

Isotopic composition of rainwater nitrate at Bermuda: The influence of air mass source and chemistry in the marine boundary layer

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[1] Emissions of anthropogenic nitrogen (N) to the atmosphere have increased tenfold since preindustrial times, resulting in increased N deposition to terrestrial and coastal ecosystems. The current sources of N deposition to the ocean, however, are poorly understood. To investigate the sources of nitrate in rainwater deposited to the ocean, two years of daily rainwater samples were collected on the island of Bermuda in the western North Atlantic. Air mass back trajectories were computed for each sample and two dominant regimes were identified: slow moving events that originate over the ocean and occur all year, and fast moving events that originate over the continental USA and occur primarily during the cool season (October–March). Marine-influenced air masses result in rainwater nitrate with lower concentrations, higher average $\delta^{15}\text{N}$, and lower average $\delta^{18}\text{O}$ (4.4 μM , -1.1% versus N_2 in air, and 69.0‰ versus Vienna SMOW, respectively) than those influenced by North American air masses (6.3 μM , -5.4% , and 75.0‰). The $\delta^{15}\text{N}$ decrease and concentration increase from marine to continental air masses are due to a change in NO_x source, with increased anthropogenic inputs associated with continental air. We suggest that heterogeneous halogen chemistry in the marine boundary layer leads to isotopic fractionation. This causes higher $\delta^{15}\text{N}\text{-NO}_3^-$ to be deposited near the coast and lower $\delta^{15}\text{N}\text{-NO}_x$ to be transported over the open ocean, yielding a low $\delta^{15}\text{N}$ for anthropogenic NO_3^- deposition. It is possible that this process also contributes to variations in $\delta^{15}\text{N}\text{-NO}_3^-$ from marine air masses. There is a negative linear correlation ($r^2 = 0.58$) between $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ which is driven by the seasonal change in trajectory influencing both the source NO_x and the nitrate formation pathways.

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1. Introduction

[2] The emissions of anthropogenic nitrogen (N) to the atmosphere, and its subsequent deposition, have increased tenfold since preindustrial times [Galloway *et al.*, 2004]. The impacts of increased N deposition to terrestrial and coastal systems are well studied [e.g., Elser *et al.*, 2009; Paerl *et al.*, 2002]; however, the implications for open ocean N biogeochemistry remain uncertain [Duce *et al.*, 2008]. Both anthropogenic and natural processes impact the amount and form of N deposition to remote marine environments,

and there have been clear increases in nitrate deposition as a result of increased anthropogenic emissions of N oxides [Elliott *et al.*, 2007; Galloway *et al.*, 2003; Hastings *et al.*, 2009; Kim *et al.*, 2011; Kodama *et al.*, 2011]. The concentration of nitric acid (HNO_3) in seawater is extremely low; therefore, deposition is a one-way process. Identifying the sources of N deposition to the open ocean is critical for understanding the biogeochemical impacts of human activities. If the N deposition is terrestrial in origin, it represents an external input to the open ocean as the reactive N chemistry over the continents is influenced heavily by anthropogenic activities; this input can be expected to change into the future [Duce *et al.*, 2008]. In contrast, if the N originates from natural sources, then it might not be a N input to the ocean as a whole (e.g., if it derives from the upper ocean), and it is in any case less likely to undergo a marked change in the coming decades.

1.1. Nitrate in the Marine Atmosphere

[3] Nitrate (NO_3^-) is the ultimate sink for atmospheric nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$), and it is an increasingly significant component of acid rain as effective sulfur dioxide

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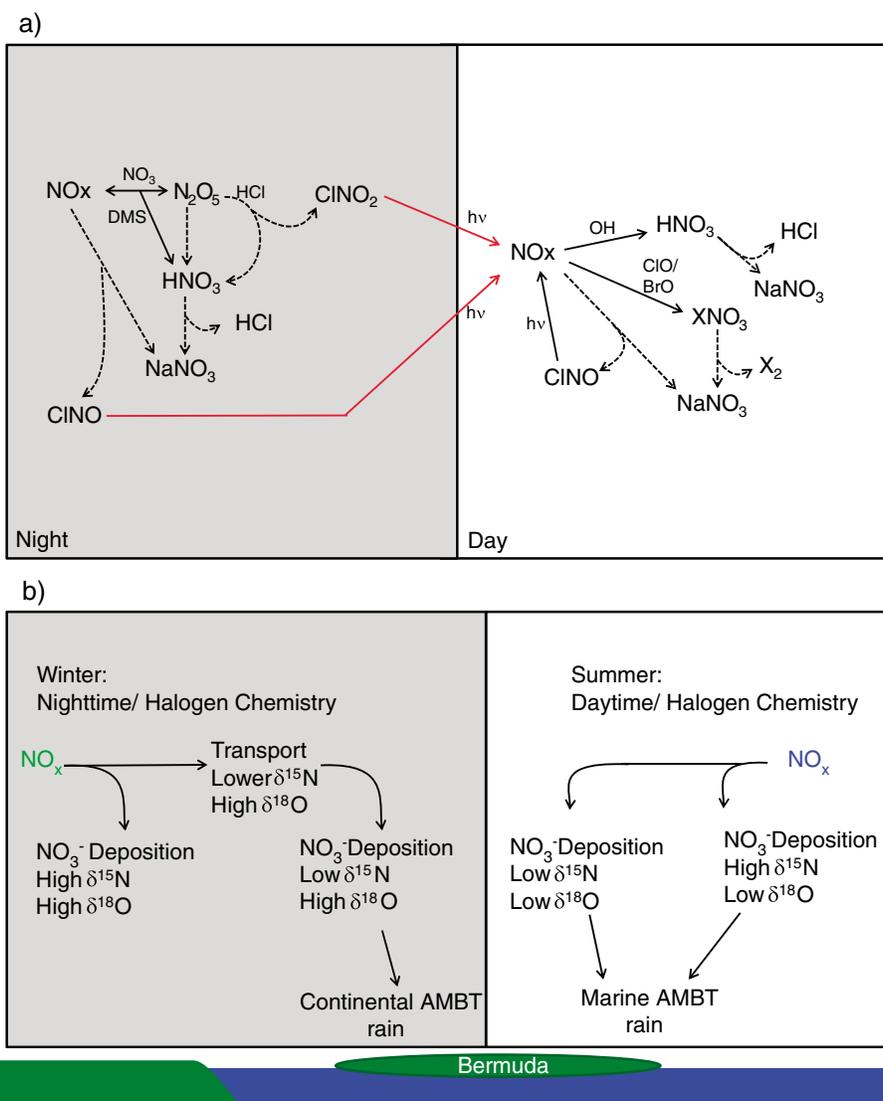
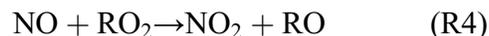


Figure 1. (a) Schematic description of the nighttime and daytime atmospheric chemical processes involving NO_x conversion to nitrate. The dashed lines indicate heterogeneous reactions, the solid lines indicate gas phase reactions, and the red solid lines that cross from night to day indicate the nighttime reservoir species that are photolyzed to NO_x in the presence of sunlight. (b) The impact of that chemistry on the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate that reaches Bermuda during continental versus marine AMBT.

regulations lead to decreases in sulfuric acid concentrations. The lifetime of NO_x is usually hours to days; thus, its conversion to longer lived reservoir species such as HNO_3 or peroxyacetyl nitrate (PAN) is needed for reactive N to be transported long distances. The atmospheric cycle of NO_x and the conversion of NO_x to NO_3^- is complex, with different processes taking place during the day and night (Figure 1a). During the day, cycling between NO and NO_2 is rapid (R1)–(R4).

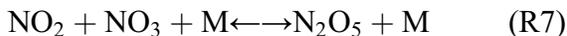
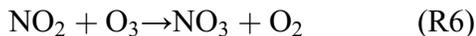


[4] The oxidation of NO to NO_2 requires ozone (R1), while the breakdown of NO_2 back to NO is photolytic and produces ozone [(R2)–(R3)]. NO can also be oxidized to NO_2 via peroxy radicals (R4), which also ultimately leads to ozone production. At night, (R2) shuts down and (R1) dominates until $[\text{NO}_2] \approx [\text{NO}_x]$. The dominant daytime sink of NO_x is the oxidation of NO_2 to HNO_3 by the hydroxyl radical (R5).

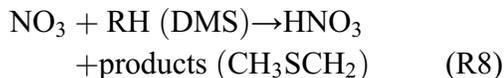


[5] During the night, when photolytic production of OH ceases, the concentration of OH decreases and NO_2 reacts preferentially with ozone to form NO_3 , the dominant nighttime oxidant. NO_2 and NO_3 then react further to form

N_2O_5 , and NO_2 and NO_3 remain in thermal equilibrium with N_2O_5 [(R6)–(R7)]; M is an unreactive body, usually N_2 .



[6] NO_3 can also be lost via gas phase reactions with volatile organic compounds (VOCs), including dimethyl sulfide (DMS) in marine areas (R8) [Stark *et al.*, 2007].



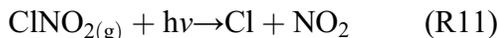
[7] The loss of N_2O_5 occurs through heterogeneous hydrolysis on aerosol particles (R9).



[8] Recent studies have shown the potential for halogens to play a significant role in NO_x and nitrate chemistry. In the presence of HCl, N_2O_5 can also react heterogeneously on aerosol particles to form both aqueous nitrate and ClNO_2 which partitions to the gas phase (R10) [Thornton *et al.*, 2010].

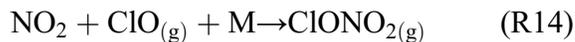


[9] It is hypothesized that the branching ratio between formation of $\text{HNO}_3(\text{aq})$ in (R9) and $\text{ClNO}_2(\text{g})$ and $\text{HNO}_3(\text{aq})$ in (R10) is determined by the relative concentrations of chloride and water in the aerosol particles. In the polluted marine boundary layer where high concentrations of NO_x and NaCl particles mix, i.e., in coastal regions, ClNO_2 is produced in high yields, exceeding previously predicted values by a factor of 2 to 30 [Osthoff *et al.*, 2008]. Maximum production of ClNO_2 has been found thus far in polluted coastal regions of the North Atlantic, with the largest fluxes occurring in the northern hemisphere winter [Erickson *et al.*, 1999]. The ClNO_2 acts as a reservoir species, building up in concentration at night and regenerating NO_x during the day through photolysis (R11).

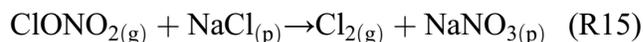


[10] The combination of (R10) and (R11) increases the lifetime of reactive N in the marine atmosphere by regenerating NO_x , in contrast to the reaction without halogen chemistry (R9), in which the conversion of N_2O_5 to aqueous nitrate aerosol ensures efficient removal of reactive N.

[11] In the presence of halides, another potential mechanism for NO_x conversion to NO_3^- is through reaction with ClO or BrO during the day to form ClONO_2 or BrONO_2 [(R12)–(R14)].



[12] First, acid displacement reactions occur when $\text{HNO}_3(\text{g})$ in continental outflow reacts with NaCl in the marine boundary layer, releasing HCl and forming $\text{NaNO}_3(\text{p})$. The HCl then reacts with OH to produce Cl radicals, which quickly form ClO by reaction with ozone; BrO is formed in an analogous manner. The ClONO_2 (or BrONO_2) formed can then combine with sea-salt aerosol to form coarse mode aerosol nitrate (R15).



[13] The conversion of HNO_3 to coarse mode NO_3^- should significantly decrease its lifetime as coarse mode particles are deposited preferentially through gravitational settling and precipitation scavenging via inertial impaction.

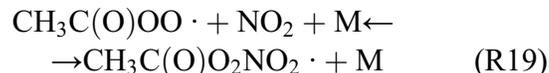
[14] NO_x can also react with sea-salt aerosol to form ClNO and NaNO_3 (R16).



[15] The ClNO produced has two potential fates, photolysis and hydrolysis [(R17)–(R18)].



[16] In polluted environments, NO_x can react with peroxyacetyl radicals to form PAN, a long lived NO_x reservoir which can be transported long distances at high altitudes. When air masses subside, PAN thermally decomposes to again form NO_2 (R19) [Fischer *et al.*, 2011, and references therein].



[17] The chemical and physical processing of NO_x and nitrate, along with the frequency and amount of precipitation as an air mass travels, controls how much reactive N will be transported to the remote marine atmosphere and the isotopic composition of reactive N.

1.2. Previous N Isotope Studies

[18] Inorganic N is the dominant form of N deposition in both polluted [Cornell *et al.*, 2003; Russell *et al.*, 1998] and remote sites [Duce *et al.*, 2008; Galloway *et al.*, 1996; Galloway *et al.*, 1982; Galloway *et al.*, 1989], and nitrate typically represents ~50% of inorganic N deposition. Previous studies have used N and O isotopes of nitrate as a tool for distinguishing nitrate sources and chemical formation pathways in polluted

[Elliott et al., 2007; Freyer, 1978] and open ocean environments [Hastings et al., 2003; Morin et al., 2009]. In the above reactions (section 1.1), as NO_x is converted to nitrate, the N atom is conserved. As such, it is generally expected that the $\delta^{15}\text{N}$ of nitrate will reflect the $\delta^{15}\text{N}$ of the NO_x source. Indeed, previous work suggests that the conversion of NO_x to nitrate imparts little isotopic fractionation [Freyer et al., 1993]. In contrast, the O atoms of atmospheric NO_x are rapidly exchanged with O_3 in (R1)–(R4). NO_2 can be converted to NO_3^- through multiple pathways, all resulting in the addition of one oxygen atom. Therefore, the $\delta^{18}\text{O}$ of nitrate is set by the oxidants that convert NO_x to nitrate (e.g., OH versus O_3).

[19] Hastings et al., [2003] showed that nitrate in Bermuda (32.27°N, 64.87°W) rain has higher $\delta^{15}\text{N}\text{-NO}_3^-$ and lower $\delta^{18}\text{O}\text{-NO}_3^-$ in the warm season (April to September; -2.1‰ and 68.6‰) as compared to the cool season (October to March; -5.9‰ and 76.9‰ ; isotope ratios are reported using the delta (δ) notation in “per mil” (‰): $\delta^{15}\text{N}_{\text{sample}} = [({}^{15}\text{N}/{}^{14}\text{N})_{\text{sample}}/({}^{15}\text{N}/{}^{14}\text{N})_{\text{N}_2 \text{ in air}} - 1] * 1000\text{‰}$ and $\delta^{18}\text{O}_{\text{sample}} = [({}^{18}\text{O}/{}^{16}\text{O})_{\text{sample}}/({}^{18}\text{O}/{}^{16}\text{O})_{\text{VSMOW}} - 1] * 1000\text{‰}$). However, the concentration of nitrate was not significantly different from the warm to the cool season (5.0 and 6.4 μM , respectively). They concluded that during the warm season there is substantial nitrate in Bermuda rain that has an isotopic signature distinct from the nitrate coming off North America, implying an alternative nitrate source over the North Atlantic. The rainwater nitrate originating from the south of Bermuda (i.e., marine air) has a $\delta^{15}\text{N}$ of $\sim 0\text{‰}$, which Hastings et al., [2003] attributed to an increased contribution from lightning NO_x . Two rain samples collected on research cruises in the Eastern Atlantic Ocean had $\delta^{15}\text{N}$ values of -1.4 and -0.9‰ [Baker et al., 2007] consistent with rains at Bermuda.

[20] One interesting and heretofore unresolved result of the Hastings et al. [2003] study is that during the cool season when North America is the air mass source region, the $\delta^{15}\text{N}\text{-NO}_3^-$ in rain is lower in Bermuda than in the United States. The N and O isotopes of nitrate in weekly rainwater collections were measured in the northeastern USA at National Atmospheric Deposition Program (NADP) sites during the same time frame as the Hastings et al., [2003] study [Elliott et al., 2007; Elliott et al., 2009], and from October to March, the rainwater $\delta^{15}\text{N}\text{-NO}_3^-$ varied from 0 to 3.5‰. In contrast, the Bermuda cool season average $\delta^{15}\text{N}$ was $-5.9 \pm 3.3\text{‰}$ ($\pm 1\text{SD}$).

[21] To investigate the sources and chemistry that influence atmospheric nitrate deposition to the ocean, two years of event-based rainwater samples were collected on the island of Bermuda. Samples were analyzed for major ion concentrations and N and O isotopic ratios of nitrate. NOAA’s Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT) was used to determine air mass history for each rainwater sample, and events were classified as originating over the continental USA or as marine in origin.

2. Methods

2.1. Sample Collection

[22] Rainwater samples were collected on the island of Bermuda (32.27°N, 64.87°W) from 1 July 2009 to 16 September 2011 ($n=155$) at an active ambient air quality monitoring site (station Prospect). All sample data including

concentrations and N and O isotopic composition of nitrate have been made publicly available at the SOLAS Project Integration Aerosol and Rain Composition and Deposition Database. Ambient air quality at this location is characterized by low levels of NO_x , SO_2 , and particulate matter (A. Peters, TSP, PM_{10} , and $\text{PM}_{2.5}$, unpublished data). The site is located atop a water catchment 65 m above sea level. It is unobstructed in all directions and is the second highest point on the island. Rainwater samples were collected in acid-washed polyethylene buckets using an automatic rain collector (Aerochem Metrics model 301). Samples were collected on an event basis and retrieved daily to limit microbial degradation of organic matter and consumption of inorganic nutrients. For all samples, the pH, rain volume, and conductivity were measured before being stored at -20°C . Freezing at -20°C is sufficient to preserve the concentration and isotopic composition of nitrate in rainwater [Hastings et al., 2003]. Field blanks were collected by placing 200 mL of deionized water into the rainwater collector overnight and then collecting the water in the same way as a rainwater sample. The full suite of chemical analyses was also performed on the field blanks to assess possible contamination from the collector or from sample handling. The concentration of nitrate in the field blanks was below the method detection limit (section 2.2).

[23] An additional 11 rainwater samples were collected on an event basis at the Bermuda Institute of Ocean Sciences from 2 July 2010 to 13 August 2010, and four rainwater samples were collected at the Tudor Hill Marine-Atmospheric Sampling Observatory tower located 23 m above sea level in March of 2010. These samples are treated in the same manner as those collected at station Prospect.

2.1. Anion Concentrations

[24] The rainwater samples were analyzed by ion chromatography for anions (Cl^- , NO_3^- , NO_2^- , SO_4^{2-}) using an ICS-1600 (Thermo Scientific Dionex, Sunnyvale, USA) at BIOS. Anions were analyzed using an IonPac AS14A 5 μm analytical column ($3 \times 150 \text{ mm}$) with an IonPac AG14A 5 μm guard column ($3 \times 30 \text{ mm}$). The mobile phase was a solution of 8 mM Na_2CO_3 and 1 mM NaHCO_3 . Calibration curves for each analyte were generated using five points over the range of 1 to 1000 μM . The instrument detection limits (defined as the concentration calculated to produce a peak height three times that of a Milli-Q water blank) were: 0.17 μM for NO_3^- , 0.08 μM for SO_4^{2-} , and 0.04 μM for Cl^- . Nitrate concentrations were also determined for a subset of samples by reduction of nitrate and nitrite to nitric oxide followed by chemiluminescence detection of nitric oxide [Braman and Hendrix, 1989]. Nitrite was below detection limit (0.15 μM) in all rainwater samples.

2.3. Nitrate Isotopic Analysis

[25] 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 at Princeton University [Casciotti et al., 2002; Sigman et al., 2001]. Natural strains of denitrifying bacteria, in this case *Pseudomonas aureofaciens*, that lack N_2O reductase activity are used to quantitatively convert NO_3^- to nitrous oxide (N_2O). The ion current ratios (m/z 45/44 and 46/44) of the resultant N_2O were measured using a modified GasBench II in line to a Thermo DeltaVPlus IRMS [Casciotti et al., 2002], allowing the coupled determination of the ${}^{15}\text{N}/{}^{14}\text{N}$

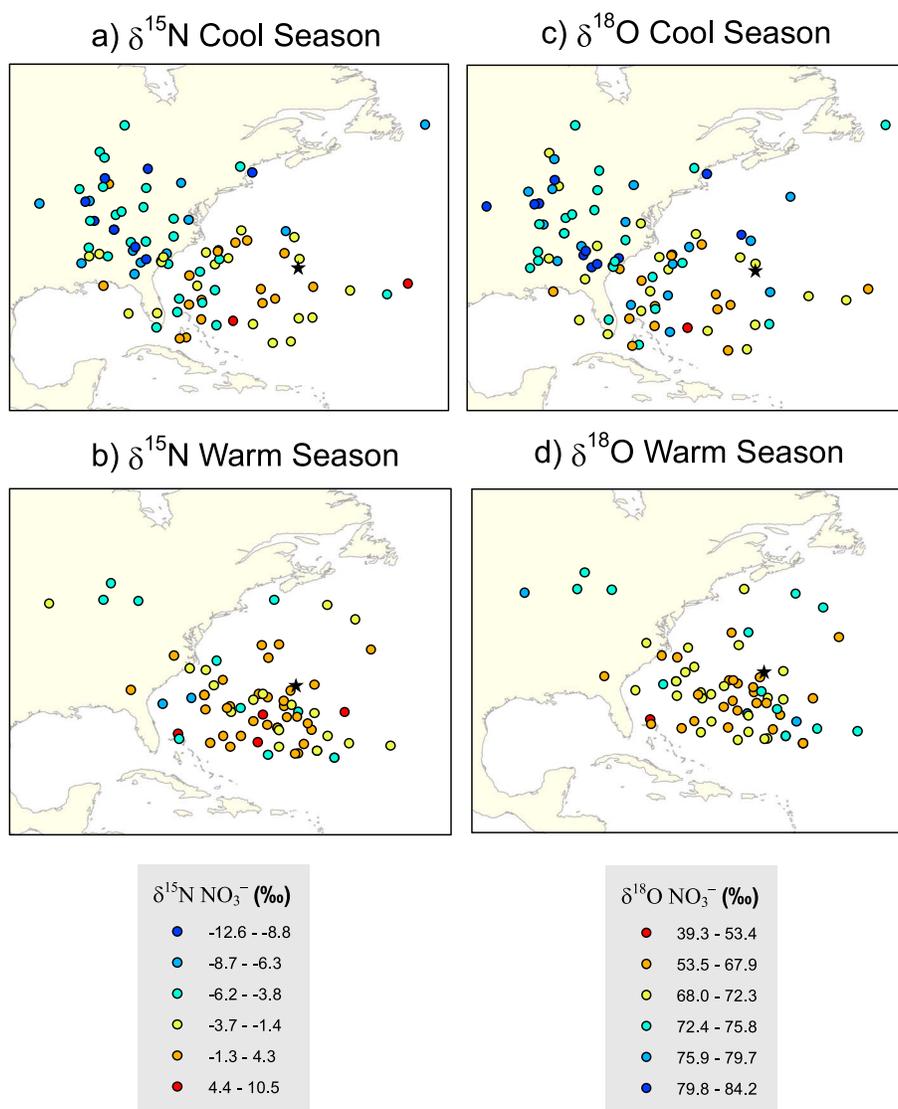


Figure 2. Geographic distribution of samples at 36 h before reaching Bermuda (shown as star), based on NOAA HYSPLIT model air mass back trajectories. Colors demark ranges in (a) $\delta^{15}\text{N-NO}_3^-$ in the cool season, (b) $\delta^{15}\text{N-NO}_3^-$ in the warm season, (c) $\delta^{18}\text{O-NO}_3^-$ in the cool season, and (d) $\delta^{18}\text{O-NO}_3^-$ in the warm season, respectively.

and $^{18}\text{O}/^{16}\text{O}$ ratios of the N_2O analyte. Individual analyses are referenced to injections of N_2O from a pure gas cylinder and then standardized through comparison to the international reference materials of IAEA-N3 and USGS34 for $\delta^{15}\text{N-NO}_3^-$, and IAEA-N3, USGS34, and USGS35 for $\delta^{18}\text{O-NO}_3^-$ (see Table S1 in the supporting information for standard values) [Bohlke *et al.*, 2003]. The $^{15}\text{N}/^{14}\text{N}$ is corrected for a bacterial culture blank quantified with each run. The $^{15}\text{N}/^{14}\text{N}$ of samples is corrected for the contribution of ^{17}O to the peak at mass 45 using an average $\Delta^{17}\text{O}$ value for Bermuda rainwater (26‰) [Hastings *et al.*, 2003]. The pooled standard deviation for all measurements of IAEA-N3 and USGS34 for $\delta^{15}\text{N-NO}_3^-$, and for all measurements of IAEA-N3, USGS34, and USGS35 for $\delta^{18}\text{O-NO}_3^-$ can be found in Table S1. All samples were measured at least in duplicate, with 50% being analyzed in triplicate or more. The pooled standard deviation from all replicate analyses

of the samples is 0.24‰ for $\delta^{15}\text{N-NO}_3^-$ and 0.79‰ for $\delta^{18}\text{O-NO}_3^-$.

2.4. Air Mass Back Trajectory Analysis

[26] To determine the source regions for each rainwater event, air mass back trajectories were computed for all sample days using NOAA's Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT v 4) with NCEP Global Data Assimilation System (GDAS) output. It is accessed via the NOAA ARL READY website at <http://www.arl.noaa.gov/ready/hysplit4.html> (NOAA Air Resources Laboratory, Silver Spring, Maryland). HYSPLIT is used to compute the trajectory of a suspended particle backward in time from a specified point, in this case the island of Bermuda, using a simple particle dispersion simulation and meteorological data. The 36 h back trajectories were chosen to represent the lifetime of NO_x . Three-dimensional

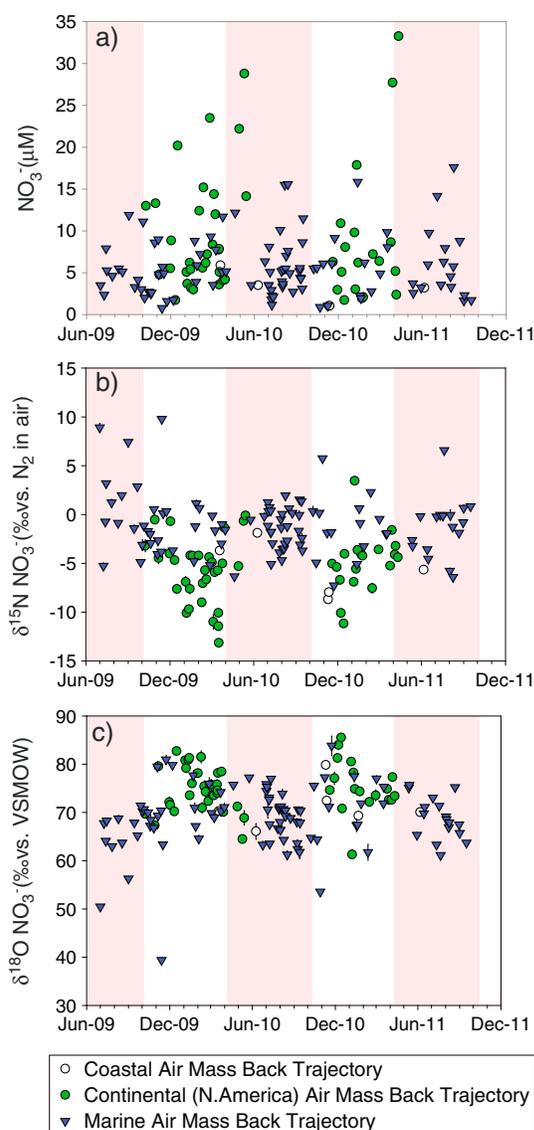


Figure 3. (a) Nitrate concentration, (b) $\delta^{15}\text{N}\text{-NO}_3^-$, and (c) $\delta^{18}\text{O}\text{-NO}_3^-$ in rain samples collected on Bermuda between June 2009 and November 2011. The pink columns denote the warm season (April to September) while the white columns denote the cool season (October to March). Error bars denote the standard deviation of replicate isotopic measurements. Where error bars are not visible, the standard deviation is smaller than the size of the marker.

trajectories were determined at three altitudes: 100 m, 2000 m, and 5000 m. Sensitivity tests to changes in initial conditions indicated that the main sources of uncertainty in the final trajectory were the starting time and the altitude, hence the use of multiple altitudes for each back trajectory. To deal with the variability associated with starting time, trajectories were run starting every hour during the rain event, or if there was uncertainty in the timing of the rain event, trajectories were run starting every hour that the sample bucket was deployed (i.e., all 24 h). The duration of the rain event was determined by cross-referencing sample collection dates with the meteorological observation archive on the Bermuda National Weather Service Web site (www.weather.bm). Five mean trajectories

were extracted from the multiple trajectories associated with a single rain event through HYSPLIT's clustering algorithm, which calculates the mean trajectory by averaging over all of the input trajectories at every hour.

3. Results

3.1. Air Mass Back Trajectory

[27] The computed and clustered back trajectories from the NOAA HYSPLIT model for the duration of each rain event show the geographic distribution of air masses 36 h prior to the collection of a rain event in Bermuda (Figures 2, S1, and S2). During the warm season, (April to September), when the Bermuda Azores high pressure system sets in, almost all events originate over the ocean with a mixture of events coming primarily from the south, but from both east and west of the island (i.e., southeast and southwest; Figures 2b, 2d). During the cool season, (October to March), the Bermuda Azores high breaks down, and there are an almost equal number of events originating over the ocean as there are over the continental USA ($n=39$ versus $n=44$, respectively; Figures 2a, 2c). The events with air mass back trajectories that originate over the continental USA tend to travel much faster and therefore much farther than events that originate over the ocean (Figures S1 and S2). Previous work at Bermuda classified events according to their season (cool versus warm); however, due to the variability in air mass source region during the cool season, season is an inadequate metric of air mass origin. Thus, the data are analyzed in terms of both the season of collection and the air mass source, which will be denoted as marine air mass back trajectory (AMBT) for the air masses that originate over the ocean, and continental AMBT for air masses that originate from the continental USA 36 h prior to arriving at Bermuda. Those few samples that had AMBT origins on the coast of the USA are classified as coastal AMBT to avoid bias in assigning them to either marine or continental AMBT categories.

3.2. Nitrate Concentrations

[28] Nitrate constituted 13–78% of total N (i.e., $\text{NO}_3^- + \text{NH}_4^+ +$ organic N) in Bermuda rainwater, with an average of 54 % across all rain samples. There were 155 rainwater samples collected between 1 July 2009 and 16 September 2011 that were analyzed for nitrate concentrations and isotopes (discussed below). The NO_3^- concentrations ranged from 0.78 to 33.3 μM (Figure 3a) with a numerical average of $6.8 \pm 5.4 \mu\text{M}$ ($\pm 1\text{SD}$ unless otherwise noted). For the different AMBT regimes, the NO_3^- concentrations ranged from 0.78 to 17.6 μM for the marine AMBT ($n=99$), 1.8 to 33.3 μM for the continental AMBT ($n=50$), and 1.1 to 5.9 μM for the coastal AMBT ($n=6$). The volume weighted average NO_3^- concentration for marine AMBT was $4.4 \pm 3.1 \mu\text{M}$, continental AMBT was $6.3 \pm 4.5 \mu\text{M}$ and for coastal AMBT was $2.1 \pm 1.1 \mu\text{M}$ (Table 1). In Bermuda rainwater measured from 1980 to 1984, the volume weighted average NO_3^- concentration was 4.57 μM in the warm season and 4.33 μM in the cool season [Moody and Galloway, 1988]. In Bermuda rainwater measured from 2000–2001, the volume weighted average NO_3^- concentration was 5.0 μM in the warm season and 6.4 μM in the cool season [Hastings et al., 2003].

Table 1. The Average (± 1 SD) Concentrations and Isotopic Ratios of N and O in Rainwater Nitrate Binned by the Source Region of the Event Air Mass Back Trajectory (AMBT)^a

	Marine	Continental	Coastal	Average of All Data
	AMBT	AMBT	AMBT	
$[\text{NO}_3^-]^{\text{b}*}$ (μM)	4.38 \pm 3.13 (99)	6.33 \pm 4.46 (50)	2.08 \pm 1.13 (6)	4.88 \pm 3.64 (155)
$\delta^{15}\text{N NO}_3^-^{\text{c}***}$ (‰)	-1.6 \pm 2.8	-5.7 \pm 2.4	-4.5 \pm 2.2	-3.1 \pm 3.3
$\delta^{18}\text{O NO}_3^-^{\text{c}***}$ (‰)	69.3 \pm 5.1	76.5 \pm 4.5	69.4 \pm 2.6	71.9 \pm 6.0
$\delta^{15}\text{N NO}_3^-^{\text{d}****}$ (‰)	-1.1 \pm 3.0	-5.4 \pm 3.2	-5.3 \pm 2.6	-2.6 \pm 3.7
$\delta^{18}\text{O NO}_3^-^{\text{d}****}$ (‰)	69.0 \pm 6.4	75.0 \pm 4.8	71.3 \pm 4.7	71.1 \pm 6.4

^aThe number of samples measured for nitrate concentrations and isotopes in each category is in parentheses.

^bVolume weighted average.

^cMass weighted average.

^dNumerical average.

*Statistically different means at the 0.0025 level $H=9.1$, Kruskal-Wallis test for nonparametric data.

** ***Statistically different means at 95% confidence interval, independent t test assuming unequal variance.

** $p < 0.0001$.

*** $p < 10^{-9}$.

[29] The NO_3^- concentrations measured in the continental and marine AMBT are statistically different (Table 1, Figure S3) (Kruskal-Wallis test for nonparametric data, $H=9.1$, $p=0.002$). Previous studies that binned rainwater by cool and warm season, and not by event-based trajectory, typically report that NO_3^- concentrations are not statistically different from the cool to the warm season in Bermuda [Galloway *et al.*, 1982; Hastings *et al.*, 2003; Moody and Galloway, 1988] and this is true in our data set as well: if the NO_3^- concentrations are binned by cool and warm season, they are not statistically different (Kruskal-Wallis test $H=0.75$, $p=0.387$). This highlights the importance of using event-based AMBT analysis, as during the cool season, the AMBT are quite variable and include a large number of marine AMBT which dilute the anthropogenic signals inherent in the continental AMBT (Figures 2, 3).

3.3. N Isotopes of Nitrate

[30] The measurements of $\delta^{15}\text{N-NO}_3^-$ in Bermuda rain ranged from -13.1 to 9.8‰ from 1 July 2009 to 16 September 2011 (Figure 3b) with a numerical average of -2.6 \pm 3.7‰ (Table 1). The $\delta^{15}\text{N-NO}_3^-$ does not correlate with $[\text{NO}_3^-]$ (Figure S4), $[\text{NH}_4^+]$, $[\text{nss-SO}_4^{2-}]$, or rainfall amount (not shown). However, the $\delta^{15}\text{N-NO}_3^-$ does correlate with $\delta^{18}\text{O-NO}_3^-$, which is discussed below (Figure 5). The mean $\delta^{15}\text{N-NO}_3^-$ for the continental AMBT was -5.4 \pm 3.2‰, and for the marine AMBT was -1.1 \pm 3.0‰. The $\delta^{15}\text{N-NO}_3^-$ for the different AMBT regimes is significantly different (independent t test, 95%, $p < 10^{-13}$). If the

continental AMBT average is weighted using the nitrate concentration and rain volume of each event, the mass-weighted average $\delta^{15}\text{N-NO}_3^-$ of -5.7 \pm 2.4‰ is also significantly lower than the marine AMBT mass-weighted average $\delta^{15}\text{N-NO}_3^-$ of -1.6 \pm 2.8‰.

[31] In previous work, the $\delta^{15}\text{N-NO}_3^-$ was binned by cool and warm season instead of marine and continental AMBT, and averages of -5.9 \pm 3.3‰ and -2.1 \pm 1.5‰ were found in the cool and warm seasons, respectively ($n=65$, [Hastings *et al.*, 2003]). For comparison, the season based $\delta^{15}\text{N-NO}_3^-$ averages for this data set were -3.9 \pm 3.8‰ ($n=87$) and -1.2 \pm 3.0‰ ($n=68$) in the cool and warm seasons, respectively, which are statistically different (independent t test, 95%, $p < 10^{-6}$). The mass-weighted average cool season $\delta^{15}\text{N-NO}_3^-$ was -4.3 \pm 2.5‰ and warm season was -1.4 \pm 3.1‰. However, the statistical significance (i.e., the p values) of the $\delta^{15}\text{N-NO}_3^-$ comparison is much stronger when the values are compared by AMBT (Table 1) as the cool season back trajectories can be quite variable. Interestingly, if the data are compared by both AMBT and season, it appears that the season does have an influence on the measured $\delta^{15}\text{N-NO}_3^-$ value (Table 2 and Figure 4a). The continental AMBT had the lowest $\delta^{15}\text{N-NO}_3^-$ values, but within all of the continental AMBT data, the mass weighted cool season average was lower than the warm season average (-6.0 \pm 2.3‰ and -3.5 \pm 1.7‰, respectively; independent t test, 95%, $p=0.02$). The marine AMBT were higher in $\delta^{15}\text{N-NO}_3^-$, but within all of the marine AMBT data, the

Table 2. The Average (± 1 SD) Concentrations and Isotopic Ratios of N and O in Rainwater Nitrate Binned by Both the Season (Cool and Warm) and the Source Region of the Events AMBT (Marine, Continental, Or Coastal)^a

	Continental AMBT	Continental AMBT	Marine AMBT	Marine AMBT
	Cool Season	Warm Season	Cool Season	Warm Season
$[\text{NO}_3^-]^{\text{b}}$ (μM)	6.23 \pm 3.58 (44)	7.02 \pm 9.13 (6)	3.82 \pm 2.92 (39)	4.85 \pm 3.26 (60)
$\delta^{15}\text{N NO}_3^-^{\text{c}}$ (‰)	-6.0 \pm 2.3	-3.5 \pm 1.7	-2.2 \pm 2.2	-1.2 \pm 3.2
$\delta^{18}\text{O NO}_3^-^{\text{c}}$ (‰)	77.2 \pm 4.3	72.2 \pm 3.7	71.7 \pm 5.2	67.7 \pm 4.3
$\delta^{15}\text{N NO}_3^-^{\text{d}}$ (‰)	-5.8 \pm 3.2	-3.0 \pm 2.1	-1.4 \pm 3.1	-0.8 \pm 3.0
$\delta^{18}\text{O NO}_3^-^{\text{d}}$ (‰)	75.6 \pm 4.7	71.3 \pm 4.4	70.3 \pm 7.8	68.2 \pm 5.1

^aThe number of samples measured for nitrate concentrations and isotopes in each category is in parentheses.

^bVolume weighted average.

^cMass weighted average.

^dNumerical average.

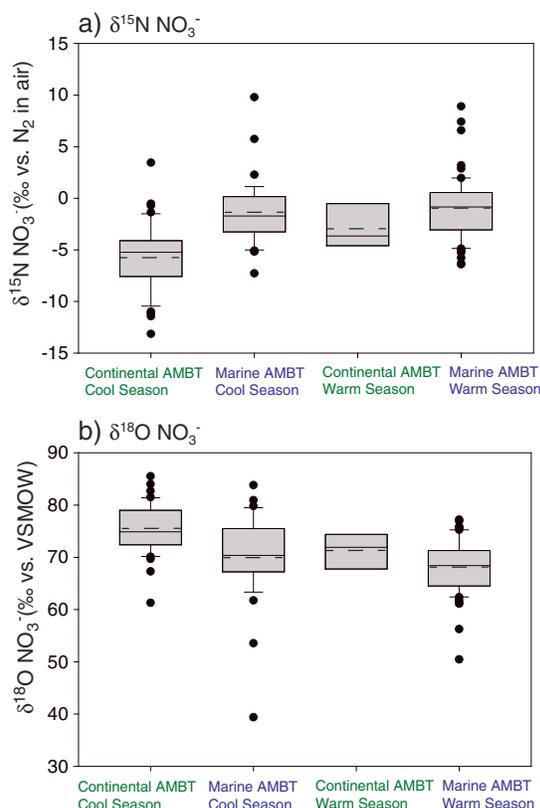


Figure 4. Box and whisker plot of (a) rainwater $\delta^{15}\text{N-NO}_3^-$ and (b) $\delta^{18}\text{O-NO}_3^-$. The solid line is the median; the dashed line is the numerical average. The whisker lines above and below the box indicate the 90th and 10th percentiles. The $\delta^{15}\text{N-NO}_3^-$ of continental AMBT cool season is statistically different than the $\delta^{15}\text{N-NO}_3^-$ of the continental AMBT warm season. The $\delta^{18}\text{O-NO}_3^-$ of continental AMBT is statistically different from the cool to the warm season, and the $\delta^{18}\text{O-NO}_3^-$ of marine AMBT is also statistically different from the cool to the warm season.

mass weighted cool season average was slightly lower than the warm season average ($-2.2 \pm 2.2\text{‰}$ and $-1.2 \pm 3.2\text{‰}$, respectively; not statistically significant).

3.4. O Isotopes of Nitrate

[32] The measurements of $\delta^{18}\text{O-NO}_3^-$ in Bermuda rain ranged from 39.4 to 85.5‰ from 1 July 2009 to 16 September 2011 (Figure 3c) with a numerical average of $71.1 \pm 6.4\text{‰}$ (Table 1). Similar to the $\delta^{15}\text{N-NO}_3^-$, the $\delta^{18}\text{O-NO}_3^-$ does not correlate with $[\text{NO}_3^-]$, $[\text{NH}_4^+]$, $[\text{nss-SO}_4^{2-}]$, or rainfall amount (not shown), but it does correlate with $\delta^{15}\text{N-NO}_3^-$ (Figure 5). The mean $\delta^{18}\text{O-NO}_3^-$ is significantly different (independent t test, 95%, $p < 10^{-9}$) for the different AMBTs, with the continental AMBT averaging $75.0 \pm 4.8\text{‰}$ and the marine AMBT averaging $69.0 \pm 6.4\text{‰}$. The mass-weighted continental AMBT average $\delta^{18}\text{O-NO}_3^-$ of $76.5 \pm 4.5\text{‰}$ was also higher than the marine AMBT mass-weighted average $\delta^{18}\text{O-NO}_3^-$ of $69.3 \pm 5.1\text{‰}$.

[33] The range of $\delta^{18}\text{O-NO}_3^-$ in the Bermuda rainwater (61.1 to 85.5‰), excluding the four samples with $\delta^{18}\text{O}$ less than 60.0‰, is consistent with rainwater nitrate measured previously in Bermuda (60.3 to 86.5‰; [Hastings et al., 2003]),

and rainwater collected at 17 National Trend Network sites in the USA ($\sim 60\text{--}90\text{‰}$; [Elliott et al., 2009]). The four samples with low $\delta^{18}\text{O}$ are also the samples with the highest $\delta^{15}\text{N-NO}_3^-$ (5.8 to 9.8‰), and they all have marine AMBT origins though only two are from the warm season.

[34] In previous work, as with the $\delta^{15}\text{N-NO}_3^-$, the $\delta^{18}\text{O-NO}_3^-$ was binned by cool and warm season instead of marine and continental AMBT and the averages were $76.9 \pm 6.3\text{‰}$ and $68.6 \pm 3.6\text{‰}$ for the cool and warm seasons, respectively ($n = 65$ [Hastings et al., 2003]). For this data set, the cool and warm season average $\delta^{18}\text{O-NO}_3^-$ were $73.1 \pm 6.7\text{‰}$ ($n = 87$) and $68.6 \pm 5.0\text{‰}$ ($n = 68$), respectively, and they are statistically different (independent t test, 95%, $p < 10^{-6}$). The mass weighted average cool and warm season $\delta^{18}\text{O-NO}_3^-$ were $74.5 \pm 4.6\text{‰}$ and $68.2 \pm 4.5\text{‰}$. As with the $\delta^{15}\text{N-NO}_3^-$, the statistical significance (i.e., the p values) of the $\delta^{18}\text{O-NO}_3^-$ comparison is much stronger when the values are compared by back trajectory. However, if the data are compared by both AMBT and season, it appears that season has even more of an influence on the measured $\delta^{18}\text{O-NO}_3^-$ than on the

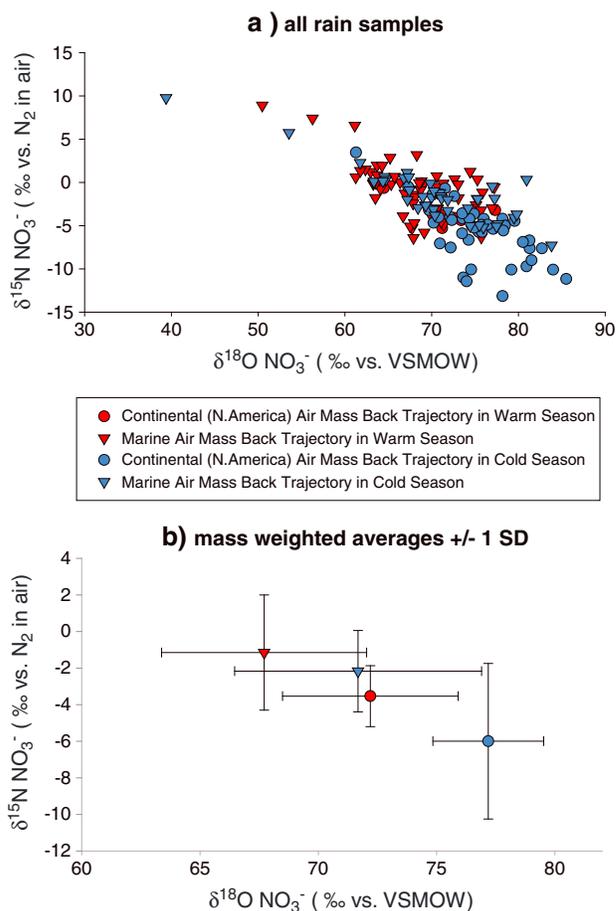


Figure 5. The relationship of $\delta^{15}\text{N-NO}_3^-$ as a function of $\delta^{18}\text{O-NO}_3^-$ for (a) all rain samples ($r^2 = 0.58$, $y = -0.44x + 28.52$, $p < 10^{-30}$) and (b) the mass weighted averages with the error bars denoting one mass-weighted standard deviation of the mean. Symbols denote the source region based on the 36 h air mass back trajectory and the color indicates the warm versus cool seasons, respectively. Note the change in scale for the x and y axes from Figures 5a to 5b.

$\delta^{15}\text{N-NO}_3^-$ (Table 2 and Figure 4). The continental AMBT had the highest $\delta^{18}\text{O-NO}_3^-$ values overall, but within all of the continental AMBT data, the cool season mass-weighted average was higher than the warm season average ($77.2 \pm 4.3\%$ and $72.2 \pm 3.7\%$, respectively; independent t test, 95%, $p < 0.02$). Likewise, the marine AMBT were lower in $\delta^{18}\text{O-NO}_3^-$, but within all of the marine AMBT data, the cool season mass weighted average was higher than the warm season mass weighted average ($71.7 \pm 5.2\%$ and $67.7 \pm 4.3\%$, respectively; independent t test, 95%, $p < 0.0001$).

3.5. Relationship Between N and O Isotopes of Nitrate

[35] Across the entire rainwater sample set, there was a negative correlation ($r^2 = 0.58$, $y = -0.44x + 28.52$, $p < 10^{-30}$) between the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of NO_3^- (Figure 5a), consistent with the previous study of rainwater N and O isotopes in Bermuda [Hastings *et al.*, 2003]. The samples cluster according to both their season (cool versus warm) and air mass history (continental versus marine) characteristics (Figure 5b). The warm season marine AMBT (highest $\delta^{15}\text{N}$ and lowest $\delta^{18}\text{O}$) and the cool season continental AMBT (lowest $\delta^{15}\text{N}$ and highest $\delta^{18}\text{O}$) are the end members, while the samples with anomalous trajectories for their season (e.g., a warm season sample with continental AMBT) fall in the middle.

4. Discussion

4.1. Rainwater Nitrate $\delta^{15}\text{N}$

[36] The $\delta^{15}\text{N}$ of nitrate should reflect the $\delta^{15}\text{N}$ of the NO_x source, overprinted by any fractionation associated with the chemical pathway that converts NO_x to nitrate. Rain events with continental AMBT origins occur primarily during the cool season (October to March) and are consistently lower in $\delta^{15}\text{N-NO}_3^-$ and higher in NO_3^- concentration than rain events from marine AMBT, which occur all year (Figure 3b). North American NO_x emissions are dominated by anthropogenic sources with $\sim 87\%$ coming from fossil fuel burning of automobiles, power plants, and industry [Zhang *et al.*, 2003]. Therefore, the lower $\delta^{15}\text{N}$ and higher concentrations during rain events with continental AMBT suggests that when air masses come from the continental USA, they bring NO_3^- with a different, and likely anthropogenic, NO_x source (Figure 1b). This interpretation is consistent with previous work on rainwater $\delta^{15}\text{N-NO}_3^-$ in this region [Hastings *et al.*, 2003], which interpreted the $\delta^{15}\text{N-NO}_3^-$ changes from the cool to the warm season as a change in NO_x source despite a lack of concurrent change in nitrate concentration in their data set. Classification by AMBT makes a stronger argument in favor of this interpretation since the $\delta^{15}\text{N-NO}_3^-$ has an even greater statistical difference, and the nitrate concentration is also found to be significantly higher with continental AMBTs than marine AMBT, although nitrate concentrations are not significantly different from cool to warm season. Therefore, we also conclude that nitrate deposition at Bermuda associated with continental AMBT from North America has a continental and thus anthropogenic NO_x source.

[37] In the few continental AMBT rain events that occurred during the warm season, the $\delta^{15}\text{N-NO}_3^-$ was significantly higher than for those that occurred during the cool season, likely as a result of mixing with the high $\delta^{15}\text{N-NO}_3^-$ present

in the warm season atmosphere near Bermuda (Figures 3b and 4a). We do not believe that this increase in $\delta^{15}\text{N}$ is due to changes in North American $\delta^{15}\text{N-NO}_3^-$ or $\delta^{15}\text{N-NO}_x$ as the summer months are when North American rainwater $\delta^{15}\text{N-NO}_3^-$ is lowest [Elliott *et al.*, 2009]. This suggests that during the cool and warm seasons, the dominant transport pathways lead to a background nitrate isotopic composition that is consistent with the default transport pattern in that season, i.e., low $\delta^{15}\text{N-NO}_3^-$ during the cool season from North American transport and higher $\delta^{15}\text{N-NO}_3^-$ during the warm season from the marine atmosphere. Thus, an anomalous trajectory for that season brings with it the $\delta^{15}\text{N}$ source signature of the NO_x , which is then mixed with the nitrate from that particular season's dominant transport pathway, diminishing the originating source signal.

[38] Interestingly, the nitrate concentration and $\delta^{15}\text{N}$ of rainwater collected in Bermuda during continental AMBT are typically lower than those of rainwater collected in the USA, the source region. The N and O isotopes of nitrate in weekly rainwater collections were measured in the northeastern USA at NADP sites [Elliott *et al.*, 2007; Elliott *et al.*, 2009]. From October to March, the rainwater $\delta^{15}\text{N-NO}_3^-$ varied from ~ 0 to 3.5% at those sites. In Bermuda rainwater during the cool season of October to March, when AMBTs almost exclusively originate over the continental USA, the $\delta^{15}\text{N-NO}_3^-$ in Bermuda rain were at their minimum ($-5.4 \pm 3.2\%$; Table 1). This is also true in previously published data on $\delta^{15}\text{N-NO}_3^-$ in Bermuda rain [Hastings *et al.*, 2003] which were collected during the same time frame as the Elliott *et al.* [2007, 2009] studies and were in the same range as those reported here ($-5.9 \pm 3.3\%$). The nitrate concentration in NADP weekly rainwater collections in the eastern USA from October to March, 2009–2011 ranged from 0.7 to 147 μM , with an average of $16.5 \pm 16.9 \mu\text{M}$ (data accessible online at www.nadp.sws.uiuc.edu [NADP, 2007]), compared to an average nitrate concentration in Bermuda rain from continental AMBT of $6.3 \pm 4.5 \mu\text{M}$. The difference in $\delta^{15}\text{N}$ and concentration of nitrate from the continental USA to Bermuda suggests that there must be loss of nitrate, or NO_x , as polluted continental air masses move off of the continent, and that this loss has a preference for ^{15}N (Figure 1b). Below we outline three potential mechanisms to explain the $\delta^{15}\text{N-NO}_3^-$ difference between North American rainwater and rainwater collected at Bermuda from North American transport, involving (1) equilibrium fractionation between NO and NO_2 over the continents, (2) heterogeneous reaction of N_2O_5 with HCl (R10), and (3) reaction of NO_2 with NaCl particles (R16).

[39] The first hypothesis is dependent on the relative concentrations of NO_x and ozone in North America and Bermuda. When NO_x concentrations are higher than ozone concentrations, equilibrium fractionation between NO and NO_2 (R1–R4) results in ^{15}N -enriched NO_2 [Freyer *et al.*, 1993]. When ozone concentrations are higher than NO_x concentrations, most of the NO_x is oxidized to NO_2 such that the $\delta^{15}\text{N-NO}_2$ is equivalent to the $\delta^{15}\text{N-NO}_x$. In Bermuda, ozone concentrations always exceed NO_x concentrations [Oltmans *et al.*, 1996; Prados *et al.*, 1999], and as a result fractionation between NO and NO_2 has previously been considered to be unimportant [Hastings *et al.*, 2003]. In the atmospheric boundary layer over North America, however, NO_x concentrations are comparable to ozone in many areas

and exceed ozone in heavy industrial zones [Liang *et al.*, 1998], causing the equilibrium fractionation between NO and NO₂ to be relevant in air masses that are subsequently transported to Bermuda. If ¹⁵N enriched NO₂ is converted to HNO₃, the higher δ¹⁵N-HNO₃ would be deposited closer to the coast, leaving behind lower δ¹⁵N-NO_x to be exported to the marine atmosphere.

[40] The second and third hypotheses are related in that both rely on fractionation between the gas and particle phases due to heterogeneous halogen chemistry. At night and in the winter, the dominant loss mechanism for NO_x is through formation of N₂O₅ via reaction of NO₂ with NO₃ radicals (Figure 1a). The potential for halides to interact with N₂O₅ forming ClNO₂ has been documented in numerous laboratory studies [Behnke *et al.*, 1997; Finlayson-Pitts, 2003], with recent direct measurements suggesting that this process is significant in the coastal marine atmosphere [Osthoff *et al.*, 2008; Pechtl and von Glasow, 2007] (see section 1.1). In the presence of NaCl particles, the N₂O₅ reacts with HCl, forming aqueous HNO₃ and releasing ClNO_{2(g)} (R10). This ClNO₂ acts as a reservoir species until the day, when it is quickly photolyzed to Cl and NO₂, recycling the original NO_x stored as N₂O₅ (R11). There is the potential for isotopic fractionation during this process as heavier isotopes are preferentially incorporated into the more stable phase: during the heterogeneous reaction of N₂O₅ on the aerosol particle, the ¹⁴N should be preferentially incorporated into the gas phase ClNO₂, leaving ¹⁵N behind in the more stable particle phase. Similarly, one might speculate based on the preference of heavier isotopes to prefer the more stable phase, that when NO₂ reacts with sea-salt aerosol to form NaNO_{3(p)} and ClNO_(g), the ¹⁵N should be preferentially incorporated into the NaNO_{3(p)} and the ¹⁴N should be preferentially incorporated into the gas phase ClNO_(g). The lifetime of a particle with respect to deposition is much shorter than the lifetime of NO₂ and as such the higher δ¹⁵N particle-associated nitrate should be deposited fairly rapidly while the lower δ¹⁵N-NO_x (from (R11) and (R17)) will persist in the atmosphere to again form nitrate, potentially contributing to a decrease in the δ¹⁵N-NO₃⁻ of deposition downwind of the continents (Figure 1b). This chemistry may also explain the smaller number of very high δ¹⁵N-NO₃⁻ (>0‰) events associated with marine AMBT (Figures 3b and 5a), as discussed immediately below. Partially because of this apparent confluence, we favor the above halogen chemistry as the explanation for the δ¹⁵N-NO₃⁻ decrease from North America to Bermuda. The impact of these processes on the δ¹⁸O-NO₃⁻ is also discussed below, in section 4.2.

[41] The previous work at Bermuda measured a δ¹⁵N-NO₃⁻ range of -4.7 to 1.4‰ in the warm season N isotopes, and this relatively high δ¹⁵N-NO₃⁻ was tentatively attributed to an increased contribution from lightning NO_x (with a δ¹⁵N of 0‰) during the warm season [Hastings *et al.*, 2003]. Indeed, improved satellite estimates of the contribution of lightning NO_x confirm an enhancement over the tropical Atlantic Ocean due to upper tropospheric transport that is not present over the Pacific Ocean. However, a lightning NO_x source at 0‰ cannot explain the regular occurrence of δ¹⁵N values above 0‰ (20% of samples > 0‰), with values up to 9.8‰ for marine AMBT. We propose two mechanisms to explain these high δ¹⁵N events, (1) the halogen chemistry described above, producing high δ¹⁵N particles in air with

a marine AMBT or (2) a higher δ¹⁵N-NO_x source, such as PAN.

[42] The halogen chemistry described above leads to the formation of aerosol nitrate with a high δ¹⁵N relative to the original NO_x load in a given air parcel. While our focus above was on the occurrence of this process in continentally derived air, it could also occur in the marine atmosphere, due to the high concentrations of sea-salt particles, and will depend on the concentrations of NO₂ and NO₃ which control the formation of N₂O₅ at night through thermal equilibrium. Unlike continental air masses, where much of the original NO_x is deposited before transport to the open ocean, resulting in consistent depletion of ¹⁵N prior to deposition, marine air masses may deposit NO₃⁻ at any stage of the atmospheric processing of NO_x. On average, this fractionation should have no net effect for marine AMBT nitrate wet deposited at Bermuda: rain would scavenge both the high δ¹⁵N aerosol formed initially in some events and the lower δ¹⁵N-NO₃⁻ from the regenerated NO_x in other events. However, the process should lead to variability in δ¹⁵N-NO₃⁻. We propose that the small number of very high δ¹⁵N marine AMBT events (Figures 3b and 5a) result from the presence of NO₃⁻ formed in the initial stages of high δ¹⁵N aerosol formation (Figure 1b).

[43] While there are certainly other possibilities that cannot be ruled out, the most plausible alternative is the continental export of PAN, a potential source of NO_x to the remote marine troposphere during the warm season. Briefly, PAN forms in urban environments where OH and aldehydes form peroxyacetyl radicals, which react with NO_x to form PAN. PAN is transported on a hemispheric scale at high altitudes due to its stability at cold temperatures. When air masses subside into the boundary layer, the lifetime of PAN decreases to ~1 h and thermal decomposition results in the release of the stored NO_x (R19, [Fischer *et al.*, 2011; Kotchenruther *et al.*, 2001]). In the South Atlantic boundary layer, PAN alone can account for almost all of the NO_x present [Heikes *et al.*, 1996]. PAN production is much higher in the Northern Hemisphere than in the Southern Hemisphere, suggesting that it could be a major contributor; however, there are few studies of PAN in the North Atlantic, making it hard to estimate its contribution to this system. While there are no measurements of the isotopic composition of PAN to date, it could have a high δ¹⁵N, as it forms in polluted atmospheres close to emissions of ¹⁵N enriched NO_x, such as coal fired power plants, which produce high δ¹⁵N-NO_x both with and without emission control technologies (δ¹⁵N-NO_x = 10‰, and 15–20‰, respectively) [Felix *et al.*, 2012]. If PAN represents a significant NO_x source during the warm season in the North Atlantic, then anthropogenic NO_x is contributing to deposition even when AMBT have not recently been over the continents. This would have significant implications and future work is necessary to assess the potential for PAN to contribute to NO_x in the North Atlantic marine atmosphere and the utility of stable isotopes of N in NO_x and nitrate to trace that contribution.

4.2. Rainwater Nitrate δ¹⁸O

[44] The high δ¹⁸O of atmospheric nitrate reflects the influence of ozone (δ¹⁸O-O₃ = 90 to 122‰ versus Vienna SMOW (VSMOW); [Johnston and Thiemens, 1997]) on the reactions that produce nitrate from NO_x [Hastings *et al.*,

2003; Michalski *et al.*, 2003]. Briefly, unlike $\delta^{15}\text{N-NO}_x$, $\delta^{18}\text{O-NO}_x$ is not conserved and is instead reset by rapid exchange with ozone during [(R1)–(R4)]. When nitrate is formed through the OH pathway favored during the summer and during the day (R5), the high $\delta^{18}\text{O}$ from ozone is diluted by that of OH, which should have a $\delta^{18}\text{O}$ close to water vapor in the troposphere ($\delta^{18}\text{O-H}_2\text{O}_{(\text{g})} = -9$ to -17% near Bermuda); (H.C. Steen-Larsen, personal communication, 2013). Thus, the variation in $\delta^{18}\text{O-NO}_3^-$ is usually interpreted as reflecting seasonal shifts in the atmospheric chemistry that converts NO_x to nitrate. During the summer, longer days and warmer temperatures lead to increased OH concentrations and lower $\delta^{18}\text{O-NO}_3^-$. During the winter, shorter days and lower temperatures lead to a greater contribution from the N_2O_5 hydrolysis pathway [(R6)–(R7), (R9)], resulting in higher $\delta^{18}\text{O-NO}_3^-$ as 5/6 of the O atoms in the 2HNO_3 formed will be from ozone. In addition, wintertime transport imports air from over North America and higher latitudes, while summertime transport tends to import air from the South: these transport changes reinforce the locally driven seasonal cycle at Bermuda to produce higher $\delta^{18}\text{O-NO}_3^-$ in the winter. The important influence of season on the $\delta^{18}\text{O}$ is also demonstrated by the increased significance of the seasonal comparison within AMBT regimes: within both the marine and continental AMBT events, the cool season rains are significantly higher in $\delta^{18}\text{O}$ than warm season rains (Figure 4b). This winter/summer and high latitude/low latitude distinction has been the focus of interpretations to date [Elliott *et al.*, 2007; Hastings *et al.*, 2003; Morin *et al.*, 2009; Wankel *et al.*, 2010].

[45] As with the nitrate N isotopes, the presence of halogens in the marine atmosphere may have an important role in the nitrate O isotopes, especially in the case of continentally produced NO_x . As discussed in section 1.1, in the presence of NaCl particles, N_2O_5 can form aqueous HNO_3 and $\text{ClONO}_{2(\text{g})}$ (R10). NO_2 can react with $\text{ClO}_{(\text{g})}$ to form ClONO_2 , or it can react with sea-salt particles to form $\text{NaNO}_{3(\text{p})}$ [(R14), (R15)]. This chemistry should increase the influence of high $\delta^{18}\text{O-O}_3$ in the formation of nitrate. For example, the aqueous HNO_3 formed from N_2O_5 and HCl (R10) should be higher in $\delta^{18}\text{O}$ than HNO_3 from N_2O_5 hydrolysis (R9) as it is not diluted with O atoms from water. Likewise, ClO is formed from Cl and ozone (R13), therefore, the $\text{NaNO}_{3(\text{p})}$ formed from ClONO_2 should also be higher in $\delta^{18}\text{O}$. The same is true as 2NO_2 molecules react with sea-salt particles to form $\text{NaNO}_{3(\text{p})}$ (R16). As a result, when polluted continental air masses move into the marine environment with high concentrations of ozone, sea-salt particles, and halogens, the NO_3^- formed should be high in $\delta^{18}\text{O}$ (Figure 1a), which is consistent with what we observe in Bermuda rainwater from continental AMBT during the cool season (Figure 3c). This chemistry further reinforces the previous interpretations of $\delta^{18}\text{O-NO}_3^-$ as the N_2O_5 pathway will be most prevalent in winter, with its lower temperatures and longer nights. Though the heterogeneous halogen chemistry is also likely to occur during marine AMBT as discussed above, the yields of ClONO_2 are highest in the winter when sea salt and ozone concentrations peak, and they correlate strongly with N_2O_5 [Osthoff *et al.*, 2008], suggesting that the influence of heterogeneous halogen chemistry on $\delta^{18}\text{O-NO}_3^-$ should be limited to the cool season. In summary, in contrast to the situation with $\delta^{15}\text{N-NO}_3^-$, the halogen chemistry simply

adds to the list of causes for the elevation of $\delta^{18}\text{O-NO}_3^-$ in the winter, and the task for future work is to parse the observed $\delta^{18}\text{O-NO}_3^-$ variations between the halogen-related and nonhalogen-related mechanisms.

4.3. Relationship of N and O Isotopes of Nitrate

[46] There is a negative linear correlation ($r^2 = 0.58$) between $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of NO_3^- in the rainwater samples (Figure 5a), consistent with the previous study of rainwater N and O isotopes in Bermuda [Hastings *et al.*, 2003]. Correlations are rarely observed between the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of atmospheric nitrate, and if any relationship is present, it is typically positive [Elliott *et al.*, 2009]. The presence of halogens and sea-salt aerosols influences the chemistry of nitrate formation in the coastal marine boundary layer. As discussed above, this chemistry can lead to a decrease in $\delta^{15}\text{N}$ from preferential removal of ^{15}N into the particle phase which deposits near the coast, leaving lower $\delta^{15}\text{N}$ NO_x or nitrate for transport to the remote marine atmosphere (Figure 1b and section 4.1). This low $\delta^{15}\text{N-NO}_3^-$ is associated with high $\delta^{18}\text{O-NO}_3^-$ due to the increased role of ozone in its formation, both because of high concentrations of ozone in the North American source region and because the continental AMBT occur almost exclusively during the cool season with lower temperatures and longer nights. During the slow and stagnant marine AMBT, the ozone signal is diluted by an increased role of OH and H_2O in the nitrate formation pathways, resulting in an overall lower $\delta^{18}\text{O-NO}_3^-$. This, in combination with an increased contribution from lightning NO_x and potentially PAN, results in higher $\delta^{15}\text{N}$ and lower $\delta^{18}\text{O}$ nitrate deposited at Bermuda associated with marine AMBT. In summary, the negative correlation of nitrate $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, thus far unique to nitrate in marine rainwater, is driven largely by the seasonal change in trajectory influencing both the source NO_x and the chemical formation pathways of nitrate.

5. Conclusions

[47] The changes in concentration and $\delta^{15}\text{N}$ of nitrate with AMBT suggest that while continental air contributes anthropogenic nitrate from North America to the subtropical surface ocean, nitrate associated with marine AMBTs comes from different NO_x sources. We hypothesize that the differences in nitrate isotopic composition between the USA and Bermuda are due to the formation and subsequent deposition of high $\delta^{15}\text{N}$ particles due to isotopic fractionation during heterogeneous halogen chemistry in the coastal marine boundary layer. This then leads to the transport of low $\delta^{15}\text{N-NO}_x$ over the North Atlantic that is subsequently deposited to Bermuda as nitrate. Our data suggest that while lightning NO_x likely plays an important role in the formation of nitrate in the marine atmosphere, a number of high $\delta^{15}\text{N-NO}_3^-$ values with marine AMBT (reaching 9.8‰) are especially hard to account for with a lightning NO_x source alone. Instead, these data are explained by the rain out of high $\delta^{15}\text{N}$ particles formed from halogen chemistry, or an additional higher $\delta^{15}\text{N-NO}_x$ source, potentially PAN. There is a seasonal predictability to the chemical pathways that form nitrate from NO_x , with greater contributions from ozone leading to higher $\delta^{18}\text{O}$ during the cool season and from continental AMBT, and with a greater role for OH leading to lower $\delta^{18}\text{O}$ during the warm

season and marine AMBT. The strong negative correlation of nitrate $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, thus far unique to nitrate in remote ecosystems, is driven by the seasonal change in trajectory influencing both the source NO_x and the pathway of nitrate formation.

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