

Isotopic evidence for source changes of nitrate in rain at Bermuda

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[1] Rainwater collected on the island of Bermuda between January 2000 and January 2001 shows pronounced seasonal variation in the nitrogen and oxygen isotopic composition of nitrate. Higher $^{15}\text{N}/^{14}\text{N}$ and lower $^{18}\text{O}/^{16}\text{O}$ ratios are observed in the warm season (April–September) in comparison to the cool season (October–March): The mean $\delta^{15}\text{N}$ of nitrate for the warm and cool seasons is -2.1‰ and -5.9‰ (versus air N_2), respectively, while the mean $\delta^{18}\text{O}$ is 68.6‰ and 76.9‰ (versus Vienna Standard Mean Ocean Water). The few cool season rain events that had high $^{15}\text{N}/^{14}\text{N}$ and low $^{18}\text{O}/^{16}\text{O}$ exhibited trajectory paths originating from the south, similar to those of warm season samples. Accordingly, the region from which air is transported to the island determines the $^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$ of the nitrate. The source region provides precursor nitrogen oxides (NO_x), influencing the $^{15}\text{N}/^{14}\text{N}$ of nitrate, and contributes to the chemistry that produces nitrate from NO_x , which determines the $^{18}\text{O}/^{16}\text{O}$ of nitrate. While the range in nitrate $^{15}\text{N}/^{14}\text{N}$ observed during the cool season is consistent with anthropogenic emissions from North America, the higher warm season $^{15}\text{N}/^{14}\text{N}$ suggests that lightning is a significant source of nitrate to Bermuda. The isotopic evidence for a significant southern source of nitrate to Bermuda helps to explain the previous observation of unexpectedly high nitrate concentrations in warm season rain. The $^{18}\text{O}/^{16}\text{O}$ of nitrate in rain at Bermuda is high throughout the year ($\delta^{18}\text{O} = 60.3$ to 86.5‰) as a result of interactions of precursor NO_x with ozone, which has a high $^{18}\text{O}/^{16}\text{O}$ ratio. The lower nitrate $^{18}\text{O}/^{16}\text{O}$ in the warm season and in cool season air masses from the south is consistent with elevated concentrations of hydroxyl radical (OH), which dilutes the isotopic signal of ozone. Our limited data set suggests that the relative importance of the OH sink for NO_x during the cool season varies spatially over as large a range as is observed between the warm and cool seasons. *INDEX*

TERMS: 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 1040 Geochemistry: Isotopic composition/chemistry; *KEYWORDS:* nitrate, isotopes, Bermuda

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1. Introduction

[2] Nitric acid (HNO_3), or nitrate (NO_3^-), is a significant contributor to acid rain, an important species in marine and atmospheric chemistry, and the dominant sink for reactive atmospheric nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$). Globally, levels of NO_x are rising due to increasing anthropogenic emissions from fossil fuel combustion, biomass burning, and aircraft emissions. The increases in anthropogenic emissions are leading to increased deposition of HNO_3 [e.g., Penner *et al.*, 1991]. In order to assess the impacts of anthropogenic inputs to the nitrogen cycle, it is important to recognize and constrain the natural production of NO_x

(and therefore NO_3^-) from soils and lightning. However, traditional approaches have been unable to successfully distinguish anthropogenic NO_3^- from that generated by natural processes.

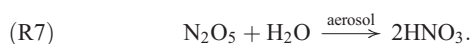
[3] The atmospheric cycle of NO_x is complex, with different processes taking place during the day and night. During the day, cycling between NO and NO_2 is rapid, controlled by the oxidation of NO by ozone (O_3) to form NO_2 and the photolysis of NO_2 back to NO:



where M is an unreactive third body. NO can also be oxidized to NO₂ via peroxy radicals, although this is generally a minor pathway of NO oxidation. The major sink for NO_x in the atmosphere is oxidation to HNO₃, which occurs during the day via



and at night via



[4] Bermuda's location, approximately 1000 km off the coast of North Carolina, has made it an important study site for the examination of pollution transport from North America to the North Atlantic Ocean [e.g., *Prospero et al.*, 1996]. The influence of continental emissions is expected to vary seasonally with the transport of air to Bermuda. During the winter and early spring (cool season), rapid transport frequently occurs from eastern North America to Bermuda [e.g., *Moody and Galloway*, 1988; *Moody et al.*, 1995]. In the summer and early fall (warm season), the Bermuda high decreases outflow from the continent and warm season transport is thus characterized by slower moving marine air masses that arrive at Bermuda from the south, southeast, and southwest [*Moody and Galloway*, 1988].

[5] Previous studies have shown that air masses transported from North America lead to the deposition of high sulfate, nitrate, and total acidity in rain at Bermuda [*Jickells et al.*, 1982; *Galloway et al.*, 1982, 1983]. On the basis of the predominant transport patterns and these studies, large anthropogenic emissions from the east coast of North America would be expected to influence cool season chemistry, while there are no obvious comparable emissions transported to Bermuda from the south during the warm season. However, *Moody and Galloway* [1988] find equal fractions of nitrate deposition associated with air from North America and air from the south of Bermuda ("Bahamas region") for samples collected over 4 years.

[6] How is it that a major seasonal variation in nitrate concentration and deposition does not occur? Two end-member alternatives arise. North American emissions may be so pervasive and the paths of transport so variable that there is essentially no seasonal variation in the supply of nitrate and its precursors from North America to Bermuda. Alternatively, we may be underestimating the contribution from sources of nitrate that take the place of North American sources during the warm season when transport to Bermuda is primarily from the south. The nitrate concentration and deposition data alone cannot distinguish between these alternatives. However, as we describe below, the stable isotopes of nitrate indicate a marked seasonal shift in the origin of the nitrate being deposited on Bermuda, clearly

supporting the latter alternative: an underappreciated source that does not originate in North America.

[7] Previous studies at other locations have used N and O isotopes as a tool for distinguishing NO₃⁻ sources. Isotope ratios are reported using delta (δ) notation in units of "per mil" (‰): δ¹⁵N_{sample} = [(¹⁵N/¹⁴N)_{sample} / (¹⁵N/¹⁴N)_{reference} - 1] × 1000 ‰ and δ¹⁸O_{sample} = [(¹⁸O/¹⁶O)_{sample} / (¹⁸O/¹⁶O)_{reference} - 1] × 1000 ‰, where the ¹⁵N/¹⁴N reference is N₂ in air and the ¹⁸O/¹⁶O reference is Vienna Standard Mean Ocean Water (VSMOW). *Heaton* [1990] presented evidence from South Africa that the δ¹⁵N of NO_x from coal combustion (+6 to +9‰) was distinctly different from that of NO_x emitted from automobiles (-13 to +2‰). *Freyer* [1991, and references therein] observed seasonal cycles in the δ¹⁵N of NO₃⁻ in rain in Jülich, Germany, and attributed higher δ¹⁵N in the winter to an increase in the importance of NO_x from fossil fuel combustion relative to soil-derived NO_x. *Russell et al.* [1998] utilized concentration, δ¹⁵N, seasonal fluxes and back trajectory analysis in an effort to determine the sources of inorganic and organic forms of nitrogen in wet deposition to the Chesapeake Bay region. In Bavaria, Germany, *Durka et al.* [1994] combined use of δ¹⁸O and δ¹⁵N of NO₃⁻ in an attempt to trace the fate of NO₃⁻ deposited from the atmosphere and quantify its impact on nitrate leaching from forested watersheds.

[8] Here we present a year-long time series of the δ¹⁵N and δ¹⁸O of NO₃⁻ in precipitation at Bermuda. Seasonal variations are observed in both isotopes of NO₃⁻. In our effort to explain the observed isotopic variations, we make use of back trajectories from the National Oceanic and Atmospheric Administration's (NOAA) Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model and results from a global chemical transport model (NOAA Geophysical Fluid Dynamics Laboratory global chemical transport model (GFDL GCTM)). The source region itself provides the nitrogen oxides that determine the ¹⁵N/¹⁴N of NO_x (and therefore nitrate). However, it is the chemistry in the air parcel that converts NO_x to nitrate and sets its ¹⁸O/¹⁶O. Thus the seasonal variation in δ¹⁵N of NO₃⁻ is interpreted in terms of NO_x source, while the seasonal change in δ¹⁸O is interpreted in terms of the chemistry that produces NO₃⁻ from NO and NO₂.

2. Methods

2.1. Sample Collection

[9] Precipitation samples were collected on the island of Bermuda (32.27°N, 64.87°W) in polyethylene buckets, using automatic rain collectors. Samples were collected on an event basis and represent only wet deposition. The samples were retrieved on a daily basis, but may at times represent more than a single precipitation event. If enough water remained after nutrient analysis at the Bermuda Biological Station for Research (BBSR), the samples were shipped frozen to Princeton University. Detailed description of the sites and results from these analyses are available from *Simmons* [2003].

[10] Between January 2000 and January 2001, samples from two different stations on Bermuda, "Prospect" and "Incinerator," were collected and analyzed for δ¹⁵N and δ¹⁸O of NO₃⁻. The Prospect site is centrally located on the island atop a water catchment ~65 m above sea level and unob-

structed in all directions. The Incinerator station is near the downtown area and is low-lying (15 m above sea level). Of the 65 samples analyzed for isotopes in this study, 50 are from Prospect and 15 are from the Incinerator station. NO_3^- concentration is reported for 72 samples from Prospect station by Simmons [2003]. For the 15 samples collected at both stations on the same date, only Prospect station data were used for volume-weighted calculation purposes. For the samples presented here, rainfall amounts varied from 0.58 to 8.74 cm.

2.2. Nitrate Concentration and Isotopic Analysis

[11] NO_3^- concentration ($[\text{NO}_3^-]$) was determined for each sample by reduction of NO_3^- and nitrite (NO_2^-) to nitric oxide (NO) followed by chemiluminescence detection of NO [Braman and Hendrix, 1989]. Typical reproducibility for this data set was 0.2 μM (1 SD). $[\text{NO}_2^-]$ was insignificant in comparison to $[\text{NO}_3^-]$ and therefore is not considered separately for the N isotope analyses.

[12] Isotopic measurements of the $^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$ ratios of NO_3^- were made using the denitrifier method (see Sigman *et al.* [2001] and Casciotti *et al.* [2002] for N and O isotope methodologies, respectively). This method is based on the isotopic analysis of nitrous oxide gas (N_2O) generated from nitrate by natural strains of denitrifying bacteria that lack N_2O reductase activity. The measurement of 45/44 and 46/44 ion current ratios (with a Thermo-Finnigan DeltaPlus IRMS in continuous flow mode) allows for coupled determination of the $^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$ ratios of the N_2O analyte. Typical reproducibility is 0.2‰ (1 SD) for $\delta^{15}\text{N}$ measurements, and 0.5‰ (1 SD) for $\delta^{18}\text{O}$ measurements. The method compares well with previously published methods but is orders of magnitude more sensitive, allowing for determination of the N and O isotopes of NO_3^- for concentrations as low as 1 μM in as little as 10 ml of sample (i.e., 10 nmol). The sensitivity of the denitrifier method was critical for this study, in which the $[\text{NO}_3^-]$ was often less than 10 μM and sample volume was limited.

[13] Analyses are referenced to atmospheric N_2 using the internationally recognized standard IAEA-NO-3, which has an assigned value for $\delta^{15}\text{N}$ of 4.7‰ versus atmospheric N_2 [Böhle and Coplen, 1995] and a reported $\delta^{18}\text{O}$ of 22.7‰ versus VSMOW [Révész *et al.*, 1997]. The $^{15}\text{N}/^{14}\text{N}$ is corrected for a blank associated with the bacterial culture (quantified with each run) and for the contribution of ^{17}O to the peak at mass 45 (see below and Sigman *et al.* [2001]). For $^{15}\text{N}/^{14}\text{N}$, corrections for the blank resulted in an average change of -0.07‰ for this data set. The $^{18}\text{O}/^{16}\text{O}$ is corrected for the blank and for exchange of oxygen atoms with water during denitrification (see below and Casciotti *et al.* [2002]), which typically resulted in a change of $+4.8\text{‰}$.

[14] Two strains of bacteria are routinely used for the isotopic analysis of NO_3^- , *Pseudomonas chlororaphis* and *Pseudomonas aureofaciens* (ATCC 13985 recently reclassified as a strain of *P. chlororaphis*). During denitrification, exchange of oxygen atoms between nitrogen oxide intermediates and water can take place [Ye *et al.*, 1991]. Oxygen exchange is quantified for each sample run by measuring incorporation of oxygen from ^{18}O -labeled water into the N_2O produced from NO_3^- . This exchange is reproducible for a given culture batch of a given age, and each day's sample run is subsequently corrected for its effect on $\delta^{18}\text{O}$ [see

Casciotti *et al.*, 2002]. *P. aureofaciens* has been shown to incorporate relatively little oxygen from water into N_2O (6% [Ye *et al.*, 1991]). In agreement with this earlier observation, we find that *P. aureofaciens* exchanges less than 10% (typically less than 3%) and is therefore suitable for $\delta^{18}\text{O}$ analysis [Casciotti *et al.*, 2002]. *P. chlororaphis*, however, has a much higher level of exchange ($\sim 60\text{--}80\%$) and is therefore not used for NO_3^- $\delta^{18}\text{O}$ analysis.

2.3. Correction to Nitrate $\delta^{15}\text{N}$ for $\delta^{17}\text{O}$ Contribution

[15] For $\delta^{15}\text{N}$ determination, a correction must be made for the contribution of $^{14}\text{N}^{14}\text{N}^{17}\text{O}$ to the peak at mass 45:

$$\delta^{15}\text{N} = 45\delta[1 + ^{17}\text{R}_{\text{std}}/(2 \times ^{15}\text{R}_{\text{std}})] - \delta^{17}\text{O}[^{17}\text{R}_{\text{std}}/(2 \times ^{15}\text{R}_{\text{std}})], \quad (1)$$

where $^{45}\delta$ is from the measured 45/44 ratio, $^{17}\text{R}_{\text{std}} = ^{17}\text{O}/^{16}\text{O} = 379.9 \times 10^{-6}$ (versus VSMOW [Li *et al.*, 1988]), and $^{15}\text{R}_{\text{std}} = ^{15}\text{N}/^{14}\text{N} = 3676.5 \times 10^{-6}$ (versus atmospheric N_2 [Coplen *et al.*, 1992; Junk and Svec, 1958]). The majority of natural samples abide by the conventional mass-dependent relationship such that $^{17}\text{R}/^{17}\text{R}_{\text{s+d}} = (^{18}\text{R}/^{18}\text{R}_{\text{s+d}})^{0.5}$ [e.g., Urey, 1947], which can be approximated as $\delta^{17}\text{O} \approx 0.5 \times \delta^{18}\text{O}$. The ^{17}R of atmospheric NO_3^- , however, does not follow this relationship with ^{18}R , that is $^{17}\text{R}/^{17}\text{R}_{\text{s+d}} \neq (^{18}\text{R}/^{18}\text{R}_{\text{s+d}})^{0.5}$ [Galanter *et al.*, 2000a; Sigman *et al.*, 2001; Michalski *et al.*, 2002, 2003]. The deviation of ^{17}R from the mass-dependent relationship with ^{18}R has been termed the “mass-independent” component. The mass-independent character of atmospheric NO_3^- is expressed by a diagnostic quantity defined as $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.5 \times \delta^{18}\text{O}$ [e.g., Miller, 2002].

[16] At high rates of exchange, the oxygen isotopic composition of N_2O reflects that of water rather than the original sample NO_3^- . Measurements made with *P. chlororaphis* (as opposed to *P. aureofaciens*) will therefore more closely resemble the “true” NO_3^- $\delta^{15}\text{N}$ with the mass-dependent assumption (i.e., $\delta^{17}\text{O} \approx 0.5 \times \delta^{18}\text{O}$). Of the 65 samples analyzed for isotopes, 36 were measured with both *P. chlororaphis* and *P. aureofaciens*, while 29 were only measured with *P. aureofaciens*. A correction factor for the samples measured with *P. aureofaciens* is determined by comparison of *P. chlororaphis* and *P. aureofaciens* data from the 36 pairs of samples.

[17] A plot of $\delta^{15}\text{N}$ from both strains of bacteria versus exchange allowed for calculation of the NO_3^- $\delta^{15}\text{N}$ at 0 and 100% exchange. At 100% exchange, the $\delta^{18}\text{O}$ of the N_2O produced from NO_3^- is equal to $\delta^{18}\text{O}$ of the water present during denitrification, and therefore $\delta^{17}\text{O} \approx 0.5 \times \delta^{18}\text{O}$; at 0% exchange, the mass-independent $\delta^{17}\text{O}$ of the sample NO_3^- is fully expressed and $\delta^{17}\text{O} = x \times \delta^{18}\text{O}$, where x is unknown. Substituting for $\delta^{17}\text{O}$ in equation (1), an average value of 0.8 for x was found for the 36 samples measured with both strains of bacteria. This value is consistent with direct observations of $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ in NO_3^- aerosol samples from the west coast of the United States [Michalski and Thiemens, 2000; Michalski *et al.*, 2003]. Consequently, $\delta^{17}\text{O} = 0.8 \times \delta^{18}\text{O}$ was substituted into equation (1) for all data collected with *P. aureofaciens*. The difference in $\delta^{15}\text{N}$ at 0% and 100% exchange (average $\Delta\delta^{15}\text{N} = -3.3 \pm 0.9\text{‰}$) could also be used to calculate $\delta^{17}\text{O}$ (and therefore $\Delta^{17}\text{O}$) of NO_3^- . However, small changes in $\delta^{15}\text{N}$ result in large

changes of $\delta^{17}\text{O}$, and therefore it is difficult to distinguish real variability from analytical variability ($\pm 8\%$) for $\Delta^{17}\text{O}$. Nevertheless, we find an average $\Delta^{17}\text{O}$ of 27‰ for NO_3^- in Bermuda rain.

2.4. Models and Statistics

[18] In section 4.1, the seasonal variations in $\delta^{15}\text{N}$ of NO_3^- are considered with respect to changes in the source of NO_3^- from the simulation of NO_x with the Geophysical Fluid Dynamics Laboratory global chemical transport model (GFDL GCTM). The GFDL GCTM has been used extensively [e.g., *Levy and Moxim*, 1989; *Kasibhatla et al.*, 1993; *Moxim et al.*, 1996; *Galanter et al.*, 2000b, and references therein], and the simulation of NO_x has been described in detail by *Levy et al.* [1999]. The GCTM explicitly separates reactive nitrogen into three classes of transported tracers: NO_x , peroxyacetyl nitrate (PAN), and HNO_3 . The model includes sources from fossil fuel combustion, biomass burning, soil-biogenic emission, lightning, aircraft emissions, and stratospheric injection. Simulations are driven by 12 months of 6-hour time-averaged wind, temperature, and precipitation fields from a general circulation model [see *Manabe et al.*, 1974; *Manabe and Holloway*, 1975], and thus are intended to be representative of a typical year.

[19] To analyze the impact of transport, back trajectories were computed for all sample days using NOAA's Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT) interactive web version model (R. R. Draxler and G. D. Rolph, HYSPPLIT Model access via NOAA ARL READY Website at <http://www.arl.noaa.gov/ready/hysplit4.html>, NOAA Air Resources Laboratory, Silver Spring, Maryland). Three-dimensional trajectories were analyzed at various levels between the surface and 500 mbar and were calculated using data from the Eta Data Assimilation System (EDAS).

[20] In the following, the $[\text{NO}_3^-]$, $\delta^{15}\text{N}$, and $\delta^{18}\text{O}$ data are divided into warm (April–September) and cool (October–March) seasons, which exhibit different predominant transport patterns (see section 3.4 for more details). The Mann-Whitney U-test (two-tailed) was used in comparing the means of the sorted data.

3. Results

[21] For 15 samples collected on the same date at both stations, $[\text{NO}_3^-]$ at the Incinerator station systematically averages higher by 2.4 μM (Figure 1a). However, no significant difference ($>0.2\%$) is seen between the mean $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of NO_3^- for these 15 paired samples. The average absolute difference between the two sampling sites is 0.60‰ for $\delta^{15}\text{N}$ (Figure 1b) and 1.4‰ for $\delta^{18}\text{O}$ (Figure 1c).

3.1. NO_3^- Concentration

[22] For the 65 precipitation samples collected between January 2000 and January 2001 for this study, $[\text{NO}_3^-]$ ranges from 1.4 to 16.8 μM , except for a rain event with unusually high $[\text{NO}_3^-]$ ($\sim 40 \mu\text{M}$) on March 6 at both stations (Figure 1a). Since this high concentration is present in samples from both stations and the isotope results are not anomalous (see below), there is no reason to suspect contamination. The volume-weighted average $[\text{NO}_3^-]$ in the warm season (April–September) is 5.0 μM and total depo-

sition is 3.1 mmol N m^{-2} , which is not significantly different from the cool season (October–March) average $[\text{NO}_3^-]$ of 6.4 μM and total deposition of 3.7 mmol N m^{-2} . Without the very high $[\text{NO}_3^-]$ observed for the March 6 sample, the volume-weighted average $[\text{NO}_3^-]$ in the cool season is 5.6 μM , with a total deposition of 3.2 mmol N m^{-2} .

[23] The lack of a significant seasonal change in $[\text{NO}_3^-]$ is consistent with and representative of the larger data set presented by *Simmons* [2003] for Bermuda rain samples collected in 2000 (see section 2.1). For precipitation samples collected between 1980 and 1984, *Moody and Galloway* [1988] found volume-weighted averages of 4.6 μM and 4.3 μM for the warm and cool seasons, respectively.

3.2. N Isotopes of NO_3^-

[24] Our measurements of $\delta^{15}\text{N}$ of NO_3^- range from -13.9 to $+1.8\%$ versus atmospheric N_2 (Figure 1b) over the course of one year. The NO_3^- $\delta^{15}\text{N}$ shows no relationship with $[\text{NO}_3^-]$ or rainfall amount (not shown). The mean $\delta^{15}\text{N}$ is significantly different ($p < 0.0001$) for the two seasons, with the warm season averaging $-2.1 \pm 1.5\%$ (± 1 SD) and the cool season averaging $-5.9 \pm 3.3\%$ (Table 1). The warm season “volume-weighted” (or deposition-weighted) average $\delta^{15}\text{N}$ of $-1.8 \pm 1.7\%$ is also significantly higher than the cool season average of $-6.8 \pm 3.7\%$. Note that the standard deviations indicate that the cool season data are more variable.

[25] The samples collected on February 23 at both stations are very low in $\delta^{15}\text{N}$ (near -14%) in comparison to the rest of the data set, but exhibit a $\delta^{18}\text{O}$ of NO_3^- within the range of the other cool season samples (Figure 1c). Although the $\delta^{15}\text{N}$ of this event does not appear to be representative, we have no reason to suspect the samples were contaminated and replicate analyses gave the same result. Thus this event is included in the data set. Moreover, our results and their interpretation (section 4) would not change without this event as the cool season would still be significantly lower ($p < 0.0001$) with a mean of $-5.4 \pm 2.7\%$, and a volume-weighted average of $-4.9 \pm 3.0\%$.

[26] All of the samples fall within the large range of previously reported $\delta^{15}\text{N}$ for precipitation NO_3^- (-16 to $+10\%$) [see, e.g., *Kendall*, 1998; *Russell et al.*, 1998, and references therein]. Average $\delta^{15}\text{N}$ measured in the eastern United States tends to be higher than typical $\delta^{15}\text{N}$ of NO_3^- seen at Bermuda. For instance, a 1-year study of $\delta^{15}\text{N}$ in bulk precipitation and throughfall at Walker Branch watershed in Tennessee showed a range of approximately -2 to $+6\%$ for NO_3^- , with an average of $+2.3 \pm 2.4\%$ [*Garten*, 1992]. *Russell et al.* [1998] observed a range in $\delta^{15}\text{N}$ of -4.0 to $+4.4\%$, with a median of -1.1% for wet deposited NO_3^- collected in the Chesapeake Bay region. *Burns and Kendall* [2002] report an average $\delta^{15}\text{N}$ for precipitation NO_3^- of -0.2% for samples collected in the Catskill Mountains of New York. Some isotopic data also exists for NO_3^- sources, or its precursor NO_x . Particulate, or dry deposited NO_3^- $\delta^{15}\text{N}$ is typically positive with values ranging from -3 to $+12\%$ [*Moore*, 1977; *Heaton*, 1987; *Freyer*, 1991; *Garten*, 1996]. *Heaton* [1990] found distinctly different $\delta^{15}\text{N}$ values for NO_x from coal combustion ($+6$ to $+9\%$) and NO_x emitted from automobiles (-13 to $+2\%$). *Hoering* [1957] shows that NO_x produced from electric

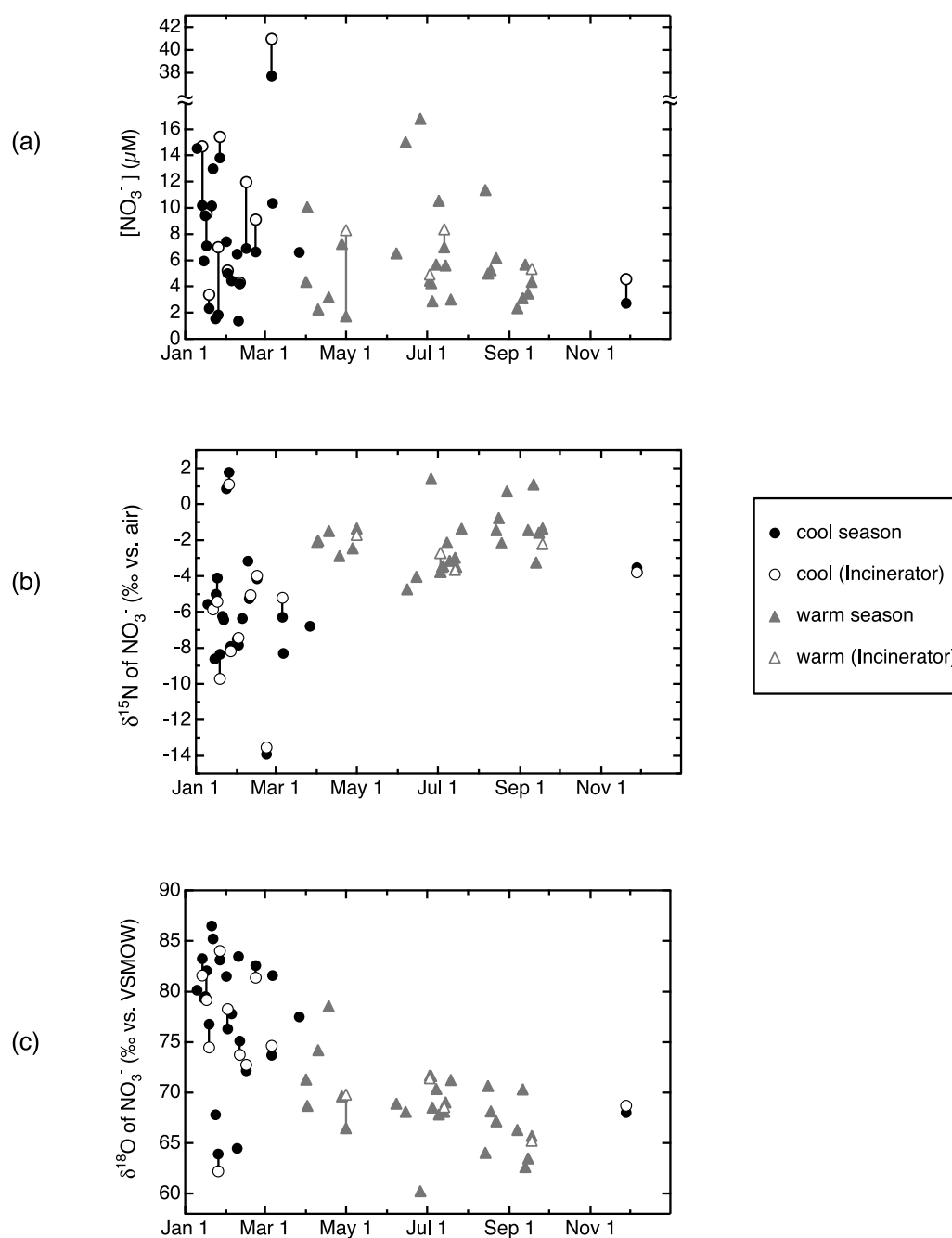


Figure 1. (a) Nitrate concentration (μM), (b) $\delta^{15}\text{N}$ of NO_3^- (‰ versus atmospheric N_2), and (c) $\delta^{18}\text{O}$ of NO_3^- (‰ versus VSMOW) in rain samples collected on Bermuda between January 2000 and January 2001. The data are divided into cool (October–March; circles) and warm (April–September; triangles) seasons. Samples from Incinerator station ($n = 15$) are shown as open symbols for the two seasons, respectively. Note the break on the y axis in Figure 1a. A tie connects samples collected on the same day at both stations (Figures 1a, 1b, and 1c). Samples from Incinerator station were systematically higher in concentration (Figure 1a), but did not show a significant difference in NO_3^- isotopes (note the overlap in Figures 1b and 1c) in comparison to Prospect station ($n = 50$).

sparks (i.e., lightning) does not differ very much from atmospheric nitrogen (-0.5 to $+1.4$ ‰).

3.3. O Isotopes of NO_3^-

[27] The $\delta^{18}\text{O}$ of NO_3^- is high in all samples, ranging from 60.3 to 86.5‰ versus VSMOW (Figure 1c), and varies seasonally. As for the $\delta^{15}\text{N}$ of NO_3^- , the $\delta^{18}\text{O}$ of

NO_3^- does not exhibit any relationship with $[\text{NO}_3^-]$ or rainfall (not shown). The warm season average of 68.6 ± 3.6 ‰ is significantly lower ($p < 0.0001$) than the cool season average of 76.9 ± 6.3 ‰ (Table 1). The warm season volume-weighted average of 68.7 ± 4.0 ‰ is also significantly lower than the cool season weighted average of 78.7 ± 5.6 ‰. As observed for $\delta^{15}\text{N}$, the $\delta^{18}\text{O}$ of NO_3^-

Table 1. Nitrate in Rainfall, Sorted by Season^a

	Warm Season (n = 30)	Cool Season (n = 35)
Total rainfall, ^b cm	61.9	59.5
Total deposition, mmol N m ⁻²	3.1	3.7
[NO ₃ ⁻], ^c μM	5.0	6.4
δ ¹⁵ N-NO ₃ ⁻ , ^c ‰	-1.8 ± 1.7	-6.8 ± 3.7
δ ¹⁵ N-NO ₃ ⁻ , ^d ‰	-2.1 ± 1.5	-5.9 ± 3.3
δ ¹⁸ O-NO ₃ ⁻ , ^c ‰	68.7 ± 4.0	78.7 ± 5.6
δ ¹⁸ O-NO ₃ ⁻ , ^d ‰	68.6 ± 3.6	76.9 ± 6.3

^aDeposition (rainfall x concentration) calculated by summing amount in each event from rainfall amounts provided by BBSR. For samples collected on the same date, only Prospect station data were used for volume-weighted calculation purposes.

^bRepresents total rainfall for the 50 Prospect samples in this study.

^c“Volume-weighted” average (weighted by [NO₃⁻] and rainfall from each event).

^dNumerical average and standard deviation (±1 SD).

is less variable in the warm season than in the cool season.

[28] High δ¹⁸O for atmospherically derived NO₃⁻ has been reported previously [Campbell *et al.*, 2002; Burns and Kendall, 2002; Williard *et al.*, 2001; Kendall, 1998; Böhlke *et al.*, 1997; Durka *et al.*, 1994]. A very large range for precipitation δ¹⁸O (~18 to 70‰, n = 110) has been reported for samples from various locations in North America [Kendall, 1998, and references therein]. A smaller range of values (55 to 75‰) has been reported for precipitation in forests of Bavaria (Germany) [Durka *et al.*, 1994]. Williard *et al.* [2001] observed seasonal variations in δ¹⁸O of NO₃⁻ in precipitation samples from Pennsylvania and West Virginia, with lower δ¹⁸O in the summer than in the winter. Kendall [1998] points out that high δ¹⁸O of precipitation NO₃⁻ in Bavaria [Durka *et al.*, 1994] may be a reflection of an anthropogenic pollution source, since other parts of central Europe further from industrial centers exhibit considerably lower δ¹⁸O of NO₃⁻. However, analyses of an ice core show δ¹⁸O of NO₃⁻ near 80‰ during the last glacial maximum [Galanter *et al.*, 2001]. The high δ¹⁸O of atmospheric NO₃⁻ is the result of interactions between NO_x and O₃ (e.g., reactions (R1)–(R3)) prior to deposition. This is discussed further in section 4.2.

3.4. Back Trajectory Analysis

[29] On the basis of the computed back trajectories from the NOAA HYSPLIT model, Figure 2 shows the geographic distribution for δ¹⁵N and δ¹⁸O of NO₃⁻ at 36-hours prior to the collection date at Bermuda. (This time frame was chosen since the lifetime of NO_x is on the order of a day.) In Figures 2a and 2b, all of the samples are shown for δ¹⁵N and δ¹⁸O of NO₃⁻. Our data show that δ¹⁵N for warm season samples (Figure 2c) is generally higher than for cool season samples (Figure 2e). In fact, only two warm season samples show a δ¹⁵N less than -4‰. In contrast, δ¹⁸O for warm season samples (Figure 2d) is lower than that observed during the cool season (Figure 2f).

[30] The model predicts that cool season samples are generally the result of air masses from continental North America, though a few originated (36 hours ago) as marine air masses. In comparison to the warm season, air masses in the cool months generally travel much farther before reaching Bermuda. In addition, the place of origin of the air masses is much more variable in the cool season. This

pattern is consistent with the higher observed variability for both δ¹⁵N and δ¹⁸O in cool season samples. In contrast, the model predicts that all of the warm season samples represent marine air masses from the North Atlantic basin or just off the east coast of the United States.

[31] The transport patterns predicted by the NOAA HYSPLIT model are similar to the predominant transport pathways defined in the trajectory cluster analysis by Moody and Galloway [1988]. The warm season is defined by trajectories arriving at Bermuda from the east, southeast, south, and southwest, and stagnant air masses that remain in the vicinity of the island (hereinafter referred to as S/EW transport). In contrast, the cool season is defined by rapid moving air parcels arriving from the west and northwest of Bermuda (hereinafter referred to as W/NW transport). To examine the isotope variability in terms of the seasonal changes in transport, the data were binned as S/EW (n = 42) or W/NW (n = 23) transport, based on the back trajectories.

[32] The average δ¹⁵N of NO₃⁻ for the S/EW samples (-2.6 ± 2.1‰) is higher than that for the W/NW samples (-7.0 ± 2.9‰) (Table 2). In contrast, the average δ¹⁸O of NO₃⁻ for S/EW samples (69.7 ± 5.1‰) is lower than the W/NW samples (79.2 ± 4.5‰). In comparison to the cool season average in Table 1, the W/NW average δ¹⁵N decreases by -1.1‰ and average δ¹⁸O increases by +2.3‰. These changes are due to the fact that 8 cool season events with high δ¹⁵N and low δ¹⁸O exhibited S/EW transport (see Figures 2e and 2f). The S/EW average δ¹⁵N and δ¹⁸O is very similar to the warm season average and significantly different (*p* < 0.0001) from the W/NW average. Thus the N and O isotopic variation observed for NO₃⁻ at Bermuda is explained equally well by seasonality (Table 1) or by transport pattern (Table 2).

4. Discussion

[33] One of the most intriguing results of this study is a correlation (*r*² = 0.56, n = 65) found between δ¹⁵N and δ¹⁸O of NO₃⁻ (Figure 3). This correlation is surprising since the ¹⁵N/¹⁴N and ¹⁸O/¹⁶O ratios are impacted by different processes prior to NO₃⁻ deposition. N atoms from the original NO_x source are conserved in reactions (R1)–(R7) above, while O atoms are exchanged with oxidizing species (i.e., O₃ and OH). As a result, the variations in δ¹⁵N of NO₃⁻ observed in this study are best interpreted as a consequence of source changes, while the δ¹⁸O of NO₃⁻ should reflect atmospheric processing of NO_x prior to deposition of NO₃⁻. Incinerator station showed systematically higher [NO₃⁻] for samples collected at both Incinerator and Prospect on the same date (section 3) and thus may be influenced by local sources. However, since the observed seasonal variations in the isotopes are much larger than the differences seen between Prospect and Incinerator stations (section 3) local sources and chemistry do not appear to have an impact on the isotopes. Regional processes must, therefore, drive the correlation we observe between δ¹⁵N and δ¹⁸O of NO₃⁻.

[34] In Figure 3 we see that warm season samples are characterized by high δ¹⁵N and low δ¹⁸O, while the cool season NO₃⁻ is typically low in δ¹⁵N and high in δ¹⁸O. Transport patterns in the cool season are more variable than those in the warm season (Figure 2). Remarkably, all of the “anomalous” cool season samples with warm season-like

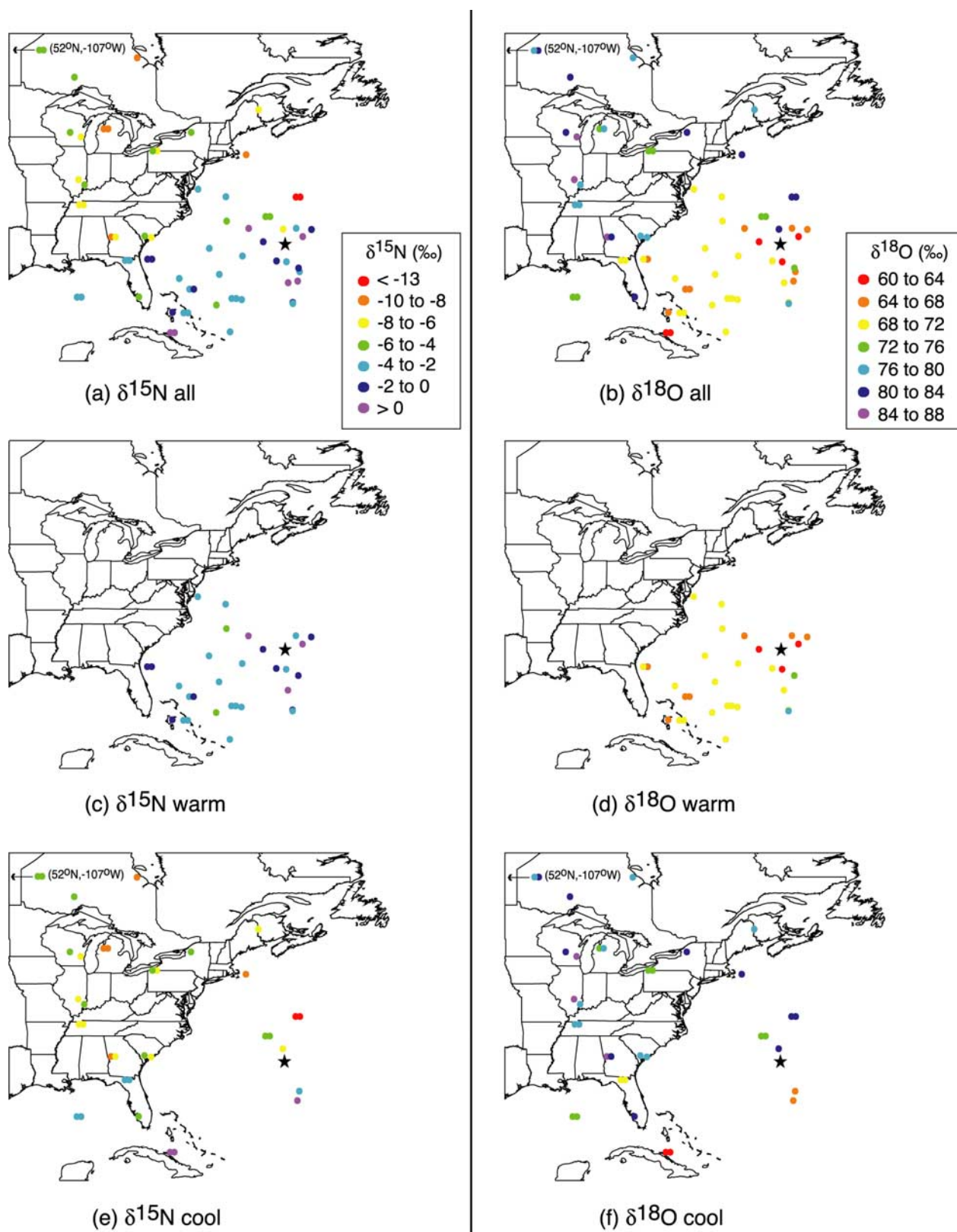


Figure 2. Geographic distribution of samples at 36-hours before reaching Bermuda (shown as a star), based on NOAA HYSPLIT model back trajectories. For dates when a sample was collected at both Incinerator and Prospect stations, one of the sample locations is shifted by 0.5° longitude so that both points can be seen. Colored points represent (a) $\delta^{15}\text{N}$ and (b) $\delta^{18}\text{O}$ of NO_3^- for all samples. The $\delta^{15}\text{N}$ of NO_3^- is shown for the (c) warm and (e) cool seasons; $\delta^{18}\text{O}$ of NO_3^- is also shown for the (d) warm and (f) cool seasons. In order to minimize the figure size, a point located in western Canada at 52°N , 107°W was shifted east, with an arrow pointing toward its original location.

Table 2. Nitrate in Rainfall, Sorted by Transport Pattern Based on Back Trajectories

	S/EW Transport (n = 42)	W/NW Transport (n = 23)
$\delta^{15}\text{N-NO}_3^-$, ^a ‰	-1.9 ± 2.3	-6.8 ± 3.2
$\delta^{15}\text{N-NO}_3^-$, ^b ‰	-2.6 ± 2.1	-7.0 ± 2.9
$\delta^{18}\text{O-NO}_3^-$, ^a ‰	68.8 ± 5.2	78.5 ± 4.7
$\delta^{18}\text{O-NO}_3^-$, ^b ‰	69.7 ± 5.1	79.2 ± 4.5

^a“Volume-weighted” average (weighted by $[\text{NO}_3^-]$ and rainfall from each event).

^bNumerical average and standard deviation (± 1 SD).

high $\delta^{15}\text{N}$ and low $\delta^{18}\text{O}$ are the result of S/EW, or warm season-type, transport patterns based on back trajectory analysis. Thus changes in transport (i.e., source region) appear to dominate both the N and O isotopic variations. For the cool season, low $\delta^{15}\text{N}$ is indicative of large inputs of anthropogenic sources from North America, while the warm season higher $\delta^{15}\text{N}$ suggests that another source is having an influence (section 4.1). The $\delta^{18}\text{O}$ difference between the two seasons is primarily driven by changes in the predominant oxidation pathway that produces NO_3^- from NO_x (section 4.2), and is consistent with regional variations in tropospheric chemistry.

4.1. Variations in $\delta^{15}\text{N}$ of NO_3^-

[35] We initially suspected that the seasonal differences in $\delta^{15}\text{N}$ of NO_3^- were due to isotopic fractionation associated with atmospheric cycling of reactive nitrogen oxides. Freyer *et al.* [1993] observed seasonal variations in $\delta^{15}\text{N}$ of NO_2 (lower in summer) in samples collected at Jülich, Germany, and found that isotopic exchange between NO and NO_2 contributes to a higher $\delta^{15}\text{N}$ in the more oxidized form. The authors determined that the seasonal variation in $\delta^{15}\text{N}$ of NO_2 is influenced by interactions among NO, NO_2 , and O_3 , oxidation of NO to NO_2 , and equilibrium isotope exchange between NO and NO_2 . The mechanisms that determined the isotopic seasonal variation of NO_2 were dependent on the NO, NO_2 , and O_3 concentrations (see reactions (R1)–(R7)) at the study site in Germany. Very high NO_x concentrations (~ 10 to 45 ppbv), moderate O_3 levels (~ 4 to 40 ppbv), and

seasonally varying NO_2 molar ratios were observed at their study site, with NO_x concentrations exceeding those of O_3 during the fall and winter.

[36] However, as acknowledged by Freyer *et al.* [1993], seasonal variations based on the above mechanisms should only be observed in areas with similar pollution levels as Jülich. Although Bermuda is not a “clean site,” O_3 concentrations (typically between 15 and 70 ppbv [Oltmans and Levy, 1992]) always exceed those of NO_x (< 0.35 ppbv [e.g., Prados *et al.*, 1999]), and thus the NO should be completely oxidized to NO_2 a majority of the time. Thus the mechanisms defined by Freyer *et al.* [1993] should not be capable of driving the seasonal variations observed for $\delta^{15}\text{N}$ of NO_3^- at Bermuda. Moreover, Freyer *et al.* [1993] observe the lowest $\delta^{15}\text{N}$ of NO_3^- when O_3 concentration is highest at Jülich during the summer; in Bermuda, the warm season is also associated with maximum O_3 concentrations [e.g., Oltmans and Levy, 1992], yet this is the period when the highest $\delta^{15}\text{N}$ of NO_3^- is observed.

[37] The $\delta^{15}\text{N}$ for cool season samples (Figure 1b) fall in the range for NO_x emitted from automobiles reported by Heaton [1990]. This is consistent with the transport of fossil fuel NO_x from the east coast of North America, which is primarily the result of vehicle emissions [U.S. Environmental Protection Agency, 2000]. The lowest $\delta^{15}\text{N}$ ($\sim -14\text{‰}$) observed at both stations on February 23 originated just to the north of Bermuda 36-hours prior to deposition (see Figure 2e). This sample is the result of a relatively slow-moving air mass that was located in New York state at 60-hours earlier, and north of the Great Lakes region at 72-hours. This sample does not exhibit an anomalous $\delta^{18}\text{O}$ (Figure 2f), and the $\delta^{15}\text{N}$ is slightly lower than the range reported for vehicle fuel combustion, its likely continental source. It is possible that fractionation during transport could alter the isotopic composition of NO_3^- and explain why studies on the east coast of the United States have attributed higher values than typically seen in this study to local emissions from fossil fuel combustion. However, based on Figures 2a–2f, the travel time to Bermuda does not appear to have a strong relationship with the isotopic composition of the rain NO_3^- .

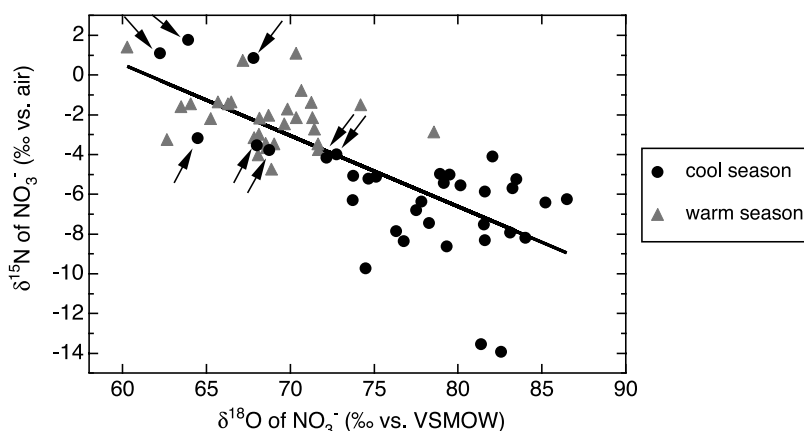


Figure 3. A plot of $\delta^{15}\text{N}$ versus $\delta^{18}\text{O}$ of NO_3^- shows a negative correlation ($r^2 = 0.56$). Arrows point to uncharacteristic cool season samples with low $\delta^{18}\text{O}$ and high $\delta^{15}\text{N}$, which also exhibit S/EW, or warm season-type, transport patterns.

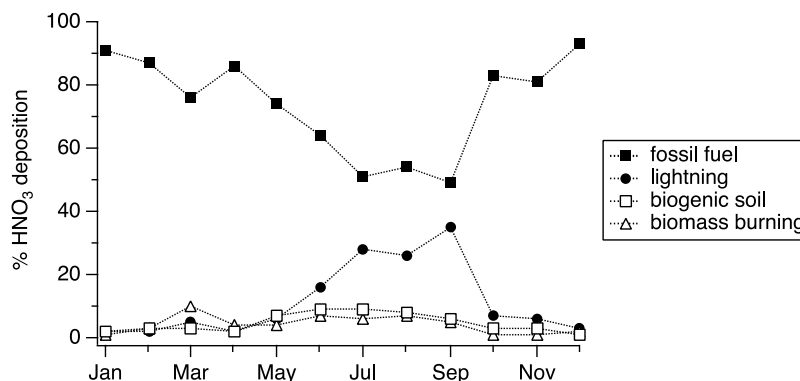


Figure 4. Percent (%) breakdown of NO_x sources that contribute to wet deposited HNO_3 at Bermuda from the GFDL GCTM simulation of NO_x . Note that these sources do not represent 100% of HNO_3 deposition, as the figure does not include the small contributions from aircraft emissions and stratospheric injection of NO_x .

[38] The seasonal change observed in $\delta^{15}\text{N}$ of NO_3^- , therefore, requires a change in the source of NO_x that correlates with the source region. A global chemical transport model (GFDL GCTM) was employed to evaluate the variability of the sources of NO_3^- deposition at Bermuda. Figure 4 shows a breakdown of the percent impact of sources of NO_x on simulated HNO_3 deposition at Bermuda during the two seasons. It should be noted that the GCTM compares well with observations at Bermuda. For a typical year, the GCTM predicts an annual wet HNO_3 deposition rate of $7.0 \text{ mmol m}^{-2} \text{ yr}^{-1}$ at Bermuda, which compares well with observations of 6.4 (1981–1988) and 4.9 (1989–1993) $\text{mmol N m}^{-2} \text{ yr}^{-1}$ [Prospero *et al.*, 1996]. The simulated volume-weighted average HNO_3 concentration for wet deposition ($5.4 \mu\text{M}$ for both seasons) also compares well with the observations in this study, and those reported by Moody and Galloway [1988].

[39] The model predicts that anthropogenic emissions from fossil fuel burning are the dominant source for NO_3^- deposition at Bermuda. In the warm season, however, lightning NO_x emissions become important, contributing $\sim 30\%$ to total HNO_3 deposition in July, August, and September (Figure 4). Observed global distributions of electrical storms suggest maximum NO_x production from lightning during summer in this region [Price *et al.*, 1997]. Pickering *et al.* [1998] predict that a significant percentage (32%) of lightning-derived NO_x occurs below 5 km in the midlatitudes, and Levy *et al.* [1996] show up to 70% contribution from lightning to total NO_x concentration below 500 mbar over the North Atlantic in July. Pickering *et al.* [1998] also note the potential presence of strong downdrafts due to intense convection over mid-latitude warm ocean currents. These studies raise lightning as a possible source of NO_3^- that could explain the N isotope variation observed in Bermuda rain.

[40] The higher $\delta^{15}\text{N}$ for warm season NO_3^- is consistent with an increased contribution of lightning NO_x ($\sim 0\%$ [Hoering, 1957]) to NO_3^- deposition. If we assume that the nitrate in Bermuda rain during the warm season has only two sources, anthropogenic emissions from North America and lightning emissions, then we can attempt to quantify the required contribution from lightning using the simple mass balance equation: $\delta^{15}\text{N}_{\text{warm-average}} \times (1) = \delta^{15}\text{N}_{\text{anthropogenic}} \times$

$(1 - x) + \delta^{15}\text{N}_{\text{lightning}} \times (x)$. Our data yield a $\delta^{15}\text{N}_{\text{warm-average}}$ of $\sim -2\%$. If we assume that $\delta^{15}\text{N}_{\text{anthropogenic}}$ is -7% (W/NW average) and that $\delta^{15}\text{N}_{\text{lightning}}$ is 0% , then we calculate a 71% contribution from lightning to total NO_3^- deposition in the warm season.

[41] Given the various assumptions that go into this calculation, this estimate is tentative, and its uncertainty is difficult to assess without more data. For instance, the $\delta^{15}\text{N}$ of other possible sources of NO_x to the North Atlantic (e.g., biomass burning, biogenic emissions) are not known and are thus excluded from this calculation. Nevertheless, the isotope data appear to suggest a greater contribution from lightning than has been previously predicted by model studies for NO_3^- deposition at Bermuda. Moreover, it is noteworthy that a large contribution from lightning in the warm season also provides a non-anthropogenic source to explain the higher than expected warm season [NO_3^-] found in this study and by Moody and Galloway [1988]. In the cool season, higher $\delta^{15}\text{N}$ of NO_3^- is observed in samples transported from the southeast and southwest of Bermuda, which suggests that lightning emissions can also be episodically important for NO_3^- deposition during the cool season.

4.2. Variations in $\delta^{18}\text{O}$ of NO_3^-

[42] The oxygen atoms of atmospheric NO_x are rapidly exchanged with O_3 in the NO/NO_2 cycle (reactions (R1) and (R2)). Therefore we expect the oxygen isotopic composition of atmospheric NO_3^- to be determined by the reactions that produce NO_3^- , not the original source of NO_x . The high $\delta^{18}\text{O}$ of precipitation NO_3^- we observe supports this conclusion. High ^{18}O , in the range of ~ 90 to 122% (versus VSMOW), is observed for tropospheric O_3 [Johnston and Thiemens, 1997; Krankowsky *et al.*, 1995]. In addition, O_3 has a mass-independent isotopic composition [Thiemens and Heidenreich, 1983], and a similar anomalous isotopic composition has been observed for atmospheric NO_3^- , a likely result of transfer from O_3 during cycling with NO_x [Galanter *et al.*, 2000a; Sigman *et al.*, 2001; Michalski *et al.*, 2003]. Results from a model study imparting a mass-independent oxygen isotopic composition in HNO_3 via exchange with O_3 agree well observations of the $\Delta^{17}\text{O}$ of atmospheric NO_3^- [Lyons, 2001, and references therein]. Finally, Röckmann *et al.* [2001] propose

that the mass-independent oxygen isotopes in tropospheric N_2O are the result of transfer from NO_2 (via reaction with NH_2) which is produced via reaction of NO and O_3 (reaction (R1)).

[43] The isotopic O_3 signal in NO_x is diluted by the reaction of NO_2 with hydroxyl radical (OH) (reaction (R4)). Although OH can be formed in the atmosphere via O_3 photolysis, the $\delta^{18}\text{O}$ of OH is expected to reflect the isotopic composition of water vapor in the troposphere [Röckmann *et al.*, 1998; Dubey *et al.*, 1997], which is typically between -30 and $+2\text{‰}$ versus VSMOW (-6 to $+2\text{‰}$ over the North Atlantic basin) (see maps and animations from the Global Network of Isotopes in Precipitation (GNIP), International Atomic Energy Agency, available at <http://isohis.iaea.org>). Using the minimum and maximum $\delta^{18}\text{O}$ reported for O_3 (90 and 122‰) and OH , we would expect (to first order) the $\delta^{18}\text{O}$ of NO_3^- to fall between 50 and 82‰ (assuming two oxygen molecules from O_3 and one from OH). In certain environments, reaction of NO with peroxy radicals can compete with O_3 to convert NO to NO_2 . The $\delta^{18}\text{O}$ of peroxy radicals is expected to be much lower than that of O_3 since the oxygen atoms should come from atmospheric O_2 ($\delta^{18}\text{O} = 23.5\text{‰}$ versus VSMOW) and could therefore contribute to some of the observations of low $\delta^{18}\text{O}$ of NO_3^- (less than 50‰) [e.g., Burns and Kendall, 2002; Williard *et al.*, 2001; Kendall, 1998, and references therein]. An additional possibility is that some of these low values (much less than 50‰) were the result of O isotope exchange during analysis of NO_3^- $\delta^{18}\text{O}$ [Casciotti *et al.*, 2002]. For instance, Révész and Böhlke [2002] report that O isotope exchange between the sample and a glass tube can occur in off-line combustion techniques used for determining $\delta^{18}\text{O}$ of NO_3^- .

[44] The most likely explanation that emerges for the $\delta^{18}\text{O}$ of NO_3^- variation observed in precipitation at Bermuda is that it reflects a shift in the predominant oxidation pathway for NO_x conversion to NO_3^- . During the warm season, particularly the summer months, photolysis produces maximum OH concentrations [e.g., Spivakovsky *et al.*, 2000] and HNO_3 production would occur primarily via reactions (R1) and (R4). On the other hand, colder temperatures, shorter days, and lower $[\text{OH}]$ during the winter would favor a greater contribution from the N_2O_5 pathway for HNO_3 formation (reactions (R5)–(R7)). N_2O_5 is thermally and photolytically unstable and a longer night would allow for significant concentrations to be reached. This seasonal change in temperature, day length and chemistry should be particularly prominent north of the subtropical island of Bermuda, and is supported by global and regional modeling studies [Dentener and Crutzen, 1993; Russell *et al.*, 1985].

[45] The N_2O_5 pathway would be expected to produce a higher $\delta^{18}\text{O}$ in deposited NO_3^- because there is a lack of dilution via reaction with OH and more interaction with O_3 . As a result of OH oxidation (reactions (R1)–(R4)), only two out of three oxygen atoms in the resulting HNO_3 would come from O_3 . For the 2HNO_3 produced from N_2O_5 , as many as five out of six of the oxygen atoms are the result of interaction with O_3 (reactions (R1) and (R5)–(R7)). Cool season samples that were the result of S/EW transport exhibit low, warm season-like, $\delta^{18}\text{O}$ of NO_3^- and are consistent with this hypothesis as well. There is a strong meridional gradient in

$[\text{OH}]$ in the winter, with higher concentrations to the south of Bermuda [Spivakovsky *et al.*, 2000]. Since the $\delta^{18}\text{O}$ is determined by the chemistry that produces the NO_3^- , the correlation with $\delta^{15}\text{N}$ (Figure 3), a source-driven signal, suggests that the spatial variation in cool season $[\text{OH}]$ produces variability in the $\delta^{18}\text{O}$ of NO_3^- that is of similar magnitude to its seasonal variation. Qualitatively, this suggests that the spatial and seasonal variations in $[\text{OH}]$ are of similar magnitude in the North Atlantic Basin.

[46] The $\delta^{17}\text{O}$ of NO_3^- is also sensitive to the chemical pathway that produces NO_3^- . Michalski *et al.* [2003] observe a strong seasonal change in $\Delta^{17}\text{O}$ (recall $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.5 \times \delta^{18}\text{O}$) and find that a seasonal trend in $\Delta^{17}\text{O}$ is controlled by the predominant NO_x chemistry that produces HNO_3 on aerosols collected in La Jolla, California. Consistent with our interpretation, Michalski *et al.* [2003] predict a shift in the chemistry that produces HNO_3 from the OH pathway (reaction (R4)) in the spring to the N_2O_5 pathway (reactions (R6)–(R7)) in the winter. OH is expected to have a mass-dependent oxygen isotopic composition because of exchange with water vapor in the troposphere, and therefore contributes to a lower $\Delta^{17}\text{O}$ during the spring. Thus it would be expected that the $\Delta^{17}\text{O}$ of NO_3^- during the warm season at Bermuda, or for air transported from the south during the cool season, should be lower than for NO_3^- from the north and west of Bermuda. Indeed, $\delta^{17}\text{O}$ calculated from $\delta^{15}\text{N}$ differences (section 2.3) results in an average $\Delta^{17}\text{O}$ of 32‰ for W/NW and 24‰ for S/EW samples.

5. Conclusions

[47] The warm season at Bermuda (April–September) is characterized by higher $\delta^{15}\text{N}$ and lower $\delta^{18}\text{O}$ of NO_3^- than the cool season (October–March). All of the cool season samples that exhibit warm season-like high $\delta^{15}\text{N}$ and low $\delta^{18}\text{O}$ are the result of warm season transport patterns. Thus the source region of air transported to Bermuda determines the seasonal variations observed in the isotopes of rain NO_3^- at Bermuda, and produces the correlation found between $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of NO_3^- . The higher warm season $\delta^{15}\text{N}$ is best interpreted as a change in the source of NO_3^- (i.e., the source of NO_x), which is consistent with observations and simulations that predict lightning as an important source of NO_x over the North Atlantic during summer months. The isotope results suggest that lightning is the dominant source contributing to NO_3^- deposition in the warm season. This lightning source of NO_x also explains the higher than expected $[\text{NO}_3^-]$ observed during the warm season in this and a previous study. This study highlights the significance of lightning as a contributor to NO_3^- deposition and underscores the importance of considering natural source impacts on reactive nitrogen chemistry, particularly in locations where the influence of anthropogenic sources may be variable.

[48] The $\delta^{18}\text{O}$ of NO_3^- is very high throughout the year as a result of NO_x and O_3 interactions in the atmosphere prior to deposition of NO_3^- . The higher $\delta^{18}\text{O}$ during the cool season reflects a shift in the predominant NO_x chemistry. Colder temperatures, shorter days, and lower $[\text{OH}]$ in the cool season would favor a larger contribution from the N_2O_5 pathway of production for NO_3^- . This pathway would result in a greater contribution from O_3 to the oxygen

isotopic composition of deposited NO_3^- , and therefore a higher $\delta^{18}\text{O}$. The similar $\delta^{18}\text{O}$ of NO_3^- observed for warm season samples and cool season rain events that originate from the south of Bermuda and the correlation between $\delta^{18}\text{O}$ (a chemistry-driven signal) and $\delta^{15}\text{N}$ (a source-driven signal) suggest that the spatial gradient in $[\text{OH}]$ in the cool season is comparable to the seasonal variation of $[\text{OH}]$.

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