Insights into anthropogenic nitrogen deposition to the North Atlantic investigated using the isotopic composition of aerosol and rainwater nitrate

Amy R. Gobel,[1] Katye E. Altieri,[1,2] Andrew J. Peters,[3] Meredith G. Hastings,[2] and Daniel M. Sigman[1]

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[1] Identifying the dominant sources of atmospheric reactive nitrogen (N_r) is critical for determining the influence of anthropogenic emissions on N_r deposition, especially in marine ecosystems. To test the influence of anthropogenic versus marine air masses, samples were collected in Bermuda, where seasonal atmospheric circulation patterns lead to greater continental transport during the cool season. The $^{15}N/^{14}N$ of aerosol nitrate (NO_3^-) indicates changes in N_r sources and its $^{18}O/^{16}O$ indicates a seasonal shift in the relative strength of pathways of NO_3^- formation. The aerosol $\delta^{15}N$-NO_3^- was consistently lower than or equal to the rainwater from the same sampling period, the opposite trend of that observed in polluted systems. We propose that this is due to $HNO_{3(g)}$ uptake onto aerosol particles with a kinetic isotope effect, lowering the aerosol $\delta^{15}N$-NO_3^- relative to residual $HNO_{3(g)}$. The aerosol $\delta^{18}O$-NO_3^- was higher than that in rainwater during the cool season, but was not different during the warm season, which we tentatively attribute to the increased importance of heterogeneous halogen chemistry on the formation of NO_3^- during the cool season. **Citation:** Gobel, A. R., K. E. Altieri, A. J. Peters, M. G. Hastings, and D. M. Sigman (2013), Insights into anthropogenic nitrogen deposition to the North Atlantic investigated using the isotopic composition of aerosol and rainwater nitrate, *Geophys. Res. Lett.*, *40*, doi:10.1002/2013GL058167.

1. Introduction

[2] The increasing deposition of anthropogenic reactive nitrogen (N_r) to the surface ocean has the potential to alter surface ocean biogeochemistry [*Duce et al.*, 2008; *Krishnamurthy et al.*, 2007]. The Sargasso Sea, in the low-nutrient core of the North Atlantic gyre, may be particularly sensitive to atmospheric inputs of N_r [*Michaels et al.*, 1993]. Moreover, because it is located downwind of major industrial centers in the eastern United States, atmospheric deposition models predict that anthropogenic activities have already substantially altered the N_r deposition to the Sargasso Sea [*Duce et al.*, 2008]. As a result, the region has been the subject of a number of studies of atmospheric deposition of N_r [e.g., *Galloway et al.*, 1989; *Knapp et al.*, 2010; *Prospero et al.*, 1996], and especially of nitrate (NO_3^-), the primary sink of atmospheric NO_x ($NO_x = NO + NO_2$) [e.g., *Hastings et al.*, 2003; *Jickells et al.*, 1982; *Moody et al.*, 1989].

[3] During the daytime, atmospheric NO_x undergoes rapid transformations via

[4] R1: $NO + O_3 \rightarrow NO_2 + O_2$

[5] R2: $NO_2 + h\nu \rightarrow NO + O$

[6] R3: $O + O_2 \rightarrow O_3$

before conversion to HNO_3 via

[7] R4: $NO_2 + OH + M \rightarrow HNO_3 + M$,

where M is an unreactive third body, usually N_2. During the nighttime, NO_x accumulates as NO_2, allowing for both the heterogeneous formation of HNO_3 via

[8] R5: $NO_2 + O_3 \rightarrow NO_3 + O_2$

[9] R6: $NO_2 + NO_3 + M \leftarrow\rightarrow N_2O_5 + M$

[10] R7: $N_2O_{5(g)} + H_2O_{(l,\ aerosol)} \rightarrow 2HNO_{3(aq)}$,

and the gas-phase reaction with hydrocarbons, especially dimethyl sulfide (DMS), in the marine boundary layer via

[11] R8: $NO_3 + RH_{(DMS)} \rightarrow HNO_3 + \text{products}\ (CH_3SCH_2)$.

[12] Heterogeneous halogen chemistry, discussed in section 3.2, may also contribute to NO_3^- formation.

[13] The $^{15}N/^{14}N$ and $^{18}O/^{16}O$ ratios of NO_3^- have been used to distinguish NO_3^- sources and chemical formation pathways in both polluted [*Elliott et al.*, 2007, 2009; *Mara et al.*, 2009; *Wankel et al.*, 2009] and remote environments [*Altieri et al.*, 2013; *Baker et al.*, 2007; *Hastings et al.*, 2003, 2004; *Morin et al.*, 2009]. The N atom is conserved during conversion from NO_x to NO_3^- (R1–R8), so the $\delta^{15}N$ ($\delta^{15}N = [(^{15}N/^{14}N)_{sample}/(^{15}N/^{14}N)_{reference} - 1]*1000$, where the reference is N_2 in air) of the final NO_3^- is taken to indicate the $\delta^{15}N$ of the NO_x source [*Altieri et al.*, 2013; *Elliott et al.*, 2007, 2009; *Hastings et al.*, 2003; *Wankel et al.*, 2009], although isotopic fractionation during formation may also influence the $\delta^{15}N$ of NO_3^- [*Freyer*, 1991; *Vicars et al.*, 2013]. In contrast, the oxygen (O) atoms are exchanged with ozone (O_3) in the nighttime pathways (R5–R8) and with both O_3 and the hydroxyl radical (OH) in the daytime pathway (R1–R4). Because O_3 has a much higher $\delta^{18}O$ ($\delta^{18}O = [(^{18}O/^{16}O)_{sample}/(^{18}O/^{16}O)_{reference} - 1]*1000$, where the reference is Vienna Standard Mean Ocean Water) than that expected for OH (+90 to +122‰ and −6 to +2‰, i.e., $H_2O_{(v)}$, respectively), the $\delta^{18}O$-NO_3^- can be used to distinguish among NO_3^- formed via the daytime (R4) and nighttime

Additional supporting information may be found in the online version of this article.

[1]Department of Geosciences, Princeton University, Princeton, New Jersey, USA.
[2]Department of Geological Sciences and Environmental Change Initiative, Brown University, Providence, Rhode Island, USA.
[3]Bermuda Institute of Ocean Sciences, St.George's, Bermuda.

Corresponding author: M. G. Hastings, Department of Geological Sciences and Environmental Change Initiative, Brown University, 324 Brook St., Box 1846, Providence, RI 02912, USA. (Meredith_Hastings@brown.edu)

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(R7–R8) pathways [*Altieri et al.*, 2013; *Elliott et al.*, 2009; *Hastings et al.*, 2003; *Wankel et al.*, 2009].

[14] The $\delta^{15}N\text{-}NO_3^-$ in rainwater ($\delta^{15}N\text{-}NO^-_{3(aq)}$) at Bermuda is significantly lower during the cool season, from October to March (-5.9 ± 3.3‰; ± 1 SD unless otherwise noted), than during the warm season, from April to September (-2.1 ± 1.5‰), corresponding to two distinct atmospheric transport regimes [*Hastings et al.*, 2003]. In the cool season, fast-moving fronts transport relatively polluted air masses from North America to Bermuda [*Jickells et al.*, 1982; *Miller and Harris*, 1985] associated with tracers for anthropogenic activity (e.g., non-sea-salt sulfate, antimony, and selenium) and high concentrations of sea-salt aerosols (e.g., coarse-mode sodium, chlorine, and calcium) due to increased wind speeds [*Arimoto et al.*, 1992; *Huang et al.*, 1999; *Wolff et al.*, 1986]. In the warm season, the Azores high pressure system develops over Bermuda, blocking most transport from North America [*Jickells et al.*, 1982] and carrying dust plumes from the Sahara over the North Atlantic [*Prospero et al.*, 1996] associated with increased mineral components (e.g., silica, aluminum, and non-sea-salt calcium) [*Arimoto et al.* 1992; *Huang et al.*, 1999; *Wolff et al.*, 1986]. Interestingly, for concurrent sampling campaigns conducted in 2000, the cool season $\delta^{15}N\text{-}NO^-_{3(aq)}$ in Bermuda (-5.9‰) [*Hastings et al.*, 2003] was much lower than that measured in the eastern United States (+0.1‰) [*Elliott et al.*, 2007], the presumed source region, which could indicate an additional NO_x source over the ocean or some isotopic transformation during transport from the U.S. to Bermuda.

[15] Aerosol NO_3^- ($NO^-_{3(p)}$) can contribute 20–65% of total NO_3^- deposition in marine environments [*Baker et al.*, 2007] and to our knowledge has not been investigated in the marine atmosphere downwind of North America, a region of high anthropogenic NO_x emissions. In addition, rainwater efficiently scavenges both particles and gases from the atmosphere. Therefore, the $\delta^{15}N\text{-}NO^-_{3(p)}$ will both influence the $\delta^{15}N\text{-}NO^-_{3(aq)}$ and illuminate the source and formation pathways of the $NO^-_{3(p)}$ itself. This study determined the N and O isotopic composition of $NO^-_{3(p)}$ to investigate the importance of anthropogenic contributions to $NO^-_{3(p)}$ and to provide insight into the formation pathways of $NO^-_{3(p)}$ in comparison to $NO^-_{3(aq)}$.

2. Methods

[16] Aerosol samples were collected in March 2010 and from June to August 2010 on the island of Bermuda at the Tudor Hill Marine-Atmospheric Sampling Observatory (32.27°N, 64.87°W) using cassette-based samplers fitted with Whatman 41 cellulose substrates. The filters were frozen until extraction into aqueous solution following the methods of *Chen et al.* [2006] and *Wankel et al.* [2009]. The extracts were subsequently analyzed for [NO_3^-], using reduction to NO followed by chemiluminescent detection of NO [*Braman and Hendrix*, 1989], and for $^{15}N/^{14}N$ and $^{18}O/^{16}O$ ratios, using the denitrifier method [*Casciotti et al.*, 2002; *Sigman et al.*, 2001]. Rainwater samples collected on an event basis from July 2009 through June 2011, including the dates of the aerosol sampling campaign, were analyzed using the same methods. NOAA's Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model was used to calculate air mass back trajectories (AMBTs) for each aerosol sample in order to confirm that specific trajectories conformed to expected seasonal atmospheric circulation patterns (Figure S2). Further detail on methods is presented in the supporting information.

3. Results and Discussion

[17] HYSPLIT AMBTs support the assumption that the seasonal designations are effective proxies for air mass source, with cool season samples originating over North America and warm season samples originating over the subtropical North Atlantic (Figures S1 and S2), consistent with the longer time series reported by *Hastings et al.* [2003] and *Altieri et al.* [2013]. Therefore, the aerosol results are considered representative of seasonal trends. Comparisons below were calculated by season, following the methods of *Hastings et al.* [2003], and using a two-tailed *t* test for populations of unequal variance, where $p < 0.05$ indicates a statistically significant difference between populations.

[18] Previous studies [*Arimoto et al.*, 1992; *Huang et al.*, 1999; *Wolff et al.*, 1986] and recent collections (Peters et al., unpublished data collected January 2007–June 2008) show that sea salt dominates the composition of Bermuda aerosols compared to mineral dust by over an order of magnitude year round. Infrequent strong dust events, usually during the summer, may cause mineral dust to reach levels comparable to sea salt concentrations [*Arimoto et al.*, 1992; *Huang et al.*, 1999; Peters et al., 2008, unpublished data]. For the samples in this study, however, AMBTs suggest little to no transport from North Africa, the main dust source to Bermuda. While we did not directly address bulk ionic composition of aerosols in this study, an (occasional) important contribution of mineral dust should not significantly affect the trends observed.

3.1. Aerosol and Rainwater $\delta^{15}N\text{-}NO_3^-$

[19] The $\delta^{15}N\text{-}NO^-_{3(p)}$ was generally lower than the $\delta^{15}N\text{-}NO^-_{3(aq)}$ for rain events concurrent with the aerosol sampling period. The difference ($\Delta\delta^{15}N = \delta^{15}N\text{-}NO^-_{3(aq)} - \delta^{15}N\text{-}NO^-_{3(p)}$) ranged from -2.9‰ to 6.0‰ and averaged 1.5‰ over the sampling period, although the populations were only significantly different during the warm season (Figure 1a). The isotopic difference between the $\delta^{15}N\text{-}NO^-_{3(p)}$ and the $\delta^{15}N\text{-}NO^-_{3(aq)}$ agrees with one other observation from the tropical North Atlantic [*Baker et al.*, 2006] but contrasts with the trend reported in polluted regions, where the $\delta^{15}N\text{-}NO^-_{3(p)}$ is consistently higher than the $\delta^{15}N\text{-}NO^-_{3(aq)}$ [*Elliott et al.*, 2009; *Freyer*, 1991; *Mara et al.*, 2009]. This difference in $\delta^{15}N$ between aerosol and rain NO_3^- is present during both the cool and warm seasons (Figure 1a). Thus, the observed difference is likely independent of the chemistry that converts NO_x to NO_3^-, which has a strong seasonal dependence, as evidenced by the seasonal distribution in $\delta^{18}O\text{-}NO_3^-$ (Figure 1b) and previous work on $\delta^{18}O\text{-}NO_3^-$ [*Hastings et al.*, 2003; *Elliott et al.*, 2009; *Wankel et al.*, 2009]. It also does not depend on AMBT, again suggesting little sensitivity to the bulk composition of the aerosol.

[20] In polluted regions, $NO^-_{3(p)}$ occurs predominantly in the fine mode as NH_4NO_3 [*Putaud et al.*, 2004], formed through the following reaction:

[21] R9: $NH_{3(g)} + HNO_{3(g)} \leftarrow\rightarrow NH_4NO_{3(p)}$

[22] *Freyer* [1991] suggested that ^{15}N is favored in the more stable solid phase, driving the $\delta^{15}N\text{-}NO^-_{3(p)}$ higher than the $\delta^{15}N\text{-}HNO_{3(g)}$. The rainwater NO_3^-, comprising both the

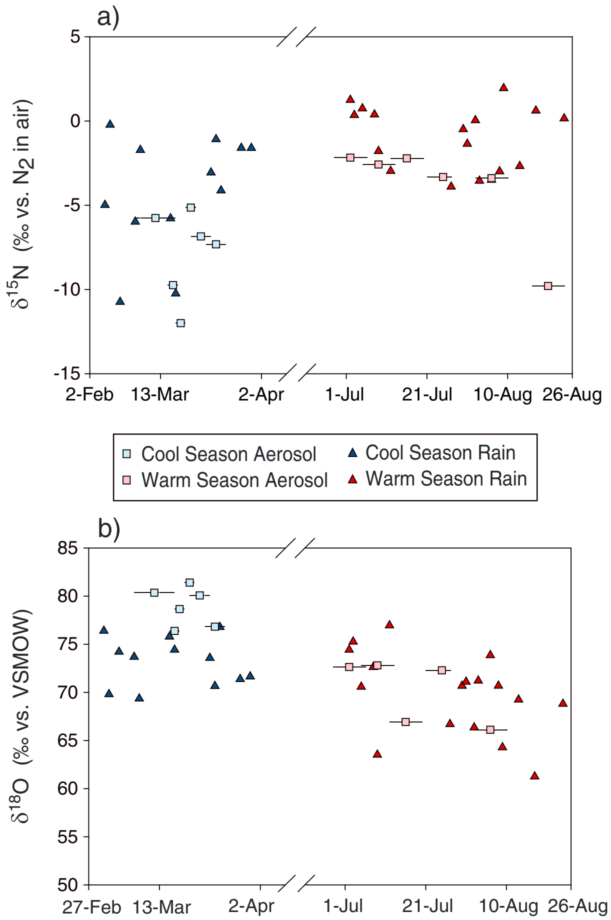

Figure 1. (a) The $\delta^{15}N\text{-}NO_{3(p)}^-$ and $\delta^{15}N\text{-}NO_{3(aq)}^-$ were lower, and (b) the $\delta^{18}O\text{-}NO_{3(p)}^-$ and $\delta^{18}O\text{-}NO_{3(aq)}^-$ were higher in the cool season than in the warm season. For rain samples that occurred during the aerosol sampling campaign, the $\delta^{15}N\text{-}NO_{3(aq)}^-$ was generally greater than or equal to the $\delta^{15}N\text{-}NO_{3(p)}^-$; and the $\delta^{18}O\text{-}NO_{3(aq)}^-$ was lower than the $\delta^{18}O\text{-}NO_{3(p)}^-$ during the cool season but was not statistically different from the $\delta^{18}O\text{-}NO_{3(p)}^-$ during the warm season. Horizontal lines through the aerosol symbols indicate the time during which the filter was deployed. In all cases, error bars for isotopic measurements for multiple filter sections were smaller than the symbol size.

higher $\delta^{15}N\text{-}NO_{3(p)}^-$ and the lower $\delta^{15}N\text{-}HNO_{3(g)}$, will therefore consistently have a lower $\delta^{15}N$ than the aerosol NO_3^-, as is observed in polluted regions. This mechanism becomes insignificant, however, when aerosols are transported into the marine atmosphere and shift from fine mode NH_4NO_3 to coarse mode through an association between $HNO_{3(g)}$ and sea salt or mineral dust particles [*Mara et al.*, 2009, and references therein]:

[23] R10: $HNO_{3(g)} + NaCl_{(p)} \rightarrow NaNO_{3(p)} + HCl_{(g)}$

[24] R11: $2HNO_{3(g)} + CaCO_{3(p)} \rightarrow Ca(NO_3)_{2(p)} + CO_{2(g)} + H_2O$

[25] Indeed, about 90% of aerosol NO_3^- is in the coarse mode in the North Atlantic marine atmosphere [*Baker et al.*, 2006]. Conversion from fine mode to coarse mode tends to be a unidirectional process; therefore, coarse mode aerosols, unlike fine mode aerosols, are not in equilibrium with $HNO_{3(g)}$ [*Keene and Savoie*, 1998]. Instead, kinetic fractionation should preferentially form $^{14}NO_{3(p)}^-$, leaving a ^{15}N-enriched pool of $HNO_{3(g)}$. The rainwater NO_3^-, integrating the lower $\delta^{15}N\text{-}NO_{3(p)}^-$ and the higher $\delta^{15}N\text{-}HNO_{3(g)}$, would yield a $\delta^{15}N$ higher than that of the aerosol NO_3^-, as observed in the data presented here and by *Baker et al.* [2006].

3.2. Aerosol and Rainwater $\delta^{18}O\text{-}NO_3^-$

[26] The $\delta^{18}O\text{-}NO_{3(p)}^-$ was significantly higher than the $\delta^{18}O\text{-}NO_{3(aq)}^-$ during the cool season but was not significantly different during the warm season (Figure 1b). Recent studies have shown the potential for halogens to play a significant role in NO_x and NO_3^- chemistry, especially in the polluted marine boundary layer near the continents [*Altieri et al.*, 2013; *Osthoff et al.*, 2008; *Thornton et al.*, 2010; *Vicars et al.*, 2013]. There, NO_x may be converted to NO_3^- through reaction with XO (X = Cl or Br) during the day to form $XONO_2$ (R12–R14). First, $HNO_{3(g)}$ in polluted plumes reacts with NaCl in the marine boundary layer, releasing HCl and $NaNO_{3(p)}$ (R10) or the analogous reaction with NaBr to form HBr. The HX then reacts with OH to produce Cl or Br radicals, which quickly form XO by reacting with ozone. The $XONO_2$ subsequently formed (R13) can then combine with sea-salt aerosol to form coarse mode $NO_{3(p)}^-$ (R14).

[27] R12: $X + O_3 \rightarrow XO + O_2$

[28] R13: $NO_2 + XO_{(g)} + M \rightarrow XONO_{2(g)}$

[29] R14: $XONO_{2(g)} + NaX_{(p)} \rightarrow X_{2(g)} + NaNO_{3(p)}$

[30] NO_x can also react with sea-salt aerosol to form XNO and $NaNO_3$ (R15).

[31] R15: $2NO_2 + NaX_{(p)} \rightarrow XNO_{(g)} + NaNO_{3(p)}$

[32] Mineral dust is assumed to play a negligible role in these reactions for two reasons: the aerosol halogens participating in these reactions can reasonably be assumed to come from sea salt, and these reactions would occur predominantly in polluted, off-shore transport from North America, when mineral dust contributions to Bermuda would be minimal. Because the coarse mode $NO_{3(p)}^-$ formed through these heterogeneous pathways derives all its O atoms from O_3, it should have a higher $\delta^{18}O$ than $HNO_{3(aq)}$ formed from N_2O_5 hydrolysis (R7). The $\delta^{18}O\text{-}NO_{3(aq)}^-$ should reflect both the high $\delta^{18}O\text{-}NaNO_{3(p)}$ and the lower $\delta^{18}O\text{-}HNO_{3(aq)}$ formed from N_2O_5 hydrolysis and other NO_3^- formation pathways (R4–R7). During the warm season, however, the OH pathway (R4) dominates NO_3^- formation and should set the $\delta^{18}O$ of both aerosols and rainwater. Thus, the direct formation of high $\delta^{18}O\text{-}NO_{3(p)}^-$ in the polluted marine boundary layer could lead to the isotopic difference between cool season rain and aerosol NO_3^-.

3.3. Seasonal characteristics of $\delta^{15}N$ and $\delta^{18}O$

[33] The range of concentrations for both $NO_{3(p)}^-$ (8.1 to 42 nmol m^{-3}; $n = 12$, Table S2) and $NO_{3(aq)}^-$ (0.8 to 33.3 μM; $n = 126$, Table S3) was consistent with other analyses in the North Atlantic [*Baker et al.*, 2006, 2007; *Hastings et al.*, 2003]. On average, dry deposition was 30% of total N (wet + dry) deposition (following the calculations of *Baker et al.* [2007] and assuming all NO_3^- was in the coarse mode). The concentrations of rainwater and aerosol NO_3^- did not vary significantly by season. However, the concentration-weighted average cool season $\delta^{15}N\text{-}NO_{3(p)}^-$ was significantly lower ($p < 0.01$) than the warm season $\delta^{15}N\text{-}NO_{3(p)}^-$ (-6.2 ± 2.0‰ and -2.6 ± 0.6‰, respectively). Consistent with the findings of *Hastings et al.* [2003], the $\delta^{15}N\text{-}NO_{3(aq)}^-$ was also significantly lower in the cool season than in the warm season (-4.3 ± 3.0‰ and -1.4 ± 3.1‰, respectively, $p < 10^{-4}$). The concentration-weighted averages for cool

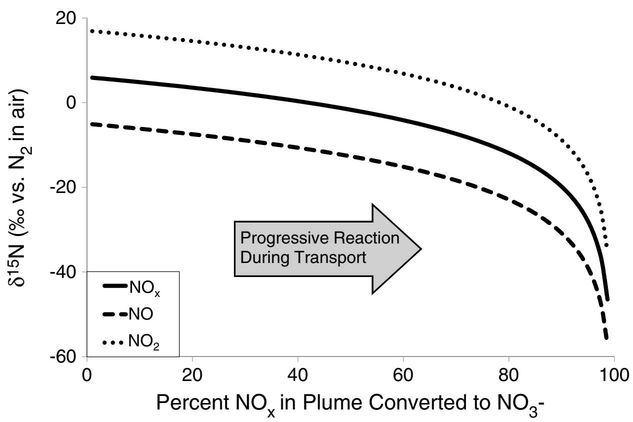

Figure 2. This model calculates the expected drop in $\delta^{15}N$ for both NO and NO_2 resulting from the conversion of ^{15}N-enriched NO_2 to HNO_3. During the winter, 65% of NO_x is removed, which could result in a decrease of ^{15}N-enriched NO_2 from +6.0‰ to −5.6‰. The HNO_3 formed is assumed to have the same $\delta^{15}N$ as its source NO_2. This may explain the difference between the $\delta^{15}N$-NO_3^- in the United States and that in Bermuda. The figure illustrates the $\delta^{15}N$-NO_x as a function of the percentage of the NO_x in the plume that has been removed from the system through deposition as NO_3^-.

season $\delta^{18}O$-$NO^-_{3(p)}$ and $\delta^{18}O$-$NO^-_{3(aq)}$ (+79.1 ± 1.7‰ and +74.7 ± 5.5‰, respectively) were significantly higher ($p < 0.01$ and $p < 10^{-4}$, respectively) than those of the warm season (+69.7 ± 3.4‰ and +67.1 ± 4.6‰, respectively).

[34] The isotopic data together with the AMBT patterns suggest a seasonal variation in NO_x source such that during the cool season, continental (and thus anthropogenic) NO_x is the primary contributor to $NO^-_{3(p)}$ deposition. However, during the cool season, both the $\delta^{15}N$-$NO^-_{3(aq)}$ (−4.3‰) and the $\delta^{15}N$-$NO^-_{3(p)}$ (−6.2‰) are distinctly lower in Bermuda than in the United States, the source region (+0.1 ± 0.2‰, winter average $\delta^{15}N$-$NO^-_{3(aq)}$ [*Elliott et al.*, 2007]; and −1.5‰, annual mean $\delta^{15}N$-$NO^-_{3(p)}$, with winter values significantly higher than summer values, although they were not reported separately [*Elliott et al.*, 2009]). The isotopic difference between NO_3^- deposition in the U.S. and Bermuda is unlikely to be driven by a significant source difference. AMBTs suggest that the air masses transported to Bermuda are representative of the regions sampled by *Elliott et al.* [2009]. Moreover, the difference was observed in the concurrent sampling events of *Elliott et al.* [2007] and *Hastings et al.* [2003], and the $\delta^{15}N$-$NO^-_{3(aq)}$ observations of the latter study are comparable to those of this study.

[35] If the ultimate source of the NO_3^- deposited in Bermuda during the cool season is the same as that of the NO_3^- deposited in the U.S. as predicted by AMBTs, then the pool of NO_x and its oxidation products must preferentially lose ^{15}N between the U.S. and Bermuda. When NO_x concentrations are high relative to O_3, equilibrium fractionation between NO and NO_2 results in ^{15}N-enriched NO_2 and ^{15}N-depleted NO [*Freyer et al.*, 1993]. By contrast, when O_3 concentrations are greater than NO_x concentrations, NO_x tends toward NO_2, such that the $\delta^{15}N$-NO_2 is expected to equal $\delta^{15}N$-NO_x. In Bermuda, O_3 concentrations always exceed NO_x concentrations [*Prados et al.*, 1999 and references therein]; therefore, fractionation between NO and NO_2 has not previously been considered important [*Hastings et al.*, 2003]. In the atmospheric boundary layer over North America, however, NO_x concentrations are comparable to O_3 in many areas and exceed O_3 in heavily industrialized zones [*Liang et al.*, 1998]. Fractionation between NO and NO_2 may therefore be important because 65% of NO_x emitted in the U.S. is deposited over the continent in the winter [*Liang et al.*, 1998], potentially altering the isotopic composition of the NO_x exported from the continent. A simple numerical model described in the supporting information that assumes 65% loss of anthropogenic NO_x with a starting $\delta^{15}N$ of +6‰ and Rayleigh fractionation with an isotope effect of 1.022 [*Freyer et al.*, 1993] results in a $\delta^{15}N$-NO_x pool of −5.6‰, consistent with NO_3^- deposition at Bermuda (Figure 2; the supporting information also includes a discussion of the model's sensitivity to the assumed isotope effect). This mechanism could be tested by following a coherent plume of NO_x and NO_3^-, as performed by *Neuman et al.* [2006] and measuring the time-dependent evolution of both the concentrations and isotopic compositions of NO_3^- and NO_x as NO_3^- is deposited during transport from the U.S. to Bermuda.

[36] Seasonal trends in the $\delta^{18}O$-NO_3^- similar to the results of this study have been observed in both aerosol [*Elliott et al.*, 2009; *Wankel et al.*, 2009] and rainwater [*Elliott et al.*, 2009, *Hastings et al.*, 2003] and are generally taken to indicate a change in the formation pathway, with the daytime reaction (R4) gaining importance during the warm season and heterogeneous nighttime reaction (R7) gaining importance during the cool season. This interpretation is consistent with the isotopic results of this study, the AMBTs, and modeled predictions of the importance of NO_3^- formation pathways [*Alexander et al.*, 2009; *Dentener and Crutzen*, 1993]. Because of the uncertainty in the absolute values, seasonal trends, and spatial variability of the $\delta^{18}O$-O_3 and $\delta^{18}O$-OH, the $\delta^{18}O$-NO_3^- alone gives us limited capacity to quantify the contributions of these pathways; nevertheless, a discussion of trends remains possible.

[37] The NO_2 + OH pathway (R4) becomes relatively more important during the warm season: increased radiation from longer days and a decreased angle of solar incidence result in greater production of OH; and decreased atmospheric transport from the U.S. results in less competition with O_3 in polluted air. The NO_3 + DMS pathway (R8) should also contribute the most in absolute terms during the warm season, when the flux of DMS to the marine atmosphere peaks [*Bates et al.*, 1992]. This pathway would tend to increase the $\delta^{18}O$-NO_3^- because NO_3, the precursor, derives all its O atoms from O_3. Since the average $\delta^{18}O$-NO_3^- decreases during the summer, we can infer that despite the likely increase in total NO_3^- formed by the NO_3 + DMS pathway compared to the cool season, the relative strengthening of the NO_2 + OH pathway drives the isotopic composition during the warm season.

[38] The N_2O_5 pathway (R7) becomes important under the opposite conditions that lead to increased importance of the NO_2 + OH pathway: longer nights, increased angle of solar incidence, and increased pollution, all occurring during the cool season, lead to the increased relative contribution of O_3. The heterogeneous halogen reactions (R12–R15) also become more important during the cool season because of the transport of halogens in polluted air and the increased salt load in the marine atmosphere due to higher wind speeds. Both halogen reactions and the N_2O_5 pathway would increase $\delta^{18}O$-NO_3^-, and thus both may contribute to the

observed trend. Future studies should pursue the quantification of these pathways through simultaneous gas, aerosol, and rainwater sampling, and combined ^{18}O and ^{17}O measurements [*Morin et al*., 2009; *Vicars et al*., 2013].

4. Conclusion

[39] The N and O isotopic composition of $NO_{3(p)}^-$ at Bermuda follows the same seasonal trends as $NO_{3(aq)}^-$: lower $\delta^{15}N$ and higher $\delta^{18}O$ during the cool season than during the warm season. The seasonal change in $\delta^{15}N$-$NO_{3(p)}^-$ is best interpreted as a seasonal change in NO_x source associated with the shift in dominant transport patterns. The cool season $\delta^{15}N$-NO_3^- observed is much lower than that of NO_3^- observed in the presumed source region in North America, a difference best explained by the loss of ^{15}N-enriched aerosols during transport of anthropogenic NO_x from North America to Bermuda, although the mechanism of this loss requires further investigation. The seasonal change in $\delta^{18}O$-$NO_{3(p)}^-$ is consistent with a cool-to-warm season shift in the relative importance of the O_3-driven nighttime and halogen chemistry versus OH-driven daytime chemistry, respectively.

[40] Aerosol $\delta^{15}N$-$NO_{3(p)}^-$ is generally lower than or equal to rainwater $\delta^{15}N$-$NO_{3(aq)}^-$ collected concurrently. A study in the marine atmosphere showed the same trend [*Baker et al*., 2007], while studies over continents showed the opposite trend [*Elliott et al*., 2007, 2009; *Freyer*, 1991; *Mara et al*., 2009]. We propose that this isotopic difference is driven by kinetic fractionation during the formation of coarse mode aerosol NO_3^- from $HNO_{3(g)}$ due to acid displacement when $HNO_{3(g)}$ reacts with sea-salt and mineral dust particles. This mechanism explains the difference in $\delta^{15}N$ between $NO_{3(p)}^-$ and $NO_{3(aq)}^-$ during both the cool and warm seasons, and why the offset over the continents is in the opposite direction. The difference between aerosol and rainwater $\delta^{18}O$-NO_3^- unique to the cool season could be driven by heterogeneous halogen chemistry in the polluted marine boundary layer leading to the formation of high $\delta^{18}O$-$NO_{3(p)}^-$. This work demonstrates the utility of isotopes as a tracer of seasonal changes in NO_x source and NO_3^- formation pathways, as well as differences in atmospheric chemistry between polluted and marine regions.

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