Integrating stable isotopes and factor analysis to delineate the groundwater provenance and pollution sources in the northwestern part of the Amman-Al Zarqa Basin, Jordan (Postprint)

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Abstract

Globally, groundwater contamination by nitrate is one of the most widespread environmental problems, particularly in arid and semiarid areas, which are characterized by low amounts of rainfall and groundwater recharge. The stable isotope composition of groundwater ($ $2H-H2O and $ $18O-H2O) and dissolved nitrate ($15N-NO3- and $ $18O-NO3-) and factor analysis (FA) were applied to explore groundwater provenance, pollution, and chemistry evolution in the northwestern part of the Amman-Al Zarqa Basin, Jordan. In this study, we collected 23 samples from the Lower Ajloun aquifer in 2021, including 1 sample from a groundwater well and 22 samples from springs. These samples were tested for electrical conductivity, total dissolved solids, pH, temperature, dissolved oxygen, the concentration of major ions (Ca2+, Mg2+, Na+, K+, HCO3-, Cl-, SO42-, and NO3-), and the stable isotope composition of groundwater and dissolved nitrate. The results revealed that groundwater in the study area is mainly Ca-Mg-HCO3 type and can be classified as fresh water, hard water, and very hard water. The range and average concentration of NO3-were 3.5-230.8 and 50.9 mg/L, respectively. Approximately 33% of the sampling points showed NO3-levels above the maximum allowable concentration of 50.0 mg/L set by the World Health Organization (WHO) guidelines for drinking water quality. The values of $ $18O-H2O and $ $2H-H2O showed that groundwater in the study area is part of the current water cycle, originating in the Mediterranean Sea, with significant evaporation, orographic, and amount effects. The values of the stable isotope composition of NO3-corresponded to $ $15N-NO3-and $ $18O-NO3-values produced by the nitrification process of manure or septic waste and soil NH4+. The FA performed on the hydrochemical parameters and isotope data resulted in three main factors, with Factor 1, Factor 2, and Factor 3, accounting for

50%, 21%, and 11% of the total variance, respectively. Factor 1 was considered human-induced factor, named "pollution factor" , whereas Factor 2, named "conservative fingerprint factor" , and Factor 3, named "hardness factor" , were considered natural factors. This study will help local researchers manage groundwater sustainably in the study area and other similar arid and semiarid areas in the world.

Full Text

Preamble

Integrating Stable Isotopes and Factor Analysis to Delineate Groundwater Provenance and Pollution Sources in the Northwestern Amman-Al Zarqa Basin, Jordan

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Abstract: Globally, groundwater contamination by nitrate represents one of the most widespread environmental problems, particularly in arid and semiarid regions characterized by low rainfall and limited groundwater recharge. This study applied stable isotope composition of groundwater (δ^2H-H_2O and δ^{18}O-H_2O) and dissolved nitrate (δ^{15}N-NO_3^-) combined with factor analysis (FA) to explore groundwater provenance, pollution, and chemical evolution in the northwestern Amman-Al Zarqa Basin, Jordan. We collected 23 samples from the Lower Ajloun aquifer in 2021, comprising 1 sample from a groundwater well and 22 samples from springs. These samples were analyzed for electrical conductivity, total dissolved solids, pH, temperature, dissolved oxygen, major ion concentrations (Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, Cl^-, SO_4^{2-}, and NO_3^-), and the stable isotope composition of groundwater and dissolved nitrate. The results revealed that groundwater in the study area is primarily Ca-Mg-HCO_3 type and can be classified as fresh, hard, and very hard water. Nitrate concentrations ranged from 3.5–230.8 mg/L, with an average of 50.9 mg/L. Approximately 33% of sampling points showed NO_3^- levels exceeding the 50.0 mg/L maximum allowable concentration set by World Health Organization (WHO) drinking water quality guidelines. The δ^{18}O-H_2O and δ^2H-H_2O values indicated that groundwater originates from Mediterranean Sea sources within the current water cycle, with significant evaporation, orographic, and amount effects. The stable isotope composition of NO_3^- (δ^{15}N-NO_3^- and δ^{18}O-NO_3^-) corresponded to values produced by the nitrification process of manure or septic waste and

soil NH_4^+. Factor analysis of hydrochemical and isotope data yielded three main factors accounting for 50%, 21%, and 11% of total variance, respectively. Factor 1 was identified as a human-induced "pollution factor," while Factor 2 ("conservative fingerprint factor") and Factor 3 ("hardness factor") were natural factors. This study provides valuable insights for sustainable groundwater management in the study area and similar arid and semiarid regions worldwide.

Keywords: stable isotope composition; δ^{15}N-NO_3^-; δ^{18}O-NO_3^-; groundwater quality; pollution sources; Jordan

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1 Introduction

The Sustainable Development Goal 6 (SDG 6), adopted by the United Nations in 2015, aims to ensure universal access to safe and affordable drinking water and sustainable water resource management by 2030. In 2019, more than 7.33$×10^{8}$ people lived in countries with high and critical levels of water stress (UN, 2019). Groundwater constitutes the vast majority of freshwater resources, yet high population growth and rapid industrialization are placing unprecedented strain on this valuable resource (Li and Qian, 2018; Li et al., 2022). Groundwater is critical for regulating the global water cycle, climate, and sustainability of human activities, particularly in arid environments with limited surface water resources (Tarawneh et al., 2019). Consequently, assessing groundwater quality, identifying pollution sources, and evaluating associated health risks have been extensively researched in recent decades (Obeidat et al., 2012; Adimalla et al., 2020; Abascal et al., 2022).

Anthropogenic nitrate represents the most widespread groundwater contaminant globally (Machiwal et al., 2018; Zhang et al., 2022). This problem is particularly acute in arid and semiarid regions like Jordan, which rely heavily on groundwater as the primary freshwater source and experience low subsurface infiltration and recharge rates (Elmeknassi et al., 2022). According to Panno et al. (2006), natural background NO_3^- concentrations typically range from 5.0 to 10.0 mg/L. However, excessive agricultural fertilizers and manure, wastewater disposal, atmospheric deposition, leachate leakage, and groundwater overpumping have caused dramatic increases in NO_3^- levels in aquatic ecosystems, surpassing both natural background levels and national/international drinking water quality guidelines (Carrey et al., 2021; Kou et al., 2021). High doses of waterborne NO_3^- can negatively impact human health (Torres-Martínez et al.,

2020), prompting the World Health Organization (WHO) to establish an upper NO_3^- concentration limit of 50.0 mg/L in drinking water (WHO, 2011). Moreover, excessive nitrate inputs can cause eutrophication of standing water bodies, species extinction in river ecosystems, acidification, algal blooms, and other ecological problems (Zhang et al., 2022). The economic impacts of nitrate pollution are also substantial, as remediation of contaminated water is extremely costly (Obeidat et al., 2021a).

Effective management of groundwater nitrate contamination requires a thorough understanding and tracing of pollution sources and the biochemical processes affecting nitrogen cycling (Gibrilla et al., 2020), as well as knowledge of nitrate distribution along flow paths and chemical transport mechanisms (Linhoff, 2022). A study by Alam et al. (2023) revealed that agricultural inputs (nitrogen fertilizers and manure) are the primary source of NO_3^- groundwater pollution in rural Bangladesh, contributing approximately 64% of nitrogen inputs, followed by pit latrines (18%). The study recommended mitigation measures including nitrogen fertilizer management strategies and farmer education programs to raise awareness of environmental impacts from fertilizer overuse. Su et al. (2022) conducted a field experimental study under irrigation and fertigation conditions to investigate moisture movement, soil salinity migration, and nitrogen transformations in soil profiles. Their results indicated that fertilizer application is the major nitrate source in soil and groundwater, while irrigation drives nitrogen transport and transformation. Managing groundwater nitrate problems remains challenging due to nitrate' s high mobility and the difficulty of tracing sources in complex hydrogeological settings (Jung et al., 2020). Hydrochemical data combined with isotope data provide a foundation for determining groundwater flow and estimating nitrate pollution origins and residence times (Jia et al., 2020). The stable isotopic composition of groundwater and nitrate has been successfully utilized for decades to address these challenges (He et al., 2022).

Source identification and apportionment of nitrate, along with controlling processes, have been addressed using the stable isotopic composition of nitrate. Determination of δ^{15}N-NO_3^- and δ^{18}O-NO_3^- helps track nitrate sources in groundwater and distinguish between natural and synthetic fertilizers, atmospheric deposition, and sewage sources (Buzeta, 2019), as different nitrate sources have distinct oxygen and nitrogen isotope signatures (Xue et al., 2009; Gutiérrez et al., 2018). Effective water resource management requires identification of pollution sources and biochemical processes affecting contaminant cycling, particularly nitrate (Popescu et al., 2015).

Jordan, covering approximately 89,210 km^2, is an arid Middle Eastern country dominated by desert with limited and scarce water resources (Al-Kharabsheh, 2020). Jordan ranks as the world' s second most water-stressed country for renewable freshwater, with approximately 61 m^3 per capita in 2021 (MWI, 2023). This crisis is worsening due to rapid population growth, agricultural expansion, increasing drought events, climate change, and inefficient water use,

placing extraordinary demands on water resources (MWI, 2023). About 70% of Jordan' s water supply comes from groundwater extraction, with 40%–50% derived from nonrenewable sources (Salameh et al., 2014). Overpumping and low recharge rates lead to groundwater depletion and quality deterioration (Al Wreikat and Al-Kharabsheh, 2020). High nitrate concentrations exceeding natural background levels and drinking water quality guidelines have been reported in many Jordanian groundwater basins (Obeidat et al., 2007; Salman et al., 2014). Hammouri and El-Naqa (2008) previously reported high nitrate concentrations in the study area groundwater. Therefore, this study investigates groundwater provenance and pollution sources in the Amman-Al Zarqa Basin, Jordan, with specific objectives: (1) identifying the provenance of the Lower Ajloun aquifer (Na' ur and Hummar aquifers) using stable isotopic composition of groundwater (δ^{18}O-H_2O and δ^{2}H-H_2O); (2) delineating main pollution sources based on stable isotopic composition of dissolved nitrate (δ^{18}O-NO_3^- and δ^{15}N-NO_3^-); and (3) determining the main biochemical processes affecting nitrogen species.

2 Study Area

The study area is located in the northwestern Amman-Al Zarqa Basin, Jordan (32°13 32 -32°20 55 N, 32°39 20 -35°56 38 E; Fig. 1 [Figure 1: see original paper]). The basin experiences a mixed arid-Mediterranean climate, with winter temperatures below 0°C and summer temperatures reaching approximately 40°C (Al-Fugara et al., 2022). Average annual rainfall varies from 319 mm in the southeast to 560 mm in the north (Fig. 1b). Agricultural land comprises approximately 33.4% of land use, followed by urban land (29.5%), bare land (28.0%), and forest (9.0%; Fig. 1c). Table 1 presents the geological and hydrogeological classification of rock types in the study area.

The geology is dominated by Upper Cretaceous Ajloun and Belqa groups, with Lower Cretaceous Kurnub sandstones outcropping in the southern part. The Kurnub sandstone is 300 m thick, white, and varicolored (Bender, 1974). The Ajloun group overlies the Kurnub sandstones and comprises five formations: Na' ur (A1 and A2), Fuheis (A3), Hummar (A4), Wadi Shueib (A5 and A6), and Wadi As Sir (A7). The A1 and A2 formations consist of 150–220 m of limestone interbedded with marl and marly limestone. The A3 formation comprises marl, marly limestone, and limestone. The A4 formation is 40–60 m thick and Cenomanian in age. The A5 and A6 formation is 75–100 m thick and consists of light grey limestone and marls. The A7 formation comprises strongly crystalline limestone, dolomitic limestone, and chert. The Balqa group (B) includes the Wadi Umm Ghudran (B1), Amman silicified limestone (B2), and Muwaqqar Chalk Marl (B3) formations. The B1 formation comprises chalk, marl, and marly limestone. The B2 formation has thicknesses of 80–120 m. The B3 formation is 60–70 m thick and Maastrichtian in age.

The aquifer systems can be separated into three primary complexes: Kurnub sandstone, Lower Ajloun (Na' ur and Hummar), and Amman/Wadi As Sir (Fig. 1e). The Kurnub sandstone aquifer is potentially useful in Jordan but is uneconomic in the study area with poor groundwater quality (Hammouri and El-Naqa, 2007). The Na' ur aquifer consists of limestone and marl overlying the Kurnub sandstone, with mean annual recharge estimated at approximately 4.5$×10^{6}$ m^3 (Al-Alawneh, 1998). The Na' ur aquifer has specific capacity, transmissivity, and hydraulic conductivity values of 0.01–12.00 m^3/h, 0.3–100.0 m^2/d, and 0.003–2.700 m/d, respectively (Salameh and Bannayan, 1993). The Hummar aquifer consists of hard, crystalline, coarse-grained, fractured dolomitic limestone with transmissivity of 32.0–300.0 m^2/d and permeability ranging from 8.1$×10^{-7}$ to 7.3$×10^{-4}$ m/s (Rimawi, 1985), receiving 5.0$×10^{6}$ to 6.0$×10^{6}$ m^3/a of recharge (Al-Alawneh, 1998). The Wadi As Sir is the most important aquifer in the basin, with permeability of 1.0$×10^{-7}–1.0×10^{-4}$ m/s and transmissivity of 10.0–6300.0 m^2/d (Al Mahamid, 2005).

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3 Methods

3.1 Sampling and Fieldwork

We collected 23 groundwater samples from the Lower Ajloun aquifer (Na' ur and Hummar aquifers) in March 2021, including 1 sample from a groundwater well and 22 samples from springs (Fig. 1c). Samples were collected at spring mouths. Prior to sampling, the well was purged to ensure representative subsurface conditions. Electrical conductivity (EC), pH, total dissolved solids (TDS), and temperature were measured in situ using a portable meter (Elite PCTS, Thermo Scientific, Waltham, USA), and dissolved oxygen (DO) was measured using a DO meter (SensoDirect 150, Lovibond, Dortmund, Germany). All groundwater samples were filtered and transferred to prewashed low-density polyethylene bottles before laboratory analysis. Samples for chemical analysis were refrigerated, while samples for δ^{15}N-NO_3^- determination were frozen before shipment to the Environmental Isotope Laboratory at the University of Waterloo, Canada. Samples for δ^{2}H-H_2O and δ^{18}O-H_2O determination were collected in 50-mL bottles and stored at room temperature until transport to the same laboratory. Field and laboratory procedures followed APHA (1998) standards. Sample coordinates were obtained using a GPS unit (GPSmap 60CSx, Garmin Ltd., Kansas, USA).

3.2 Laboratory Chemical Analyses

Concentrations of Na^+, K^+, Ca^{2+}, Mg^{2+}, and Cl^- were determined using an ion chromatograph (Dionix ICS-1600, Thermo Fisher Scientific, Sunnyvale, USA). Concentrations of SO_4^{2-} and NO_3^- were determined using a spectrophotometer (Lovibond 712005, Spectro Direct, Dortmund, Germany). HCO_3^- concentration was determined by titration. Total hardness (TH; mg/L) was calculated using

the following formula (Todd, 1980):

$$TH = 2.497(Ca^{2+}) + 4.11(Mg^{2+})$$

where Ca^{2+} (mg/L) and Mg^{2+} (mg/L) represent the concentrations of calcium and magnesium, respectively. Analytical uncertainty was less than 4%, with samples analyzed in triplicate. The anion-cation balance method was used to verify analytical correctness, with reproducibility within $±$10% error limits (Appelo, 2005):

$$Error = \frac{\Sigma cations - \Sigma anions}{\Sigma cations + \Sigma anions} \times 100$$

where Σcations is the total ionic concentration of cations (mol/L) and Σanions is the total ionic concentration of anions (mol/L).

3.3 Stable Isotope Composition

The $^{15}N/^{14}N$ and $^{18}O/^{16}O$ of NO_3^-, as well as the $^{18}O/^{16}O$ and $^{2}H/^{1}H$ of water, were determined at the Environmental Isotope Laboratory, University of Waterloo, Canada. The $^{15}N/^{14}N$ and $^{18}O/^{16}O$ of NO_3^- were determined using a N_2O chemical denitrifier (GVI Trace Gas Iso Prime, Elemental Microanalysis, Okehampton, UK) following the technique described by McIlvin and Altabet (2005). Analytical precision was $±$0.3‰ for $^{15}N/^{14}N$ and $±$0.8‰ for $^{18}O/^{16}O$ of NO_3^-. A liquid water isotope analyzer (T-LWIA-45-EP, Los Gatos Research, California, USA) determined the $^{18}O/^{16}O$ and $^{2}H/^{1}H$ of water with analytical precisions of $±$0.2‰ and $±$0.8‰ for ^{18}O and ^{2}H, respectively. Ratios were calculated using:

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

where δsample (‰) and Rsample are the $^{15}N/^{14}N$, $^{2}H/^{1}H$, or $^{18}O/^{16}O$ of the sample relative to the international reference, and Rstandard is the corresponding ratio of the standard. The international reference for $\delta^{15}N$ is N_2 in atmospheric air, while Vienna Standard Mean Ocean Water (VSMOW) is used for $\delta^{18}O$ and $\delta^{2}H$ values.

3.4 Chloro-Alkaline Index (CAI)

The CAI is widely used to investigate ion exchange processes in groundwater (Toumi et al., 2015) and can be calculated using (Schoeller, 1977):

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

where Cl^-, Na^+, and K^+ (mol/L) represent the concentrations of chloride, sodium, and potassium, respectively.

3.5 Principal Component Analysis (PCA) and Factor Analysis (FA)

PCA is a multivariate statistical technique widely used in groundwater quality assessment (Obeidat et al., 2013; Wu et al., 2014). This study used PCA to analyze main hydrochemical and isotopic parameters, including 14 variables: major ion concentrations, EC, TDS, pH, temperature, DO, and stable isotope composition of groundwater and dissolved nitrate. Data suitability for PCA was confirmed by a Kaiser-Meyer-Olkin (KMO) test value of 0.726 (>0.500) and a Bartlett test value of 0.00 (<0.05). Variables were selected based on eigenvalues greater than 1.00. Varimax rotation was employed to maximize factor coefficient variance and better interpret processes influencing groundwater chemistry. SPSS 13 software performed all PCA and FA calculations.

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4 Results and Discussion

4.1 General Hydrochemistry

Groundwater physicochemical parameters depend on rock weathering, recharge water quality, ion exchange, river base leakage, evaporation, and human activities. Characterizing groundwater chemistry helps evaluate hydrogeochemical features and assess suitability for irrigation and drinking (Rezaei et al., 2020; Ren et al., 2021). Table 2 presents descriptive statistics for hydrochemical parameters, along with WHO (2011) and Jordan Standards and Metrology Organization (2015) guidelines.

Potassium showed the highest coefficient of variation (CV), followed by NO_3^-, Cl^-, Na^+, SO_4^{2-}, and Mg^{2+}, indicating diverse sources and processes governing these ions. The lowest CV was for HCO_3^- (19.6%), suggesting a single spatial source. Calcium was the dominant cation, followed by Mg^{2+}, Na^+, and K^+. The dominant anion was HCO_3^-, followed by Cl^-, NO_3^-, and SO_4^{2-}. pH values ranged from 7.3–8.6 (average 7.7), indicating slightly alkaline groundwater within WHO (2011) and Jordanian standards. DO ranged from 4.6–11.6 mg/L (average 7.5 mg/L). TDS varied from 324.0–1030.0 mg/L (average 539.3 mg/L), while EC ranged from 457.0–1423.0 µS/cm (average 758.9 µS/cm; Fig. 2 [Figure 2: see original paper]). All EC values were within permissible limits for drinking water.

Total hardness ranged from 152.4–426.4 mg/L, classifying groundwater as hard to very hard. Calcium enters the aquatic environment predominantly through weathering of calcium-rich rocks such as limestone, which dominates the study area (Meybeck, 1987), with agricultural fertilizer as an additional source (Weyhenmeyer et al., 2019). Calcium concentrations ranged from 44.3–156.0 mg/L (average 81.9 mg/L), with approximately 57% of samples exceeding WHO (2011)

maximum limits, though all samples met Jordanian standards. Magnesium concentrations ranged from 5.9–32.3 mg/L (average 14.0 mg/L), while sodium ranged from 10.3–80.5 mg/L (average 26.8 mg/L). No samples exceeded WHO or Jordanian limits for Mg^{2+} or Na^{+}. Magnesium and sodium originate from carbonate mineral decomposition, silicates, evaporites, and atmospheric input, with agricultural operations and sewage effluents as additional sodium sources (Afroza et al., 2009; Hem, 1985). Potassium ranged from 0.1–26.0 mg/L. Bicarbonate concentrations varied from 64.0–128.0 mg/L (average 96.9 mg/L). Chloride ranged from 14.2–139.1 mg/L (average 47.2 mg/L), while sulfate ranged from 13.0–117.7 mg/L (average 33.4 mg/L). Chlorides and sulfates originate from water-rock interactions, seawater encroachment, industrial waste, or domestic sewage (Venkatesan et al., 2021). All samples met drinking water standards for these parameters.

Nitrate concentrations varied from 3.5–230.8 mg/L (average 50.9 mg/L; Fig. 2b). We categorized NO_3^- concentrations into three groups: (1) <10.0 mg/L (low risk, 4% of samples); (2) 10.0–50.0 mg/L (human impact, 61% of samples); and (3) >50.0 mg/L (exceeding WHO guidelines, 35% of samples). EC showed significant positive correlations with TDS, NO_3^-, Cl^-, SO_4^{2-}, Na^+, and Ca^{2+} (Table 3), indicating substantial influence from processes involving these parameters. Nitrate was significantly correlated with Cl^- and SO_4^{2-}, suggesting common sources such as fertilizers, sewage, and animal waste.

4.2 Natural Processes Contributing to Groundwater Chemical Composition

The Piper diagram is a common tool for deducing hydrochemical facies and processes influencing water chemistry. Figure 3 [Figure 3: see original paper] shows that Ca-Mg-HCO_3 type accounts for 44% of samples, followed by Ca-Mg-Cl type (39%) and Ca-Mg-SO_4 type (17%). The Ca-Mg-HCO_3 type reflects primary regional rock formations (limestone and dolomite) and represents recently recharged freshwater uncontaminated by human activity (El Yaouti et al., 2009). The Ca-Mg-Cl type indicates mixing of highly saline solutions (e.g., domestic wastewater) with uncontaminated freshwater, followed by ion exchange processes (Selvam et al., 2016).

Although the Gibbs diagram was originally developed for surface water chemistry (evaporation, weathering, precipitation; Gibbs, 1970), it has been extensively applied to groundwater hydrochemistry (Liu et al., 2023; Samtio et al., 2023; Yang et al., 2023; Zhang et al., 2023). The Gibbs diagram revealed that all samples plot in the rock dominance zone (Fig. 4 [Figure 4: see original paper]), indicating rock weathering as the main natural process controlling groundwater hydrochemistry. Evaporation is not dominant, as confirmed by negative correlations between Na^+ and TDS and between Cl^- and TDS. Sajil Kumar and James (2016) demonstrated that evaporation increases TDS when Na^+ or Cl^- is constant.

A Chadha diagram was used to classify natural waters and identify controlling hydrogeochemical processes (Chadha, 1999). Groundwater in the study area falls into two fields (Fig. 5 [Figure 5: see original paper]): (1) recharge water field (Ca-Mg-HCO_3 type, ~35% of samples), where alkaline earths and weak acidic anions exceed alkalis and strong acidic anions, creating temporary hardness; and (2) ion exchange field (Ca-Mg-Cl type, ~65% of samples), where alkaline earths exceed alkali metals and strong acidic anions exceed weak acidic anions, creating permanent hardness (Barzegar et al., 2017). Two exchange processes were identified: (1) reverse ion exchange, where Ca^{2+} and Mg^{2+} in the host aquifer are replaced by Na^+ and K^+ in water, hardening groundwater (Zaidi et al., 2015; Abu-Alnaeem et al., 2018; Tiwari et al., 2019); and (2) base ion exchange, where K^+ and Na^+ in the host aquifer are replaced by Ca^{2+} and Mg^{2+} in water, softening groundwater. Approximately 52% of samples had negative CAI values, while 28% had positive values (Fig. 5c), indicating both processes affect groundwater chemistry, though CAI values ranging from -0.20 to 0.36 suggest the exchange process is not intense.

The relationship between (Ca^{2+}+Mg^{2+})-($SO_4{}^{2-}$+$HCO_3{}^-$) and (Na^++K^+)-Cl^- confirmed ion exchange as a fundamental process affecting groundwater chemistry (Fig. 5d). The relationship between Ca^{2+}+Mg^{2+} and $HCO_3{}^-$ also indicated ion exchange, as most samples plot below the 1:1 reference line (Fig. 6). The $HCO_3{}^-$ to Cl^- ratio is a good indicator of groundwater salinization (Ayadi et al., 2018). Approximately 70% of samples had $HCO_3{}^-/Cl^-$ >1.0, indicating freshwater recharge. To assess carbonate mineral dissolution, we analyzed the relationship between Cl^- and $Ca^{2+}/HCO_3{}^-$ (Fig. 6b). Abu-Alnaeem et al. (2018) showed that calcite dissolution yields $Ca^{2+}/HCO_3{}^-$ 1.0, while dolomite dissolution yields 0.5. All samples had $Ca^{2+}/HCO_3{}^-$ >1.0, indicating ion exchange affects groundwater chemistry. A significant linear relationship (r=0.87; P<0.01) between ($NO_3{}^-$+Cl^-)/$HCO_3{}^-$ and TDS demonstrated human impacts on groundwater chemistry (Jalali, 2009), confirmed by significant correlation between $NO_3{}^-$ and Cl^-, indicating domestic wastewater as a primary pollution source (Reddy et al., 2009).

Table 4 shows PCA results for hydrochemical parameters, δ^2H-H_2O, δ^{18}O-H_2O, δ^{15}N-$NO_3{}^-$, and δ^{18}O-$NO_3{}^-$. Factor 1 accounted for 50% of total variance with strong positive loadings on EC, Cl^-, $SO_4{}^{2-}$, $NO_3{}^-$, Na^+, Ca^{2+}, and K^+, clearly indicating anthropogenic impacts and termed "pollution factor." Infiltration of domestic wastewater frequently increases hydrochemical parameter levels (Wang et al., 2017; Zhu et al., 2019). The $NO_3{}^-$-$SO_4{}^{2-}$ connection demonstrated impacts from synthetic fertilizers and domestic wastewater (Das and Nag, 2017; Aravinthasamy et al., 2020). Factor 2 accounted for 21% of variance with strong positive loadings on δ^2H-H_2O, δ^{18}O-H_2O, and δ^{18}O-$NO_3{}^-$, termed "conservative fingerprint factor." The association of δ^{18}O-$NO_3{}^-$ with δ^2H-H_2O and δ^{18}O-H_2O confirmed nitrification, as bacterially nitrified nitrate should contain two oxygen atoms from groundwater and one from air (Kendall et al., 2007). Factor 3 accounted for 11% of variance with very strong loadings on Mg^{2+} and $HCO_3{}^-$, termed "hardness factor" since Mg^{2+} is a major hardness component. The

Mg^{2+}-HCO_3^- association reflects freshwater recharge and water-rock interaction (Prasanna et al., 2010).

4.3 Stable Isotope Composition of Groundwater (δ^2H-H_2O and δ^{18}O-H_2O)

Meteorological factors including temperature, rainfall amount, continental effect, altitude, and latitude strongly affect water stable isotope composition. Both δ^2H and δ^{18}O are widely used to understand temporal and geographic isotope variability trends in precipitation (Rozanski et al., 1993; Dutton et al., 2005). Table 5 shows that δ^{18}O varied from -7.0‰ to -5.9‰ (average -6.7‰) and δ^2H ranged from -32.5‰ to -26.6‰ (average -29.7‰).

The δ^2H-δ^{18}O relationship (Fig. 7 [Figure 7: see original paper]) was plotted alongside the global meteoric water line (GMWL), Mediterranean meteoric water line (MMWL), and Jordan' s local meteoric water line (LMWL; Bajjali, 2012). Groundwater samples plotting near the LMWL and MMWL indicated Mediterranean water recharge. Samples were divided into two groups: Group 1 (21 samples) had δ^{18}O (-7.0‰ to -6.4‰) and δ^2H (-32.5‰ to -27.5‰) values between the LMWL and MMWL, indicating a common Mediterranean meteoric origin. Group 2 (2 samples) had δ^{18}O (-5.9‰ to -5.8‰) and δ^2H (-26.6‰ to -27.9‰) values between the MMWL and GMWL, indicating mixed sources and δ^{18}O enrichment relative to Group 1.

The study area lies in the Mediterranean bioclimatic region, characterized by abundant cool, wet winter precipitation and pronounced summer drought (Bajjali, 2012). Kattan (2019) identified precipitation-generating air mass sources over the Middle East as the Atlantic Ocean, North Pole via Eastern Europe, Siberian Plateau, North Africa, and Red Sea. All samples had d-excess values of 19.1‰-25.6‰ (average 23.6‰), consistent with central and northern Jordan rainfall values of 23.0‰-25.6‰. A significant inverse correlation ($r=-0.76$; $P<0.01$) between δ^{18}O and d-excess indicated evaporation effects, while a significant negative correlation ($r=-0.76$; $P<0.01$) between δ^{18}O and altitude demonstrated orographic effects with δ^{18}O depletion of -0.2‰ per 100 m, consistent with the global average depletion of -0.15‰ to -0.50‰ per 100 m (Aeschbach-Hertig et al., 2007). A significant negative correlation ($r=-0.61$; $P<0.01$) between δ^{18}O and rainfall amount was also observed. According to Bajjali (2012), the eastern highlands of the Jordan Rift Valley force air masses upward, preventing Mediterranean crossing.

The relationship between stable isotopes and TDS helps delineate groundwater chemistry processes (Liu et al., 2023). Specifically, δ^{18}O and d-excess reveal contributions from mineral dissolution, evaporation, and precipitation (Qu et al., 2023). d-excess decreases during evaporation but remains constant during mineral dissolution (Dansgaard, 1964). δ^{18}O increases significantly during evaporation, decreases when mixing with rainwater, and increases slightly or remains constant during mineral dissolution (Qu et al., 2023). Figure 8 [Fig-

ure 8: see original paper] shows most samples exhibited no significant d-excess or $\delta^{18}O$ changes with increasing TDS, signifying mineral dissolution or other salinity sources. The TDS-NO_3^- relationship showed covariation, indicating anthropogenic groundwater salinity sources (Fig. 8).

4.4 Stable Isotope Composition of Dissolved Nitrate (δ^{15}N-NO_3^- and δ^{18}O-NO_3^-)

The stable isotope composition of dissolved nitrate ($\delta^{15}N$ and $\delta^{18}O$) is a powerful tool for tracing nitrate sources and cycling processes, as different nitrate sources have distinct isotopic compositions (Kendall, 1998; Silva et al., 2000). Typical δ^{15}N-NO_3^- values are: manure/sewage nitrification (7.0‰-20.0‰), atmospheric nitrate (-13.0‰-13.0‰), synthetic fertilizer nitrate (-3.0‰-3.0‰), and natural soil organic matter (3.0‰-5.0‰) (Mayer et al., 2002; Lee et al., 2008; Xue et al., 2009; Gutiérrez et al., 2018; Obeidat et al., 2021b). Typical δ^{18}O-NO_3^- values are: nitrification-derived nitrate (-15.0‰-15.0‰), atmospheric nitrate (25.0‰-70.0‰), and synthetic fertilizer nitrate (17.0‰-25.0‰) (Durka et al., 1994; Mayer et al., 2002; Kendall et al., 2007; Xue et al., 2009). Biological, chemical, and physical processes (nitrification, denitrification, assimilation, volatilization) cause fractionation that modifies nitrate isotopic composition (Kaown et al., 2009).

In the study area, δ^{15}N-NO_3^- ranged from 2.6‰ to 13.7‰ (average 7.0‰) and δ^{18}O-NO_3^- ranged from 1.1‰ to 7.4‰ (average 3.0‰) (Table 5). Figure 9 [Figure 9: see original paper] shows nine samples fall in the "manure or septic waste" category, with δ^{15}N-NO_3^- (8.2‰-13.7‰) and δ^{18}O-NO_3^- (1.5‰-7.4‰) matching nitrification of wastewater or manure. These samples had NO_3^- concentrations of 12.4–230.8 mg/L, exceeding natural background (5.0–10.0 mg/L), indicating domestic wastewater as the pollution source. Nine samples fell in the overlapping "soil NH_4^+" and "manure or septic waste" window, with δ^{15}N-NO_3^- of 3.7‰-7.4‰ and δ^{18}O-NO_3^- of 1.1‰-5.5‰. The groundwater well sample had 3.5 mg/L NO_3^- (within natural background), while other samples ranged from 13.8–54.3 mg/L (exceeding background). The well sample' s isotopic composition suggests soil NH_4^+ as the nitrate source, while other samples indicate domestic wastewater. Five samples fell in the overlapping window of "manure or septic waste," "soil NH_4^+," and "NH_4^+ in fertilizers and precipitation," with δ^{15}N-NO_3^- of 1.6‰-4.3‰. A significant positive correlation between Cl^- and $\delta^{15}N$ ($r=0.74$; $P<0.01$) confirmed domestic waste as the primary nitrate source.

4.5 Biogeochemical Processes

Nitrification is the NH_4^+ transformation to nitrate catalyzed by autotrophic bacteria or archaea (Kendall, 1998). Denitrification converts nitrates to gaseous nitrogen species under reducing conditions (Brandes and Devol, 1997; Koba et al., 1997). ^{14}N is preferentially deposited during nitrification. δ^{18}O-NO_3^- values from nitrification vary from -5‰ to 15‰ depending on δ^{18}O-H_2O and oxygen gas values (Durka et al., 1994; Mayer et al., 2001). In the study area,

δ^{18}O-NO_3^- ranged from 1.1‰ to 7.4‰ (average 3.0‰), significantly lower than fertilizer nitrate (17.0‰–25.0‰) and atmospheric nitrate (25.0‰–70.0‰), indicating nitrification as the main biochemical process affecting nitrogen species, with wastewater and soil NH_4^+ as primary sources. δ^{18}O-H_2O values vary between –25.0‰ and 4.0‰, while atmospheric oxygen is approximately 23.5‰. δ^{18}O-NO_3^- from bacterial nitrification typically ranges from –10.0‰ to 10.0‰ (Kendall et al., 2007). Using measured groundwater δ^{18}O values and assuming atmospheric oxygen δ^{18}O of 23.5‰, theoretical δ^{18}O-NO_3^- values ranged from 2.4‰ to 3.1‰ (average 2.6‰), within the measured range (1.1‰–7.4‰). The average measured δ^{18}O-NO_3^- (3.0‰) was consistent with the theoretical nitrification value. Denitrification requires specific conditions (Gutierrez et al., 2018): low DO (1.0–2.0 mg/L), electron donors, denitrifying bacteria, trace nutrients, nitrate, temperature (25°C–35°C), and pH (5.5–8.0). These conditions are absent in the study area, where DO exceeds 4.0 mg/L and groundwater temperature remains below 25°C.

5 Conclusions and Recommendations

Integrated hydrochemical methods, environmental isotope techniques, and multivariate statistical analysis successfully explored groundwater provenance, quality, and pollution in the Amman-Al Zarqa Basin, Jordan. Domestic wastewater intrusion into fresh groundwater has deteriorated water quality and shifted hydrochemical facies from Ca-Mg-HCO_3 to Ca-Mg-Cl and Ca-Mg-SO_4 types. Groundwater originates from Mediterranean Sea rainfall as part of the current water cycle, as evidenced by stable isotope composition. Altitude and rainfall amount are the main factors controlling groundwater stable isotope composition. Domestic wastewater is the primary pollution source, as indicated by dissolved nitrate stable isotope composition. Nitrification is the main biochemical process governing nitrogen species, while water-rock interaction (dissolution and cation exchange) is the primary natural process affecting groundwater quality. These results provide decision-makers with an important tool for implementing effective groundwater protection measures. We strongly recommend adopting best management practices and efficient land use planning, including improved agricultural practices (fertilization, manure application, animal manure storage) and sanitation techniques (better pit latrine and septic tank design, sewer leakage control).

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