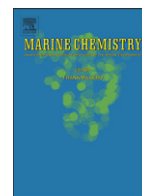




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The flux and isotopic composition of reduced and total nitrogen in Bermuda rain

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ABSTRACT

The concentration and $^{15}\text{N}/^{14}\text{N}$ ratio of total nitrogen (TN) were measured in precipitation samples collected at Bermuda between January and December 2000. By correcting for nitrate, analyzed previously, the concentration and $\delta^{15}\text{N}$ of “reduced” N (RN, i.e., ammonium + organic N) were also determined. The TN precipitation flux ($\sim 10\text{--}19\text{ mmol N m}^{-2}\text{ yr}^{-1}$) is twice the NO_3^- precipitation flux, and the mass-weighted annual average $\delta^{15}\text{N}$ of TN, -2.3‰ , is higher than the $\delta^{15}\text{N}$ of NO_3^- in the same samples (-4.5‰), indicating that RN has an annual average $\delta^{15}\text{N}$ of -0.6‰ . While neither the concentration nor the flux of RN ($6.8\text{ }\mu\text{M}$ and $5.2\text{ mmol N m}^{-2}\text{ yr}^{-1}$, respectively) in precipitation shows statistically significant seasonal variation, the $\delta^{15}\text{N}$ of RN varies significantly from -2.7‰ in the cool season to 1.5‰ in the warm season. This seasonality in the $\delta^{15}\text{N}$ of RN is similar to that of NO_3^- , implying that RN and NO_3^- in precipitation may have related sources or, more speculatively, mechanisms of inter-conversion. Additionally, the seasonality of the RN $\delta^{15}\text{N}$ at Bermuda is similar to that of typical ammonium concentrations in precipitation at Bermuda, both showing maxima in the spring and late summer, raising the possibility that the maxima in the RN $\delta^{15}\text{N}$ derives from ammonium at those times. Finally, the low $\delta^{15}\text{N}$ of the TN flux will cause it to have an effect on the $\delta^{15}\text{N}$ of Sargasso Sea thermocline NO_3^- that is in the same sense as the effect of N_2 fixation, with slightly greater isotopic leverage. If the atmospheric TN flux is not marine-derived, it could explain a substantial fraction of the previously documented upward decrease in NO_3^- $\delta^{15}\text{N}$ from deep water into the thermocline of the Sargasso Sea, for example, ~ 20 to 35‰ of it, assuming a N_2 fixation rate of $45\text{ mmol N m}^{-2}\text{ yr}^{-1}$ as estimated by Hansell et al. [Hansell, D.A., Bates, N.R., and Olson, D.B., 2004. Excess nitrate and nitrogen fixation in the North Atlantic Ocean. *Mar. Chem.*, 84:243–265].

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1. Introduction

The modern marine nitrogen (N) cycle is an active area of research because of the direct link of N to the global carbon cycle, especially in the ocean, where it has been suggested that N commonly limits photosynthesis (Falkowski et al., 1998). In spite of the significance of N for marine primary productivity, the magnitudes and distributions of the fluxes of N to and from the ocean are still poorly known. While it is agreed that the deposition of atmospheric N is not the dominant source of new N to the global ocean, determining its flux and ecological importance in specific marine environments has been the focus of considerable effort (Baker et al., 2003; Cornell et al., 1995;

Duce et al., 2008; Fanning, 1989; Knap et al., 1986; Michaels et al., 1993; Paerl, 1985; Spokes and Jickells, 2005).

Identifying the different forms of N present in atmospheric deposition has improved our understanding of their utility as a source of N to organisms in surface waters, while measurements of the isotopic composition of the N in precipitation have helped constrain the sources and processing of atmospheric N (Carrillo et al., 2002; Cornell et al., 1995; Hastings et al., 2003; Jickells et al., 2003; Kelly et al., 2005; Russell et al., 1998). Much of this work has been carried out on wet and/or dry deposition in the North Atlantic basin. Similarly, numerous studies of marine N fluxes and cycling have been focused in the North Atlantic Ocean, especially in the Sargasso Sea (Altabet, 1988; Gruber and Sarmiento, 1997; Hansell et al., 2004; Lipschultz et al., 2002). However, the large-scale importance of wet deposition in the North Atlantic Ocean, and in particular in regional N isotope budgets, remains uncertain (Altabet, 1988; Knapp et al., 2005).

Nitrate (NO_3^-) with a $\delta^{15}\text{N}$ of as low as 2‰ has been observed in the upper thermocline of the North Atlantic, decreasing upward from a NO_3^- $\delta^{15}\text{N}$ of 5.3‰ at the base of the thermocline (Karl et al., 2002; Knapp et al., 2005) ($\delta^{15}\text{N}$, in per mil versus atmospheric $\text{N}_2 = \{ \{ (^{15}\text{N}/^{14}\text{N})_{\text{sample}} /$

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$(^{15}\text{N}/^{14}\text{N})_{\text{reference}}]-1)*1000$, where the reference is atmospheric N_2 . Along with related observations from the North Pacific and the Arabian Sea (Brandes et al., 1998; Liu et al., 1996; Sigman et al., 2005), this large inventory of low- $\delta^{15}\text{N}$ NO_3^- is perhaps most easily explained by the remineralization of newly fixed N, which has a $\delta^{15}\text{N}$ of ~ -2 to 0‰ (Carpenter et al., 1997; Hoering and Ford, 1960; Minigawa and Wada, 1986). The thermocline inventory of low- $\delta^{15}\text{N}$ NO_3^- , when paired with a time scale over which this geochemical signature has accumulated, provides a means for estimating regional rates of N_2 fixation (Knapp et al., 2008). One potential complication for such N_2 fixation rate estimates, however, is the contribution of low- $\delta^{15}\text{N}$ N from precipitation; the $\delta^{15}\text{N}$ of NO_3^- in precipitation at Bermuda is on average ~ -4 ‰ (Hastings et al., 2003), which would also contribute to the low- $\delta^{15}\text{N}$ NO_3^- in the thermocline of the North Atlantic gyre and consequently lower the N_2 fixation rate required to generate this isotopic signal (Baker et al., 2007). Similarly, wet and dry atmospheric deposition have N:P ratios several fold to several orders of magnitude higher than the “Redfield” N:P ratio of 16:1 that generally characterizes marine planktonic biomass (Baker et al., 2003, 2007; Carbo et al., 2005; Duarte et al., 2006; Ozyoy, 2003; Schroth et al., 2001; Sutula et al., 2001). Therefore, atmospheric deposition may bias geochemical estimates of N_2 fixation that depend upon deviations of NO_3^- and phosphate (PO_4^{3-}) concentration ratios from Redfield proportions (Deutsch et al., 2001, 2007; Gruber and Sarmiento, 1997; Hansell et al., 2004, 2007).

Hastings et al. (2003) investigated the sources and atmospheric chemistry contributing to NO_3^- deposition based on the isotopes of NO_3^- ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, where $\delta^{18}\text{O}$, in per mil, = $\{[(^{18}\text{O}/^{16}\text{O})_{\text{sample}}]/(^{18}\text{O}/^{16}\text{O})_{\text{reference}}]-1\} * 1000$, where the reference is Vienna Standard Mean Ocean Water, or VSMOW) and back-trajectory analysis for rain samples collected on Bermuda between January 2000 and January 2001. Using a subset of the samples from the Hastings et al. (2003) study and methods described in Knapp et al. (2005), we analyzed the concentration and isotopic composition of total N (TN), approximately the sum of NO_3^- , dissolved organic N, and ammonium (NH_4^+). We use these data and those from Hastings et al. (2003) to constrain the significance of TN in wet deposition as a flux of both N and ^{15}N to the Sargasso Sea. We aim to address two questions in this regard: (1) What is the quantitative significance of TN in wet deposition as a source of new N to organisms in Sargasso Sea surface waters? and (2) To what degree does the flux of TN in wet deposition affect the use of stable isotopes as a tool to reconstruct rates of N_2 fixation in this environment? In addition, by differencing the results for TN and NO_3^- , we gain information on the concentration and isotopic signature of “reduced N” (RN, approximately the sum of dissolved organic N and NH_4^+), which has implications for its sources and its relationship to NO_3^- in rainfall.

2. Methods

2.1. Sample collection

Collection of the wet deposition samples is described in Hastings et al. (2003) and references therein. Briefly, rain samples were collected daily after wet deposition events on the island of Bermuda at two stations, “Prospect” and “Incinerator”. Since the same precipitation samples were analyzed for their chemical composition at Bermuda (e.g., Simmons, 1997, and unpublished data; data available from BIOS Air Quality Program), as well as by Hastings et al. (2003) for NO_3^- concentration ($[\text{NO}_3^-]$) and NO_3^- $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ analysis, the number of samples with sufficient remaining volume for TN concentration ($[\text{TN}]$) and TN $\delta^{15}\text{N}$ analysis was fewer than the number of samples analyzed in both previous studies (e.g., $n=56$ in this study vs. $n=65$ in Hastings et al., 2003). Samples were stored at -20 °C upon collection and between all analyses, which has been sufficient to preserve the concentration and isotopic composition of NO_3^- in rainwater (Hastings et al., 2003) and both NO_3^- and TN in previously analyzed seawater samples that have undergone multiple freeze/thaw cycles (Knapp et al., 2005). Moreover, since TN concentration and isotopic

composition was the focus of this study, any changes in speciation that may have taken place should not affect our results, unless a dissolved species converted to a gas (e.g., N_2O and/or N_2) that was then lost upon opening of the sample container. For the precipitation samples collected at Bermuda, the warm season is defined as April through September and the cool season as October through March.

2.2. TN concentration and isotopic analysis

[TN] was determined using persulfate oxidation to convert organic nitrogen to NO_3^- (Solorzano and Sharp, 1980, as modified by Knapp et al., 2005), followed by chemiluminescent detection of NO_3^- (Braman and Hendrix, 1989). The RN concentration ($[\text{RN}]$) was determined by subtracting the $[\text{NO}_3^-]$ reported for each sample in Hastings et al. (2003) from the [TN]. Thus, RN includes any NH_4^+ as well as dissolved and particulate organic nitrogen present in these unfiltered wet deposition samples. The average standard deviation associated with replicate ($n>2$) measurements of an individual sample for each analytical method is ± 0.2 μM for $[\text{NO}_3^-]$ analysis and ± 0.3 μM for [TN] analysis; the propagated error for determining [RN], calculated by adding the standard deviations for $[\text{NO}_3^-]$ and [TN] analysis in quadrature (Taylor, 1982), is ± 0.4 μM . While nitrite (NO_2^-) is included with NO_3^- in the above analytical methods, its concentration, measured by ion chromatography, was insignificant in these samples (Hastings et al., 2003), so that we refer to the $\text{NO}_3^- + \text{NO}_2^-$ pool as “ NO_3^- ”.

The $\delta^{15}\text{N}$ of TN and RN was determined by adapting the denitrifier method for NO_3^- $\delta^{15}\text{N}$ analysis described by Sigman et al. (2001) and Casciotti et al. (2002) for TN $\delta^{15}\text{N}$ analysis according to Knapp et al. (2005). The average standard deviation for replicate analysis of an individual sample for NO_3^- $\delta^{15}\text{N}$ is ± 0.2 ‰, and for replicate analysis of an individual TN $\delta^{15}\text{N}$ sample is ± 0.3 ‰. The $\delta^{15}\text{N}$ of RN is determined by subtracting the $[\text{NO}_3^-]$ and the $\delta^{15}\text{N}$ of NO_3^- of each sample (from Hastings et al. (2003)) from the [TN] and TN $\delta^{15}\text{N}$ by mass balance:

$$\delta^{15}\text{N} \text{ of RN} = \left([\text{TN}] \times \delta^{15}\text{N}_{\text{TN}} - [\text{NO}_3^-] \times \delta^{15}\text{N}_{\text{NO}_3^-} \right) / ([\text{TN}] - [\text{NO}_3^-]). \quad (1)$$

The propagated error for the calculation of RN $\delta^{15}\text{N}$, determined using a Monte Carlo method (Press et al., 1992), and assuming duplicate analysis of a single sample and the standard deviations of the measurements given above, is ± 0.6 ‰.

Seasonal and annual average fluxes of TN and RN were calculated from daily rain samples collected between January and December of 2000 at a single station (“Prospect”) on Bermuda where enough sample volume remained for [TN] and TN $\delta^{15}\text{N}$ analysis ($n=41$), similar to calculations of NO_3^- fluxes in Hastings et al. (2003). Calculations of both numerical and volume-weighted (in parentheses) seasonal and annual average concentrations, and numerical and mass-weighted (in parentheses) seasonal and annual average $\delta^{15}\text{N}$ of both RN and TN are listed in Table 1, and include all of the 41 samples used to calculate fluxes, as well as seven additional samples also collected at the “Prospect” station in September 1999 and January 2001. The remaining eight samples were collected at the “Incinerator” station on the same day that a sample from the “Prospect” station was collected, and thus were not included in flux or averaging calculations to avoid double-weighting the same precipitation event.

3. Results

3.1. RN and TN concentrations and fluxes

The [RN] of samples ranges from 1.1 to 51.4 μM , with an annual volume-weighted average of 6.9 μM , and similar seasonal volume-weighted concentration averages of 6.4 and 7.5 μM for the warm and cool seasons, respectively (Table 1). Typically, RN comprises $\sim 50\%$ of the [TN] throughout the year (annual volume-weighted average [TN] is 12.3 μM , and $[\text{NO}_3^-]$ is 5.7 μM) (Table 1, Fig. 1). The elevated $[\text{NO}_3^-]$ and [RN] in

Table 1

Seasonal and annual numerical average precipitation N values (volume-weighted or mass-weighted averages in parentheses) and fluxes

	Cool season average concentration (μM)	Warm season average concentration (μM)	Annual average concentration (μM)	Cool season average $\delta^{15}\text{N}$ (‰)	Warm season average $\delta^{15}\text{N}$ (‰)	Annual average $\delta^{15}\text{N}$ (‰)	Cool season flux (mmol N m^{-2})	Warm season flux (mmol N m^{-2})	Annual flux ($\text{mmol N m}^{-2} \text{yr}^{-1}$) ^a
NO_3^-	8.4 (6.5)	6.0 (5.0)	7.1 (5.7)	-5.9 (-6.8)	-2.1 (-1.9)	-3.9 (-4.5)	2.6	3.0	5.6
RN	8.5 (7.5)	8.3 (6.4)	8.4 (6.9)	-3.6 (-2.7)	-0.2 (1.5)	-1.8 (-0.6)	1.8	3.3	5.2
TN	16.8 (13.8)	14.2 (11.1)	15.4 (12.3)	-4.7 (-4.6)	-0.8 (0.0)	-2.6 (-2.3)	4.3	6.0	10.0

[RN] and [TN] are not significantly different between the warm and cool seasons, but RN $\delta^{15}\text{N}$ and TN $\delta^{15}\text{N}$ are statistically significantly different between the warm and cool season beyond the 0.025 and 0.005 confidence levels, respectively. The warm season is defined as April through September, and the cool season as October through March.

^a Fluxes (rainfall \times concentration) calculated by summing fluxes for each depositional event ($n=41$) from rainfall amounts provided by BIOS. For samples collected at both sampling stations on the same date, only Prospect station data were used for volume-weighted and flux calculation purposes.

March and the high [RN] in May each result from only one sample and thus may not be representative of a monthly average (Fig. 1b), although the isotopic composition of both the March and the May samples is not extraordinary (Fig. 1a). The results reported in Table 1 include these samples; if the March and May data are excluded, the annual volume-weighted average [RN] falls from 6.9 to 6.4 μM . The annual RN flux is $\sim 5.2 \text{ mmol N m}^{-2} \text{yr}^{-1}$, with $\sim 3.3 \text{ mmol N m}^{-2}$ and $\sim 1.8 \text{ mmol N m}^{-2}$ falling during the warm and cool seasons, respectively (Table 1).

The range in [TN] is 2.4 to 62.4 μM . The annual volume-weighted average [TN] is 12.3 μM , and the warm and cool seasons' volume-weighted average [TN] are 11.1 μM and 13.8 μM , respectively (Table 1), which are not statistically different from each other. Excluding the two (March and May) samples with very high [TN], the annual volume-weighted average [TN] is 11.4 μM , and the warm and cool seasons' volume-weighted average [TN] are 10.7 μM and 12.3 μM , respectively. Annually, the TN flux is $\sim 10 \text{ mmol N m}^{-2} \text{yr}^{-1}$, with the warm season accounting for 6.0 mmol N m^{-2} , and the cool season 4.3 mmol N m^{-2} (Table 1).

Our sample set is not ideal for estimation of RN and TN fluxes, in that insufficient sample remained from all rainfall events to be analyzed for [TN] and TN $\delta^{15}\text{N}$. If, instead of calculating an annual TN flux based on the reduced sample set as described in Section 2.2, annual fluxes are calculated using the volume-weighted annual average [RN] and [TN], and then multiplied by the total water deposition for 2000 (K. Simmons and A. Peters, pers. comm.), our estimated annual RN and TN fluxes would be roughly twice as large, $\sim 10 \text{ mmol N m}^{-2} \text{yr}^{-1}$ and $19 \text{ mmol N m}^{-2} \text{yr}^{-1}$, respectively (Table 2).

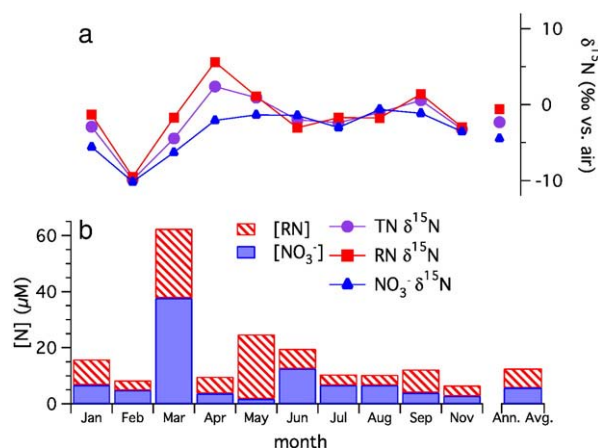


Fig. 1. Monthly and annual mass-weighted averages of TN $\delta^{15}\text{N}$ (circles), RN $\delta^{15}\text{N}$ (squares), and $\text{NO}_3^- \delta^{15}\text{N}$ (triangles) (a), and volume-weighted [NO₃⁻] (shaded area), [RN] (cross-hatched area) and [TN] (sum of shaded and cross-hatched area) (b) versus month at Bermuda. Standard deviation for each measurement is approximately the symbol size for both TN and RN $\delta^{15}\text{N}$; smaller than the symbol size for $\text{NO}_3^- \delta^{15}\text{N}$ (a); smaller than the thickness of the box line for [NO₃⁻]; and roughly double the thickness of the box line for [RN] (b).

3.2. $\delta^{15}\text{N}$ of RN and TN

Unlike the concentrations of RN and TN, their $\delta^{15}\text{N}$ has statistically significant seasonal variations. The Kruskal–Wallis test for non-parametric data (Triola, 2001) indicates that the mass-weighted average $\delta^{15}\text{N}$ of RN in the cool and warm seasons (-2.7% vs. 1.5% , respectively) are significantly different beyond the 0.025 confidence level, and the cool and warm season TN $\delta^{15}\text{N}$ are significantly different beyond the 0.005 confidence level (-4.6% and 0.0% , respectively; see Table 1). These findings are similar to Hastings et al.'s (2003) observation of statistically significantly lower average $\text{NO}_3^- \delta^{15}\text{N}$ in cool season than in warm season precipitation (mass-weighted averages from this study were -6.8% vs. -1.9% , respectively); of course, the isotopic changes in TN are partly derived from changes in NO_3^- . Both the annual and the cool season $\text{NO}_3^- \delta^{15}\text{N}$ are moderately ($r^2=0.34$ in both cases) but statistically significantly correlated with RN $\delta^{15}\text{N}$, while the warm season $\text{NO}_3^- \delta^{15}\text{N}$ are weakly ($r^2=0.03$) and not significantly correlated with RN $\delta^{15}\text{N}$ (Fig. 2; reduced major axis (RMA) regression lines shown to guide the eye, although r^2 value is independent of the type of linear regression used). The annual mass-weighted averages for the $\delta^{15}\text{N}$ of RN, NO_3^- and TN are -0.6% , -4.5% and -2.3% , respectively (Table 1).

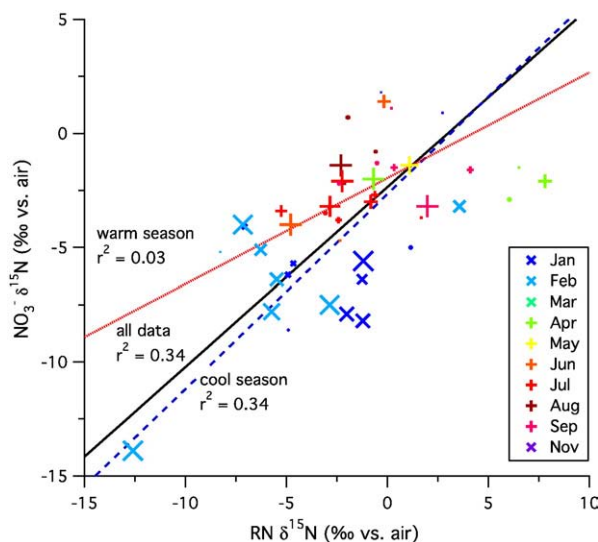


Fig. 2. $\text{NO}_3^- \delta^{15}\text{N}$ vs. RN $\delta^{15}\text{N}$ for cool season ("x" symbols) and warm season ("+" symbols) with reduced major axis (RMA) linear regression lines to guide the eye for all of the data (solid line), cool season data (dashed line) and warm season data (dotted line). The symbol size is proportionate to the [TN] in each sample. The cool season and the annual $\text{NO}_3^- \delta^{15}\text{N}$ and RN $\delta^{15}\text{N}$ data sets are statistically significantly correlated, although the warm season data alone are not significantly correlated. See online for color version of symbols corresponding to month of collection.

4. Discussion

4.1. Precipitation TN flux and sources of new N to the Sargasso Sea

The magnitude of the TN flux calculated from these wet deposition samples generally agrees with previous regional precipitation N flux estimates, as do comparisons of the constituents of the TN flux. For example, previous calculations of the wet deposition flux of NO_3^- at Bermuda range from 2 to 11 $\text{mmol N m}^{-2} \text{yr}^{-1}$ (Knap et al., 1986; Prospero et al., 1996, and references therein), and are consistent with the estimate for the wet deposition flux of NO_3^- at Bermuda for 2000, 7 $\text{mmol N m}^{-2} \text{yr}^{-1}$ (Hastings et al., 2003) (Table 2). The wet deposition NO_3^- flux based on the samples analyzed here, $\sim 5.6 \text{mmol N m}^{-2} \text{yr}^{-1}$ (Table 1), is different than the Hastings et al. (2003) flux estimate due to the reduced sample set in this study (see Sections 2.1 and 2.2 above). The few measurements of wet deposition TN fluxes made at Bermuda that include discrete measurements of both inorganic and organic forms of N are typically twice as large as wet deposition flux estimates of NO_3^- alone (Cornell et al., 1995; Knap et al., 1986), and are similar to the wet deposition TN flux estimate presented here, 10 $\text{mmol N m}^{-2} \text{yr}^{-1}$ using only measured rain events and 19 $\text{mmol N m}^{-2} \text{yr}^{-1}$ if using the annual rainfall flux (Tables 1 and 2). In other regional studies, in particular, those from the east coast of the United States, NO_3^- commonly represents roughly the same fraction of the [TN] as in these wet deposition samples (e.g., Keene et al., 2002; Russell et al., 2003), but often have higher [TN] than the Bermuda data set.

Most marine dry deposition N flux estimates are small compared to the wet deposition TN flux presented here (e.g., 0.1 to 1.0 $\text{mmol N m}^{-2} \text{yr}^{-1}$, Carrillo et al., 2002; Heath and Huebert, 1999), and we do not expect that including the dry deposition N flux at Bermuda would substantially alter the magnitude and/or isotopic composition of the wet + dry TN flux based on the wet deposition estimate presented here. Some recent aerosol TN flux estimates are considerably larger than the wet deposition TN flux estimates discussed here, e.g., 100 $\text{mmol N m}^{-2} \text{yr}^{-1}$ (Duarte et al., 2006), and/or make up a larger fraction of wet + dry TN deposition in coastal ecosystems (e.g., $\sim 43\%$, Russell et al., 2003). However, the highest aerosol N deposition rates in Duarte et al. (2006) were measured in coastal regions nearest the source of Saharan dust plumes, and so these estimates probably do not apply to rates of dry deposition of N at Bermuda. Indeed, measurements of $\text{NO}_3^- + \text{NH}_4^+$ in wet + dry deposition at Bermuda from 1981 through 1993 range from ~ 7 to 11 $\text{mmol N m}^{-2} \text{yr}^{-1}$ (Prospero et al., 1996), one to two orders of magnitude smaller than the N dry deposition fluxes reported in Duarte et al. (2006). Additionally, measurements made at Bermuda during the

warm season suggest that only $\sim 4\%$ of the wet + dry NH_4^+ flux and $\sim 24\%$ of the wet + dry NO_3^- flux occur as dry deposition (Turekian, 2000).

Nonetheless, we note that the N:P ratios of the aerosol samples in Baker et al. (2003), Baker et al. (2007) and Duarte et al. (2006) are also much higher than the Redfield N:P ratio of 16:1, and that the depositional areas of these studies are near the regions of large positive thermocline gradients in N:P concentration ratios documented in Gruber and Sarmiento (1997) and Hansell et al. (2004), which were attributed to N_2 fixation (see Hansell et al., 2007 for further discussion). Although our wet deposition samples may include some aerosol N scoured out during deposition events (Todd et al., 2003), the magnitude of our wet deposition TN flux should be considered a lower bound for the wet + dry TN flux at Bermuda, since dry deposition samples were not collected in this study. We note that we do not expect dry deposition to have a markedly different isotopic signature than TN in wet deposition, at least during the warm season, since Turekian (2000) reports a $\delta^{15}\text{N}$ of $\sim -2.1\%$ for springtime dry deposited NO_3^- , the same as the average $\delta^{15}\text{N}$ of NO_3^- in these warm season wet deposition samples.

The magnitude of our wet deposition TN flux estimate is small compared to estimates of the dominant flux of new N to Sargasso Sea surface waters, NO_3^- mixed up from the subsurface (840 $\text{mmol N m}^{-2} \text{yr}^{-1}$; Jenkins and Doney, 2003) (Table 2). However, the magnitude of the TN wet deposition flux is comparable to biological (i.e., bottle incubation) estimates of N_2 fixation rates in the Sargasso Sea (8–15 $\text{mmol N m}^{-2} \text{yr}^{-1}$; Achilles, 2004; Orcutt et al., 2001), although geochemical (i.e., nutrient ratio calculation) estimates of N_2 fixation in the North Atlantic Ocean are typically several fold higher (e.g., 45–72 $\text{mmol N m}^{-2} \text{yr}^{-1}$) (Gruber and Sarmiento, 1997; Hansell et al., 2004) (Table 2). Moreover, the average $\delta^{15}\text{N}$ of the TN precipitation flux (-2.3%) is lower than the $\delta^{15}\text{N}$ of newly fixed N (~ -2 to 0% ; Carpenter et al., 1997; Hoering and Ford, 1960; Minigawa and Wada, 1986) and thus is more divergent from the $\delta^{15}\text{N}$ of mean ocean NO_3^- of $\sim 5\%$ (Sigman et al., 2000). Consequently, for a flux of equal magnitude, precipitation would have a similar or greater impact on the regional $\delta^{15}\text{N}$ budget. A concern raised by our data is that the TN precipitation flux can account for a sizable fraction of the low $\delta^{15}\text{N}$ - NO_3^- in the thermocline of the Sargasso Sea previously attributed to the remineralization of newly fixed N (Karl et al., 2002; Knapp et al., 2005). Here we estimate the fraction (“X”) of depression in NO_3^- $\delta^{15}\text{N}$ observed in the Sargasso Sea thermocline that may be attributable to wet deposition according to the expression:

$$X = \frac{\Delta\delta^{15}\text{N}_{\text{ppt}} * \text{TN ppt flux}}{(\Delta\delta^{15}\text{N}_{\text{N}_2 \text{ fix}} * \text{N}_2 \text{ fix flux} + \Delta\delta^{15}\text{N}_{\text{ppt}} * \text{TN ppt flux})} \quad (2)$$

where $\Delta\delta^{15}\text{N}_{\text{ppt}}$ represents the difference between the $\delta^{15}\text{N}$ of NO_3^- below the thermocline in the Sargasso Sea (5.3%; Knapp et al., 2005) and the $\delta^{15}\text{N}$ of the mean mass-weighted precipitation TN flux (-2.3%); TN ppt flux represents the wet deposition TN flux (10 to 19 $\text{mmol N m}^{-2} \text{yr}^{-1}$); $\Delta\delta^{15}\text{N}_{\text{N}_2 \text{ fix}}$ represents the difference between the $\delta^{15}\text{N}$ of NO_3^- below the thermocline in the Sargasso Sea (5.3‰) and the $\delta^{15}\text{N}$ of newly fixed N (-1%); and “ N_2 fix flux” represents one geochemical estimate of the regional rate of N_2 fixation (45 $\text{mmol N m}^{-2} \text{yr}^{-1}$, based on an intermediate Sargasso Sea N_2 fixation rate estimate from Hansell et al., 2004). This yields a value for X of 0.21 to 0.34, indicating that TN in the wet deposition flux can account for ~ 20 to 35% of the low $\delta^{15}\text{N}$ - NO_3^- in the Sargasso Sea thermocline, with the remainder of the ^{15}N depletion resulting from the remineralization of N_2 fixation inputs.

This calculation is for quantitative illustration only, for the following reasons. First, it assumes that the Hansell et al. (2004) N_2 fixation flux estimate is correct. Of particular relevance here, since N_2 fixation and atmospheric deposition will both increase the thermocline $[\text{NO}_3^-]:[\text{PO}_4^{3-}]$ ratio, Hansell et al. (2004) recognized that their

Table 2
Magnitude and $\delta^{15}\text{N}$ of fluxes of new N to surface waters of the Sargasso Sea

Flux type	Magnitude ($\text{mmol N m}^{-2} \text{yr}^{-1}$)	$\delta^{15}\text{N}$ of flux	Reference
NH_4^+ ppt	6		Jickells et al. (1982)
NH_4^+ ppt	5		Knap et al. (1986)
NO_3^- ppt	9		Jickells et al. (1982)
NO_3^- ppt	6		Knap et al. (1986)
NO_3^- ppt	7	-4.6%	Hastings et al. (2003)
DIN ppt	16		Jickells et al. (1982)
$\text{NO}_3^- + \text{NH}_4^+$ ppt	25		Michaels et al. (1993)
$\text{NO}_3^- + \text{NH}_4^+$ ppt	8–11		Prospero et al. (1996)
DON ppt	10		Prospero et al. (1996)
TN ppt	6–30		Knap et al. (1986)
TN ppt	10 (19) ^a	-2.3%	This study
In situ N_2 fix	8–15		Orcutt et al., 2001; Achilles (2004)
Geochem	45–72		Gruber and Sarmiento, 1997;
N_2 fix			Hansell et al., 2004
NO_3^- from subsurface	840	2.4%	Jenkins and Doney (2003) (NO_3^- $\delta^{15}\text{N}$ from Knapp et al., 2005)

^a Flux of 19 $\text{mmol N m}^{-2} \text{yr}^{-1}$ is calculated by multiplying annual volume-weighted average [TN] by total annual rain amount; see Section 3.1.

estimate of N_2 fixation may need to be lowered by roughly the rate of atmospherically deposited N (see also [Hansell et al., 2007](#)). In this case, our calculated proportion of the thermocline $NO_3^- \delta^{15}N$ lowering due to deposition would increase. The inherent circularity of this situation derives from the simple fact that N_2 fixation and atmospheric N deposition similarly affect both the N isotopes and the N:P ratio of the Sargasso Sea thermocline. A second caveat in our calculation is that it assumes that all of the RN in the precipitation flux is accessible to biogeochemical N transformations in the upper water column. However, even if a portion of the RN in precipitation were adequately recalcitrant to survive into the thermocline, it is most likely that it would be degraded on the time scale of residence there and would thus enter the thermocline NO_3^- pool.

The final caveat that we highlight, and arguably the most interesting, is that some fraction of the TN in rainfall may be derived from the surface ocean by gaseous emission or sea spray (e.g., NH_4^+ , [Jickells et al., 2003](#)). The fraction of the TN flux that derives from Sargasso Sea surface waters is obviously not, in net, a fixed N input to the ocean. In this case, our TN flux calculation of 10 to 19 $mmol N m^{-2} yr^{-1}$ would overestimate the amount of TN in deposition that is a source of new N to the Sargasso Sea, and Eq. (2) would not be an appropriate measure of the impact of the TN in wet deposition on the $\delta^{15}N$ of NO_3^- in the Sargasso Sea thermocline. Any emission of N to the atmosphere would probably not represent a net loss of N from the oceans, though, since the residence time of NH_4^+ in the atmosphere is on the order of hours to several days ([Cornell et al., 2003](#); [Smith et al., 2007](#)), and so the NH_4^+ would likely be re-deposited to the Atlantic Ocean. Traditionally, evaluating whether N in atmospheric deposition represents a source of “new” N to oceanic surface waters or is simply a “reflux” of N from the ocean to the atmosphere and back again depended primarily upon the magnitude and direction of the atmospheric/oceanic ammonia+ammonium ($NH_3+NH_4^+$) concentration gradient (e.g., [Quinn et al., 1996](#)). However, recent work has shown that temperature plays an important role in determining the direction and magnitude of the air/sea $NH_3+NH_4^+$ flux ([Bell et al., 2007](#); [Johnson et al., 2008](#)). Revised calculations with previous measurements ([Quinn et al., 1996](#)) that include a greater importance of the temperature term in this flux calculation suggest that even in oligotrophic regions of the ocean such as the Sargasso Sea, where surface water NH_4^+ concentrations ($[NH_4^+]$) are low, the direction of the air/sea $NH_3+NH_4^+$ flux may be from the sea to the air ([Johnson et al., 2008](#)).

4.2. Reduced N isotopic composition and source constraints

While the [RN] does not vary throughout the year, the $\delta^{15}N$ of RN exhibits temporal variation that appears similar to that of $NO_3^- \delta^{15}N$

([Fig. 1](#)), which has been interpreted as the result of seasonal variation in N sources ([Hastings et al., 2003](#)). This analogous variation in the isotopic composition of RN implies that both RN and NO_3^- have seasonally distinct sources. The bulk of air arriving at Bermuda during the warm season (April through September) is of marine (tropical Atlantic) origin, while air masses arriving during the cool season are typically of continental (North American) origin (e.g., [Hastings et al., 2003](#); [Jickells et al., 1982](#); [Miller and Harris, 1985](#)). As was found previously for the NO_3^- isotopes ([Hastings et al., 2003](#)), there is more variation in RN $\delta^{15}N$ within the cool season than during the warm season. For the NO_3^- isotopes, back-trajectory analysis showed that this could be explained by variations in source region ([Hastings et al., 2003](#)), and the cool season correlation in $\delta^{15}N$ between NO_3^- and RN suggests the same explanation for the latter ([Fig. 2](#)).

Previous studies indicate that the $[NH_4^+]$ in precipitation at Bermuda is similar to that of the $[NO_3^-]$, which implies that NH_4^+ dominates the RN pool in wet deposition ([Jickells et al., 1982](#); [Knap et al., 1986](#)). While measurements of both $[NH_4^+]$ and $NH_4^+ \delta^{15}N$ may help constrain sources of RN, there was insufficient sample volume to carry out these analyses on this sample set. Thus, in the context of this study, we cannot confidently separate the RN pool into its constituent fractions. It has been suggested that alkyl nitrates are likely recovered as NO_3^- ([Keene et al., 2002](#)). We did not explicitly analyze this component of wet deposition. However, the high $\delta^{18}O$ and $\Delta^{17}O$ of NO_3^- ($\Delta^{17}O \approx \delta^{17}O - 0.5 \times \delta^{18}O$) observed in Bermuda precipitation ([Hastings et al., 2003](#)) suggests that alkyl nitrates are not an important source of the NO_3^- deposited, since formation of alkyl nitrates is expected to be influenced by the low $\delta^{18}O$ and $\Delta^{17}O$ of atmospheric oxygen and/or water vapor ([Hastings and Alexander, 2006](#)).

A comparison of our RN data with $[NH_4^+]$ measurements made on two sets of precipitation samples collected at Bermuda between 1980 through 1988 (at station “Harbor Radio”) and 1989 through 1996 (at station “Tudor Hill”) suggests an interesting correlation ([Fig. 3](#); [J. Galloway, in preparation](#)). The monthly mass-weighted average RN $\delta^{15}N$ and monthly volume-weighted average $[NH_4^+]$ both show peaks in spring (April) and late summer/early fall (July through September). The RN $\delta^{15}N$ data set is moderately but statistically significantly correlated with the 1980 through 1988 $[NH_4^+]$ data, while the correlation with the 1989 through 1996 data set is not significant ($r^2=0.53$ and 0.33, respectively, with RMA regression lines shown, [Fig. 3b](#)). These comparisons suggest that NH_4^+ may contribute to our RN samples with higher $\delta^{15}N$. [Hastings et al. \(2003\)](#) find that anthropogenic sources contribute substantially to NO_3^- deposition at Bermuda throughout the year, with a relative maximum in April, and [Huang et al. \(1999\)](#) observe a strong spring and weaker fall maxima in pollution-derived elements such as Sb, which they attribute to transport of polluted air masses from North America to Bermuda.

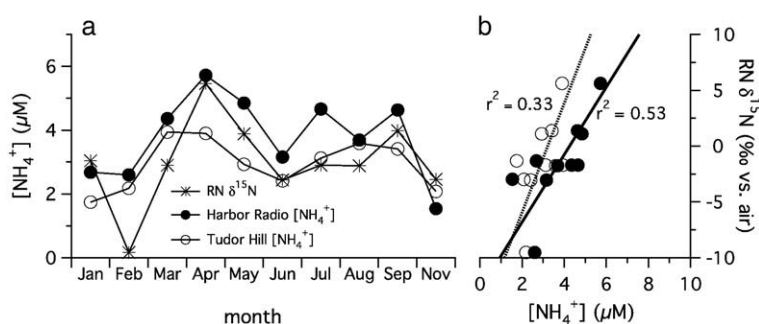


Fig. 3. Monthly mass-weighted average RN $\delta^{15}N$ from this data set (asterisk symbols) and volume-weighted $[NH_4^+]$ from the 1980 through 1988 (“Harbor Radio”, filled circles) and 1989 through 1996 (“Tudor Hill”, open circles) sample sets vs. month in precipitation at Bermuda (a), and monthly mass-weighted average RN $\delta^{15}N$ vs. monthly volume-weighted average $[NH_4^+]$ from the 1980 through 1988 (filled circles) and 1989 through 1996 (open circles) sample sets, and corresponding RMA regression lines to guide the eye (solid and dashed lines, respectively) (b). While the 1980–1988 (Harbor Radio) $[NH_4^+]$ data set is statistically significantly correlated with the RN $\delta^{15}N$ data, the 1989–1996 (Tudor Hill) data set is not.

This pattern broadly fits our observed spring and fall maxima in RN $\delta^{15}\text{N}$, and is also consistent with a North American source for the peak $[\text{NH}_4^+]$ observed at the same time.

The marine emission of NH_3 has also been postulated as a source of NH_4^+ to the atmosphere (Galloway et al., 1995, 2004; Gibb et al., 1999; Jickells et al., 2003; Quinn et al., 1988; Zhuang and Huebert, 1996). The temporal correlation between $[\text{NH}_4^+]$ and RN $\delta^{15}\text{N}$ is intriguing with regard to this possibility as well. The April maxima in $[\text{NH}_4^+]$ and RN $\delta^{15}\text{N}$ coincide with the period after the spring bloom near Bermuda (Steinberg et al., 2001). During this post-bloom period, NH_4^+ cycling is likely rapid. While this is interesting to note, we cannot directly determine from the data reported here if marine sources of $\text{NH}_3 + \text{NH}_4^+$ are important in driving changes in RN $\delta^{15}\text{N}$, and the isotopic data of Jickells et al. (2003) argue against this possibility.

Finally, it has been suggested that the oxidation of RN is a source of NO_3^- in precipitation (Hoering, 1957). The modest similarity in the temporal trends of $\delta^{15}\text{N}$ in RN and NO_3^- in our samples, as well as the observation that the $\delta^{15}\text{N}$ of RN is on average $\sim 4\%$ higher than that of NO_3^- , are both consistent with NO_3^- being derived from RN. Comparisons with previous measurements of the $\delta^{15}\text{N}$ of NO_3^- , NH_4^+ and/or DON in precipitation (Carrillo et al., 2002; Cornell et al., 1995; Freyer, 1978; Garten, 1992; Heaton, 1987; Russell et al., 1998) have not helped to resolve this or other questions of source for our samples. In sum, our data are apparently consistent with the derivation of some atmospheric NO_3^- from RN, although they by no means require it.

A surprising finding from past studies of Bermuda rain is that the magnitude of the NO_3^- flux is only weakly seasonal, despite a large warm season decrease in transport from North America (Moody and Galloway, 1998). Hastings et al. (2003) suggested that lightning provides a substantial atmospheric source of NO_3^- during the warm season, when air over Bermuda is generally from the South. Combining several of the possibilities described above provides an interesting alternative scenario for a marine source: if marine NH_3 emission contributes to warm season atmospheric [RN] and RN $\delta^{15}\text{N}$ over Bermuda, and if a fraction of that RN is converted to NO_3^- , then it might contribute to the substantial $[\text{NO}_3^-]$ and higher $\delta^{15}\text{N}$ of NO_3^- in warm season rain at Bermuda. The plausibility of this scenario could be tested by a variety of approaches, including a more systematic study of the forms of N and the isotopic composition of Bermuda rain than we have yet accomplished.

5. Conclusion

The magnitude of the wet deposition TN flux at Bermuda, $\sim 10\text{--}19 \text{ mmol N m}^{-2} \text{ yr}^{-1}$, is comparable to biological estimates of N_2 fixation rates in regional surface waters, and it is less than but still not trivial in comparison to regional geochemical estimates of N_2 fixation. Moreover, because its average $\delta^{15}\text{N}$, -2.3% , is at the lower end of the estimates for the $\delta^{15}\text{N}$ of N added by oceanic N_2 fixation (~ -2 to 0%), wet deposition has leverage by which to lower the $\delta^{15}\text{N}$ of NO_3^- in the thermocline of the Sargasso Sea. Thus, atmospheric deposition of N may substantially reduce the rate of oceanic N_2 fixation required to generate the low- $\delta^{15}\text{N}$ NO_3^- pool observed in subtropical thermoclines (Brandes et al., 1998; Karl et al., 2002; Knapp et al., 2005; Liu et al., 1996). One twist to this result is that anthropogenic fixed N in the atmosphere has been increasing rapidly (Duce et al., 2008), such that the $\text{NO}_3^- \delta^{15}\text{N}$ in the thermocline of the Sargasso Sea may have recently decreased. Of course, this entire line of reasoning assumes that the low- $\delta^{15}\text{N}$ portion of TN in wet deposition at Bermuda does not itself originate from the evasion of N from Atlantic surface waters.

While the magnitude of the RN flux does not change statistically significantly between seasons, the $\delta^{15}\text{N}$ of the RN does, implying that terrestrial sources (during the cool season) have a lower $\delta^{15}\text{N}$ than marine sources (during the warm season), which is consistent with the seasonal trends observed for NO_3^- in wet deposition at Bermuda (Hastings et al., 2003). This finding also motivates interest in some

specific unknowns, including (1) the importance of evasion of NH_3 from the surface ocean as a source of RN in the marine atmosphere, and (2) the potential for conversion of RN to NO_3^- , and vice versa. More generally, our data provide incentive for more complete regional and temporal studies of the concentration, isotopes, and chemical composition of the RN fraction, as well as direct measurements of the isotopic composition of the suspected dominant regional sources of N.

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