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^{17}O-excess traces atmospheric nitrate in paleo groundwater of the Saharan desert

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Abstract

Saharan paleo groundwater from the Hasouna area of Libya contains up to 1.8 mM of nitrate, the origin of which is still disputed. Herein we show that a positive ^{17}O-excess in NO_3^- ($\Delta^{17}O_{NO_3} = \delta^{17}O_{NO_3} - 0.52\,\delta^{18}O_{NO_3}$) is preserved in the paleo groundwater. The ^{17}O-excess provides an excellent tracer of atmospheric NO_3^-, which is caused by the interaction of ozone with NO_x via photochemical reactions, coupled with a non-mass dependent isotope fractionation. Our $\Delta^{17}O_{NO_3}$ data from 0.4 to 5.0 ‰ ($n = 28$) indicate that up to $x[NO_3^-]_{atm} = 20$ mol % of total dissolved NO_3^- originated from the Earth's atmosphere. High $\Delta^{17}O_{NO_3}$ values correspond to soils that are barren in dry periods, while low $\Delta^{17}O_{NO_3}$ values correspond to more fertile soils. Coupled high $\Delta^{17}O_{NO_3}$ and high $x[NO_3^-]_{atm}$ values are caused by a sudden wash out of dry deposition of atmospheric NO_3^- on plant or soil surfaces within humid-wet cycles. The individual isotope and chemical composition of the Hasouna groundwater can be followed by a binary mixing approach using the lowest and highest mineralized groundwater as end-members without considering evaporation. Using the $\delta^{34}S_{SO_4}$ and $\delta^{18}O_{SO_4}$ isotope signature of dissolved sulfate, no indication is found for a superimposition by denitrification, e.g. involving pyrite minerals within the aquifers. It is suggested that dissolved sulfate originates from the dissolution of calcium sulfate minerals during groundwater evolution.

1 Introduction

The accumulation of nitrate in groundwater is a well-known phenomenon occurring worldwide (Clark and Fritz, 1997; Kendall, 1998). Individual NO_3^- sources and mechanisms for its accumulation depend strongly on the environmental conditions during recharge, infiltration, and aquifer storage. High NO_3^- concentrations of paleo groundwater from Hasouna area (Libya) have been measured for decades, but the NO_3^- origin is still hotly debated (El-Baruni et al., 1985; Milne-Home and Sahli, 2007). Deciphering the source of NO_3^- for Saharan groundwater in Libya is highly challenging, as the present arid conditions preclude appreciable recharge (Edmunds, 2006).

The source of dissolved NO_3^- in groundwater is commonly attributed to (i) anthropogenic origin, including leaching of fertilisers or animal waste, (ii) the dissolution of evaporite deposits, (iii) leaching of organic or inorganic nitrogen from soils, and (iv) atmospheric deposition (e.g., Clark and Fritz, 1997; Saccon et al., 2013, and references therein). Ancient Saharan groundwater of Hasouna (Libya) was recharged under environmental conditions that did not allow for an anthropogenic impact, but natural provenances of dissolved NO_3^- of the paleo groundwater have not yet been deciphered and quantified.

Evidence for NO_3^- origin is traditionally obtained by measuring $^{15}N/^{14}N$ and $^{18}O/^{16}O$ ratios (Amberger and Schmidt, 1987; Kendall, 1998). From $\delta^{15}N_{NO_3}$ and $\delta^{18}O_{NO_3}$ data, the NO_3^- provenances can be evaluated, and reaction mechanisms like denitrification may be deduced by considering changes in NO_3^- concentration and mass dependent isotope fractionation (MDF) (Kendall, 1998). However, throughout complex processes of nitrogen conversion in soils and within the aquifer $\delta^{15}N_{NO_3}$ and $\delta^{18}O_{NO_3}$ values of dissolved NO_3^- can be strongly overprinted (e.g. by (de)nitrification; Xue et al., 2009).

More recently, a triple stable isotope approach using $^{18}O/^{16}O$ and $^{17}O/^{16}O$ signals in NO_3^- was successfully applied to identify exclusively NO_3^- of atmospheric origin. Atmospheric NO_3^- ($NO^-_{3,atm}$) is characterized by a ^{17}O-excess according to the expression:

$$\Delta^{17}O = \delta^{17}O - 0.52\,\delta^{18}O, \tag{1}$$

where non-mass dependent isotope fractionation (NMDF) during the formation of ozone, followed by photochemical reactions between atmospheric NO_x and O_3 to NO_3^-, results in non-zero $\Delta^{17}O_{NO_3}$ values (Michalski et al., 2003; Thiemens, 2006). Böhlke et al. (1997), for instance, found evidence from $^{15}N/^{14}N$ and $^{18}O/^{16}O$ isotope analyses for the atmospheric source of NO_3^- for nitrate-rich salts in Atacama (Chile) and Mojave

Desert (California). The atmospheric origin of NO_3^- in the Atacama deposits has been confirmed by a pronounced ^{17}O-excess (Michalski et al., 2004a). Since then $NO^-_{3,atm}$ was quantified using the ^{17}O-excess for various desert deposits and dissolved NO_3^- in modern groundwater, lakes, and wet depositions (Darrouzet-Nardi et al., 2012; Dejwakh et al., 2012; Li et al., 2010; Michalski et al., 2004b, 2005; Tsunogai et al., 2010, 2011; Nakagawa et al., 2013).

The aim of the present study is to trace the origin of NO_3^- in Saharan paleo groundwater by using $^{15}N/^{14}N$ ratios and triple stable isotopes of oxygen. In addition, a reaction of nitrate with pyrite (FeS_2) in the aquifers can act as a potential nitrate sink, which has already been shown for European shallow aquifers (e.g., Böttcher et al., 1990; Zhang et al., 2012). This requires the analyses of the stable isotope signatures of dissolved sulfate. Furthermore, ancient recharge and climate conditions are reconstructed by using a multi-element and isotope approach.

2 Study area and sample sites

The Hasouna well field is located about 700 km south of Tripoli (Libya) within the Cambro-Ordovician Nubian Sandstone Aquifer System (Fig. 1). This system comprises one of the world's largest paleo groundwater aquifers, which had been recharged at about 30 ± 10 and 10 ± 3 ka BP based on ^{14}C dating (Edmunds et al., 2003; Edmunds and Wright, 1979; Guendouz et al., 1998; Milne-Home and Sahli, 2007; Sonntag et al., 1978). Strong evidence exists for enhanced precipitation in north Africa during these time periods. However, individual epochs for humidity and groundwater recharge periods are still disputed, Pleistocene and Holocene humid periods in north Africa have been deduced from the records stored in lacustrine fresh-water sediments (Rognon, 1987), wadi river systems (Kuper and Kröpalin, 2006), travertine (Carrara et al., 1998), paleobotanic investigations (Doherty et al., 2000), rock art dating and varnish-coating of petroglyphs (Dietzel et al., 2008), dating of aragonitic mollusk shells (Blackwell et al., 2012), together with cyclicity of geochemical signals observed in marine sediments of the Eastern Mediterranean that are influenced by the Nile river hydrology (Wehausen and Brumsack, 1999; Lourens et al., 2001).

The aquifer consists predominately of fractured sandstone ranging from ≈ 500 to 1500 m thickness, with thin interbeds of marine limestone and marl. The sandstone itself is mostly quartzitic sandstone, but occasionally carbonate cement occurs. In the study area, the main Cambro-Ordovician Sandstone aquifer is overlain by a shallow carbonate aquifer with a basal aquitard, predominantly composed of marly limestone, clay and shale.

Groundwater in the study area of Jabal Hasouna was discovered during oil exploration in the 1960s (Edmunds, 2006). A large number of wells has been installed as part of the Great Man-made River Project, which brings up to ≈ 6 Mm^3 of fresh water per day to the Mediterranean (Salem, 1992; Abdelrhem et al., 2008). The average spacing of the total 484 wells is ≈ 1.5 km, with individual discharges of ≈ 50 $L\,s^{-1}$ covering ≈ 4000 km^2 (Binsariti and Saeed, 2000).

3 Materials and methods

Sampling of Hasouna groundwater from 28 wells was carried out in the year 2007, with sampling depths between 323 and 555 m. Coding and sampling site locations are summarized in Table 1 and shown in Fig. 1.

3.1 Chemical composition

Temperature and pH of the groundwater were measured in-situ with pH meter WTW 330 and pH electrode WTW SenTix 41, having a precision of ±0.03 pH units (calibrated on-site using pH 4.0 and 7.0 WTW standard buffer solutions). Concentration of dissolved O_2 was analysed in the field using WTW Oxi 325 and WTW CellOx325, having an analytical precision of ±0.2 $mg\,L^{-1}$. Sampled solutions were filtered in the field through 0.45 µm cellulose acetate membranes, and one aliquot was acidified. The samples were stored in polyethylene and hermetically sealed glass vessels for Lab analyses. Concentrations of dissolved anions were analysed in non-acidified samples by ion chromatography (Dionex DX 500) with an analytical precision of about ±3 %. Alkalinity was obtained by potentiometric titration of non-acidified samples from the gas-tight glass vessels with an uncertainty of about ±5 %. In the acidified solutions (2 % HNO_3), cations were analysed by inductively-coupled optical emission spectroscopy with a precision of better than ±5 % (Perkin Elmer Optima ICP-OES 4300; Merck multi-element standard). Calculation of saturation indices with respect to calcite ($SI_{calcite}$) and gypsum (SI_{gypsum}) was performed with the computer code PHREEQC (Parkhurst and Appelo, 1999) and the phreeqc.dat database.

3.2 Stable isotopes

Additional samples were gathered for analysing the D/H and $^{18}O/^{16}O$ distribution in H_2O. The stable isotopes of hydrogen were measured using a Finnigan DELTA plus XP mass spectrometer working in continuous flow mode by the chromium reduction technique (Morrison et al., 2001). The oxygen isotope composition was measured with a Finnigan DELTA plus mass spectrometer using the classic CO_2-H_2O equilibrium method (Horita et al., 1989). The δD_{H_2O} (analytical precision: ±0.1 ‰) and $\delta^{18}O_{H_2O}$ values (±0.03 ‰) are given relative to the Vienna Mean Ocean Water (VSMOW). As an example, the definition of δ values is given for the D/H distribution in H_2O by the expression:

$$\delta D_{H_2O} = (R_s/R_{st} - 1)\ 10^3\ (‰), \tag{2}$$

where R_s and R_{st} are the respective analysed isotope ratios (D/H) for the measured sample and standard (VSMOW), respectively. The $\delta^{34}S_{SO_4}$ and $\delta^{18}O_{SO_4}$ values of dissolved sulfate were measured on $BaSO_4$ that was precipitated from acidified solutions by the addition of barium chloride. The solids were washed and dried and further anal-

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◀| |▶
◀ ▶
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

ysed by means of continuous-flow isotope-ratio monitoring mass spectrometry (CirmMS) using a Thermo Scientific Finnigan Delta+ mass spectrometer at MPI-MM Bremen, Germany (according to Böttcher et al., 2001 and Kornexl et al., 1999). Respective precisions of sulfur and oxygen isotope measurements were ±0.3 ‰ and ±0.5 ‰, and results are reported in relation to the VCDT and VSMOW scales, respectively.

Separate samples were taken for isotope analyses of dissolved NO_3^-. Analyses were carried out using the bacterial denitrifier technique in combination with the N_2O decomposition method (Casciotti et al., 2002; Kaiser et al., 2007; Morin et al., 2008; Savarino et al., 2007). The $\delta^{15}N_{NO_3}$, $\delta^{18}O_{NO_3}$, and $\Delta^{17}O_{NO_3}$ values (^{17}O-excess) of dissolved NO_3^- are given with respect to the atmospheric N_2(AIR) and VSMOW standard, and were measured with uncertainties of ±0.5 ‰, ±2 ‰, and ±0.5 ‰, respectively.

4 Results and discussion

4.1 Ion content and mixing approach

The analysed compositions of the sampled groundwater from the Hasouna area are summarized in Table 1. The investigated Hasouna groundwater display near neutral pH values (pH = 7.0 ± 0.5) at slightly elevated temperatures, ranging from 27 to 35 °C. The concentration of dissolved oxygen is $5.5 \pm 0.8\,\mathrm{mg\,L^{-1}}$ ($n = 9$). Dissolved cations and anions generally occur in the quantitative sequences of $Na^+ > Ca^{2+} > Mg^{2+} > K^+ > Sr^{2+}$ and $Cl^- > HCO_3^- > SO_4^{2-} > NO_3^-$, respectively (Table 1). The average deviation from electrical neutrality for the aqueous solutions is 3.6 meq % with a maximum of about 5 meq %, which verifies the quality of ion content analysis. Except for nitrate, the chemical composition of the groundwater is within the limits for drinking water. In ≈ 85 % of the analysed Hasouna groundwater, the maximum contaminant level (MCL) of the World Health Organization (WHO, 2004) for NO_3^- in drinking water of 0.71 mM is exceeded (Table 1).

All analysed groundwater is undersaturated with respect to gypsum ($SI_{gypsum} \leq -0.93$). However, approximately 20 % of the groundwater (6 of 28 samples) are slightly supersaturated with respect to calcite ($-0.50 \leq SI_{calcite} \leq 0.18$; Table 1). If the analysed calcium concentration is reduced by the proportion gained from calcium carbonate dissolution by considering the dissolution of magnesium carbonates like dolomite ($[Ca^{2+}] + [Mg^{2+}] - 0.5[HCO_3^-]$), a calcium (reduced) to sulfate ratio of 1 is obtained (Fig. 2). This relationship typically results from the uptake of gaseous CO_2 (e.g., in soil horizons) and subsequent dissolution of limestone and/or dolostone (e.g. calcite and/or dolomite; Dietzel et al., 1997). Dissolution of calcite and dolomite during the evolution of the groundwater seems reasonable, as both minerals have been documented in rock core samples from Hasouna well fields (Sahli, 2006). The congruent dissolution of calcium sulfates, like gypsum, causes the calcium (reduced) to sulfate ratio of 1 (Fig. 2).

The dissolved ions cover a broad concentration range, where ion concentrations are well correlated. For instance, the correlation of Na^+ and Cl^- concentrations is shown in Fig. 3a. As groundwater samples #165 and #152 bracket the full observed range, their chemical composition is used for a binary mixing approach according to the expression:

$$[i]_{groundwater} = x_{\#152} \cdot [i]_{\#152} + (1 - x_{\#152}) \cdot [i]_{\#165}, \qquad (3)$$

where $x_{\#165} + x_{\#152} = 1$ (refer to solid green line in Fig. 3a). In this expression [i] denotes the concentration of the dissolved ion ($i = Na^+$ or Cl^-) of the respective solution. The terms $x_{\#165}$ and $x_{\#152}$ are the volume fractions of groundwater samples #165 and #152, which yield the ion concentration range of the Hasouna groundwater. Analogous relationships are found for all dissolved ions (e.g., Ca^{2+} vs. NO_3^- in Fig. 3b). If seawater is assumed for a mixing end-member solution, the mixing approach of Eq. (3) fails, as in most cases the ion ratios of the groundwater are inconsistent with seawater. This is shown by the calcium (reduced) to sulfate ratio of the Hasouna groundwater of about 1 (Fig. 2), which differs significantly compared to that of sea water (≈ 60; assuming ancient seawater composition close to modern conditions; Drever, 2002). Additionally, an evaporation trend for #165 to reach the composition of #152 is not consistent with the measured data (dotted arrows in Fig. 3a and b). This is even valid if a decrease of Ca^{2+} concentration through calcite precipitation ($SI_{calcite} = 0$) is considered, which may be induced by evaporation (solid arrow in Fig. 3b). Thus, the solution chemistry of the Hasouna groundwater can be best explained by mixing of the two end-member solutions #165 and #152.

As an exception, the concentration of silicic acid is nearly constant in all groundwater samples ($[Si(OH)_4] = 0.22 \pm 0.02$ mM; $n = 28$) and reflects the solubility of quartz at the average temperature of the Hasouna groundwater ($K_{quartz} = [Si(OH)_4] = 0.22$ mM at 31 °C; Rimstidt, 1997). Thus, the concentrations of silicic acid in the acient Hasouna groundwater from the Nubian Sandstone Aquifer are clearly controlled by quartz-water interaction considering thermodynamic equilibrium, which is typically found for ancient groundwater in quartz-dominated aquifers (Rimstidt, 1997, and references therein).

4.2 Stable isotopes of water and climate record

The δD_{H_2O} and $\delta^{18}O_{H_2O}$ values of the analysed Saharan groundwater range from −73.2 to −64.6 ‰ and from −9.97 to −8.75 ‰, respectively (Table 1). The isotope values fall below the modern Global Meteoric Water Line (GMWL) and Local Meteoric Water Line (LMWL is given for Sfax, southern Tunisia; see Fig. 4). Our isotope data are very close to former results reported for paleo groundwater from Hasouna, Murzuq Basin, Wadi Ash Shati Valley, Arab Jamahiriya in Libya and paleo groundwater from southern Tunisia (Abid et al., 2012; Milne-Home and Sahli, 2007; Salem et al., 1980; Sonntag et al., 1978; Srdoč et al., 1980). From the isotope composition of our Hasouna groundwater the local Paleo Meteoric Water Line

$$\delta D_{H_2O} = 8.0\,\delta^{18}O_{H_2O} + 6.3, \quad R^2 = 0.82 \tag{4}$$

is estimated (see Fig. 4). The lower deuterium excess (d-excess = $6.3 = \delta D - 8.0\,\delta^{18}O$) for the paleo groundwater compared to that of modern precipitation (12±2 ‰) is caused by decreasing moisture deficit (increase in relative humidity) of the air above sea water during evaporation (Sonntag et al., 1978). As air moisture deficit is positively correlated with temperature, lower paleo temperature and higher paleo humidity are suggested from the lower d-excess (Kendall and Doctor, 2004).

In accordance with the overall shift of Saharan paleo groundwater to low δD_{H_2O} and $\delta^{18}O_{H_2O}$ values compared to apparent local precipitation (in Sfax and Tripoli, Fig. 4) it is postulated that the Hasouna groundwater was recharged under paleoclimatic conditions, which were cooler and much more humid compared to the modern situation (Clark and Fritz, 1997; Edmunds, 2006). As an analogy to the above mentioned mixing approach, an evaporation effect for Hasouna paleo groundwater (e.g. subsequent to precipitation or during infiltration) can be ruled out, as the slope of the regression line for the isotope data is similar to the MWLs (Craig, 1961; Kendall and Doctor, 2004).

4.3 Stable isotopes of nitrate, origin and potential overprints

The $^{18}O/^{16}O$ and $^{15}N/^{14}N$ distributions of the dissolved NO_3^- for the Hasouna groundwater range from 6.9 to 17.4 ‰ and from 6.6 to 9.1 ‰, respectively (Fig. 5), in relation to the isotope ranges of different sources for NO_3^- (see Kendall, 1998; Böhlke et al., 1997). Our measured $\delta^{15}N_{NO_3}$ and $\delta^{18}O_{NO_3}$ values are almost within the range of a microbial origin for NO_3^- (e.g. obtained by nitrification in soils), where $^{18}O/^{16}O$ is incorporated from apparent H_2O and O_2, and $^{15}N/^{14}N$ is derived from organic matter (Fig. 5).

In modern groundwater the isotope composition of NO_3^- might be modified within pyrite-bearing aquifers by microbial NO_3^- reduction via oxidation of iron sulfides (Böttcher et al., 1990; Zhang et al., 2010, 2012; Saccon et al., 2013). This overprint can be followed by a characteristic superimposition of the sulfur and oxygen isotope composition of dissolved SO_4^{2-} (e.g., Zhang et al., 2011, 2012). The measured narrow range of $\delta^{34}S_{SO_4}$ and $\delta^{18}O_{SO_4}$ values in Hasouna groundwater of +10.5 ± 0.7 ‰ vs. VCDT and +10.4 ± 0.8 ‰ vs. VSMOW (n = 10; see Table 1), respectively, is surprising, considering the observed wide range in SO_4^{2-} concentrations (1.3 to 4.3 mM, see Fig. 6). In addition, no significant correlation of the above isotope data with the NO_3^- concentrations exists. This behaviour indicates that the source of dissolved sulfate was not coupled to nitrate reduction. Thus pyrite-oxidation driven nitrate reduction is considered to be insignificant. In addition, the heavy sulfur isotope values exclude significant contribution, at least from biogenic pyrite oxidation. If isotopically light sulfur would have been modified by later microbial sulfate reduction under essentially closed system conditions (e.g., Hartmann and Nielsen, 2012) to reach heavy residual sulfate values, one would expect an equilibration of the oxygen isotope signature of sulfate with the surrounding bulk water (Fritz et al., 1989). Using the fractionation factors derived by Fritz et al. (1989) much heavier oxygen isotope values for water are expected. The isotope data of the dissolved sulfate are close to values reported for Permian evaporites (Böttcher, 1999; Mittermayr et al., 2012; Nielson, 1979; $\delta^{34}S_{SO_4} = +11 \pm 1$ ‰), but differ significantly from the isotope values of modern Mediterranean seawater $\delta^{34}S_{SO_4} = +21$ ‰; Böttcher et al., 1998; Fig. 6). Unfortunately, details regarding the hydrogeological conditions of the groundwater remain unknown, in particular respect to the regional occurrence and distribution of calcium sulfate horizons. However, our hydrogeochemical findings and isotope values support the dissolution of gypsum during subterranean groundwater evolution, as shown by the relationship in Fig. 2. Moreover, the correlation for the concentrations of dissolved Sr^{2+} vs. Ca^{2+} of Hasouna groundwater ($[Sr^{2+}] = 0.0058 \cdot [Ca^{2+}]$, $R^2 = 0.83$; see values in Table 1) is typically found, where evaporite gypsum deposits are dissolved (e.g., Dietzel and Kirchhoff, 2003). Thus, from the solution chemistry of the groundwater as well as from the known occurrence of evaporites on the Saharan platform (Turner and Sherif, 2007), and occasionally documented gypsum in core samples from Hasouna well fields (Sahli, 2006), we reasonably assume salt dissolution as the dominant source for the dissolved sulfate. This conclusion is also supported by the above mentioned narrow range of stable isotope data with respect to SO_4^{2-}, with no correlation of isotope data and SO_4^{2-} concentrations (Fig. 6).

A pronounced trend toward higher $\delta^{18}O_{NO_3}$ and lower $\delta^{15}N_{NO_3}$ values is obvious for elevated NO_3^- concentrations (solid green arrow in Fig. 5). This trend cannot result from denitrification (dashed arrow; Böttcher et al., 1990; Kendall, 1998; Granger et al., 2010), but might be best explained by an impact of NO_3^- from atmospheric deposition. The $\delta^{15}N_{NO_3}$ data of desert NO_3^- deposition are close to the atmospheric value of 0 ‰, and the range of $\delta^{18}O_{NO_3}$ values may further indicate supply of atmospheric NO_3^- (e.g. Böhlke et al., 1997).

The origin of nitrate can be constrained by considering the minor oxygen isotope, and evaluating both the $\delta^{17}O_{NO_3}$ and $\delta^{18}O_{NO_3}$ values. All Hasouna paleo groundwater measured here exhibit a positive ^{17}O-excess up to $\Delta^{17}O_{NO_3} \approx 5$ ‰, which is attributed to NMDF during conversion of atmospheric NO_x and O_3 to $NO^-_{3\,(atm)}$ (Table 1; Kendall and Doctor, 2004; Michalski et al., 2004a; Thiemens, 2001). In Fig. 7a, the ^{17}O-excess vs. the traditional $\delta^{18}O_{NO_3}$ value is displayed. A potential secondary (de)nitrification or reduction impact can be followed by a shift parallel to the terrestrial fractionation trend (horizontal arrows indicate MDF effect). For the given isotope data of NO_3^- in Fig. 7a, an overall relationship with a slope of 0.342 is obtained from least squares regression, which fits well with the $\Delta^{17}O_{NO_3}$ end-member, the atmospheric photochemical NO_3^- (Michalski et al., 2004a; see Fig. 7a). The deviation from the overall correlation of isotope data, which is given by the green dashed line in Fig. 7a, can be explained by MDF effects.

The formation of $NO^-_{3,atm}$ is linked to the most important oxidants in the atmosphere: O_3. The respective $\Delta^{17}O$ of atmospheric NO_3^-, gained from the conversion of atmospheric NO_x and O_3, can be followed by three major reaction pathways involving NO_2, O_3, OH^- and H_2O (Gao and Marcus, 2001; Savarino, 2000; Michalski et al., 2003). The proportion of $NO^-_{3,atm}$ for the former reaction paths and corresponding precipitation rates can be obtained from global climate models, which finally results in $\Delta^{17}O_{NO_{3,atm}}$ of about +25 ‰, a value well corroborated by atmospheric observations (Michalski et al., 2003; Morin et al., 2008; Alexander et al., 2009). In contrast, microbial-induced nitrification in soils results in $\Delta^{17}\mathrm{O}_{\mathrm{NO}_{3,\mathrm{soil}}} = 0$ ‰. The individual ^{17}O-excess of dissolved NO_3^- of the analysed Saharan groundwater, $\Delta^{17}\mathrm{O}_{\mathrm{NO}_{3,\mathrm{soil}}}$ an be used to calculate the fraction of atmospheric NO_3^- vs. the total NO_3^- concentration according to the expression:

$$x[\mathrm{NO}_3^-]_{\mathrm{atm}} = \frac{\Delta^{17}\mathrm{O}_{\mathrm{NO}_3}}{\Delta^{17}\mathrm{O}_{\mathrm{NO}_{3,\mathrm{atm}}}} \cdot 100\,(\%) \tag{5}$$

Considering the measured $\Delta^{17}\mathrm{O}_{\mathrm{NO}_3}$ values of the groundwater from 0.4 to 5 ‰ in Table 1 and $\Delta^{17}\mathrm{O}_{\mathrm{NO}_{3,\mathrm{atm}}} \approx +25$ ‰, individual proportions from 1.6 up to 20.0 % for atmospheric origin with respect to the total dissolved NO_3^- are obtained. Interestingly, $x[\mathrm{NO}_3^-]_{\mathrm{atm}} \approx 20$ % is consistent with the proportion of non-recycled atmospheric NO_3^- vs. total NO_3^- estimated from $\delta^{18}\mathrm{O}_{\mathrm{NO}_3}$ data of unsaturated zone moisture in the arid Badain Jaran Desert (China; Gates et al., 2008).

Our $x[\mathrm{NO}_3^-]_{\mathrm{atm}}$ data results in a maximum NO_3^- concentration, which is gained from atmospheric origin, of $[\mathrm{NO}_3^-]_{\mathrm{atm}} = 0.34$ mM in the Saharan groundwater #152 at highest total NO_3^- concentration (see Table 1). Lower concentrations of NO_3^- from atmospheric origin are related to lower total NO_3^- concentrations (e.g. groundwater #165 with $[\mathrm{NO}_3^-]_{\mathrm{atm}} = 0.02$ mM).

Thus, the $\Delta^{17}\mathrm{O}_{\mathrm{NO}_3}$ values of dissolved nitrate in the Hasouna Aquifer clearly reveal that NO_3^- is a mixture between NO_3^- transferred from the atmosphere and NO_3^- gained from nitrification. At elevated NO_3^- concentrations of the groundwater, the highest concentrations of atmospheric NO_3^-, as well as the highest fractions of atmospheric NO_3^- vs. the total NO_3^- concentration ($x[\mathrm{NO}_3^-]_{\mathrm{atm}}$) are found.

5 Implications for paleo climate conditions during recharge

In analogy to the ion concentrations, a binary mixing approach that considers the end-member solutions #165 and #152 is consistent with the ^{17}O-excess in Hasouna paleo groundwater. This mixing approach is displayed by a linear correlation of $\Delta^{17}O_{NO_3}$ values vs. $1/[NO_3^-]$ in Fig. 7b, where elevated $NO_{3,atm}^-$ proportions (higher ^{17}O-excess) are obtained at high total NO_3^- concentrations (e.g., groundwater #152). Such elevated $NO_{3,atm}^-$ proportions can be explained by an impact of flood events as shown by Michalski et al. (2004b) from monitored values during storm events in Devil Canyon watershed (southern California, USA). $\Delta^{17}O_{NO_3}$ maximum values are caused by a sudden wash out of dry deposition of atmospheric NO_3^-, which was accumulated through long term arid conditions to which plant or soil surfaces have been exposed. Wash out during storm flow periods and flood events enhances the mobilization of NO_3^-, and corresponding high NO_3^- concentrations occur in the recharging groundwater as reported by Chiwa et al. (2010) for a small forested watershed.

Accordingly, for the present case, it is predicted that dry periods have alternated with heavy precipitation and flood events, where infiltration of solutions occurred leaving the ^{17}O-excess of NO_3^- preserved. These environmental conditions during recharge coincides well with results from pollen analyses in the Saharan desert (Libya), where past climate oscillations between wet and dry periods are documented at about 8–10 ka BP (Mercuri, 2008). Preserved $\Delta^{17}O_{NO_3} > 0$ ‰ clearly indicates that $NO_{3,atm}^-$ underwent limited biological processing, as time for infiltration through soil horizons was limited (Michalski et al., 2004b). Limited NO_3^--biotic interaction periods are confirmed by the uniform sulfur and oxygen isotope composition of SO_4^{2-} and in particular by $\delta^{18}O_{NO_3}$ values, which change in the direction to atmospheric NO_3^- at elevated NO_3^- concentrations. The latter relationship is opposite to what would be expected to occur during denitrification (Fig. 5).

The local distribution of $NO_{3,atm}^-$ proportions on total dissolved NO_3^- of the Hasouna groundwater is analogous to that of the NO_3^- content shown in Fig. 1, as $\Delta^{17}O_{NO_3}$ is negatively correlated to $1/[NO_3^-]$ (see Fig. 7b). Spatial variability in $x[NO_3^-]_{atm}$ and $[NO_3^-]$ is attributed to paleoclimatic conditions during recharge and to an associated paleo biosphere response. Atmospheric components suggest rather uniform deposition over time, and the soil content depends on soil type, its volume, and biological activity. Thus, a relative increase in $x[NO_3^-]_{atm}$ can be caused by (i) longer lasting dry periods with subsequent precipitation events and/or (ii) a local surface covered by less fertile soils. High $\Delta^{17}O_{NO_3}$ values of Hasouna groundwater reflect soils more barren in the dry periods, while low $\Delta^{17}O_{NO_3}$ values correspond to more fertile soils. Combining the climate record from the isotope composition of the water with the $\Delta^{17}O_{NO_3}$ data, elevated $x[NO_3^-]_{atm}$ values are correlated to less negative δD_{H_2O} and $\delta^{18}O_{H_2O}$ values (see groundwater samples #152 vs. #165 in Figs. 4 and 7b). This relationship traces longer lasting dry periods and more barren soils for these dry periods at relatively warmer climate conditions.

6 Conclusions

In the present study we used an integrated hydrogeochemical and isotope approach to trace the origin of NO_3^- and to reconstruct the paleoclimatic conditions during recharge of Saharan groundwater in the area of Hasouna, Libya. We applied the outstanding feature of $\Delta^{17}O_{NO_3}$ values to trace atmospheric NO_3^- as the ^{17}O-excess of dissolved NO_3^- is not being affected by terrestrial fractionation processes (MDF) (Kendall and Doctor, 2004). Our ^{17}O-excess data clearly show that in the present Saharan groundwater up to 20 mol% of the dissolved NO_3^- originates from the atmosphere, with the remaining NO_3^- related to microbial sources (Table 1). To our knowledge, this is the first study where ^{17}O-excess of NO_3^- is measured in paleo groundwater, verifying that $\Delta^{17}O_{NO_3}$

values survived up to thousands of years and can be still used to estimate $NO_{3,atm}^-$ proportion of total dissolved NO_3^- during ancient recharge. Aerobic conditions documented by the presence of dissolved O_2 and the isotope composition of dissolved sulfate within the Saharan aquifer have allowed dissolved NO_3^- from paleo recharge to persist until present. This nitrogen trap has formed a still underestimated N reservoir for N-cycling and balancing (see also Gates et al., 2008). The NO_3^- content within the aquifer is predetermined by paleo recharge conditions. Thus, for the management of water supply by using Saharan groundwater from Hasouna well fields, elevated NO_3^-concentrations have to be considered as a long-lasting challenge.

The assumption of groundwater mixing within the aquifer seems to be reasonable, considering that paleo groundwater with a huge variability in salinity is regionally documented. For instance, for the Zimam aquifer with enhanced salinities and elevated NO_3^- concentrations up to 1.1 mM (El-Baruni et al., 1985; located close to #152), significant leakage into the underlying Cambro-Ordovician sandstone aquifer through fractures in limestone and dolostone is postulated (Binsariti and Saeed, 2000). To understand the groundwater evolution in more detail, a sophisticated modeling approach using more refined age models and all respective hydrogeochemical parameters must be considered.

An evaporation trend is reflected by neither solution chemistry nor the δD_{H_2O}–$\delta^{18}O_{H_2O}$ relationship. Low d-excess as well as low δD_{H_2O} and $\delta^{18}O_{H_2O}$ values clearly indicate that the groundwater of the Hasouna basin was recharged under cooler and more humid climate compared to the current conditions along the coastal areas of Libya. The negative correlation between $\Delta^{17}O_{NO_3}$ values and reciprocal NO_3^- concentrations traces longer lasting dry periods, and more barren soils corresponding to warmer climate conditions. Past alternating arid periods and strong precipitation events occurred. The accumulated $NO_{3,atm}^-$ is washed out from plant or soil surfaces. Subsequently, rapid infiltration through the subsurface without significant evaporation of water had been recharged the Saharan paleo groundwater of Hasouna.

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Table 1. Composition of Saharan paleo groundwater from wells of Hasouna area (Libya). No.: well number (see Fig. 1). T: Temperature in °C. [ ]: Concentrations are given in mM, except for $O_{2(aq)}$ in $\mathrm{mg\,L^{-1}}$. Δ_{eq}: Derivation from electrical neutrality in meq %. Site positioning of the wells are given in coordinates X and Y and well depths, D, in meter. $\delta^{18}O_{H_2O}$ and δD_{H_2O} values of the groundwaters are given in ‰ (VSMOW). $\delta^{34}S_{SO_4}$ and $\delta^{18}O_{SO_4}$ values for the isotope composition of dissolved sulfate are related to VCDT and VSMOW standard, respectively, and given in ‰. $\delta^{15}N_{NO_3}$, $\delta^{18}O_{NO_3}$, $\delta^{17}O_{NO_3}$ and $\Delta^{17}O_{NO_3}$ values of the dissolved NO_3^- are given in ‰ relative to the AIR and VSMOW standard, respectively. $x[NO_3^-]_{atm}$: proportion of dissolved NO_3^- from atmospheric origin in respect to total dissolved NO_3^- in %.

No.	T	pH	[Ca^{2+}]	[Mg^{2+}]	[Sr^{2+}]	[Na^+]	[K^+]	[$Si(OH)_4$]	[SO_4^{2-}]	[Cl^-]	[HCO_3^-]	[NO_3^-]	[$O_{2(aq)}$]	Δ_{meq}	X	Y	D
13	33.0	6.66	2.48	1.33	0.0129	4.23	0.143	0.22	1.63	4.63	3.26	0.54	n.a.	1.5	466 214	3 200 767	535
32	33.2	6.85	2.64	1.30	0.0167	6.64	0.157	0.25	1.77	5.91	3.19	0.76	n.a.	5.0	448 816	3 204 106	499
39	32.7	6.85	2.94	1.49	0.0170	7.42	0.149	0.23	1.83	6.50	3.80	0.95	4.3	5.3	456 039	3 196 409	345
51	29.6	6.74	3.03	1.35	0.0184	9.24	0.149	0.21	2.26	8.43	2.79	0.87	n.a.	4.8	461 602	3 180 497	555
60	30.6	6.54	3.95	1.73	0.0248	12.90	0.171	0.22	2.99	11.21	4.10	1.27	n.a.	4.4	471 372	3 171 846	539
72	33.0	7.12	3.09	1.35	0.0186	8.61	0.136	0.21	2.20	8.71	2.88	1.31	n.a.	1.1	450 790	3 188 993	550
84	35.1	6.79	2.31	1.00	0.0127	5.52	0.136	0.23	1.34	4.43	3.48	0.69	6.5	4.6	434 200	3 202 598	500
89	30.7	7.11	3.63	1.43	0.0200	10.43	0.140	0.24	3.06	8.51	2.71	1.48	5.5	5.2	440 533	3 182 417	453
100	29.9	7.08	2.13	1.19	0.0239	4.57	0.136	0.22	1.50	4.32	3.15	0.69	n.a.	1.1	435 694	3 222 835	500
121	34.4	7.05	3.45	1.41	0.0201	12.57	0.123	0.22	2.63	11.11	3.31	0.81	6.8	4.9	428 000	3 193 342	500
126	30.4	7.18	3.75	1.76	0.0223	13.43	0.146	0.21	3.52	10.74	3.03	1.50	5.4	5.4	431 590	3 186 822	500
134	29.3	6.76	3.25	1.38	0.0192	10.26	0.175	0.21	2.91	7.81	3.00	1.27	4.8	5.3	434 819	3 175 353	500
138	28.9	7.24	2.74	1.06	0.0138	6.67	0.113	0.21	2.14	4.60	3.48	0.88	5.6	4.6	436 464	3 169 606	500
139	28.9	7.46	2.28	0.84	0.0129	4.94	0.091	0.21	1.72	3.78	2.51	0.88	n.a.	3.4	437 292	3 168 351	500
145	29.8	7.00	3.29	2.18	0.0189	9.31	0.128	0.22	2.83	8.13	3.61	1.24	n.a.	4.9	442 758	3 161 113	417
149	28.1	7.40	3.01	1.45	0.0175	8.47	0.133	0.21	2.69	7.60	2.54	1.18	n.a.	2.7	443 135	3 171 020	500
151	28.3	7.00	4.52	2.67	0.0252	13.53	0.173	0.21	3.99	12.25	3.61	1.70	5.7	5.3	446 133	3 171 021	500
152	28.8	7.03	4.51	2.66	0.0275	14.51	0.212	0.24	4.32	13.87	2.51	1.84	5.1	4.4	447 659	3 171 097	500
154	27.2	7.08	3.18	1.50	0.0200	9.95	0.156	0.23	2.93	8.18	3.03	1.18	n.a.	3.6	453 209	3 147 514	524
165	28.1	7.24	2.15	0.63	0.0105	3.47	0.058	0.26	1.53	1.92	2.76	0.59	n.a.	4.8	461 003	3 133 483	500
179	28.1	7.06	3.74	1.10	0.0179	9.57	0.136	0.22	3.20	7.67	3.11	1.20	n.a.	3.0	471 484	3 115 183	343
181	29.7	7.03	3.08	0.91	0.0152	8.89	0.127	0.21	2.86	7.49	2.95	1.02	n.a.	−0.5	473 701	3 112 417	323
286	28.6	7.02	3.34	1.02	0.0168	9.48	0.130	0.22	2.82	7.70	2.87	1.07	n.a.	3.3	474 363	3 114 298	500
372	27.3	7.37	3.37	1.18	0.0207	10.37	0.130	0.24	3.01	8.79	2.79	1.36	n.a.	1.9	488 456	3 132 366	400
384	29.0	7.40	2.69	0.79	0.0151	5.65	0.189	0.24	1.61	4.73	2.98	0.78	n.a.	4.9	493 410	3 115 655	500
442	30.8	7.01	2.39	1.20	0.0150	4.99	0.131	0.22	1.46	4.65	3.23	0.79	n.a.	3.3	460 267	3 205 047	332
453	34.6	6.82	2.15	1.21	0.0131	5.79	0.141	0.24	1.77	4.52	3.87	0.47	n.a.	1.2	439 845	3 232 454	453
478	29.8	7.01	3.06	0.77	0.0225	6.61	0.115	0.22	2.99	5.19	2.36	0.71	n.a.	0.7	463 888	3 109 085	451

n.a.: not analysed

Table 1. Continued.

No.	$SI_{calcite}$	SI_{gypsum}	$\delta^{18}O_{H_2O}$	δD_{H_2O}	$\delta^{34}S_{SO_4}$	$\delta^{18}O_{SO_4}$	$\delta^{15}N_{NO_3}$	$\delta^{18}O_{NO_3}$	$\delta^{17}O_{NO_3}$	$\Delta^{17}O_{NO_3}$	$x[NO_3^-]_{atm}$
13	−0.50	−1.40	−9.75	−73.2	n.a.	n.a.	9.1	6.9	4.1	0.5	2.0
32	−0.31	−1.37	−9.68	−71.8	n.a.	n.a.	8.4	8.3	6.1	1.8	7.1
39	−0.20	−1.33	−9.72	−72.0	n.a.	n.a.	8.5	13.4	9.5	2.5	10.1
51	−0.49	−1.24	−9.17	−67.6	n.a.	n.a.	7.9	10.4	8.0	2.6	10.4
60	−0.44	−1.08	−8.75	−65.6	n.a.	n.a.	7.4	11.7	10.0	3.9	15.7
72	−0.04	−1.25	−9.46	−67.0	n.a.	n.a.	7.4	13.5	10.7	3.7	14.7
84	−0.34	−1.50	−9.77	−69.0	9.6	9.4	8.9	7.6	4.9	0.9	3.8
89	−0.07	−1.07	−9.51	−69.5	10.9	11.7	7.2	12.3	10.9	4.5	18.0
100	−0.19	−1.48	n.a.	n.a.	n.a.	n.a.	8.5	7.6	4.7	0.7	3.0
121	−0.02	−1.17	−9.39	−68.3	9.3	9.2	8.3	10.4	7.4	2.0	8.0
126	0.04	−1.04	−9.15	−69.5	11.0	11.3	6.9	15.0	12.8	5.0	20.0
134	−0.43	−1.13	−9.58	−70.4	11.0	11.2	6.6	16.1	12.6	4.2	16.9
138	0.07	−1.26	−9.94	−71.6	11.1	10.3	7.2	13.6	9.7	2.6	10.5
139	0.10	−1.38	−9.97	−73.1	n.a.	n.a.	7.1	11.9	8.9	2.7	10.8
145	−0.10	−1.16	−9.52	−69.8	10.3	9.6	7.1	14.7	11.3	3.7	14.6
149	0.10	−1.17	−9.69	−69.0	n.a.	n.a.	7.1	15.4	12.1	4.1	16.4
151	−0.04	−0.95	−9.32	−68.0	10.1	10.6	7.0	17.4	13.7	4.7	18.6
152	−0.16	−0.93	−9.20	−67.5	10.2	10.6	7.5	14.8	12.4	4.7	18.8
154	−0.15	−1.13	−9.30	−67.4	n.a.	n.a.	8.6	16.4	11.1	2.6	10.3
165	−0.09	−1.42	−9.90	−72.8	n.a.	n.a.	7.7	9.8	6.1	1.0	4.0
179	−0.08	−1.03	−9.26	−68.3	11.1	10.5	8.0	10.9	7.6	1.9	7.7
181	−0.18	−1.13	−9.08	−69.3	n.a.	n.a.	8.7	10.6	7.6	2.1	8.4
286	−0.18	−1.11	−9.17	−68.8	n.a.	n.a.	8.5	12.9	9.1	2.4	9.6
372	0.13	−1.09	−9.09	−64.6	n.a.	n.a.	8.9	10.2	7.2	1.9	7.6
384	0.18	−1.36	n.a.	n.a.	n.a.	n.a.	8.6	8.1	5.7	1.5	6.0
442	−0.19	−1.46	−9.74	−72.0	n.a.	n.a.	8.4	9.8	5.5	0.4	1.6
453	−0.31	−1.43	−9.62	−70.3	n.a.	n.a.	8.6	9.1	5.8	1.1	4.3
478	−0.28	−1.09	n.a.	n.a.	n.a.	n.a.	7.8	9.1	6.5	1.8	7.1

n.a.: not analysed

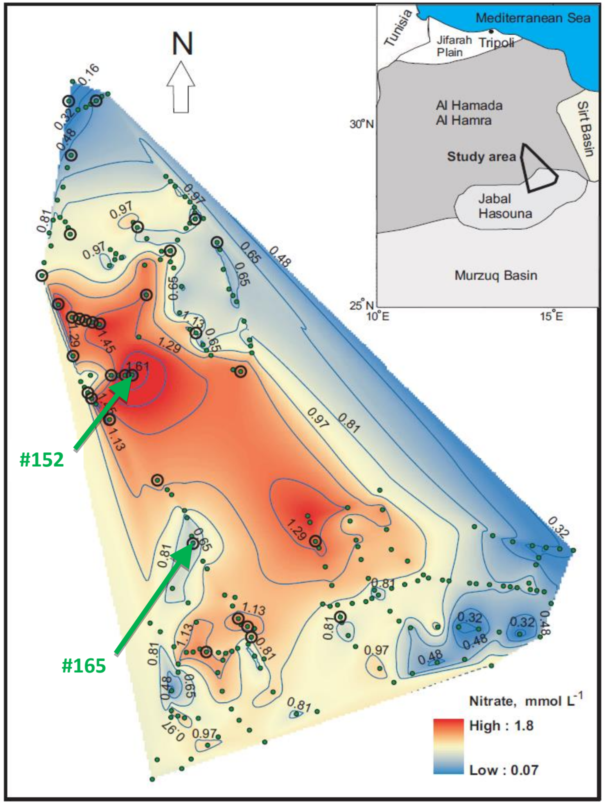

Fig. 1. Sampling sites (○; $n = 28$) and distribution of nitrate in paleo groundwater from Hasouna, Libya. Isolines are obtained from a total of 57 NO_3^- analyses of paleo groundwater from wells (●).

Title Page
Abstract
Introduction
Conclusions
References
Tables
Figures
◀◀
▶▶
◀
▶
Back
Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

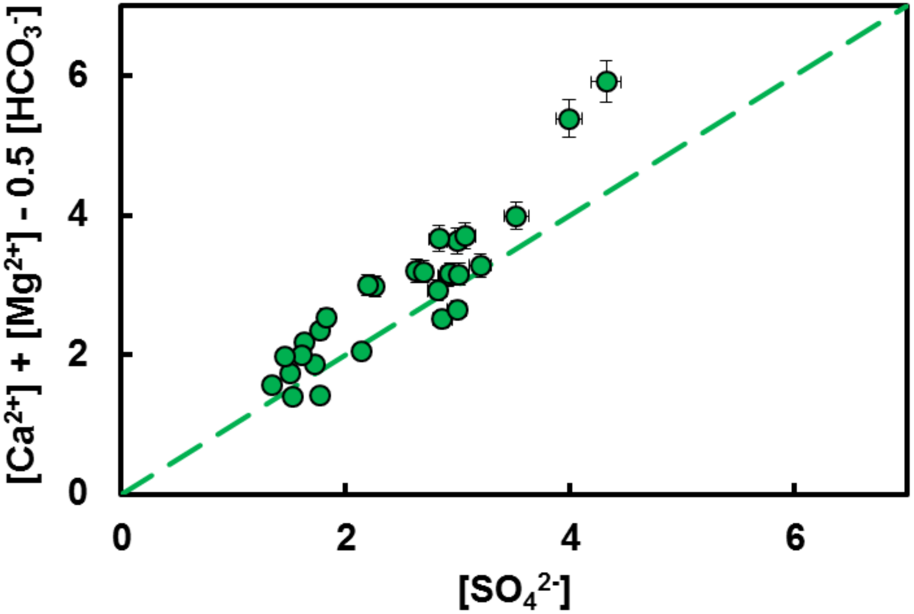

Fig. 2. Calcium concentration reduced by the proportion gained from calcium carbonate dissolution by considering dolostone dissolution ($[Ca^{2+}] + [Mg^{2+}] - 0.5\ [HCO_3^-]$, mM) vs. the concentration of dissolved sulfate, $[SO_4^{2-}]$ (mM). The linear relationship with a slope of 1 fits the composition of the Hasouna groundwaters quite well and reflects the dissolution of calcium sulfate minerals, like gypsum.

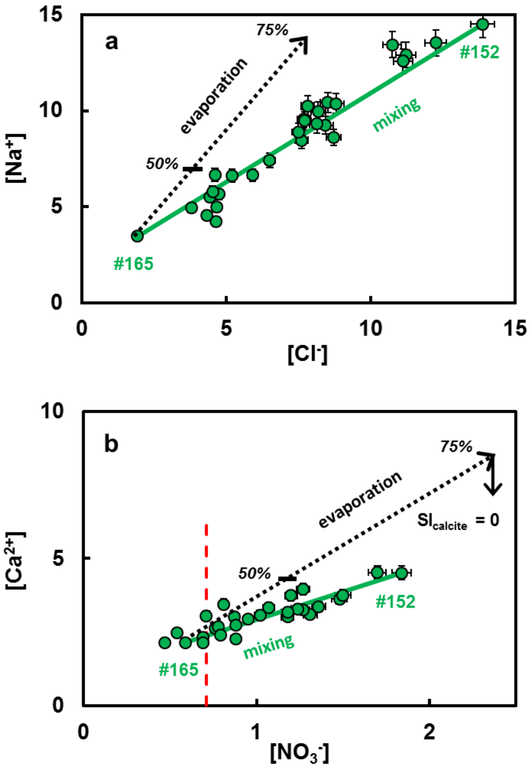

Fig. 3. Chemical composition of groundwater from Hasouna, Libya. **(a)** Na^+ vs. Cl^- concentration. **(b)** Ca^{2+} vs. NO_3^- concentration. Values are given in mM. Solid green lines: Mixing between end-member solutions #165 and #152 with lowest and highest ion concentrations, respectively. Dotted arrows: Chemical trend for evaporation of solution #165, where 50 and 75 % denote ion concentrations at respective loss of H_2O by evaporation. Solid arrow: Decrease of Ca^{2+} concentration by considering calcite precipitation to reach $SI_{calcite} = 0$. Dashed red line: MCL for NO_3^- in drinking water according to WHO (WHO, 2004).

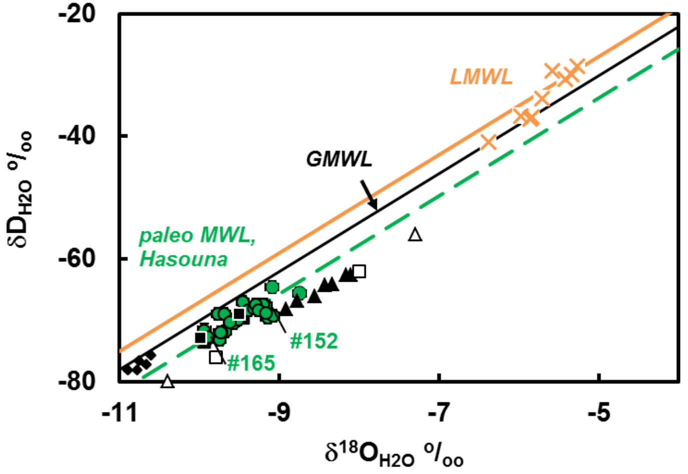

Fig. 4. Stable hydrogen and oxygen isotope composition of groundwater from north Africa. Paleo groundwater displays lower stable isotope values and an elevated d-excess compared to modern precipitation, which indicates recharge under cooler and more humid climate conditions vs. modern climate conditions. The analytic inaccuracies lay within the size of the symbols. Isotope composition of Modern Eastern Mediterranean seawater is out the displayed range, comprising δ^{18}O values from 0.3 to 2.5 ‰ and δD values ≈ 0 ‰ (Gat, 2010). ●: Hasouna, Libya (this study); ■: Hasouna, Libya, isotope range (Milne-Home and Sahli, 2007); □: Murzuq Basin, Libya, isotopic range (Sonntag et al., 1978); △: Arab Jamahiriya, Libya (Srdoè et al., 1980); ▲: South Tunisia (Abid et al., 2012); ♦: Wadi Ash Shati Valley, Libya (Salem et al., 1980). X: Groundwater recharged by modern precipitation close to Tripoli (own data). GMWL: Global Meteoric Water Line (δD = 8 δ^{18}O + 10; Craig, 1961). LMWL: Local Meteoric Water Line for Sfax metereological station, southern Tunisia (yellow line: δD = 8 δ^{18}O + 13; Abid et al., 2012). Paleo MWL: Paleo Meteoric Water Line estimated from isotopic data of the present study by least square method (dashed green line: Eq. 4).

Title Page
Abstract
Introduction
Conclusions
References
Tables
Figures
◀◀
▶▶
◀
▶
Back
Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

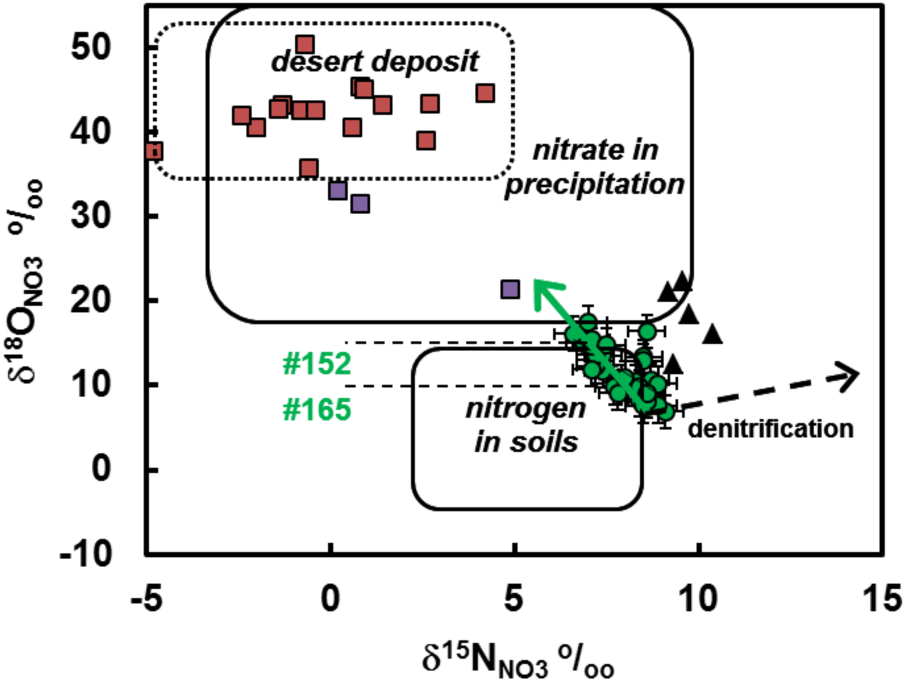

Fig. 5. $^{18}O/^{16}O$ vs. $^{15}N/^{14}N$ distribution in nitrate (adapted from Kendall, 1998). $\delta^{18}O_{NO_3}$ and $\delta^{15}N_{NO_3}$ values are referred to the VSMOW and AIR standards, respectively. ●: Hasouna groundwater (this study), where the solid green arrow displays an increase in NO_3^- concentration; ▲: Hasouna groundwater (Milne-Home and Sahli, 2007); 🟥 and 🟪: NO_3^--rich deposit of Atacama (Chile) and Mojave desert (California), respectively (Böhlke et al., 1997).

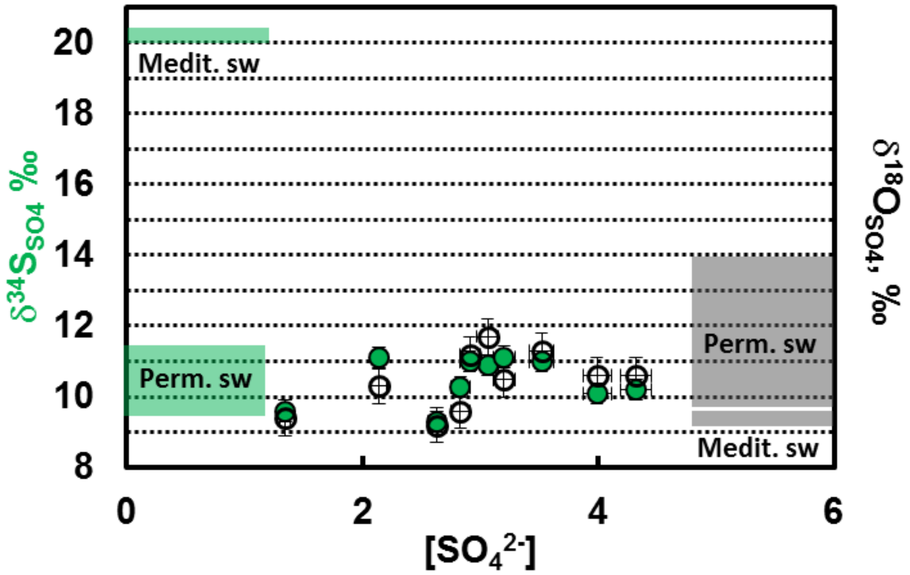

Fig. 6. The isotope composition as a function of the concentration of dissolved sulfate. Green and open circles denote $\delta^{34}S_{SO_4}$(VCDT) and $\delta^{18}O_{SO_4}$ (VSMOW) values, respectively. The presented $\delta^{34}S_{SO_4}$ and $\delta^{18}O_{SO_4}$ ranges of dissolved sulfate of modern Mediterranean seawater (Medit. sw) and Permian sulfate (Perm. sw) are from Böttcher et al. (1998), Böttcher (1999), Faure and Mensing (2005), Mittermayr et al. (2012), and Nielson (1979).

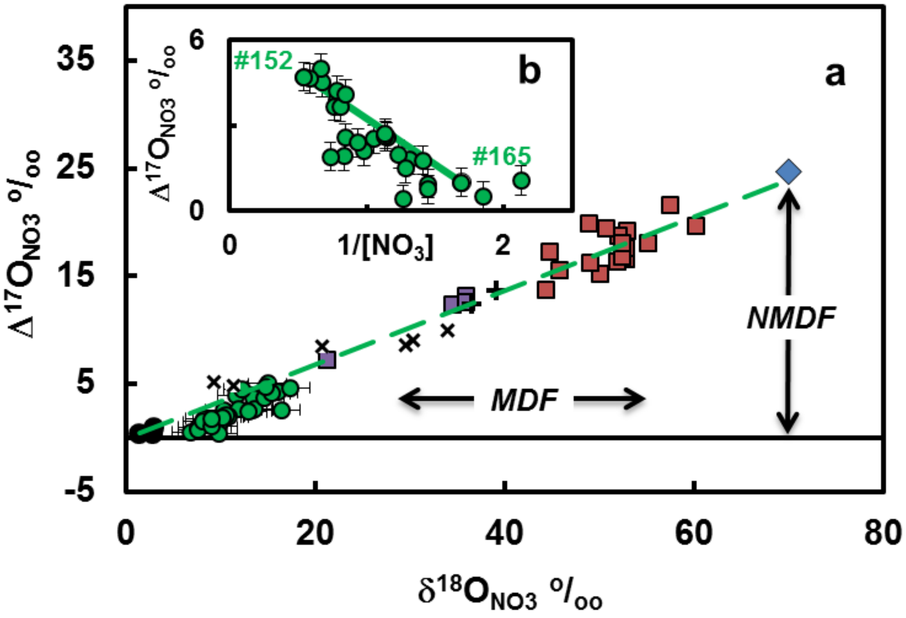

Fig. 7. (a) ^{17}O-excess ($\Delta^{17}O_{NO_3}$) vs. $\delta^{18}O_{NO_3}$ value of Hasouna groundwaters. **(b)** Mixing approach for #165 and #152 end-member solutions, where the ^{17}O-excess of dissolved NO_3^- and the reciprocal NO_3^- concentration (mM) can be followed by a linear relationship. Isotope values are related to the VSMOW standard. ●: Hasouna groundwater, Libya (this study); ■ and ■: NO_3^--rich deposit of Atacama (Chile) and Mojave desert (California), respectively (Michalski et al., 2004a). •: Groundwater from Mojave desert (Michalski et al., 2004a). **x**: Stream water from San Gorgonio and Devil Canyon at storm flow event (California; Michalski et al., 2004b). **+**: NO_3^--rich deposit of Kumutag (China; Li et al., 2010); ♦: Atmospheric photochemical NO_3^- (Michalski et al., 2004a). Solid horizontal line: Terrestrial isotope fractionation line considering MDF. Dashed green line: regression line for all given data ($\Delta^{17}O_{NO_3} = 0.342\ \delta^{18}O_{NO_3}$; $R^2 = 0.978$).