



Sources of aerosol nitrate to the Gulf of Aqaba: Evidence from $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate and trace metal chemistry

Scott D. Wankel^{a,b,*}, Ying Chen^e, Carol Kendall^b, Anton F. Post^d, Adina Paytan^c

^a Department of Organismic and Evolutionary Biology, 16 Divinity Avenue, Room 3092, Harvard University, Cambridge, MA 02138, United States

^b United States Geological Survey, 345 Middlefield Road, MS 434, Menlo Park, CA 94025, United States

^c University of California Santa Cruz, Institute of Marine Sciences, 1156 High Street, Santa Cruz, CA 95064, United States

^d H. Steinitz Marine Biological Laboratory, Hebrew University, Eilat, Israel

^e Center for Atmospheric Chemistry Study Department of Environmental Science and Engineering Fudan University, Shanghai 200433, China

ARTICLE INFO

Article history:

Received 25 June 2008

Received in revised form 27 January 2009

Accepted 27 January 2009

Available online 10 February 2009

Regional terms:

Israel

Gulf of Aqaba

Eilat

Keywords:

Nitrogen cycle

Nitrate

Aerosols

Nitrogen isotopes

Oxygen isotopes

Atmospheric particulates

ABSTRACT

The nitrogen (N) and oxygen (O) isotopic composition ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) of water soluble aerosol nitrate was measured in aerosol samples collected in Eilat, Israel, from August 2003 to November 2004. During this period $\delta^{15}\text{N}$ values ranged from -6.9% to $+1.9\%$ and $\delta^{18}\text{O}$ from $+65.1\%$ to $+84.9\%$ and exhibited strong seasonal variability with higher average $\delta^{15}\text{N}$ values observed in the summer and higher $\delta^{18}\text{O}$ values in the winter. Nitrate isotopic composition was compared with bulk chemical composition and extractable ion and trace metals on co-collected samples linking nitrate isotopic composition to various sources of aerosols to this region. Atmospheric processes impacting the isotopic signatures of nitrate were also considered.

Based on back trajectory analyses, the majority of NO_3^- came from air masses originating over the Mediterranean Sea (34%), Western Europe (20%) and the local Negev desert (19%), which contain a larger anthropogenic imprint compared to southern and eastern air masses which are dominated by mineral dust. The potential role of reactive mineral dust aerosols as a regulator of NO_3^- isotopic composition is considered; however, based on factor analysis, neither $\delta^{15}\text{N}$ nor $\delta^{18}\text{O}$ were associated with mineral dust components (such as Fe or Al), but rather with anthropogenic indicators such as Cu, Cd, P and Pb. Seasonality in primary NO_x cycling reactions driven by seasonal changes in solar radiation, relative humidity and temperature also influence the observed isotopic signatures. The isotope data, together with trace element analysis, suggests that seasonal variations in both $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ are related to both NO_x source and transport processes as well as NO_x chemical reactions in the atmosphere.

The flux-weighted $\delta^{15}\text{N}$ of aerosol NO_3^- in this area averaged -2.6% making aerosol deposition a substantial contributor of low $\delta^{15}\text{N}$ nitrogen to the oligotrophic waters of the Gulf of Aqaba. Thus, while the flux of atmospheric N to oligotrophic marine systems is smaller than the upward flux of NO_3^- from deep water, it nonetheless represents an important source of new N having a low $\delta^{15}\text{N}$. Further, if this low $\delta^{15}\text{N}$ signature is not considered, it could interfere with N-fixation estimates based on isotopic composition of dissolved nitrate or particulate organic nitrogen. Thus, atmospheric deposition should be constrained for accurate estimates of marine N-fixation when based on $\delta^{15}\text{N}$ in the ocean. Indeed, in the Gulf of Aqaba, low upper water $\delta^{15}\text{N}_{\text{NO}_3}$ values could be related to inputs of atmospheric NO_3^- as well as N-fixation.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Atmospheric deposition to the ocean represents a potentially important new source of nitrogen supporting primary production, particularly in oligotrophic regions of the world (Chen and Siefert, 2004; Duarte et al., 2006; Duce et al., 1991; Spokes and Jickells, 2005). Fluxes of atmospheric nitrogen (N) may occur in many forms

including nitrate (as aerosol NO_3^- or HNO_3 vapor), organic nitrogen (N_{org}) and ammonium (NH_4^+) and may fall as either wet or dry deposition. In especially arid regions of the world, such as the Red Sea, dry deposition, in the form of aerosolized particulates, represents the most dominant (and often the only) form of atmospheric N deposition (Kouvarakis et al., 2001). The chemical composition of these particulate aerosols often reflects their origin, such as mineral dust from deserts, sea salt, industrial processing byproducts or vehicular exhaust. Studies of aerosol deposition to the ocean have been made in the open Atlantic and Pacific oceans (e.g., Arimoto et al., 1995; Baker et al., 2003, 2007; Chen and Siefert, 2004) as well as more regional seas including, but not limited to, the Mediterranean Sea (Bonnet and

* Corresponding author. Present permanent address: Biology Labs, 16 Divinity Avenue, Room 3092, Cambridge, MA 02138, United States. Tel.: +1 617 495 9156; fax: +1 617 495 8848.

E-mail address: swankel@oeb.harvard.edu (S.D. Wankel).

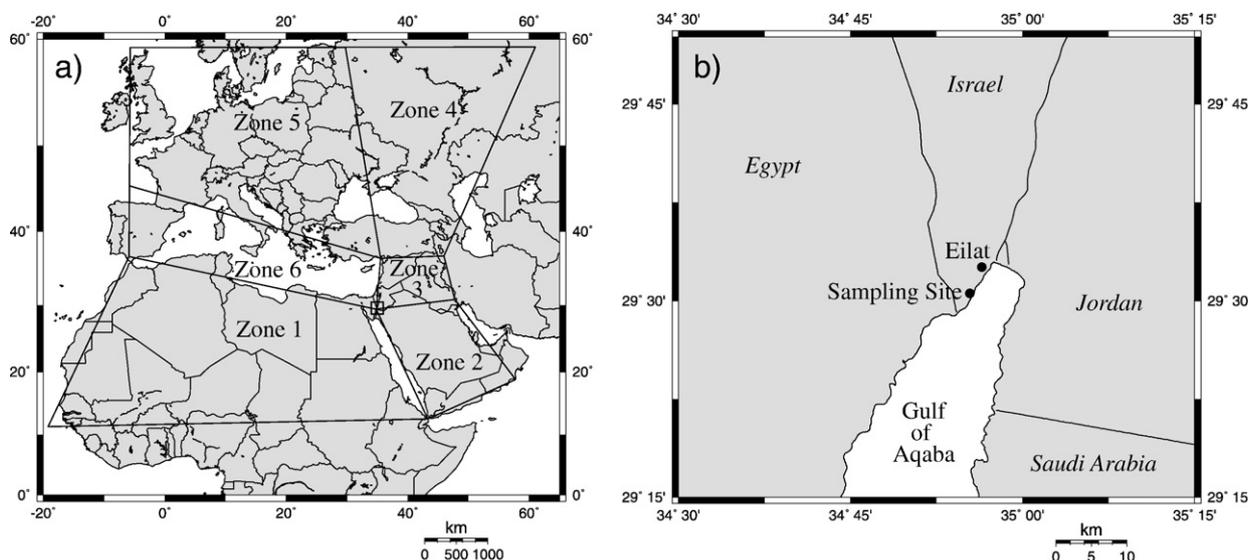


Fig. 1. a) Map of air mass source regions based on 5-day back trajectories binned into six zones and b) map of local aerosol sample collection site in Eilat, Israel.

Guieu, 2006; Guieu et al., 1997; Herut et al., 2001; Kocak et al., 2005; Migon et al., 1997; Ridame et al., 1999).

This study uses the dual isotopic composition of aerosol NO_3^- ($\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$) as a tracer of aerosol nitrate sources by analyzing its relationship with soluble and bulk major ions and trace metal chemistry of aerosols deposited in the Gulf of Aqaba. Nitrate N stable isotopic composition has been largely viewed as reflecting NO_x ($\text{NO} + \text{NO}_2$) sources, because nitrogen atoms are conserved during transformations of NO_x to NO_3^- in the atmosphere (Freyer, 1978; Freyer, 1991; Hastings et al., 2003; Heaton, 1990; Moore, 1977). On the other hand, $\delta^{18}\text{O}$ of aerosol NO_3^- is considered to be mostly related to oxidation pathways in the atmosphere (Freyer et al., 1993; Hastings et al., 2003, 2004; Michalski et al., 2003; Morin et al., 2007). By using the N and O isotopic composition we aim to better understand the variability of atmospheric N sources to the Gulf of Aqaba, which in turn will help to evaluate the impact of future urban development and industrialization on these inputs of N to this and other oligotrophic ocean regions.

To date little work has been done to characterize the dual isotopic composition of atmospheric N deposition to the surface ocean and no such data is available for the Gulf of Aqaba, an area with significant atmospheric deposition and low surface water nitrate (NO_3^-) concentrations. Specifically, the Gulf of Aqaba represents a small-scale, easy to access, regional analog of larger oligotrophic systems. It is surrounded by arid lands (African, Arabian and local Negev deserts; Fig. 1) and receives negligible river discharge or atmospheric wet deposition (Ganor and Foner, 1996; Reiss and Hottinger, 1994). With the exception of biological N-fixation, atmospheric aerosol deposition largely represents the only important external input of new N into this ecosystem. Using a suite of aerosol major ion and trace metal soluble and bulk concentrations and air mass back-trajectories together with variations in $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$, we evaluate potential sources of atmospherically derived N to this region and the utility of the isotopic composition of nitrate as a source fingerprinting tool in arid regions. To this end, we explore relationships of nitrate isotopic composition with aerosol source indicators for mineral dust and anthropogenic pollutants in order to shed light on whether $\delta^{15}\text{N}$ and/or $\delta^{18}\text{O}$ are reflective of NO_x sources, atmospheric chemical processes such as oxidation pathway, gas phase or surface chemistry or a combination of these parameters.

2. Background on atmospheric nitrate isotopic composition

Nitrate (including both particulate aerosol NO_3^- and vapor phase HNO_3) represents the primary sink of atmospheric NO_x (e.g., $\text{NO} + \text{NO}_2$) which originates from both natural and anthropogenic sources

(Fig. 2). Oxidation of NO_x to NO_3^- takes place via complex interactions between NO_x and ultimately two primary oxidants, ozone (O_3) and OH radicals, with both reactions resulting in a rapid transfer of oxygen atoms from OH and O_3 to NO_x as noted by empirical (Savarino et al., 2007), modeling (Lyons, 2001) and isotopic studies (Michalski et al., 2003). These oxidation reactions are influenced by many factors including temperature, humidity, solar radiation and the availability of reactive aerosol surfaces. For example, because oxidation of NO_x by OH is photochemical, this reaction is generally more important during summer, when days are longer, ultraviolet radiation is highest (Rohrer and Berresheim, 2006) and other pathways are inhibited. As another example, mineral dust can serve as an important surface for reactions, such as N_2O_5 hydrolysis (Fig. 2), and the production of aerosol NO_3^- (Mogili et al., 2006).

Because N atoms are conserved throughout these oxidation reactions, the isotopic composition of the source of N to the NO_x pool is generally considered to be retained in the sink term of aerosol

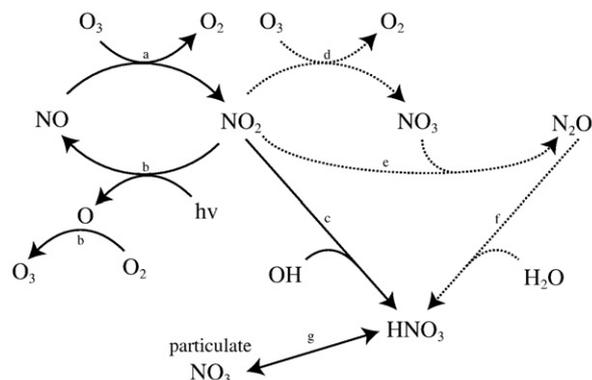


Fig. 2. Simplified depiction of NO_x cycling pathways leading to the formation of aerosol HNO_3 (or NO_3^-). During the daytime (solid lines) cycling between NO and NO_2 is rapid. The oxidation of NO to NO_2 (reaction a) is controlled by O_3 , while the breakdown of NO_2 back to NO (reaction b) is photolytic and results in the production of O_3 . The primary daytime sink of NO_x is the oxidation of NO_2 to HNO_3 by the hydroxyl radical (reaction c). Thus, the oxygen isotopic composition of HNO_3 formed from this pathway reflects the contribution of 2/3 O_3 and 1/3 OH. During the nighttime (dashed lines), oxidation of NO_2 to NO_3 is again carried out by O_3 (reaction d) with both NO_2 and NO_3 reacting to form N_2O_5 (reaction e). N_2O_5 is then hydrolyzed (reaction f) to form HNO_3 , which again serves as a sink for atmospheric NO_x . The oxygen isotopic composition of HNO_3 formed from this pathway reflects the contribution of 5/6 O_3 and 1/6 H_2O . Finally, a dynamic equilibrium exists between HNO_3 vapor and particulate aerosol NO_3^- (reaction g), with deposition of the particulate phase generally serving the dominant role in delivery of atmospheric NO_3^- to the earth's surface.

NO_3^- . However, short term environmental variations (e.g. temperature, relative humidity, etc.) can lead to shifts in equilibrium between various components of the NO_x pool which may have some impact on isotopic composition. For example, low relative humidity and high temperatures will cause a shift in the equilibrium between HNO_3 and particulate NO_3^- (Morino et al., 2006), such that particulate NO_3^- , which represents the major sink for aerosol deposition, would be isotopically lighter than under cooler, wetter conditions. Similarly, under high O_3 conditions, the equilibrium between NO and NO_2 is shifted towards NO_2 (Fig. 2), a primary precursor of HNO_3 , such that $\delta^{15}\text{N}_{\text{NO}_3}$ values would be lower than under low O_3 conditions (Freyer et al., 1993).

Reported values of $\delta^{15}\text{N}$ of atmospherically derived NO_3^- , from both wet and dry deposition, range widely (Elliott et al., 2007; Hastings et al., 2003, 2004; Heaton, 1990; Heaton et al., 2004; Kendall, 1998; Russell et al., 1998; Yeatman et al., 2001). In large part this can be explained by variations in the $\delta^{15}\text{N}$ values for both natural and anthropogenic NO_x sources. For example, $\delta^{15}\text{N}$ of NO_x from coal power plants tend to have higher $\delta^{15}\text{N}$ values (+6 to +13‰; (Heaton, 1990)), while vehicle exhaust has been shown to have lower $\delta^{15}\text{N}$ values (−13 to +6‰; (Amman et al., 1999; Heaton, 1990; Moore, 1977)). Another study showed that both agricultural and urban emissions have elevated values as high as +19‰ being characteristic of such anthropogenic N sources (Yeatman et al., 2001). Indeed, Elliott et al. (2007) demonstrated a strong correlation between wet deposition $\delta^{15}\text{N}_{\text{NO}_3}$ and stationary source (e.g., power plant facilities) NO_x emissions in the northeastern US, with higher $\delta^{15}\text{N}$ values (up to +3.2‰) found in areas impacted by higher NO_x emissions.

$\delta^{18}\text{O}$ values of atmospheric nitrate are generally found to fall between +65 and +95‰ (Hastings et al., 2003, 2004; Kendall, 1998; Kendall et al., 2007) (though lower values were reported using earlier techniques, which may have been compromised due to analytical interferences; see (Revesz and Böhlke, 2002)). The range of $\delta^{18}\text{O}$ values, which are largely from studies in northern temperate latitudes, exhibits a strong and consistent seasonality (with higher values during winter and lower during the summer). This seasonality has been interpreted as reflecting variability in the relative importance of the dominant oxidation pathways which are influenced by the changing amount of solar radiation (and to some degree temperature) throughout the year. It has been suggested that ozone, which is the main source of oxygen atoms for atmospheric NO_3^- , donates approximately 5/6 of the NO_3^- oxygen atoms during winter and only 2/3 during summer (Hastings et al., 2003; Michalski et al., 2003; Savarino et al., 2008). During summer, longer days allow increased photolysis of NO_2 and NO_3 lessening the importance of the N_2O_5 hydrolysis pathway. In addition, higher UV during summer leads to increased OH concentrations and a higher proportion of oxidation via OH (Rohrer and Berresheim, 2006). Both phenomena promote more incorporation of oxygen atoms from OH (generally thought to have a low $\delta^{18}\text{O}$, near atmospheric water $\delta^{18}\text{O}$ (Dubey et al., 1997)) and consequently result in lower $\delta^{18}\text{O}_{\text{NO}_3}$ values observed during summer. Thus, it is generally believed that $\delta^{15}\text{N}$ is most reflective of sources of NO_x , while $\delta^{18}\text{O}$ tends to reflect NO_x oxidation chemistry.

3. Methods

3.1. Aerosol sample collection and chemical analyses

Aerosol samples were collected using a Total Suspended Particle Sampler placed on a roof (about 10 m above the ground level) at the Inter-University Institute of Marine Sciences (IUI) in Eilat, a few meters off the northwest coast of the Gulf of Aqaba (29°31'N, 34°55'E, Fig. 1). Aerosol samples were taken at least once/week over a 24 h period with an air flow of 2.5–2.8 $\text{m}^3 \text{h}^{-1}$. The sampler collected four samples simultaneously: two filter samples were used for water extraction and strong acid digestion to measure soluble and bulk chemical components, respectively, while one of the other filters was used for nitrate isotope analyses. Samples were extracted with Milli-Q

water (of constant $\delta^{18}\text{O}$) following the procedure described in Chen et al. (2006) and approximately 30 ml of the extraction solution was filtered, refrigerated and kept in the dark for NO_3^- isotope analysis.

The sampling technique was designed to collect the NO_3^- fraction associated with particulate aerosol only; HNO_3 vapor, which would have passed through the filter was not targeted in the sampling strategy. Potential losses or overestimates of aerosol NO_3^- due to NO_3^- volatilization or HNO_3 adsorption, respectively, were minimized by the use polycarbonate filters rather than Teflon, quartz or cellulose filters which have been shown to exhibit extensive losses at temperatures >25 °C (Schaap et al., 2004) and substantial HNO_3 adsorption (Savoie and Prospero, 1982; Schaap et al., 2004). Furthermore it has been shown that evaporative losses are <5% at high mass loadings (>144 $\mu\text{g cm}^{-2}$ filter) as was consistently observed in our study (Chang et al., 2000; Wang and John, 1988).

Soluble anions (F^- , formate, oxalate, methansulfonic acid, Cl^- , Br^- , SO_4^{2-} , NO_2^- , NO_3^- , and PO_4^{3-}) and cations (NH_4^+ , Na^+ , K^+ , Mg^{+2} , and Ca^{+2}) were measured via ion chromatography while soluble trace elements were measured via ICP-OES (Al, Ca, Cu, Fe, K, Mg, Na, Ni, P, Pb, and Zn). Bulk trace elemental analysis was carried out after a strong-acid microwave digestion and measurement on an ICP-MS (Al, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Se, V, Zn). For detailed collection and analytical procedures see Chen et al. (2008).

3.2. Nitrate isotopes

Nitrate N and O stable isotopic composition was analyzed using the denitrifier method (Sigman et al 2001; Casciotti et al 2002). Internationally recognized nitrate isotope standards USGS 34, USGS 35 and IAEA-N3 (Böhlke et al., 2003) were used for necessary analytical corrections along with an internal lab nitrate standard. Analytical precision based on duplicate sample analyses was $\pm 0.3\%$ for both $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$. Because atmospheric nitrate contains a large mass-independent ^{17}O anomaly (Michalski et al., 2004a; Michalski et al., 2003), use of the denitrifier method for $\delta^{15}\text{N}$ measurements requires that a correction be made for the contribution of mass-independent ^{14}N - ^{14}N - ^{17}O to the analyte N_2O (see Hastings et al (2003, 2004) for more detail). Thus, $\delta^{15}\text{N}$ values were corrected based on measured $\delta^{18}\text{O}$ values and the relationship observed by others (Kaiser et al., 2007; Michalski et al., 2003, 2004a, b) between $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$. On average $\delta^{15}\text{N}$ values were decreased by ~1.4‰ compared to un-corrected values.

The denitrifier method involves conversion of both NO_3^- and NO_2^- to N_2O for analysis. As such, while the $\delta^{15}\text{N}$ values reported here represent the combined pools of NO_2^- and NO_3^- , the presence of NO_2^- interferes with analyses of $\delta^{18}\text{O}_{\text{NO}_3}$ and may result in substantial errors (Casciotti and Mcilvin, 2007; Casciotti et al., 2002). Without prior removal of NO_2^- (Granger et al., 2006) or separate NO_2^- analyses and correction by mass balance (Casciotti et al., 2007; Casciotti and Mcilvin, 2007), this analytical artifact precludes the measurement of $\delta^{18}\text{O}_{\text{NO}_3}$ in samples containing substantial NO_2^- .

The analyses presented here did not include separate analysis or prior removal of NO_2^- . Hence, our $\delta^{18}\text{O}_{\text{NO}_3}$ analyses contained an analytical artifact, the magnitude of which is proportional to the amount of NO_2^- in the sample (which ranged from 0 up to 11% and averaged 3.3%) as well as the $\delta^{18}\text{O}$ of the respective NO_2^- and NO_3^- . We apply a correction to account for this artifact based on the following assumptions about the $\delta^{18}\text{O}$ of the contaminating NO_2^- and its contribution to the measured $\delta^{18}\text{O}_{\text{NO}_3}$. The samples were stored at 4 °C in the dark for approximately 120 days before isotopic analysis. Based on evidence presented by Casciotti et al (2007), we expect that NO_2^- in the sample had reached isotopic equilibrium with the water ($\delta^{18}\text{O}_{\text{water}} = -13.5\%$, measured). Assuming an equilibrium isotope effect for exchange between water and NO_2^- at 4 °C of 18‰ (Mcilvin and Casciotti, 2006) we can calculate a $\delta^{18}\text{O}$ value of ~+4.5‰ ($\pm 1\%$) for the NO_2^- in our samples. Knowing this isotope value and the NO_2^- concentration in our samples we can use an isotope mass balance

Table 1
Seasonal comparison of flux-weighted isotope values and nitrogen fluxes.

Season	Region	N	Fluxes ($\mu\text{mol m}^{-2} \text{day}^{-1}$)						$\delta^{15}\text{N}_{\text{NO}_3}$	$\delta^{18}\text{O}_{\text{NO}_3}$
			NO_3^-	NO_2^-	NH_4^+	TSN	Org N			
Summer	Mid March–mid Oct	28	31.7	1.0	17.8	57.0	6.5	-1.7	+77.3	
Winter	Mid Oct–mid March	23	38.8	1.1	21.0	70.7	9.8	-3.4	+80.5	

Mean fluxes are calculated as $\mu\text{mol m}^{-2} \text{d}^{-1}$ from each 24 h period sampled (summer = 28; winter 23). Errors are 1 standard deviation.

calculation to correct for the artifact. In addition—because the data were corrected based on $\delta^{18}\text{O}_{\text{NO}_3}$ standards, the $\delta^{18}\text{O}_{\text{NO}_2}$ needs to be converted to the $\delta^{18}\text{O}_{\text{NO}_3}$ scale (see (Casciotti and Mcilvin, 2007) for more complete discussion). We use a value of 25‰ for the fractionating branching reaction between NO_3^- and NO_2^- during the denitrifier method. Thus, depending on the proportion of NO_2^- in the sample, our initial $\delta^{18}\text{O}_{\text{NO}_3}$ values have been corrected to higher values by an average of 3.3‰ (with corrections ranging from 0.0‰ to 10.9‰). Note that the adjustments to the $\delta^{18}\text{O}$ values are too small to impact the $\delta^{15}\text{N}$ corrections discussed above. There are clearly potential errors involved in making such corrections, namely in the $\delta^{18}\text{O}$ value of NO_2^- used for the correction. We estimate the error associated with the correction to be on the order of $\pm 4.4\%$ (calculated by using an appropriate range of values for the unknown parameters used in calculating the $\delta^{18}\text{O}$ of NO_2^-). Nonetheless, because NO_2^- is generally only a very small component in most of our samples—the error associated with the correction of $\delta^{18}\text{O}_{\text{NO}_3}$ values is on average $\pm 0.4\%$ (i.e., the final correction to the $\delta^{18}\text{O}_{\text{NO}_3}$ values was much smaller than the estimate error associated with the $\delta^{18}\text{O}$ values of NO_2^-). Despite this limitation, we note that the range of values recorded is much larger than can be explained by NO_2^- interference alone, and thus we believe it represents true variability in the oxygen isotopic composition of the NO_3^- .

3.3. Back trajectory analysis

For analyzing the origins of air masses transporting aerosols, 5 day back trajectories were carried out using the NOAA HY-SPLIT program (Draxler, 2002) and samples were binned into one of six primary source zones corresponding to the region in which the air mass spent at least 60% of the time during the preceding 5 days. Back trajectories were calculated for the 700 mb surface which was suggested as the most representative surface for the mixing layer and thus most reliable for assessing both long and short range transported material available for dry deposition (Kallos et al., 1998). The air mass sectors identified were (Fig. 1): North Africa (Sahara desert, Z1), Arabian peninsula (Z2), the local region including Israel, Jordan, Syria, Iran and Iraq (Z3), Eastern Europe (Z4), Western Europe (Z5) and the Mediterranean Sea (Z6).

3.4. Flux calculations

Using a particle deposition model (Jacobson, 2004), dry deposition velocities for each sample, based on the size distribution of aerosol

particles in each specific sample, were calculated. The velocity was calculated as the sum of particle sedimentation speed in air and its deposition against a series of resistances at the air–water interface, which depend on particle size and the meteorological and physical conditions in the troposphere (see more details in (Jacobson, 2004) and (Chen et al., 2006)). The meteorological inputs for each date, including surface pressure (HPA), surface temperature (K), temperature (K) and wind speed (cm s^{-1}) at reference height (10 m) were obtained from the NOAA archived FNL METEOROGRAM database. A dust particle density of 2.6 g cm^{-3} was used (Chin et al., 2002) which is considered typical of mineral dust, which dominates aerosols in the study area. The calculated aerosol deposition speeds were combined with the concentrations (soluble fraction) of each analyzed element to estimate the elemental deposition flux. Dry deposition flux of aerosol-associated N was calculated as the product of the concentration of soluble N species in the aerosol sample and the average deposition velocity of the particles calculated for each sampling event (e.g. specific concentrations and velocities for each sampling date).

4. Discussion

4.1. Temporal and spatial patterns of N deposition

The sampling period for this study spanned just over one full year. For the purposes of temporal analysis, the data were divided into the ‘summer’ (mid March to mid October) and ‘winter’ seasons (mid October to mid March). However, due to an instrument error resulting in the loss of samples between Jan 2004 and March 2004, there is a slight bias of samples collected during summer ($n = 28$) as compared to winter ($n = 23$). Average fluxes of aerosol soluble NO_2^- and NH_4^+ were not statistically different between summer and winter, although on average higher fluxes were found during winter (Table 1) (in the discussion that follows, the term ‘statistically significant’ is used to describe values for p of 0.05 or less). In contrast, NO_3^- , total soluble N (TSN) and organic N (by difference) were statistically higher during winter than summer.

Nitrogen species fluxes varied significantly among zones (Table 2). Average NO_3^- , NO_2^- and NH_4^+ fluxes (in $\mu\text{mol m}^{-2} \text{d}^{-1}$) from air masses originating among the different zones ranged from 27 (E. Europe) to 49 (Local), 0.8 (W. Europe) to 1.5 (Arabian Desert) and from 13.8 (E. Europe) to 32.9 (Arabian Desert), respectively. Organic N and TSN also ranged from 3.8 (E. Europe) to 14.5 (Local) and 42 (E. Europe) to 78 (Local), respectively. In fact, the highest average daily fluxes of all nitrogen species originate from the three desert regions (zones 1, 2 and 3) corresponding to the high total suspended particle loads of air masses from these locations (Chen et al., 2007).

However, while the three desert zones represented the highest average daily fluxes (when considered on an individual sample basis) the contribution of N to the Gulf of Aqaba from these zones on an annual basis was not the highest. This is because the occurrence of air masses originating from within each zone and arriving at the Gulf was not equally distributed throughout the year with air masses

Table 2
Spatial comparison of nitrogen fluxes from each air mass source region (zones 1–6).

Zone	Region	N	Fluxes ($\mu\text{mol m}^{-2} \text{day}^{-1}$)				
			NO_3^-	NO_2^-	NH_4^+	TSN	Org N*
1	Saharan Desert	7	43.1 \pm 21.8	0.8 \pm 0.6	22.3 \pm 14.3	76.6 \pm 38.1	10.4 \pm 7.2
2	Arabian Desert	3	40.0 \pm 18.3	1.5 \pm 1.1	32.9 \pm 6.0	87.8 \pm 24.0	13.3 \pm 2.6
3	Negev Desert (local region)	8	49.0 \pm 21.6	1.3 \pm 1.8	27.7 \pm 10.1	92.4 \pm 34.3	14.5 \pm 7.0
4	E. Europe	6	26.9 \pm 11.2	1.3 \pm 0.8	13.8 \pm 5.4	52.0 \pm 21.4	3.8 \pm 3.8
5	W. Europe	14	29.8 \pm 15.8	0.8 \pm 0.4	18.8 \pm 11.4	55.4 \pm 24.8	6.0 \pm 4.6
6	Mediterranean Sea	22	32.5 \pm 12.9	1.0 \pm 0.9	15.4 \pm 10.5	55.9 \pm 20.7	7.0 \pm 3.9

Mean fluxes are calculated as $\mu\text{mol m}^{-2} \text{d}^{-1}$ from each 24 h period sampled. Errors are 1 standard deviation. Note that fluxes for each zone were only calculated for days when air masses originated from that zone.

*Organic N calculated by difference.

Table 3
Spatial comparison of estimated annual nitrogen loads from air mass source region (zones 1–6).

Zone	Region	N	Estimated annual load ($\mu\text{mol m}^{-2}$)									
			NO_3^-		NO_2^-		NH_4^+		TSN		Org N*	
			Load	%	Load	%	Load	%	Load	%	Load	%
1	Saharan Desert	7	1836	14	35	10	950	14	3264	14	443	15
2	Arabian Desert	3	731	6	28	8	601	9	1602	7	243	8
3	Negev Desert (local region)	8	2383	19	63	17	1348	19	4498	19	704	24
4	E. Europe	6	1113	6	47	11	553	6	1898	8	184	4
5	W. Europe	14	2542	20	67	18	1601	23	4722	20	513	17
6	Mediterranean Sea	22	4356	34	132	36	2055	29	7482	32	940	32

Loads are estimated as the mean flux from each region multiplied by the number of days/year that aerosols are expected to originate from within that zone (based on our annual sampling). Hence, for zones in which air masses do not originate very often, even a high flux will not necessitate a high load.

*Organic N calculated by difference.

originating from two zones, the west (Mediterranean) and northwest (W. Europe) ~61% of the time yet only 5% of the time from the southeast (Arabian Desert) (Tables 2 and 3). Furthermore, documented NO_x emissions from western Europe can indeed be high, with more than 60% attributable to power generation combustion sources according to the European Pollutant Emission Register (eper.ec.europa.eu/eper) and with annual NO_x concentrations in excess of $40 \mu\text{g m}^{-3}$ in regions such as northern Italy according to the European Environment Agency reports for 2004 and 2005 (www.eea.europa.eu/themes/air). Consequently, while fluxes of NO_3^- , NH_4^+ and Org N originating from over zones 1, 2 and 3 (the more southern and desert regions) consistently have the highest daily average values (i.e., when dust rich air masses originated from these regions), because air masses originate most often from zones 5 and 6 (~74% of the time), the majority of the aerosol-associated nitrogen load on an annual basis originates from three of the six zones: the Mediterranean Sea (zone 6), Western Europe (zone 5) and the local Negev desert (zone 3) (Table 3). The N compounds arriving from the various zones may originate from different N sources and also may have undergone distinct chemical reaction in the atmosphere during transport, both of which could be reflected in the isotopic composition of the aerosol nitrate deposited in Eilat.

4.2. Nitrate N isotopic composition

A considerable span of $\delta^{15}\text{N}$ values was observed in our samples, ranging from -6.9‰ to $+1.9\text{‰}$ (Fig. 3) which falls well within the wide range of previously reported values for atmospheric NO_3^- (Burns

and Kendall, 2002; Elliott et al., 2007; Hastings et al., 2003; Heaton et al., 2004; Kendall et al., 2007; Russell et al., 1998; Savarino et al., 2007; Yeatman et al., 2001). The flux-weighted $\delta^{15}\text{N}$ value over the entire sampling period was -2.6‰ , although this value is calculated from the whole dataset which is slightly biased toward more summer sampling dates. $\delta^{15}\text{N}$ values were significantly positively correlated with NO_3^- fluxes only during summer ($r^2 = 0.22$), with no significant relationships observed between $\delta^{15}\text{N}$ and NO_3^- during the winter or the entire year. The positive correlation between NO_3^- flux and $\delta^{15}\text{N}$ value in summer is consistent with a pattern influenced by variable contribution of NO_3^- from an isotopically distinct N source with an elevated $\delta^{15}\text{N}$. The higher fluxes which are associated with higher $\delta^{15}\text{N}$ values can be explained as resulting from variable contribution from an anthropogenic, possibly power generation source, emitting NO_x with high $\delta^{15}\text{N}$ (and contributing to higher NO_3^-) to the area particularly during summer.

Seasonality is a common feature reported in studies of the isotopic composition of atmospheric nitrate (Elliott et al., 2007; Hastings et al., 2003, 2004; Kendall et al., 2007; Savarino et al., 2007). In this study, average $\delta^{15}\text{N}$ values during the summer were -2.1‰ and were significantly higher than average winter values (-3.7‰). Mean concentration-weighted (or 'flux-weighted') $\delta^{15}\text{N}$ values for summer (-1.7‰) were also higher than for winter (-3.5‰) and were slightly higher than the seasonal un-weighted averages. Thus, in contrast to some other studies (Elliott et al., 2007; Yeatman et al., 2001) who observed higher $\delta^{15}\text{N}$ values in winter, we observe lower winter $\delta^{15}\text{N}$ values, a trend that is likely related to seasonally controlled changes in air mass source region and their respective anthropogenic imprint (see below).

4.3. Nitrate O isotopic composition

$\delta^{18}\text{O}_{\text{NO}_3}$ values ranged from $+66.1$ to $+85.3\text{‰}$ and are typical of the range of values observed in other studies of atmospherically derived nitrate (Böhlke et al., 1997; Burns and Kendall, 2002; Hastings et al., 2003, 2004; Kendall et al., 2007; Savarino et al., 2007). Higher values were generally observed during winter (Fig. 3), consistent with prior studies of atmospheric nitrate which suggest a greater transfer of O_3 oxygen into the NO_x pool due to seasonally lower oxidation by OH radicals because of lower solar radiation (Rohrer and Berresheim, 2006). However, a much higher degree of variability was observed here as compared with previous studies, which, while perhaps not surprising in light of the corrections for NO_2^- discussed above, may still be related to seasonal irradiance variability, possible effects of atmospheric chemical reactions during transport to the site, or to the reactivity of aerosol NO_x on mineral dust surfaces (see below).

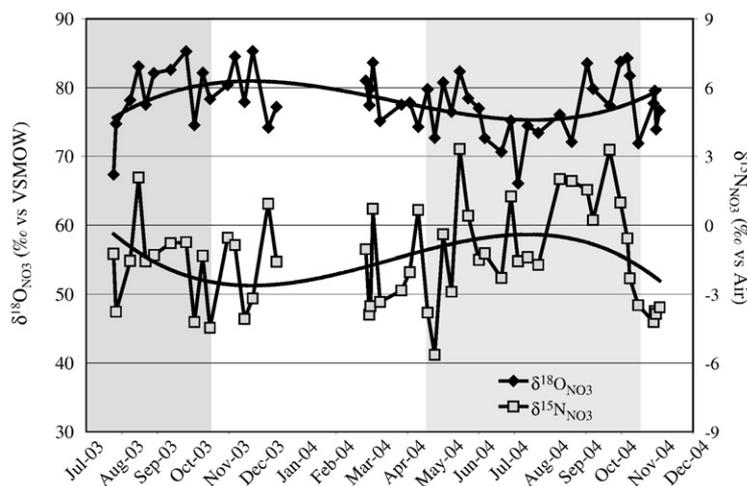


Fig. 3. Temporal variation of aerosol $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$. Gray regions indicate samples from the warmer 'summer' time period. Curved lines are best-fit third order polynomial.

Table 4
Flux-weighted nitrate isotope values for each zone.

Zone	Region	N	$\delta^{15}\text{N}_{\text{NO}_3}$	$\delta^{18}\text{O}_{\text{NO}_3}$	Seasonal occurrence	
					Summer	Winter
1	Saharan Desert	6	-4.7	+80.5	1	5
2	Arabian Desert	2	-3.5	+78.3	0	2
3	Negev Desert (local region)	8	-3.0	+81.5	0	8
4	E. Europe	5	-2.9	+79.9	4	1
5	W. Europe	10	-2.3	+74.8	9	1
6	Mediterranean Sea	20	-1.5	+78.3	14	6

Note the slightly smaller sample sizes due to a loss of 9 samples during analytical instrument failure. Higher $\delta^{15}\text{N}_{\text{NO}_3}$ values were observed from northern zones 4–6, while higher $\delta^{18}\text{O}$ values were observed from zones 1 and 3. Also–note that seasonality plays a large role in the air mass source regions with aerosols originating from zones 1–3 mostly during winter and from zones 4–6 mostly during summer.

In Eilat, due to the lower latitude ($\sim 29^\circ\text{N}$; as compared to Hastings et al (2003) (32.5°N) and Elliott et al (2007) ($40\text{--}47^\circ\text{N}$)) the seasonality of light irradiance is small and the observed isotopic variability is probably more influenced by the effects of chemical reactions occurring in the atmosphere during transport to the site. Indeed, $\delta^{18}\text{O}$ values were significantly positively correlated with NO_3^- fluxes during both summer ($r^2=0.17$) and winter ($r^2=0.27$) as well as the whole year ($r^2=0.37$). This correlation is intriguing and may suggest the influence of a source signature as discussed above for the $\delta^{15}\text{N}$ (e.g. increased contribution from a source with higher $\delta^{18}\text{O}$ values in the winter). However, the range of observed $\delta^{18}\text{O}$ values for atmospheric nitrate is not consistent with any known source signature (e.g., power plant emissions, vehicular exhaust or soil emissions, etc.), but rather reflects the higher values expected from atmospheric reactions and the variable proportion of oxidation reactions involving ozone ($\delta^{18}\text{O}\sim 90$ to 120% ; (Johnston and Thiemens, 1997), and OH ($\delta^{18}\text{O}\sim -20$ to 0% ; (Dubey et al., 1997)). The correlation is therefore related to variability in the relative contribution of the various atmospheric NO_x oxidation reactions which produce aerosol NO_3^- . It is also possible that samples containing high amounts of mineral dust, the surface of which is highly reactive (Hanisch and Crowley, 2001; Mogili et al., 2006), may contribute to higher aerosol NO_3^- content originating from such reactions (Chen et al., 2007). Indeed, aerosol input from sources with high mineral dust content is dominant during winter when $\delta^{18}\text{O}$ tends to be high. Thus, the seasonal dominance of desert regions as air mass source areas during winter may contribute to the observed correlations between $\delta^{18}\text{O}$ and NO_3^- fluxes (a combination of lower irradiance and high reactive particle surfaces).

The flux-weighted $\delta^{18}\text{O}$ value over the entire sampling period was $+78.9\%$ (and is slightly biased towards more summer samples). In contrast to the $\delta^{15}\text{N}$ data, the flux-weighted mean $\delta^{18}\text{O}$ value for summer ($+77.3\%$) was statistically lower than for winter ($+80.5\%$; $p=0.04$) and high variability of $\delta^{18}\text{O}$ values was present during all seasons. Interestingly, $\delta^{18}\text{O}$ values are higher overall as compared with other studies (even without correcting for NO_2^- interference, the flux-weighted $\delta^{18}\text{O}$ values for summer ($+74.3\%$) and winter ($+77.9\%$) are at the high end of those in previously reported studies). Hastings et al (2003, 2004) reported flux-weighted $\delta^{18}\text{O}$ values of $69\text{--}70\%$ during the warm season and $77\text{--}78\%$ during the cool season in both low latitude (Bermuda rain) and high latitude (Greenland snow) regions.

4.4. Spatial patterns in nitrate isotopic composition

As shown in Table 4, there is considerable variation in average flux weighted $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values among the six different source zones. In general $\delta^{15}\text{N}$ values from the Mediterranean Sea region and the European continent (zones 4–6) were higher, while lower values originated from over the Saharan and Arabian deserts (zones 1–3) (Fig. 4). In contrast, average $\delta^{18}\text{O}$ values, while more variable overall,

tended to be higher from over the Saharan and Negev deserts (zones 1 and 3), while lower in air masses coming from Western Europe (zone 5) suggesting that different regions may have unique isotopic source signatures. However, there is also a strong seasonal bias to air mass source regions (Table 4). For example, during the summer period 96% of all aerosol dust originated from north and/or northwest (zones 4–6), while during the winter, 70% originated from the south and/or southwest (zones 1–3). Indeed the higher $\delta^{15}\text{N}$ values originating from over the European continent likely reflect inputs from stationary NO_x emitting sources in these more urban zones such as power plants (Elliott et al., 2007). The seasonality in the $\delta^{15}\text{N}$ values is related to the sources of air masses during these two seasons, as was found by others (Hastings et al., 2003; Hastings et al., 2004). Additionally, due to the pronounced seasonality in air mass source locations between the summer and winter seasons, the observed correlation between NO_3^- flux and $\delta^{18}\text{O}$ is likely highly influenced by this seasonality rather than source region. Higher daily fluxes (although lower annual contribution) and higher $\delta^{18}\text{O}$ values were seen originating mostly during the summer from zones 1 and 3, while lower fluxes (and higher loads) and generally lower $\delta^{18}\text{O}$ values emanated from the more northern zones 5 and 6. Hence, because the origination of air masses from within these source regions is also heavily influenced by time of year, the variability in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ can be explained by seasonality in sources as well as transport (e.g. atmospheric chemical processing). We suspect that like in other studies the N isotopes reflect mostly seasonal changes in source signatures while the O isotopic signature is dominated by seasonally varying atmospheric oxidation reactions.

4.5. Correlations between trace elements and nitrate isotopic composition

In light of the type of temporal variability observed in the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ data and their spatial relation to geographical source regions, we turn to the relationships of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ with trace metal chemistry as an independent means for helping to differentiate variability in isotopic composition. A wide range of soluble and bulk ions and trace elements were analyzed in conjunction with the current study (Chen et al., 2007, 2008, 2006). These data showed relatively high concentrations of Al, Fe and Mn in bulk aerosols over the Gulf of Aqaba, consistent with a high amount of mineral dust in the region. In addition elevated amounts of Cu, Cd, Ni, Zn and P, consistent with an anthropogenic influence, were observed particularly in aerosols

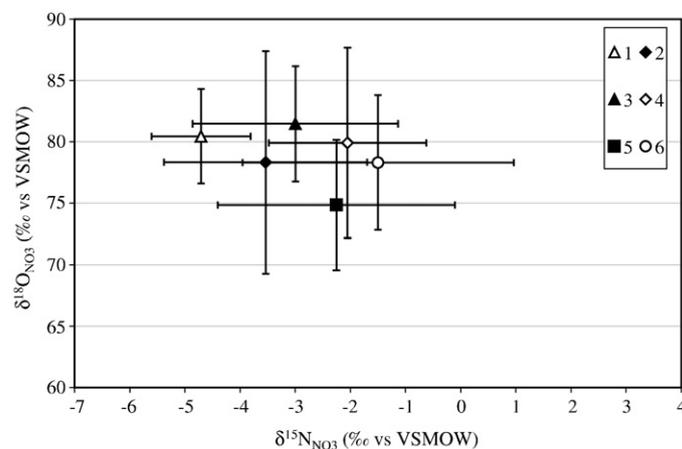


Fig. 4. Flux-weighted average $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ values for each air mass source zone. Error bars represent one standard deviation. Note that desert regions (especially zones 1 and 3) which tended to be more important during the winter months have lower $\delta^{15}\text{N}$ and generally higher $\delta^{18}\text{O}$, while the opposite is true for the more northern regions (especially zone 5). Results suggest that higher $\delta^{15}\text{N}_{\text{NO}_3}$ values are associated with an anthropogenic NO_x source influence from Europe and the Mediterranean. The lower $\delta^{18}\text{O}$ values observed from these regions is mostly influenced by the fact that these regions are the dominant source regions during summer when reaction of NO_x with ozone is less pronounced.

associated with air masses originating from over Western Europe and/or the Mediterranean Sea (Chen et al., 2008). In contrast, air masses originating from over the Saharan desert, while elevated in Al and Fe, were relatively depleted in Cu, Cd, Ni, Pb and P. Local air masses (Negev and Arabian deserts) had high amounts of Pb, Ni and V (likely from fossil fuel combustion) as well as Ca and P (apatite mineral) (Chen et al., 2008).

$\delta^{15}\text{N}$ was significantly ($p < 0.05$; two-tailed) positively correlated with bulk aerosol concentrations of Ca ($p = 0.01$), P ($p = 0.01$) and Cd ($p = 0.02$). High levels of both Ca and P in aerosols is interpreted as originating from local mineral sources (limestone and apatite common to the Negev) which are also associated with relatively local short range transport of aerosols from populated areas in Israel that have not been washed out by rain events. Chen et al (2008), also found that P had an enrichment factor (i.e., amount not attributable to mineral dust) of >10 , suggesting an additional influence, at least partially, by anthropogenic sources. Indeed, high Cd is also strongly correlated with anthropogenic sources (Bilos et al., 2001; Chen et al., 2008). This correlation indicates that $\delta^{15}\text{N}_{\text{NO}_3}$ tends to be higher when aerosols are influenced by anthropogenic sources.

$\delta^{18}\text{O}$ was significantly ($p < 0.05$) positively correlated with concentrations of soluble Br^- ($p < 0.01$), SO_4^{2-} ($p = 0.02$), nss-SO_4^{2-} ($p = 0.02$), NO_3^- ($p < 0.001$), PO_4^{3-} ($p < 0.01$), K^+ ($p = 0.02$), Ca^{+2} ($p = 0.03$), Cu ($p = 0.03$), Cd ($p = 0.04$) and Pb ($p = 0.03$). It is possible that the correlation with sea salt related components (Br^- , K^+ and SO_4^{2-}) indicates a relation to sea salt aerosol particles which may provide reactive surfaces for N_2O_5 hydrolysis (leading to more influence of O_3 and higher $\delta^{18}\text{O}$ values). The correspondence of higher $\delta^{18}\text{O}$ values with elements found enriched in anthropogenic sources (Cd, Pb, Cu) may suggest the anthropogenic components also promote those NO_x oxidation reactions which favor incorporation of ozone.

Kocak et al (2005) used factor analysis to explain variation in aerosol ionic composition in the eastern Mediterranean, finding 5 significant factors which accounted for 94% of the total variance, including marine, crustal, combustion, biogenic and photochemical. Using a similar approach we explored the variability of bulk trace metals, soluble ions and trace metals and nitrate isotopic composition. However, because our dataset contains only 51 time-point measurements, the inclusion of all analytes would be inappropriate for factor analysis (Tabachnick and Fidell, 1996). Therefore, we selected representative components for known constituents of aerosols in the region (Chen et al., 2008; Kocak et al., 2005) including: anthropogenic (Cd, Cu), marine (soluble Na and SO_4^{2-}), Saharan mineral (Al, Fe), Negev local dust (Ca, P), photochemical (C_2O_4 , NO_3^-), combustion (non-sea-salt SO_4^{2-} , TSN), and Arabian sources (Pb, Ni). We then used a factor analysis to investigate groupings of parameters into common factors.

The results of the varimax-rotated factor analysis (which also included $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) are summarized in Table 5. Factor loadings smaller than 0.32 were considered to be insignificant (Tabachnick and Fidell, 1996). We found that the data could be interpreted based on four factors that explained 82% of the total variance. The first factor explained 27%, contained heavy loadings for Cu, Al, Fe, Ca, and Ni and is attributed to a crustal component probably originating from the Saharan, Negev and Arabian deserts. The second factor, explaining 21% of the variance, had high loadings for $\delta^{18}\text{O}_{\text{NO}_3}$, Cd, NO_3^- , TSN and Pb and moderate loadings for SO_4^{2-} , Cu, P and nss-SO_4^{2-} . Here, the linkage appears evident between sources of N (as TSN, and NO_3^-) from both local combustion (Pb) and more distantly derived (Cu, Cd) anthropogenic sources. The inclusion of $\delta^{18}\text{O}_{\text{NO}_3}$ among these loadings is intriguing and may point to a linkage between oxidative pathways and anthropogenic sources, which should be further investigated. However, the correspondence between season and air mass source region (i.e., lower $\delta^{18}\text{O}$ values during summer occurring concomitantly with periods of higher delivery of Cd and Cu from European sources) may explain this linkage.

Table 5

Varimax rotated factor analysis results and probable source type for each component.

Parameter	Component			
	1	2	3	4
$\delta^{15}\text{N}$			0.31	0.65
$\delta^{18}\text{O}$		0.66		
Cu	0.63	0.49		0.49
Cd		0.53		0.76
Soluble Na				
SO_4^{2-}		0.43	0.81	
Al	0.99			
Fe	0.99			
Ca	0.96			
P				0.77
Oxalate			0.80	
NO_3^-		0.68	0.58	
nss-SO_4^{2-}		0.47	0.75	
TSN		0.81	0.46	
Pb	0.35	0.74		0.38
Ni	0.91			
Variance	27.4	21.0	19.1	14.5
Explained				
Source	Crustal	Anthro/Local & Europe	Marine/Photochemical	Anthro/Europe

Trace elements are bulk digest samples.

Factor three, which explains an additional 19% of the total variance, is strongly loaded in SO_4^{2-} , nss-SO_4^{2-} , extractable Na and oxalate and suggests the influence of marine aerosols. The presence of oxalate may indicate secondary reactions on reactive sea-salt aerosols from the photo-oxidation of aromatic hydrocarbons (Kawamura and Sakaguchi, 1999). Finally, the fourth factor, which probably represents a separate anthropogenic component, explains 15% of the variance and was highly loaded in $\delta^{15}\text{N}$, Cd and P and moderately loaded in Cu and Pb.

4.6. Chemical reactions involving precursors of aerosol nitrate

The aerosol nitrate measurements presented here are not without potential sources of error, including evaporative loss of semi-volatile NH_4NO_3 or adsorption of HNO_3 onto the filter surface. Although the hot and dry climate of Eilat tends to increase the chances of evaporative loss of particulate ammonium nitrate, our filter type and the high sampled aerosol mass on the filters (all $>2500 \mu\text{g}$) should substantially decrease the impact of any evaporation and/or HNO_3 adsorption. Moreover, mineral dust is the major aerosol component in this desert-surrounding region and nitrate in such samples is often associated with the coarse mode dust particles (Savoie and Prospero, 1982; Spokes et al., 2000) and thus present in the form of stable compounds like $\text{Ca}(\text{NO}_3)_2$ which are even less susceptible to evaporation. Hence, although we cannot easily quantify the potential impact of these evaporation and adsorption processes on our nitrate concentration estimates (or isotopic composition) we expect them to be small because of the high aerosol load and filter type used in our samples.

While we believe that the data presented accurately represent aerosol NO_3^- , the interaction between HNO_3 vapor and aerosol NO_3^- prior to deposition could influence the observed aerosol $\delta^{15}\text{N}_{\text{NO}_3}$ values. Specifically, because the aerosol samples contained substantial NH_4^+ and a dynamic equilibrium is known to exist between NH_4NO_3 and HNO_3 , it is likely that the partitioning of NO_3^- between these two phases could have an effect on the isotopic composition of aerosol NO_3^- . While the equilibrium fractionation factor between these two species remains uncharacterized (to the best of our knowledge), we can assume that the equilibrium fractionation segregates an isotopically lighter fraction into the vapor phase (i.e., HNO_3). Hence, under conditions which favor a greater fraction of vapor phase (e.g., high temperature and low relative humidity; (Morino et al., 2006)), we might expect the $\delta^{15}\text{N}$ of the aerosol fraction to increase. Indeed, using the NOAA Archived Meteorology database (www.arl.noaa.gov/)

ready/amet.html) to calculate daily average values for relative humidity and surface temperature together with modeled partitioning between NH_4NO_3 and HNO_3 (Morino et al., 2006) we would predict a larger proportion of dry deposition to be in the form of HNO_3 in Eilat particularly during summer (data not shown). This situation should drive aerosol $\delta^{15}\text{N}_{\text{NO}_3}$ values higher, consistent with our observations of higher $\delta^{15}\text{N}$ during summer (Fig. 3). While the seasonality of temperature and relative humidity may indeed account for some portion of the seasonal trend in $\delta^{15}\text{N}$, we note that no correlation was observed between temperature and/or relative humidity and NO_3^- or NH_4^+ flux, $\delta^{15}\text{N}_{\text{NO}_3}$ or $\delta^{18}\text{O}_{\text{NO}_3}$.

Scavenging of the isotopically lighter HNO_3 phase by sea-salt and/or mineral surfaces (Dentener et al., 1996; Guimbaud et al., 2002; Hanisch and Crowley, 2001; Song and Carmichael, 1999) could lead to a decrease in $\delta^{15}\text{N}$ of aerosol NO_3^- . In fact it is possible that air masses originating from marine and desert regions may have a higher propensity for scavenging HNO_3 , leading to overall lower aerosol $\delta^{15}\text{N}_{\text{NO}_3}$ values in the dataset as a whole. Indeed, air masses arriving from desert regions had on average lower $\delta^{15}\text{N}$ values than those from non-desert regions, and it is possible that this mechanism may play some role in the control of aerosol $\delta^{15}\text{N}_{\text{NO}_3}$. However, no correlations were observed between $\delta^{15}\text{N}_{\text{NO}_3}$ and total suspended particulate (TSP, the best proxy for total dust content) both within the whole dataset and within individual seasons or zones.

Additionally, mineral dust has been shown to serve as a highly reactive surface for N_2O_5 hydrolysis (Mogili et al., 2006) and therefore may play a role in $\delta^{18}\text{O}_{\text{NO}_3}$ as well. Mineral dust may serve to favor the incorporation of oxygen atoms from N_2O_5 , which should have an isotopic composition closer to ozone and would lead to an overall increase in $\delta^{18}\text{O}$ of particulate NO_3^- when dust concentrations are high. However, again no correlations were observed between $\delta^{18}\text{O}_{\text{NO}_3}$ and TSP, whether within the entire dataset or broken up into zones or seasons, suggesting these phenomena may only play secondary roles in controlling aerosol nitrate isotopic composition.

In addition to adsorption and equilibrium reactions (e.g., vapor phase–solid phase), a set of photochemical steady-state reactions (Fig. 2), including NO oxidation by ozone and NO_2 photolysis, may also play a role in controlling the nitrogen isotopic composition of aerosol NO_3^- in some systems (Freyer et al., 1993). Polluted systems with abundant ozone exhibit higher NO_2 levels resulting in lower $\delta^{15}\text{N}$ of NO_2 and ultimately lower $\delta^{15}\text{N}$ of aerosol NO_3 . In addition, higher ozone levels are observed in the Mediterranean during summer (Kouvarakis, et al., 2002) which would result in lower $\delta^{15}\text{N}$ values during summer contrary to our data. Accordingly, while all of these processes may have some impact on the nitrate isotopic compositions reported here, they constitute only secondary effects which may contribute to increased noise about the mean rather than primary controls on isotopic variability.

4.7. Implications for aerosol nitrate inputs to surface waters

The contribution of atmospherically derived NO_3^- to the surface waters of the Gulf of Aqaba and other similar oligotrophic, dry climate regions has the potential to be quite important. Terrestrial inputs in these regions are scarce and surface water nitrogen concentrations are extremely low. Accordingly, atmospheric deposition of nitrogen may be important as a new nitrogen source particularly during periods of water column stratification.

Importantly these regions are also suggested to be areas with potentially extensive N-fixation resulting from low available nitrogen sources in the surface area. Time and space integrated nitrogen fixation estimates have been made based on nitrogen isotopic composition of particulate organic matter and NO_3^- within the thermocline (Karl and Michaels, 2001; Mino et al., 2002; Pantoja et al., 2002; Sachs et al., 1999; Thunell et al., 2004). Most often, the $\delta^{15}\text{N}$ values of both particulate organic matter and nitrate in these

areas are substantially lower than underlying deep water and have been used to implicate N-fixation, which is known to contribute $\delta^{15}\text{N}$ of $\sim 0\text{‰}$ (Brandes and Devol, 2002; Hoering and Ford, 1960; Minagawa and Wada, 1986).

However, given the fact that the atmospheric flux of NO_3^- to the ocean typically exhibits $\delta^{15}\text{N}$ values even lower than those of N-fixation, these interpretations may be subject to reevaluation. In the Gulf of Aqaba – the flux weighted annual average $\delta^{15}\text{N}_{\text{NO}_3}$ input is -2.6‰ , which would lead to low $\delta^{15}\text{N}$ values for POM from surface waters and low values for NO_3^- in the thermocline where POM is regenerated and oxidized. Without accounting for atmospheric inputs, nitrogen fixation estimates using this approach may be grossly overestimated. In the Gulf of Aqaba, particularly during summer when the water column is stratified, fluxes of atmospheric nitrate, which have been estimated to supply up to 35% of the soluble inorganic nitrogen (Chen et al., 2007), could lower the $\delta^{15}\text{N}$ of organic matter by as much as 0.7‰. Thus, estimates of N-fixation based on $\delta^{15}\text{N}$ of organic matter should take this component into account.

5. Conclusions

Investigation of the aerosol nitrate dual isotopic composition and related chemical composition and source origin over the Gulf of Aqaba indicates that $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ vary seasonally in this region. The $\delta^{15}\text{N}_{\text{NO}_3}$ is heavily influenced by seasonal changes in air mass source regions which are dominated by mineral dust (desert sources) in the winter and urban areas with anthropogenic impacts (NO_x emission) in the summer. The $\delta^{18}\text{O}_{\text{NO}_3}$ is affected by seasonally changing solar radiation which determines the relative impact of ozone and OH oxidation reactions in the atmosphere. In summary, anthropogenic N sources seem to play an important role in controlling the variability of $\delta^{15}\text{N}$, with higher values generally indicative of more anthropogenic influence (e.g., power generation). Relationships with Cd and Cu seem to suggest the influence from the European and Mediterranean regions on $\delta^{15}\text{N}$, and the links with Ca and P as well as with Pb, implicate the more immediate Israel region also as an important contributor to aerosol based N deposition. Chemical reactions involving NO_3^- precursors, which can be particularly sensitive to relative humidity, temperature, solar radiation and the presence of reactive mineral surfaces may also play a role in regulating the $\delta^{15}\text{N}_{\text{NO}_3}$ in this desert region. $\delta^{18}\text{O}$ is generally reflective of oxidation chemistry and usually strongly related to season, however, its moderate relation here to anthropogenic sources may suggest some influence of anthropogenic constituents on the chemical reactions occurring during long range transport in the atmosphere. The overall higher $\delta^{18}\text{O}$ values observed in this study compared to those reported from other regions in the world may be attributed to a greater degree of interactions with mineral dust aerosols leading to increased N_2O_5 hydrolysis on reactive surfaces and higher HNO_3 nucleation. However, the lack of any substantial correlation between $\delta^{18}\text{O}$ and the crustal component in the factor analysis, indicates that while mineral dust surfaces are undoubtedly important reaction sites, and may lead to overall higher and more variable $\delta^{18}\text{O}$ values, their direct role in controlling $\delta^{18}\text{O}$ values in this area is limited and does not overwhelm the seasonality control. Finally, the annual flux weighted $\delta^{15}\text{N}$ in this area is very low (-2.6‰), having important implications for estimates of marine N fixation using $\delta^{15}\text{N}$ in oligotrophic waters.

Acknowledgements

We are grateful to Dorit Golan and Mark Chernihovsky for assistance with aerosol sample collection; the Paytan Lab for field work assistance and our colleagues at the Interuniversity Institute for Marine Science in Eilat, Israel for assisting in data collection and providing laboratory space and equipment during the study. Additionally, we would like

to thank two anonymous reviewers for their helpful insight and constructive comments on earlier versions of this manuscript. This study is supported by the NASA New Investigator Program NAG5-12663 to AP and the NATO–Science for Peace SfP project 982161 to AP and AFP. Support for CK and SDW was provided in part by the USGS National Research Program.

References

- Amman, M., et al., 1999. Estimating the uptake of traffic-derived NO₂ from 15 N abundance in Norway spruce needles. *Oecologia* 118, 124–131.
- Arimoto, R., et al., 1995. Trace elements in the atmosphere over the North Atlantic. *Journal of Geophysical Research* 100, 1199–1213.
- Baker, A., Kelly, S., Biswas, K., Witt, M., Jickells, T., 2003. Atmospheric deposition of nutrients to the Atlantic Ocean. *Geophysical Research Letters* 30 (24). doi:10.1029/2003GL018518.
- Baker, A., et al., 2007. Dry and wet deposition of nutrients from the tropical Atlantic atmosphere: links to primary productivity and nitrogen fixation. *Deep Sea Research* 1 54, 1704–1720.
- Bilos, C., Columbo, J., Skorupa, C., Rodriguez-Presa, M., 2001. Sources, distribution and variability of airborne trace metals in La Plata City area, Argentina. *Environmental Pollution* 111, 149–158.
- Böhlke, J., Eriksen, G.E., Revesz, K.M., 1997. Stable isotope evidence for an atmospheric origin of desert nitrate deposits in northern Chile and southern California, USA. *Isotope Geoscience* 136, (135–152).
- Böhlke, J., Mroczkowski, S., Coplen, T.B., 2003. Oxygen isotopes in nitrate: new reference materials for 18O:17O:16O measurements and observations on nitrate–water equilibration. *Rapid Communications in Mass Spectrometry* 17, 1835–1846.
- Bonnet, S., Guieu, C., 2006. Atmospheric forcing on the annual iron cycle in the western Mediterranean Sea: a 1 year survey. *Journal of Geophysical Research* 111 (C09010). doi:10.1029/2005JC003213.
- Brandes, J.A., Devol, A.H., 2002. A global marine fixed nitrogen isotopic budget: implications for Holocene nitrogen cycling. *Global Biogeochemical Cycles* 16 (4), 1120.
- Burns, D.A., Kendall, C., 2002. Analysis of δ¹⁵N and δ¹⁸O of nitrate to differentiate nitrate sources in runoff at two watersheds in the Catskill Mountains of New York. *Water Resources Research* 38, (5).
- Casciotti, K.L., McIlvin, M.R., 2007. Isotopic analyses of nitrate and nitrite from reference mixtures and application to Eastern Tropical North Pacific waters. *Marine Chemistry* 107 (2), 184–201.
- Casciotti, K.L., Sigman, D.M., Galanter-Hastings, M., Böhlke, J.K., Hilker, A., 2002. A Bacterial method for the measurement of the oxygen isotope composition of nitrate in marine and fresh waters. *Analytical Chemistry* 74, 4905–4912.
- Casciotti, K.L., Böhlke, J.K., McIlvin, M., Mroczkowski, S., Hannon, J., 2007. Oxygen isotopes in nitrite: analysis, calibration and equilibration. *Analytical Chemistry* 79, 2427–2436.
- Chang, M.C., Sioutas, C., Kim, S., Gong, H., Linn, W.S., 2000. Reduction of nitrate losses from filter and impactor sampler by means of concentration enrichment. *Atmospheric Environment* 34, (85–98).
- Chen, Y., Siefert, R., 2004. Seasonal and spatial distributions and dry deposition fluxes of atmospheric total and labile iron over the tropical and sub-tropical North Atlantic Ocean. *Journal of Geophysical Research* 109 (D09305). doi:10.1029/2003JD003958.
- Chen, Y., Street, J., Paytan, A., 2006. Comparison between pure-water- and seawater-soluble nutrient concentrations of aerosols from the Gulf of Aqaba. *Marine Chemistry* 101, 141–152.
- Chen, Y., et al., 2007. Estimates of atmospheric dry deposition and associated input of nutrients to Gulf of Aqaba seawater. *Journal of Geophysical Research* 112 (D04309). doi:10.1029/2006JD007858.
- Chen, Y., et al., 2008. Sources and fluxes of atmospheric trace elements to the Gulf of Aqaba, Red Sea. *Journal of Geophysical Research* 113 (D05306). doi:10.1029/2007JD009110.
- Chin, M., Ginoux, P., Kinne, S., Torres, O., Holben, B.N., Duncan, B.N., Martin, R.V., Logan, J.A., Higurashi, A., Nakajima, T., 2002. Tropospheric aerosol optical thickness from the GOCART model and comparison with satellite and sun photometer measurements. *Journal of the atmospheric sciences* 59, 461–482.
- Dentener, F.J., Carmichael, G.R., Zhang, Y., Levlieveld, J., Crutzen, P.J., 1996. Role of mineral aerosol as a reactive surface in the global troposphere. *Journal of Geophysical Research* 101 (D17), 22869–22890.
- Draxler, R., 2002. HYSPLIT-4 user's guide. NOAA Technical Memo, pp. 230.
- Duarte, C.M., et al., 2006. Aerosol inputs enhance new production in the subtropical northeastern Atlantic. *Journal of Geophysical Research* 111 (G04006). doi:10.1029/2005JG000140.
- Dubey, M., Mohrschladt, R., Donahue, N.M., Anderson, J.G., 1997. isotope specific kinetics of hydroxyl radical (OH) with water (H₂O): testing models of reactivity and atmospheric fractionation. *Journal of Physical Chemistry* 101, 1494–1500.
- Duce, R.A., et al., 1991. The atmospheric input of trace species to the world ocean. *Global Biogeochemical Cycles* 5, 193–259.
- Elliott, E.M., et al., 2007. Nitrogen isotopes as indicators of NO_x source contributions to atmospheric nitrate deposition across the Midwestern and Northeastern United States. *Environmental Science & Technology* 41 (22), 7661–7667.
- Freyer, H., 1978. Preliminary 15 N studies on atmospheric nitrogenous trace gases. *Pure and applied physics* 116 (2–3), 393–404.
- Freyer, H., 1991. Seasonal variations in 15 N/14 N ratios in atmospheric nitrate species. *Tellus* 43, 34–44.
- Freyer, H., Kley, D., Volz-Thomas, A., Kobel, K., 1993. On the interaction of isotopic exchange processes with photochemical reactions in the atmospheric oxides of nitrogen. *Journal of Geophysical Research* 98, 14791–14796.
- Ganor, E., Foner, H., 1996. The mineralogical and chemical properties and the behavior of Aeolian Saharan dust over Israel. The impact of desert dust across the Mediterranean. Kluwer Academic Press.
- Granger, J., Sigman, D.M., Prokopenko, M.G., Lehmann, M.F., Tortell, P.D., 2006. A method for nitrite removal in nitrate N and O isotope analyses. *Limnology and Oceanography: Methods* 4, 205–212.
- Guieu, C., et al., 1997. Atmospheric input of dissolved and particulate metals to the north western Mediterranean. *Deep Sea Research II* 44, 665–674.
- Guimbaud, C., Arens, F., Gutzwiller, L., Gaggeler, H.W., Ammann, M., 2002. Uptake of HNO₃ to deliquescent sea-salt particles: A study using the short-lived radioactive isotope tracer ¹³N. *Atmospheric Chemistry and Physics* 2, 249–257.
- Hanisch, F., Crowley, J.N., 2001. heterogeneous reactivity of gaseous nitric acid on Al₂O₃, CaCO₃, and atmospheric dust samples: a Knudsen cell study. *Journal of Physical Chemistry* 105 (13), 3096–3106.
- Hastings, M.G., Sigman, D.M., Lipschultz, F., 2003. Isotopic evidence for source changes of nitrate in rain at Bermuda. *Journal of Geophysical Research* 108 (D24), 4790.
- Hastings, M.G., Steig, E.J., Sigman, D.M., 2004. Seasonal variations in N and O isotopes of nitrate in snow at Summit, Greenland: implications for the study of nitrate in snow and ice cores. *Journal of Geophysical Research* 109, D20306.
- Heaton, T., 1990. 15 N/14 N ratios of NO_x from vehicle engines and coal-fired power stations. *Tellus* 42, 304–307.
- Heaton, T.H.E., Wynn, P., Tye, A.M., 2004. Low 15 N/14 N ratios for nitrate in snow in the high Arctic (79 N). *Atmospheric Environment* 38, 5611–5621.
- Herut, B., Nimmo, M., Medway, A., Chester, R., Krom, M., 2001. Dry atmospheric inputs of trace metals at the Mediterranean coast of Israel (SE Mediterranean): sources and fluxes. *Atmospheric Environment* 35, 803–813.
- Hoering, T.C., Ford, H.T., 1960. The isotope effect in the fixation of nitrogen by Azotobacter. *Journal of the American Chemical Society* 82, 376–378.
- Jacobson, M.Z., 2004. Sedimentation, dry deposition and air-sea exchange. In: Jacobson, M.Z. (Ed.), *Fundamentals of Atmospheric Modelling*. Cambridge University Press, pp. 661–672.
- Johnston, J.C., Thiemens, M.H., 1997. The isotopic composition of tropospheric ozone in three environments. *Journal of Geophysical Research* 102 (D21), 25395–25404.
- Kaiser, J., Hastings, M.G., Houlton, B.Z., Röckmann, T., Sigman, D.M., 2007. Triple oxygen isotope analysis of nitrate using the denitrifier method and thermal decomposition of N₂O. *Analytical Chemistry* 79 (2), 599–607.
- Kallos, G., Kotroni, K., Lagouvardos Papadopolous, A., 1998. On the long range transport of air pollutants from Europe to Africa. *Geophysical Research Letters* 25, 619–622.
- Karl, D.M., Michaels, A.F., 2001. Nitrogen cycle. In: Steele, J.H., Thorpe, S.A., Turekian, K. (Eds.), *Encyclopedia of Ocean Science Academic Press*, London, pp. 1876–1884.
- Kawamura, K., Sakaguchi, F., 1999. Molecular distributions of water soluble dicarboxylic acids in marine aerosols over the Pacific Ocean including the tropics. *Journal of Geophysical Research* 104, 3501–3509.
- Kendall, C., 1998. Tracing nitrogen sources and cycling in catchments. In: Kendall, C., McDonnell, J.J. (Eds.), *Isotope Tracers in Catchment Hydrology*. Elsevier, Amsterdam, pp. 519–576.
- Kendall, C., Elliott, E.M., Wankel, S.D., 2007. Tracing anthropogenic inputs of nitrogen to ecosystems. In: Michener, R.H., Lajtha, K. (Eds.), *Stable isotopes in ecology and environmental science*. Blackwell Publishing, p. 592.
- Kocak, M., Kubilay, N., Herut, B., Nimmo, M., 2005. Dry atmospheric fluxes of trace metals (Al, Fe, Mn, Pb, Cd, Zn, Cu) over the Levantine Basin: a refined assessment. *Atmospheric Environment* 29, (2289–2300).
- Kouvarakis, G., Mihalopoulos, N., Tselepidis, A., Stavrakakis, S., 2001. On the importance of atmospheric inputs of inorganic nitrogen species on the productivity of the Eastern Mediterranean Sea. *Global Biogeochemical Cycles* 15 (4), 805–817.
- Kouvarakis, G., Vrekoussis, M., Mihalopoulos, N., Kourtidis, K., Rappenglueck, B., Gerasopoulos, E., Zerefos, C., 2002. Spatial and temporal variability of tropospheric ozone (O₃) in the boundary layer above the Aegean Sea (eastern Mediterranean). *Journal of Geophysical Research* 107 (D18). doi:10.1029/2000JD000081.
- Lyons, J.R., 2001. Transfer of mass-independent fractionation on ozone to other oxygen-containing molecules in the atmosphere. *Geophysical Research Letters* 28, 3231–3234.
- McIlvin, M.R., Casciotti, K.L., 2006. Method for analysis of δ¹⁸O in water. *Analytical Chemistry* 78 (7), 2377–2381.
- Michalski, G., Böhlke, J., Thiemens, M.H., 2004a. Long term atmospheric deposition as the source of nitrate and other salts in the Atacama Desert, Chile: new evidence from mass independent oxygen isotopic compositions. *Geochimica et Cosmochimica Acta* 68 (20), 4023–4038.
- Michalski, G., et al., 2004b. Tracing atmospheric nitrate deposition in a complex semiarid ecosystem using D¹⁷O. *Environmental Science & Technology* 38, 2175–2181.
- Michalski, G., Scott, Z., Kabling, M., Thiemens, M.H., 2003. First measurements of D¹⁷O in atmospheric nitrate. *Geophysical Research Letters* 30 (16), 1870.
- Migon, C., Journal, B., Nicolas, E., 1997. Measurement of trace metal wet, dry and total atmospheric fluxes over the Ligurian Sea. *Atmospheric Environment* 40, 889–896.
- Minagawa, M., Wada, E., 1986. Nitrogen isotope ratios of red tide organisms in the East China Sea: a characterization of biological nitrogen fixation. *Marine Chemistry* 19 (3), 245–259.
- Mino, Y., Saino, T., Suzuki, K., Maranon, E., 2002. Isotopic composition of suspended particulate nitrogen in surface waters of the Atlantic Ocean from 50 N to 50 S. *Global Biogeochem. Cycles* 16 (4). doi:10.1029/2001GB001635.
- Mogili, P.K., Kleiber, P.D., Young, M.A., Grassian, V.H., 2006. N₂O₅ hydrolysis on the components of mineral dust and sea salt aerosol: comparison study in an environmental aerosol reaction chamber. *Atmospheric Environment* 40, 7401–7408.

- Moore, H., 1977. The isotopic composition of ammonia, nitrogen dioxide and nitrate in the atmosphere. *Atmospheric Environment* 11, 1239–1243.
- Morin, S., Savarino, J., Bekki, S., Gong, S., Bottenheim, J., 2007. Signature of Arctic surface ozone depletion events in the isotope anomaly (D17O) of atmospheric nitrate. *Atmospheric Chemistry and Physics Discussions* 7, (1451–1469).
- Morino, Y., et al., 2006. Partitioning of HNO₃ and particulate nitrate over Tokyo: effect of vertical mixing. *Journal of Geophysical Research* 111, (D15215).
- Pantoja, S., Repeta, D.J., Sachs, J.P., Sigman, D.M., 2002. Stable isotope constraints on the nitrogen cycle of the Mediterranean Sea water column. *Deep Sea Research I* 49 (9), 1609–1621.
- Reiss, J., Hottinger, L., 1994. *The Gulf of Aqaba Ecological Paleontology*. Ecological Studies, 50. Springer, New York. 354 pp.
- Revesz, K.M., Böhlke, J., 2002. Comparison of δ¹⁸O measurements in nitrate by different combustion techniques. *Analytical Chemistry* 74 (20), 5410–5413.
- Ridame, C., Guieu, C., Loye-Pilot, M., 1999. Trend in total atmospheric fluxes of aluminum, iron and trace metals in the northwestern Mediterranean over the past decade (1985–1997). *Journal of Geophysical Research* 104, 30127–30138.
- Rohrer, F., Berresheim, H., 2006. Strong correlation between levels of tropospheric hydroxyl radicals and solar ultraviolet radiation. *Nature* 442 (7099), 184–187.
- Russell, K., Galloway, J.N., Macko, S.A., Moody, J., Scudlark, J., 1998. Sources of nitrogen in wet deposition to the Chesapeake Bay region. *Atmospheric Environment* 32, 2453–2465.
- Sachs, J.P., Repeta, D.J., Goericke, R., 1999. Nitrogen and carbon isotopic ratios of chlorophyll from marine phytoplankton. *Geochimica et Cosmochimica Acta* 63 (9), 1431–1441.
- Savarino, J., Kaiser, J., Morin, S., Sigman, D.M., Thiemens, M.H., 2007. Nitrogen and oxygen isotopic constraints on the origin of atmospheric nitrate in coastal Antarctica. *Atmospheric Chemistry and Physics Discussions* 7, 1925–1945.
- Savarino, J., Battacharya, S.K., Morin, S., Baroni, M., Doussin, J.F., 2008. The NO + O₃ reaction: a triple oxygen isotope perspective on the reaction dynamics and atmospheric implications for the transfer of the ozone isotope anomaly. *Journal of Chemical Physics* 128 (19), 194303.
- Savoie, D.L., Prospero, J., 1982. Particle-size distribution of nitrate and sulfate in the marine atmosphere. *Geophysical Research Letters* 9, 1207–1210.
- Schaap, M., et al., 2004. Artefacts in the sampling of nitrate studied in the “INTERCOMP” campaigns of EUROTRAC-AEROSOL. *Atmospheric Environment* 38 (38), 6487–6496.
- Sigman, D.M., Casciotti, K.L., Andreani, M., Barford, C., Galanter, M., Böhlke, J.K., 2001. A Bacterial Method for the Nitrogen Isotopic Analysis of Nitrate in Seawater and Freshwater. *Analytical Chemistry* 73 (17), 4145–4153.
- Song, C.H., Carmichael, G.R., 1999. The aging process of naturally emitted aerosol (sea-salt and mineral aerosol) during long range transport. *Atmospheric Environment* 33 (14), 2203–2218.
- Spokes, L.J., Jickells, T., 2005. Is the atmosphere really an important source of reactive nitrogen to coastal waters? *Continental Shelf Research* 25 (16), 2022–2035.
- Spokes, L.J., Yeatman, S., Cornell, S., Jickells, T., 2000. Nitrogen deposition to the eastern Atlantic Ocean: the importance of south-easterly flow. *Tellus* 52, (37–49).
- Tabachnick, B., Fidell, L., 1996. *Using Multivariate Statistics*. Harper Collins College Publishers, New York. 880 pp.
- Thunell, R.C., Sigman, D.M., Muller-Karger, F., Astor, Y., Varela, R., 2004. Nitrogen isotope dynamics of the Cariaco Basin, Venezuela. *Global Biogeochemical Cycles* 18, GB3001.
- Wang, H.C., John, W., 1988. Characteristics of the Berner Impactor for sampling inorganic ions. *Aerosol Science and Technology* 8, 157–172.
- Yeatman, S., Spokes, L.J., Dennis, P., Jickells, T., 2001. Comparisons of aerosol nitrogen isotopic composition at two polluted coastal sites. *Atmospheric Environment* 25, 1307–1320.