation, and rock-water interaction (Clark and Fritz, 2013). The δ^{18}O and δ^2H values of groundwater in the study area showed very slight variations (CV = 8.5% for δ^{18}O; CV = 9.5% for δ^2H), where the values ranged from -6.3‰ to -4.8‰ with an average of -5.5‰ for δ^{18}O, and from -28.7‰ to -20.7‰ with an average of -24.7‰ for δ^2H. The stable isotopic composition of groundwater from the three aquifers (A1/2, A4, and B2/A7) was plotted using a ^{2}H-^{18}O diagram [Figure 9: see original paper]. The stable isotopic composition of precipitation in Jordan (i.e., the Local Meteoric Water Line (LMWL; Bajjali, 2012)), the Global Meteoric Water Line

(GMWL), and the Eastern Mediterranean Meteoric Water Line (MMWL) were also plotted. The $\delta^{18}O$ values of precipitation in Jordan ranged from -7.3‰ to -3.5‰, and the $\delta^{2}H$ values ranged from -33.2‰ to -19.9‰. The $\delta^{18}O$ and $\delta^{2}H$ values of the groundwater samples fell close to local precipitation and the MMWL, indicating that groundwater in the study area has been recharged from Mediterranean meteoric water. The samples were clustering along a well-defined local evaporation line (LEL), which fits the following equation:

$$\delta^{2}H = 4.89\delta^{18}O + 2.17$$

However, the samples clustered in three groups. The first group had $\delta^{18}O$ and $\delta^{2}H$ values ranging from -5.1‰ to -4.8‰ and from -22.8‰ to -20.7‰, respectively. This group involved five samples, with two samples from A4 aquifer (samples 4 and 16) and three samples from B2/A7 aquifer (samples 10, 12, and 17), and it was isotopically enriched due to evaporation effect. The second group had $\delta^{18}O$ and $\delta^{2}H$ values ranging from -5.78‰ to -5.38‰ and from -26.84‰ to -23.97‰, respectively; it involved nine samples, with two samples from the A1/2 aquifer (samples 1 and 6), four samples from the A4 aquifer (samples 11, 13, 14, and 15), and three samples from the B2/A7 aquifer (samples 3, 5, and 9). The third group was relatively depleted in $\delta^{18}O$ and $\delta^{2}H$ values compared with the first and second groups. It had $\delta^{18}O$ and $\delta^{2}H$ values ranging from -6.3‰ to -6.2‰ and -28.7‰ to -27.8‰, respectively, and involved one sample from the A1/2 aquifer (sample 2), one sample from the A4 aquifer (sample 8), and one sample from the B2/A7 aquifer (sample 7). Samples 7 and 8 were taken from two wells with depths of 285 and 283 m, respectively, implying a well depth effect on the isotope composition of the groundwater.

The air masses that produce rains in the Middle East come from different areas, such as the Siberian Plateau, the Northern Pole via Eastern Europe, Atlantic Ocean, northern Africa, and the Red Sea (Kattan, 2019). Bajjali (2012) showed that cold and dry continental air masses stemming from the European continent come in contact with the warm Mediterranean Sea water, resulting in rapid evaporation and large-scale convergence. The deuterium excess (d-parameter) of the groundwater ($d = 2\times\delta^{2}H - 8\times\delta^{18}O$) ranged from 16.2‰ to 21.8‰ with an average of 19.3‰, which is slightly lower than that of local precipitation (ranging from 16.6‰ to 25.6‰ with an average of 21.7‰). Variation in the d-parameter may indicate mixing of water from different sources having different isotopic signatures (El-Sayed et al., 2018).

A single-factor analysis of variance test (ANOVA) was performed to determine if there is a significant difference between the $\delta^{18}O$ and $\delta^{2}H$ values for samples collected from the three aquifer units. The test showed no significant difference in $\delta^{18}O$ values for A1/2 and A4 aquifers, because the F-calculated value (1.14) was smaller than the F-critical value (5.32), and the P-value obtained (0.32) was greater than 0.05. The test also revealed no significant difference in $\delta^{18}O$ values for A1/2 and B2/A7 aquifers, as the F-calculated value (1.04) was smaller

than the F-critical value (5.32), and the P-value calculated (0.34) was greater than 0.05. The test showed no significant difference in $\delta^{18}O$ for A4 and B2/A7 aquifers, because the F-calculated value (0.12) is smaller than the F-critical value (4.75), and the P-value obtained (0.73) is greater than 0.05. The test clearly indicated that the groundwater of the three aquifers has the same recharging sources, that is Mediterranean rainfall.

The relationship of $\delta^{18}O$ values with Cl^- concentration in the three aquifers (A1/2, A4, and B2/A7) is depicted in [Figure 10: see original paper], where a very significant correlation was found for the A4 aquifer (r = 0.92) and for the B2/A7 aquifer (r = 0.98), indicating a strong evaporation effect. A moderate correlation (r = 0.51) was found for the A1/2 aquifer, indicating a moderate evaporation effect. The relationship between $\delta^{18}O$ values and the d-parameter of groundwater in the Wadi Shueib is presented in [Figure 10: see original paper]. The three aquifers exhibited very significant correlations (r = 0.98 for the A1/2 aquifer; r = 0.84 for the A4 aquifer; and r = 0.96 for the B2/A7 aquifer) between $\delta^{18}O$ values and the d-parameter, indicating a strong evaporation effect on the isotopic composition of the groundwater.

3.4 $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ Values of Groundwater

The $\delta^{15}N\text{-}NO_3^-$ values of groundwater in the study area ranged from 6.0‰ to 11.3‰ with an average of 8.7‰, and the $\delta^{18}O\text{-}NO_3^-$ values ranged from 1.6‰ to 5.9‰ with an average of 3.4‰ (Table 2). The $\delta^{15}N\text{-}NO_3^-$ values of the A1/2 aquifer ranged from 9.0‰ to 11.3‰ with an average of 9.9‰, and from 4.0‰ to 5.9‰ with an average of 4.9‰, respectively. The A4 aquifer had $\delta^{15}N\text{-}NO_3^-$ values in the range of 6.0‰-11.1‰ with an average of 8.6‰, and $\delta^{18}O\text{-}NO_3^-$ values in the range of 1.8‰-5.8‰ with an average of 3.4‰, respectively. The B2/A7 aquifer had $\delta^{15}N\text{-}NO_3^-$ values in the range of 6.1‰-10.4‰ with an average of 8.3‰, and $\delta^{18}O\text{-}NO_3^-$ values in the range of 1.6‰-4.8‰ with an average of 2.8‰, respectively.

The relationship plot of $\delta^{15}N$ and $\delta^{18}O$ was used to identify the sources of nitrate in the study area [Figure 11: see original paper] (Kendall et al., 2007). About 59% of the samples (samples 1, 2, 4, 5, 6, 10, 11, 12, 16, and 17) fell in the source "manure/septic waste" window. These samples represented the three aquifers in the study area: samples 1, 2, and 6 of the A1/2 aquifer; samples 4, 11, and 16 of the A4 aquifer; and samples 5, 10, 12, and 17 of the B2/A7 aquifer. These samples had $\delta^{15}N\text{-}NO_3^-$ values in the range of 8.6‰ to 11.3‰ and $\delta^{18}O\text{-}NO_3^-$ values in the range of 1.6‰ to 5.9‰, which are in compliance with the stable isotopic composition of nitrate derived from the nitrification of wastewater/manure (Widory et al., 2004; Kendall et al., 2007; Xue et al., 2009; Adebowale et al., 2019; Danni et al., 2019; Zhang and Wang, 2020). The $\delta^{15}N\text{-}NO_3^-$ values of wastewater in the study area were 9.3‰ and 7.4‰, respectively (Grimmeisen et al., 2017). The NO_3^- concentration of the above samples ranged from 19.0 to 74.0 mg/L, which is above the natural background concentration of NO_3^- (5.0–10.0 mg/L) (Panno et al., 2006). Thus, the source of this group

of samples can be considered manure/septic waste.

In addition, the stable isotopic composition of seven samples (samples 3, 7, 8, 9, 13, 14, and 15) fell in the crossing window of the sources manure/septic waste and soil NH_4^+. The δ^{15}N-NO_3^- values of these samples ranged from 6.0‰ to 7.8‰, and the δ^{18}O-NO_3^- values ranged from 1.8‰ to 3.1‰. Except sample 7, which had NO_3^- concentration (7.0 mg/L) within the natural background concentration (5.0–10.0 mg/L), the NO_3^- concentration of this group of samples ranged from 26.0 to 39.0 mg/L, which is higher than the natural background concentration. Sample 7 was collected from a well tapping the B2/A7 aquifer (well depth of 283 m) and had δ^{15}N-NO_3^- and δ^{18}O-NO_3^- values of 6.1‰ and 2.6‰, respectively. Samples 3 and 9 were collected from the B2/A7 aquifer, and samples 8, 13, 14, and 15 were collected from the A4 aquifer. Accordingly, nitrate isotope composition of sample 7 indicated soil NH_4^+ origin of nitrate, whereas samples 3, 8, 9, 13, 14, and 15 had wastewater/manure source of nitrate. This is supported by the results of analysis of total coliform and Escherichia coli reported by several studies carried out in the study area (Al-Kharabsheh and Al-Kharabsheh, 2014). Average values of total coliform were found to be in the range of 10.1–11,741.7 MPN/100 mL in ten springs in the study area (Al-Kharabsheh and Al-Kharabsheh, 2014). These springs had the following samples in this study: samples 1 and 2 of the A1/2 aquifer; samples 3, 5, 9, 10, 12, and 17 of the B2/A7 aquifer; and samples 4 and 11 of the A4 aquifer. Escherichia coli was also detected in three springs with values as follows: 5.0 MPN/100 mL for sample 5, 13.0 MPN/100 mL for sample 3, and 110.0 MPN/100 mL for sample 10 (Zemann et al., 2015). All these springs emerge from the B2/A7 aquifer.

Chloride has been used as a conservative tracer of groundwater contamination (Koh et al., 2010; Baily et al., 2011; Jiang et al., 2016; Anornu et al., 2017). Plotting Cl^- concentration vs. δ^{15}N-atmospheric air revealed a significant correlation (r = 0.73), indicating that manure/septic waste is a major source of nitrate in groundwater in the study area [Figure 12: see original paper].

A single-factor analysis of variance test (ANOVA) was performed to determine if there is a significant difference between the δ^{15}N-NO_3^- and δ^{18}O-NO_3^- values for the three aquifers. The test showed no significant difference between the δ^{15}N-NO_3^- values for the A1/2 and A4 aquifers, as the F-calculated value (2.55) was smaller than the F-critical value (5.32), and the P-value calculated (0.15) was greater than 0.05. No significant difference was found between the δ^{15}N-NO_3^- values for the A1/2 and B2/A7 aquifers, as the F-calculated value (1.01) was smaller than the F-critical value (5.32), and the P-value calculated (0.34) was greater than 0.05. No significant difference was found between the δ^{15}N-NO_3^- values for the A4 and B2/A7 aquifers, as the F-calculated value (0.10) was smaller than the F-critical value (4.75), and the P-value calculated (0.76) was greater than 0.05.

The ANOVA test revealed a significant difference between the δ^{18}O-NO_3^- values for the A1/2 and A4 aquifers, since the F-calculated value (8.36) was greater

than the F-critical value (5.32), and the P-value calculated (0.02) was smaller than 0.05. The test revealed no significant difference between the δ^{18}O-NO_3^- values for the A1/2 and B2/A7 aquifers, as the F-calculated value (2.53) was smaller than the F-critical value (5.32), and the P-value calculated (0.10) was greater than 0.05. The test also showed no significant difference between the δ^{18}O-NO_3^- values for the A4 aquifer and the B2/A7 aquifer, because the F-calculated value (0.57) was smaller than the F-critical value (4.75), and the P-value calculated (0.47) was greater than 0.05. The results of the ANOVA test indicated that the three aquifer units (A1/2, A4, and B2/A7) have a common source of nitrate, primarily domestic wastewater.

Groundwater in the Wadi Shueib had δ^{18}O-NO_3^- values (average of 3.4‰) that were much lower than those for nitrate in fertilizers (17.0‰ to 25.0‰) and atmospheric nitrate (25.0‰ to more than 70.0‰). This indicated that nitrification was the main biological transformation process of nitrogen species, and nitrate was mainly derived from the nitrification of wastewater/manure. The δ^{18}O-NO_3^- values produced from nitrification should be in the range from -10.0‰ to 10.0‰, since water had δ^{18}O values in the range from -25.0‰ to 4.0‰, and atmospheric oxygen had a value of about 23.5‰ (Durka et al., 1994; Kendall et al., 2007). We calculated the theoretical δ^{18}O-NO_3^- produced by microbial nitrification for the groundwater in the study area based on the measured δ^{18}O values of the groundwater, assuming δ^{18}O value of atmospheric oxygen of 23.5‰, according to the following equation (Kendall et al., 2007):

$$\delta^{18}\text{O-NO}_3^- = \frac{2}{3}\delta^{18}\text{O-H}_2\text{O} + \frac{1}{3}\delta^{18}\text{O-O}_2$$

The theoretical δ^{18}O-NO_3^- values in the groundwater resources in the study area ranged from 3.7‰ to 4.6‰ with an average of 4.2‰, which were higher than the measured δ^{18}O-NO_3^- values in the range of 1.6‰-5.9‰ with an average of 3.4‰. About 71% of the samples had theoretical δ^{18}O-NO_3^- values higher than the measured δ^{18}O-NO_3^- values. The high theoretical δ^{18}O-NO_3^- values can be attributed to the high δ^{18}O-H_2O values, which ranged from -6.3‰ to -4.8‰ with an average of -5.5‰, showing a strong evaporation effect. In general, the average measured δ^{18}O-NO_3^- value (3.4‰) was consistent with the average theoretical δ^{18}O-NO_3^- value (4.2‰) for nitrification.

The relationship between δ^{15}N-NO_3^- and δ^{18}O-NO_3^- values provided useful information about the denitrification process taking place within the aquifer. The relationship between δ^{15}N-NO_3^- and δ^{18}O-NO_3^- values for all samples (n = 17) representing the three aquifers showed a moderate correlation (r = 0.50). However, splitting the samples based on aquifer source [Figure 12: see original paper] revealed that there was a very significant correlation (r = 0.86) between δ^{15}N-NO_3^- and δ^{18}O-NO_3^- for samples collected from the A4 aquifer (n = 7). Two groups of samples can be observed: the first group included samples 4, 11, and 16. This group had high values of δ^{15}N-NO_3^- (from 10.0‰ to 11.1‰) and δ^{18}O-NO_3^- (from 3.7‰ to 5.8‰). These values corresponded to nitrate derived

from nitrification of manure/septic waste. The same group showed a moderate negative correlation (r = -0.38) between NO_3^- concentration and $\delta^{15}N$ values [Figure 12: see original paper], signifying denitrification. Thus, the isotopic data of this group indicated both source and process signals. The second group included samples 8, 13, 14, and 15. This group had $\delta^{15}N\text{-}NO_3^-$ values in the range of 6.0‰-7.8‰ and $\delta^{18}O\text{-}NO_3^-$ values in the range of 1.8‰-2.6‰. A moderate positive correlation existed (r = 0.47) between NO_3^- concentration and $\delta^{15}N$ values [Figure 12: see original paper].

Additionally, two groups of samples (n = 7) collected from the B2/A7 aquifer can be delineated. The first group covered samples 10, 12, and 17; these samples showed a very significant correlation (r = 0.95) between $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values in the range of 9.2‰-10.4‰ and 1.6‰-2.9‰, respectively, which corresponded to nitrate derived from nitrification of manure/septic waste. A very significant negative correlation (r = -0.96) existed between NO_3^- concentration and $\delta^{15}N$ values for this group, which signified denitrification [Figure 12: see original paper]. The second group covered samples 3, 5, 7, and 9. This group also showed a very significant correlation (r = 0.97) between $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values. A very significant positive correlation (r = 0.99) existed between NO_3^- concentration and $\delta^{15}N$ values for this group. The A1/2 aquifer showed no clear relationship between $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values for the groundwater collected from this aquifer.

4 Conclusions

We used conventional hydrochemical methods in conjunction with isotopic methods to investigate groundwater chemistry evolution and sources of pollution in the Wadi Shueib catchment area. Groundwater is fresh, belonging to hard to very hard water. Results revealed that dissolution of aquifer minerals as well as reverse ion exchange are the main natural processes affecting groundwater chemistry in the study area. The stable isotopic composition of groundwater ($\delta^2H\text{-}H_2O$ and $\delta^{18}O\text{-}H_2O$) showed that it is of meteoric origin, being recharged by Mediterranean rainfall and undergoing strong evaporation. NO_3^- concentration signifies contamination of groundwater resources due to anthropogenic activities. Nitrate isotopes ($\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$) showed that nitrified wastewater/manure is the main source of contamination of groundwater in the study area. No significant differences were found in the chemistry and isotope values of the three aquifers, indicating that these aquifers are hydraulically interconnected and have common sources/processes influencing water chemistry and pollution. Nitrification and denitrification are the main transformation processes of nitrogen species in the study area. Although the aquifer system is unconfined, denitrification might occur in anaerobic pockets within the aquifer. Hydrogeological interconnectivity between the three aquifer units was supported by the similar nitrate isotope contents of the three aquifers, as well as the results of statistical tests.

The use of nitrate isotopes in this study has provided new insights into the

sources of contamination of groundwater resources in the study area, an issue which cannot be tackled by hydrochemical tools alone. Sustainable management of groundwater resources in the study area necessitates application of best management practices and proper land use planning. Connecting the study area to a sewerage system as a preventive measure of water resources pollution is highly recommended. The results of the study are an important tool for decision makers to enact effective water protection policies.

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Note: Figure translations are in progress. See original paper for figures.