Interbasin isotopic correspondence between upper-ocean bulk DON and subsurface nitrate and its implications for marine nitrogen cycling

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[1] Measurements to date have shown that both bulk and high molecular weight marine dissolved organic nitrogen (DON) have a $^{15}N/^{14}N$ that is substantially higher than the $^{15}N/^{14}N$ of suspended particulate organic nitrogen (PN_{susp}) found in the same surface waters (with $\delta^{15}N$ of ~4 to 5‰ and ~−1 to 1‰, respectively). Moreover, the concentration and $^{15}N/^{14}N$ of DON are much less dynamic than those of PN_{susp}. These observations raise questions regarding the role of DON in the upper ocean nitrogen (N) cycle. In this study, the concentration and $^{15}N/^{14}N$ of nitrate and DON was measured in the upper 300 m of the oligotrophic North Atlantic and North Pacific Oceans. Comparing these two regions, the average DON concentration in the upper 100 m is similar, between 4.5 and 5.0 μM, but the average $\delta^{15}N$ of DON is significantly different, 3.9‰ versus air in the North Atlantic and 4.7‰ in the North Pacific. This difference parallels a similar isotopic difference between shallow nitrate in these two regions; at 200 m in the North Atlantic, the $\delta^{15}N$ of nitrate is 2.6‰, while it is 4.0‰ in the North Pacific. This isotopic correlation between surface DON and subsurface nitrate indicates that DON is actively participating in the upper ocean N cycle of each region. We describe a conceptual model that explains the elevation of the $^{15}N/^{14}N$ of DON relative to surface ocean PN_{susp} as well as the interbasin difference in the $^{15}N/^{14}N$ of DON. In this model, DON is produced from PN_{susp} without isotopic fractionation but DON is removed by fractionating processes. The ammonium and simple organic N compounds released by DON decomposition reactions are reassimilated by algae into the PN_{susp} pool, as an integral part of the ammonium-centered cycle that lowers the $^{15}N/^{14}N$ of PN_{susp} relative to the nitrate supply from below. This interpretation is consistent with the understanding of the chemical controls on isotope fractionation and is analogous to the previously posed explanation for the $^{15}N/^{14}N$ elevation of herbivorous zooplankton. In addition, it explains a lack of correlation between in situ N_2 fixation rates and DON concentration and $^{15}N/^{14}N$ on short time scales.

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1. Introduction

[2] Dissolved organic nitrogen (DON) is thought to play a central role in the microbial loop and thus in the metabolism of the ocean [*Azam et al.*, 1983]. However, fundamental questions remain about this complex pool of marine nitrogen. DON can be produced by numerous biological mechanisms, including direct release from living marine microbes, cell death, viral lysis, and grazing [*Bronk and Steinberg*, 2008, and references therein]. Still, a mechanistic understanding of how, when, and why DON is produced under different oceanographic conditions remains elusive [*Azam*, 1998]. Similarly, it has been shown that various constituents of DON, especially amino acids and urea, can be assimilated by phytoplankton and bacteria [e.g., *Palenik and Morel*, 1990; *Bronk et al.*, 2007; *Mulholland and Lee*, 2009]. However, in the oligotrophic surface ocean, these simple compounds are minor constituents of DON [e.g., *McCarthy et al.*, 1996, 1997; *Aluwihare et al.*, 2005; *Kaiser and Benner*, 2008, 2009]. It is possible that more complex

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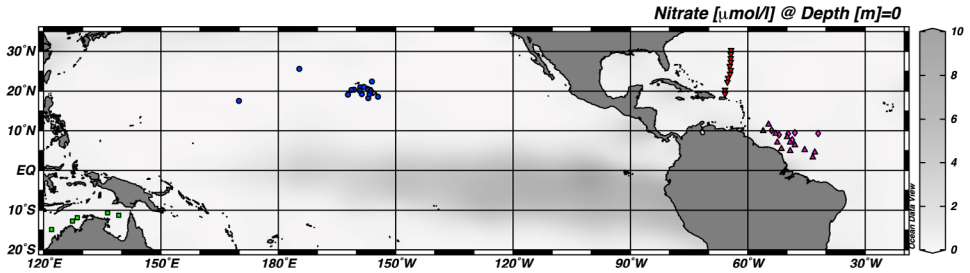

Figure 1. Cruise and station map overlaid upon World Ocean Atlas 2005 [*Garcia et al.*, 2006] annually averaged surface ocean [NO_3^-]. Samples were collected in November 1999 above the North Australian shelf (green filled squares); in January–February 2001 and July–August 2001 in the Central Western Atlantic ("MP1," pink diamonds, and "MP3," purple triangles, respectively); in October 2002 in the Sargasso Sea (BVAL 32) (filled red inverted triangles); and in July–August 2003 in the North Pacific (MP9) (filled blue circles).

forms of DON are also directly available to phytoplankton and bacteria. However, it could be that DON is a large reservoir of highly diverse, relatively recalcitrant organic N containing compounds that can be broken down into simple, commonly utilized forms of N (e.g., ammonium, amino acids) which are then rapidly assimilated.

[3] In spite of its dynamic role in surface ocean N cycling, characterization of the DON pool has proven challenging due to its apparently recalcitrant composition and its low concentration in the ocean. Tangential-flow ultrafiltration and resins have been used to concentrate and de-salt marine DON for chemical and isotopic characterization [e.g., *Benner et al.*, 1992; *McCarthy et al.*, 1996; *Benner et al.*, 1997; *McCarthy et al.*, 1997, 1998; *Aluwihare et al.*, 2005; *McCarthy et al.*, 2007; *Guo et al.*, 2009; *Kaiser and Benner*, 2009]. However, the high-molecular weight DON (HMW DON) that is captured by ultrafiltration represents only ~20 to 35% of the bulk DON pool [*Benner et al.*, 1992, 1997], leaving the balance of the marine DON pool largely uncharacterized.

[4] In addition, determination of in situ DON fluxes is hindered by the heterogenous and largely unknown composition of the bulk surface ocean DON pool. ^{15}N-labeled model organic compounds are added to culture or mesocosm experiments to constrain DON fluxes (see review by *Mulholland and Lomas* [2008, and references therein]). However, because these model compounds do not appear to be a substantial component of the standing DON pool in surface waters, it is not known how these fluxes relate to the production and consumption of in situ DON.

[5] To better constrain oligotrophic surface ocean DON sources and cycling, the concentration and isotopic composition of bulk DON were measured in samples collected in the Sargasso Sea, the Western Tropical North Atlantic Ocean, the North Pacific Ocean, as well as over the North Australian shelf. Additionally, the concentration and δ^{15}N of nitrate (NO_3^-) in the upper 400 m was measured (where $\delta^{15}N = \{[(^{15}N/^{14}N)_{sample}/(^{15}N/^{14}N)_{reference}] - 1\}$ and where the reference is atmospheric N_2). Finally, during several of the cruises, at the same stations where our geochemical samples were collected, euphotic zone N_2 fixation rates were measured by others using biological assay techniques. Based on these data, we derive a conceptual model for the role of DON in the upper ocean cycling of N and its isotopes.

2. Methods

2.1. Sample Collection

[6] Samples were collected from Niskin bottles deployed on a rosette into acid-cleaned, sample-rinsed 60 mL HDPE bottles that were frozen at −20°C until analysis. The date, latitude, longitude and depth of all samples are reported in Data Set S1 in the auxiliary material.[1]

2.1.1. North Atlantic Ocean Samples

[7] DON and NO_3^- samples were collected on three cruises in the North Atlantic Ocean. In October 2002 unfiltered seawater samples were collected along a meridional transect between Bermuda and Puerto Rico at each degree of latitude between ~30° N and ~19° N (Figure 1) aboard the R/V Weatherbird II as part of the BVAL 32 cruise carried out by the Bermuda Institute of Ocean Sciences (hereafter referred to as the "BVAL 32" cruise) (n = 108). In addition, surface water (~1 m) DON samples were collected in the Western Tropical North Atlantic Ocean during two MANTRA/PIRANA "Biocomplexity" cruises from January through February 2001 (hereafter referred to as "MP1") (n = 6) and July through August 2001 (hereafter referred to as "MP3") (n = 12), aboard the R/V Seward Johnson and R/V Knorr, respectively (Figure 1). MP1 and MP3 samples were collected by an underway, towed fish [*Vink et al.*, 2000] and filtered through a 0.2 μm cartridge filter (MSI Calyx polypropylene) via peristaltic pump.

2.1.2. North Pacific Ocean and North Australian Shelf Samples

[8] DON and NO_3^- samples were collected on two cruises in the Pacific Ocean. Unfiltered seawater samples were collected in July through August 2003 aboard the R/V Revelle on a MANTRA/PIRANA "Biocomplexity" cruise (hereafter

[1] Auxiliary material data sets are available at ftp://ftp.agu.org/apend/gb/2010gb003878. Other auxiliary material files are in the HTML. doi:10.1029/2010GB003878.

referred to as "MP9") (n = 136) between latitudes 18°N and 28°N, and longitudes 170°E and 154°W, although most samples were collected within 5° of the Hawaiian Islands (Figure 1). Additionally, surface water (~5 m) DON samples (n = 5) were collected from North Australian shelf waters in November 1999 on the R/V Ewing (hereafter referred to as the "Australia 1999" cruise) from a deployed zodiac using a peristaltic pump and filtered through a 0.2 μm MSI Calyx polypropylene cartridge filter following the protocols described for the North Atlantic MP1 and MP3 cruises.

2.2. Nitrate and DON Concentration Analysis

[9] The concentration of NO_3^- ($[NO_3^-]$) was determined by chemiluminescent analysis [*Braman and Hendrix*, 1989] in a configuration yielding a detection limit of ~0.05 μM. Nominal $[NO_3^-]$ measurements include nitrite (NO_2^-), but NO_2^- concentrations are negligible (typically <0.05 μM; see *Lipschultz* [2001] for the Sargasso Sea and *Fujiki et al.* [2008] for the North Pacific Gyre). The average standard deviation for replicate $[NO_3^-]$ analyses from an individual sample is ±0.1 μM.

[10] The concentration of DON ([DON]) was determined using persulfate oxidation to convert DON to NO_3^- [*Solórzano and Sharp*, 1980], adapted according to *Knapp et al.* [2005]. The resulting $[NO_3^-]$ was then measured using chemiluminescence as described above. In cases where samples were not filtered (i.e., those from the BVAL 32 and MP9 cruises), [DON] measurements are truly measures of the total N concentration ([TN]) in a sample. In the upper 100 m of most sampling locations, however, where the $[NO_3^-]$ is below the detection limit, ≥90% of TN is present as DON [*Abell et al.*, 2000], and so these are essentially measures of [DON]. In the subsurface (i.e., >100 m) where the $[NO_3^-]$ is above the detection limit, [DON] is determined by subtracting the $[NO_3^-]$ from the [TN] of a sample. The average standard deviation for duplicate [DON] analyses of individual samples that have undetectable levels of NO_3^- in the sample is ±0.30 μM, and the propagated error for [DON] when NO_3^- is present is 0.32 μM.

2.3. NO_3 and DON δ^{15}N Analysis

[11] The isotopic composition of NO_3^- was determined using the "denitrifier" method [*Sigman et al.*, 2001; *Casciotti et al.*, 2002] on samples with $[NO_3^-]$ >0.5 μM. The standard deviation associated with replicate NO_3^- δ^{15}N analyses of an individual sample is ±0.2‰. The δ^{15}N of DON was determined according to *Knapp et al.* [2005], where DON samples were oxidized to NO_3^- by persulfate oxidation (as described above in section 2.2), acidified to a pH range of 3 to 4, and measured as per NO_3^- by the denitrifier method. In samples with measurable NO_3^-, the δ^{15}N of DON is calculated by mass balance by subtracting the $[NO_3^-]$ and NO_3^- δ^{15}N from the [TN] and TN δ^{15}N measurements. In surface samples with undetectable levels of NO_3^-, the standard deviation associated with duplicate analysis of a sample for DON δ^{15}N is ±0.3‰. For subsurface samples with $[NO_3^-]$ approximately equal to the [DON], the propagated error for the calculation of DON δ^{15}N using a Monte Carlo method [*Press et al.*, 1992], and assuming duplicate analysis of a single sample and the standard deviations for [TN], $[NO_3^-]$ and NO_3^- δ^{15}N given above, is ±0.6‰.

3. Results

3.1. NO_3^- and Bulk DON Concentration

[12] The $[NO_3^-]$ data from the BVAL 32 and MP9 cruises are consistent with previous work in the Sargasso Sea [e.g., *Michaels and Knap*, 1996; *Knapp et al.*, 2005] and in the North Pacific gyre [e.g., *Fujiki et al.*, 2008], with higher $[NO_3^-]$ in the shallow subsurface (i.e., 100 to 400 m) in the North Pacific than in the North Atlantic (Figures 2, S1, and S2 and Data Set S1). Most of the Australia 1999 cruise was over shallow (<100 m depth) shelf areas. Typically, the surface water samples collected on the Australia 1999, MP1 and MP3 cruises had undetectable levels of NO_3^-, although the 5 November sample from the Australia 1999 cruise had 0.45 μM NO_3^-, and station 46 on the MP1 cruise had 0.45 μM NO_3^-.

[13] The range in bulk [DON] from all depths on all cruises was 3.0 to 8.1 μM (Figure 3), with lower [DON] observed at greater depths (Figures 2a, S1, and S2). Within the upper 100 m, 90% of [DON] was between 4.0 and 5.5 μM (total range 3.4 to 8.1 μM). The average [DON] of samples collected in the upper 100 m on BVAL 32 and MP9 are not statistically distinguishable, 4.7 μM and 4.8 μM, respectively (Figures 2a, 4b, S1a, and S2a and Table 1), and exhibit a similar concentration gradient from the upper 100 m to 200 m (Figures 2a, S1a and S2a). The average [DON] decreases significantly ($p < 0.005$; Kruskal-Wallis test for non-parametric data [*Triola*, 2001]) to 3.7 and 3.8 μM at 200 m in the North Atlantic and North Pacific, respectively, indicating a net addition of ~1 μM DON in the upper 100 m of both basins, relative to the background [DON] exchanged with the shallow thermocline (Figure 2a and Table 1). In the North Atlantic, half of this change in concentration (~0.5 μM) occurs between the upper 60 m and the 80–100 m depth interval, and the other 0.5 μM [DON] change occurs between 100 m and 200 m (both statistically significant changes, Figure 2a). However, in the North Pacific, the largest break in [DON] is between 100 m and 200 m (Figure 2a). These interbasin differences in [DON] with depth are consistent with previous observations from the Sargasso Sea and the North Pacific [*Harrison et al.*, 1992; *Hansell and Carlson*, 2001; *Knapp et al.*, 2005; *Fujiki et al.*, 2008].

[14] The surface water samples from the Australia 1999 and from the MP1 and MP3 cruises to the Western Tropical North Atlantic have a similar range in bulk [DON] (Figure 3). The [DON] of MP1 and MP3 samples range from 3.8 to 7.1 μM, and samples from the Australia 1999 cruise range from 3.4 to 8.1 μM (Figure 3 and Data Set S1).

3.2. NO_3^- and DON δ^{15}N

[15] The depth profiles of NO_3^- δ^{15}N from the BVAL 32 and MP9 cruises are comparable to previous measurements (e.g., those by *Knapp et al.* [2005, 2008] in the Sargasso Sea and *Sigman et al.* [2009] for the North Pacific), although the shallow thermocline NO_3^- δ^{15}N data in *Casciotti et al.* [2008] from station ALOHA are lower than the data reported here. In general, the δ^{15}N of NO_3^- in the thermocline of the North Pacific is higher than in the North Atlantic (Figures 2b, S1,

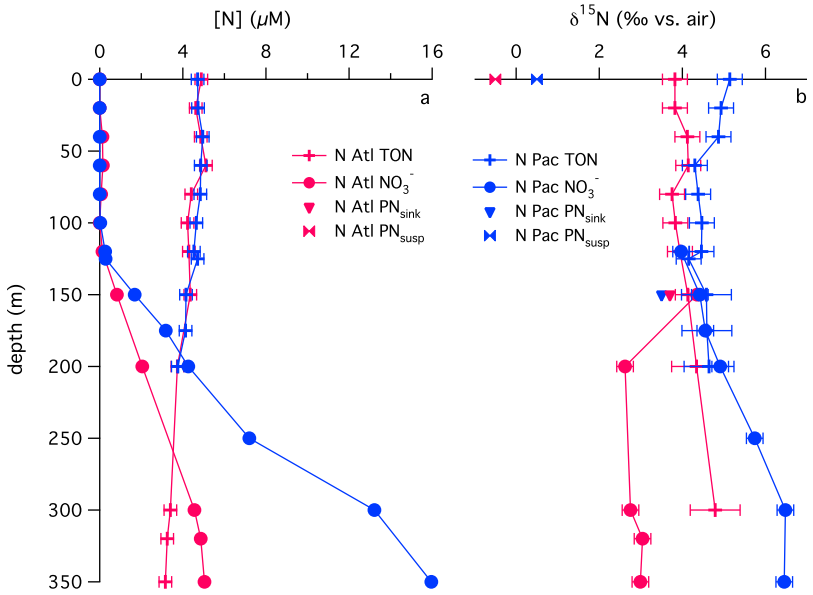

Figure 2. (a) Depth versus cruise average [NO_3^-] (filled circles) and [DON] (plus symbols) for the BVAL 32 (red) and MP9 (blue) cruises, and (b) depth versus cruise average NO_3^- δ^{15}N (filled circles) and DON δ^{15}N (plus symbols) for the BVAL 32 (red) and MP9 (blue) cruises. The standard deviation (for [NO_3^-] and NO_3^- δ^{15}N) and propagated error (for [DON] and DON δ^{15}N) are shown as error bars; for [NO_3^-] the error bars are smaller than the size of the symbol. Suspended (PN_{susp}) (bowties) and sinking (PN_{sink}) (inverted triangles) particulate organic nitrogen δ^{15}N for the North Atlantic (red) are from *Altabet* [1988] and for the North Pacific (blue) are from *Casciotti et al.* [2008] and *Dore et al.* [2002], respectively, in Figure 2b.

and S2) because of denitrification occurring in the oxygen minimum zones of the Eastern Tropical Pacific [*Brandes et al.*, 1998; *Sigman et al.*, 2009]. The average NO_3^- δ^{15}N at 200 m is 4.0‰ in the North Pacific, and 2.6‰ in the Sargasso Sea (Figure 2b and Table 1).

[16] The range in DON δ^{15}N in all samples from all depths was the same as the range in DON δ^{15}N of samples from the upper 100 m, the typical euphotic zone depth for these cruises, between 1.1 and 6.1‰, although 90% of DON had a δ^{15}N between 3.4 and 5.5‰ (Figures 3 and 5 and Data Set S1). The average DON δ^{15}N for the upper 0 to 100 m was 3.9‰ ± 0.5‰ (1 S.D.) and 4.7‰ ± 0.5‰ (1 S.D.) for the BVAL 32 and MP9 cruises, respectively (Figure 2b and Table 1). Comparison of the average DON δ^{15}N in mixed

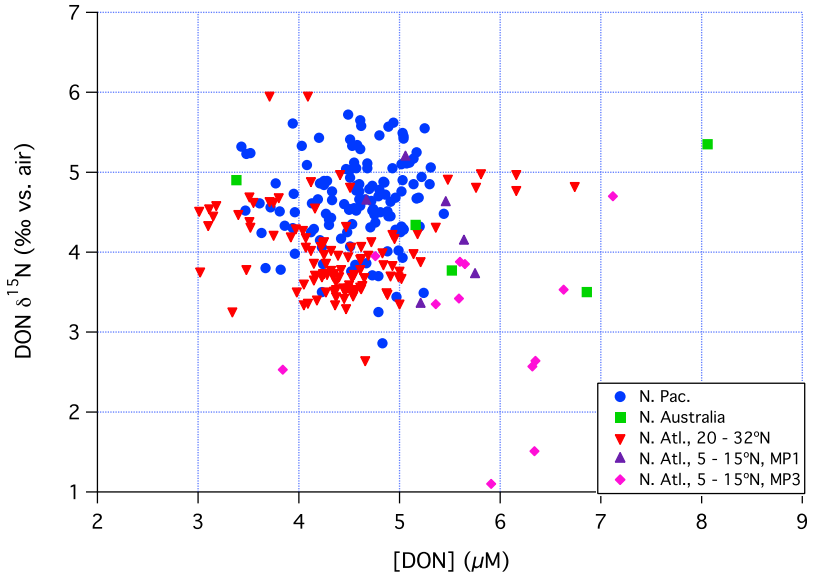

Figure 3. Bulk DON δ^{15}N versus [DON] for all samples collected at all depths on all cruises, including upper 100 m samples from all cruises as well as subsurface samples in the North Pacific (MP9) and North Atlantic (BVAL 32) cruises; symbols follow from Figure 1.

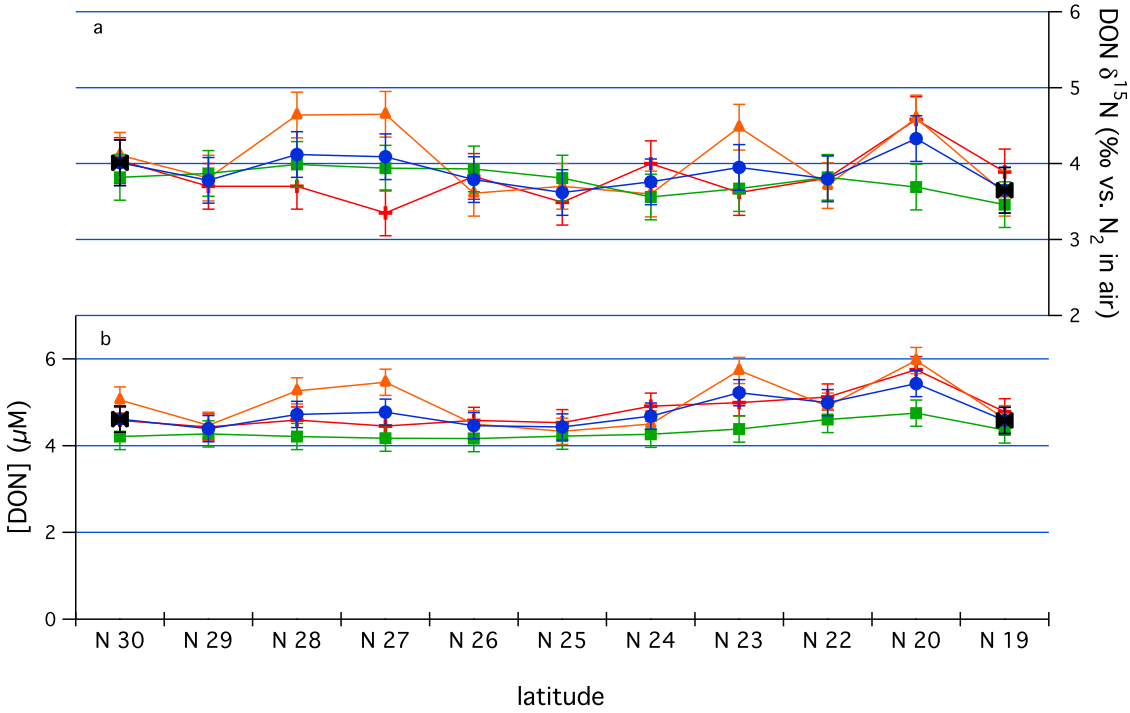

Figure 4. (a) Average DON δ^{15}N for the BVAL 32 transect in the upper 0 and 20 m samples (red crosses), 40 and 60 m samples (orange filled triangles), and 80 and 100 m samples (green filled squares) versus latitude; average of all samples in the upper 100 m at each station (blue filled circles), and average of all samples in the upper 100 m at northern (30°N) and southern (19°N) stations (black filled bow-ties). (b) Average [DON] for same samples; symbols follow Figure 4a. The propagated error for [DON] and DON δ^{15}N are shown as error bars.

layer samples alone (the upper ~40 m during both cruises) suggests an even larger interbasin DON δ^{15}N difference, 3.8‰ in the North Atlantic and 5.0‰ in the North Pacific. The 0 to 100 m average bulk DON δ^{15}N from BVAL 32 and MP9 are slightly lower than the HMW DON δ^{15}N previously reported for similar sites in the North Atlantic (3.9‰ for bulk versus 4.1‰ for HMW DON) and North Pacific (4.7‰ for bulk versus 5.4‰ for HMW DON) (HMW DON δ^{15}N data from *Meador et al.* [2007]). Nevertheless, these data show the same sense and a comparable magnitude of Pacific-to-Atlantic isotopic difference, as do other HMW DON δ^{15}N data from Atlantic- and Pacific-influenced waters of the Arctic Ocean [*Benner et al.*, 2005]. The average (±1 S.D.) surface ocean bulk DON δ^{15}N from the Australia 1999 cruise is 4.4 ± 0.8‰, from the MP1 cruise is 4.5 ± 0.7‰, and from the MP3 cruise is 3.1 ± 1.0‰ (Figures 3 and 5a).

[17] While [DON] gradients with depth are essentially identical in the Sargasso Sea and North Pacific gyre, the changes in DON δ^{15}N with depth appear to differ between the two basins. The average δ^{15}N of DON at 200 m in the Sargasso Sea is 4.3‰ (Figure 2b and Table 1), similar to previous measurements [*Knapp et al.*, 2005], and is statistically higher than the average DON δ^{15}N in the upper 100 m, 3.9‰. By mass balance, this surface-to-subsurface gradient in DON δ^{15}N implies that the ~1 μM DON that has accumulated in the upper 100 m of the Sargasso Sea has a δ^{15}N of ~2.4‰ ± 1.1‰. In the North Pacific gyre, however, at 200 m the average DON δ^{15}N is 4.6‰, insignificantly different from the 0 to 100 m average DON δ^{15}N of 4.7‰ (Figure 2b and Table 1). This implies that the δ^{15}N of the 1 μM DON added in the upper 100 m of the North Pacific is ~5.3‰ ± 1.1‰ (i.e., indistinguishable from the δ^{15}N of the background DON).

[18] As noted above in section 2.1.1 and 2.1.2, our DON measurements from the BVAL 32 and MP9 cruises are in fact measures of total organic nitrogen (TON) since these samples were not filtered. While PN_{susp} is typically ≤10% of the oligotrophic surface ocean TON concentration ([TON])

Table 1. Average Values for Samples Collected on the Bermuda to Puerto Rico Cruise (N. Atl.) and MP9 Cruise (N. Pac.)

	[TN] (μM)		TN δ^{15}N (‰ Versus Air)	
	N. Atl.	N. Pac.	N. Atl	N. Pac
Avg. upper 40 m	4.8	4.8	3.8‰	5.0‰
Avg. upper 100 m	4.7	4.8	3.9‰	4.7‰
Avg. at 200 m	3.7	3.8	4.3‰	4.6‰
Δ (100 m – 200 m)	1.0	1.0	2.4‰	5.3‰
PN_{susp}[a]	0.25	0.25	−2.0‰	−3.8‰
DON[b]	0.75	0.75	3.9‰	8.3‰
	$[NO_3^-]$ (μM)		NO_3^- δ^{15}N (‰ Versus Air)	
	N. Atl.	N. Pac.	N. Atl.	N. Pac.
Avg. at 200 m	2.05	4.26	2.6‰	4.0‰

[a]The contribution of PN_{susp} to the 1 μM pool of TN that accumulates in the upper 100 m of both the North Atlantic and North Pacific.
[b]The contribution of DON to the 1 μM pool of TN that accumulates in the upper 100 m of both the North Atlantic and North Pacific.

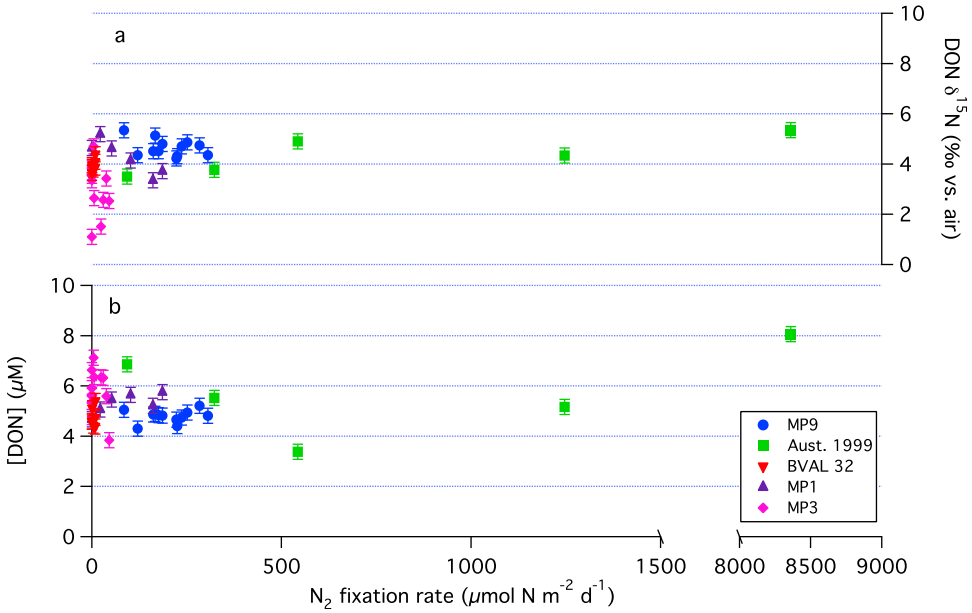

Figure 5. (a) Average upper 100 m DON δ^{15}N for each station versus N_2 fixation rate and (b) average upper 100 m [DON] for each station versus N_2 fixation rate; colors and symbols follow from Figure 1 and correspond to the cruise the samples were collected on. Note the break in *x* axis scale between 1500 and 8000 μmol N m^{-2} d^{-1}. Propagated errors for [DON] and DON δ^{15}N are shown as error bars. N_2 fixation rates from the Australia 1999 (D. Capone et al., manuscript in preparation), MP1 and MP3 [*Capone et al.*, 2005], and Bermuda to Puerto Rico (K. M. Achilles, unpublished thesis, 2004) cruises are *Trichodesmium* spp.-specific, depth-integrated rates. N_2 fixation rates for the MP9 cruise are bulk, depth integrated rates and include contributions from all diazotrophs [Sohm et al., 2011].

[*Abell et al.*, 2000], the gradients we report in [TON] and TON δ^{15}N with depth are small, so it is appropriate to consider what fraction of the surface to subsurface gradients described above is attributable to changes in PN_{susp} over the same depth range. Since PN_{susp} samples were not collected on these cruises, we use previously reported data from the Sargasso Sea [*Altabet*, 1988; *Michaels et al.*, 1994; *Michaels and Knap*, 1996] and the North Pacific gyre [*Dore et al.*, 2002; *Fujiki et al.*, 2008] to determine these gradients. As was observed for [DON], the change in the concentration of PN_{susp} ([PN_{susp}]) between the upper 100 m and at 200 m is the same between both basins. In each case, [PN_{susp}] decreases by ~0.25 μM between the upper 100 m and 200 m, and thus most (0.75 μM) of the 1 μM [TON] depth gradient can be attributed to changes in [DON] over the same depth range (Table 1).

[19] However, the bulk of the change in TON δ^{15}N between surface and subsurface waters results from changes in PN_{susp} δ^{15}N with depth, and not from changes in the δ^{15}N of DON. In the North Atlantic, the 0.25 μM decrease in [PN_{susp}] between the upper 100 m and at 200 m corresponds to a change in the δ^{15}N of PN_{susp} over the same depth range of ~4.5‰ (e.g., from −0.2‰ in the surface to 4.3‰ at 200 m) [*Altabet*, 1988]. This difference implies that the 0.75 μM of DON accumulating in the upper 100 m of the North Atlantic has a δ^{15}N of ~3.9‰ ± 1.3‰, which is similar to subsurface DON δ^{15}N (4.3‰), and is higher than the δ^{15}N of NO_3^- at 200 m, 2.6‰ (Table 1). In the North Pacific, the change in the δ^{15}N of PN_{susp} over the same depth range is ~5.5‰ (i.e., from −0.5‰ in the surface to 5.0‰ at 200 m) [*Dore et al.*, 2002]. Thus, in the North Pacific, of the 1 μM TON accumulating in the upper 100 m, 0.75 μM is DON which would appear to have a δ^{15}N of ~8.3‰ ± 1.3‰ (Table 1), which is higher than the δ^{15}N of DON in the subsurface (4.6‰) as well as the δ^{15}N of NO_3^- at 200 m (4.0‰). While we emphasize that these calculations are very sensitive to small changes in [PN_{susp}] and PN_{susp} δ^{15}N, they imply that the bulk of the change in TON δ^{15}N between the upper 100 m and at 200 m in the North Atlantic is due to changes in the δ^{15}N of PN_{susp} over that depth range, and not due to changes in the δ^{15}N of DON. Similar results were found by *Knapp et al.* [2005] for samples collected at the Bermuda Atlantic Time series Study site.

3.3. Comparison of DON Data to N_2 Fixation Rates

[20] Areally integrated N_2 fixation rates from these five cruises in oligotrophic waters vary by ~four orders of magnitude, from 0.05 to 8400 μmol N m^{-2} d^{-1} (Figure 5). The majority of these cruises took place during or immediately following the season of peak N_2 fixation rates in these regions [*Orcutt et al.*, 2001; *Dore et al.*, 2002], in the summer or early fall, with the exception of MP1 which took place in the Western Tropical North Atlantic Ocean in January, where seasonality is in any case reduced due to its low latitude. In addition, the BVAL 32 cruise sampled across a southward increase in previously reported in situ N_2 fixation rates [*Orcutt et al.*, 2001; K. M. Achilles, Bioavailability of iron to *Trichodesmium* colonies and other ecologically important cyanobacterial cultures: Implications for global carbon and nitrogen cycling, unpublished Ph.D. thesis, University of Delaware, 2004]. Measured and modeled atmospheric dust fluxes also increase southward along

this transect [e.g., *Prospero et al.*, 1996; *Gao et al.*, 2001] which may alleviate iron-stress for N_2 fixing organisms [*Kustka et al.*, 2003], and maximum winter mixed layer depths also shoal to the south [e.g., *Kara et al.*, 2003]. All of these gradients would support an equator-ward increase in the importance of N_2 fixation relative to subsurface NO_3^- as a source of new nitrogen to the euphotic zone along BVAL 32. Among the wide range of N_2 fixation rates measured on all five cruises, notably high rates were encountered in North Australian shelf waters (rates of ~1000 to 8361 μmol N m^{-2} d^{-1}, Figure 5) [*Montoya et al.*, 2004; D. Capone et al., manuscript in preparation, 2011]. The lowest N_2 fixation rates were found in the Sargasso Sea, with intermediate rates found at most of the stations in the North Pacific and in the Western Tropical North Atlantic (Figure 5), consistent with previous work [e.g., *Montoya et al.*, 2004; *Capone et al.*, 2005, and references therein].

[21] In spite of the spatial and temporal variations in N_2 fixation rates and other physical parameters, little difference in upper 100 m [DON] or DON δ^{15}N was observed (Figures 2–5). A positive relationship between N_2 fixation rate and upper ocean [DON] was expected based on previous field [*Karl et al.*, 1992; *Lenes et al.*, 2001], culture [*Mulholland et al.*, 2004; *Mulholland and Bernhardt*, 2005], and experimental studies of nitrogen release by a prominent diazotroph in these waters, *Trichodesmium* [*Capone et al.*, 1994; *Glibert and Bronk*, 1994]. All of these previous studies suggest that N_2 fixing organisms are capable of shunting a significant fraction of their newly fixed N into the DON pool. However, no such relationship was observed in the measurements reported here (Figure 5b). Since the δ^{15}N of newly fixed N is ~ −2 to 0‰ [*Hoering and Ford*, 1960; *Minagawa and Wada*, 1986; *Carpenter et al.*, 1997], if newly fixed N resides in the DON pool, one might expect inverse correlations between N_2 fixation rate and the δ^{15}N of DON, as well as between [DON] and the δ^{15}N of DON. Again, no such inverse correlations were observed (Figures 3 and 5a).

[22] Even the "extreme" [DON] and/or DON δ^{15}N values from these data sets fail to show a correspondence with N_2 fixation rate. For example, the high [DON] and low DON δ^{15}N values from the Tropical Western North Atlantic Ocean (MP3 samples, Figure 5a) correspond to low, not high, N_2 fixation rates within this data set. In addition, while the highest [DON] in the data set corresponds to the highest N_2 fixation rate (observed in North Australian shelf waters), the DON δ^{15}N for this same sample is among the highest in the data set, failing to show a direct relationship with N_2 fixation. These observations indicate that the surface ocean DON pool is not responsive to discrete events of rapid N_2 fixation.

[23] We suspect that the difference in the average δ^{15}N of bulk DON between the MP1 and MP3 cruises, sampled in similar regions of the Western Tropical North Atlantic, reflects the seasonal influence of the Amazon river [e.g., *Cooley and Yeager*, 2006; *Del Vecchio and Subramaniam*, 2004; *Subramaniam et al.*, 2008]. The MP3 cruise occurred during July through August, when the Amazon River experiences peak discharge, while MP1 occurred during January through February, when discharge from the Amazon River to the ocean is lowest [e.g., *Richey et al.*, 1989; *Zakharova et al.*, 2006]. Since the average bulk DON δ^{15}N on MP1, 4.5‰, is similar to bulk DON δ^{15}N from the Sargasso Sea, ~4.0‰, the lower bulk DON δ^{15}N observed on MP3, 3.1‰, may be due to the incorporation of low-δ^{15}N material from Amazon River-influenced waters [e.g., *Hedges et al.*, 2000; *Brandes and Devol*, 2002] into oceanic surface water samples. Moreover, these bulk DON δ^{15}N values from MP1 are similar to HMW DON δ^{15}N values reported by *Meador et al.* [2007] for samples collected in the same region.

4. Discussion

4.1. Explaining the High δ^{15}N of Bulk DON

[24] While definitive constraints are methodologically limited, previous studies have indicated that bulk DON has a residence time in the upper ocean of many months to years. For example, at both the Bermuda Atlantic Time-series Study (BATS) and Hawaii Ocean Time-series (HOT) sites, surface ocean [DON] changes ≤1 μM over the year [*Hansell and Carlson*, 2001; *Knapp et al.*, 2005; *Fujiki et al.*, 2008]. Moreover, during winter mixing events at both the BATS and HOT sites, the majority of surface ocean DON, i.e., ≥3 μM, persists after mixing and exposure to subsurface microbes that remineralize a portion of the surface DON pool, demonstrating that on average, the bulk surface ocean DON pool persists for timescales longer than a year. In addition, the lack of significant gradients in [DON] across subtropical gyres also indicates that rates of turnover of the surface ocean DON pool are slow [e.g., *Hansell and Waterhouse*, 1997; *Bates and Hansell*, 1999].

[25] The DON δ^{15}N results reported here and previously [*Knapp et al.*, 2005] support the view that the majority of the DON pool is long-lived in the surface ocean. First, while the δ^{15}N of PN_{susp} varies with time at BATS [*Altabet*, 1988; *Altabet et al.*, 1991], comparatively small gradients in the δ^{15}N of DON are observed both with depth and over the course of a year [*Knapp et al.*, 2005]. Second, in the subtropical surface waters of both the North Atlantic and North Pacific, the δ^{15}N of DON is ~4‰ higher than the mean δ^{15}N of the PN_{susp} pool. While this finding does not require a slow exchange between the two pools, it indicates that the input and/or loss processes are not the same for DON as for the more isotopically variable PN_{susp} pool. Finally, the lack of evidence for a direct link between in situ N_2 fixation rate and either [DON] or the δ^{15}N of DON is consistent with a DON pool that does not rapidly absorb N from the other upper ocean pools, in this case, the euphotic zone diazotrophs.

[26] However, a second important finding from this study indicates that surface ocean DON is impacted by primary productivity occurring within a given gyre. Specifically, the ~0.8‰ difference in the average bulk euphotic zone DON δ^{15}N between the North Atlantic and North Pacific basins corresponds to a similar isotopic difference in the δ^{15}N of subsurface NO_3^- in the two regions (Figure 2 and Table 1), and subsurface NO_3^- has previously been shown to be the dominant source of new N to surface waters in both subtropical gyres [*Altabet*, 1988; *Knapp et al.*, 2005; *Casciotti et al.*, 2008; *Johnson et al.*, 2010]. These bulk DON δ^{15}N data also parallel a similar isotopic offset between the δ^{15}N of HMW DON observed in the North Atlantic and North Pacific, which represents ~30% of the bulk DON pool

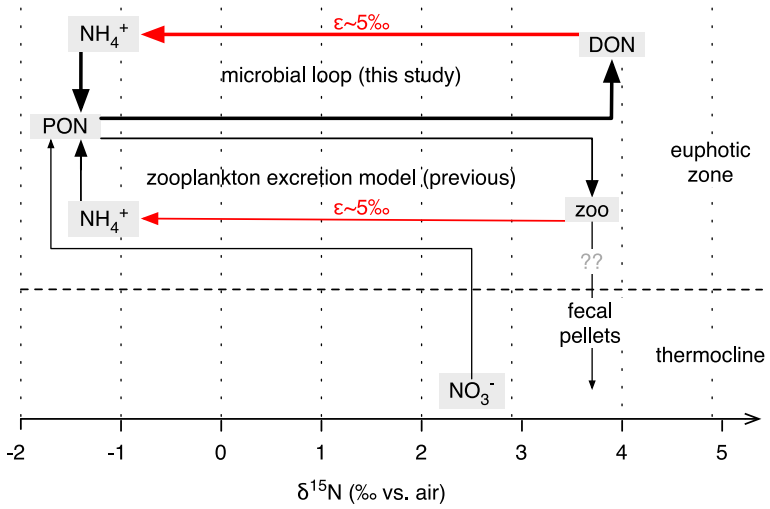

Figure 6. Schematic representation of oligotrophic surface ocean partitioning of nitrogen isotopes. Red arrows indicate processes with substantial N isotope discrimination that are important to euphotic zone N isotope distribution (i.e., NO_3^- assimilation is not red because the imported NO_3^- pool is completely consumed). In the model proposed here, DON breakdown and deamination leave DON higher in δ^{15}N and produce low-δ^{15}N NH_4^+ and other simple N compounds that are assimilated into the PON pool, lowering its δ^{15}N. Our concentration and isotope data indicate that the net accumulation of high-δ^{15}N DON in the euphotic zone is adequate to explain the ^{15}N-depletion of the PN_{susp} pool (see text). The traditional zooplankton excretion model involves effectively the same dynamic, with zooplankton N metabolism and excretion releasing low-δ^{15}N NH_4^+. While zooplankton biomass is a small fraction of the fixed N in the surface ocean, this model posits that their production of sinking fecal pellets leads to the preferential export of ^{15}N from the euphotic zone, explaining how PN_{susp} δ^{15}N evolves to much lower δ^{15}N than the NO_3^- supply from below. However, as indicated by the "??," it is not clear if the export of fecal pellets is sufficient to generate the high δ^{15}N of sinking matter that is observed and required by this model (see text).

[*Benner et al.*, 2005; *Meador et al.*, 2007], suggesting that the interbasin difference is not specific to a given molecular weight fraction.

[27] The accumulated data suggest that, while DON has a residence time adequately long to make it seem unresponsive in surface waters, it is actively involved in the N cycling of subtropical gyres. Here we propose a conceptual model (Figure 6) that considers previously recognized processes capable of producing and consuming DON, and the likelihood for these processes to cause changes in the isotopic composition of DON consistent with our observations. The conceptual model explains: 1) the difference in δ^{15}N between the larger, slowly responding bulk DON pool and the smaller, more rapidly cycling PN_{susp} pool in the surface ocean, and 2) the connection between the δ^{15}N of surface ocean DON and the δ^{15}N of NO_3^- supplied from the shallow subsurface.

[28] In this model, DON is produced by exudation, cell lysis or particle solubilization [*Bronk and Steinberg*, 2008, and references therein]. Direct exudation of DON by primary producers could occur with fractionation; whether this happens is not currently known. However, DON production by cell lysis or the solubilization of particulate organic matter is unlikely to occur with significant fractionation. Cell lysis is necessarily indiscriminate with respect to stable isotopes, except to the degree that the soluble versus insoluble N-bearing compounds have different δ^{15}N. The solubilization of particulate organic matter is also unlikely to involve substantial N isotope fractionation since the breaking of N-bearing bonds most likely plays a minor role in this process. Even with respect to the stable isotopes of carbon, the bonds of which are much more likely to be involved in the solubilization process, there is likely to be minimal net fractionation [e.g., *Druffel et al.*, 1992; *McArthur et al.*, 1992; *Hayes*, 1993]. Thus, we expect DON to be produced with a δ^{15}N similar to the particulate N from which it derives.

[29] In contrast, the release of biologically active N from DON in surface waters likely occurs with isotope fractionation. Hydrolysis reactions breaking common C-N bonds, converting amide to amine (e.g., peptide hydrolysis) and amine to ammonia (deamination) have been shown to have significant isotope effects (ε of 3 to 10‰) [*O'Leary and Kluetz*, 1972; *Macko et al.*, 1986; *Bada et al.*, 1989; *Silfer et al.*, 1992] (where the isotope effect $\varepsilon = (^{14}k/^{15}k - 1)*1000$, where ^{14}k and ^{15}k are the rate coefficients for the ^{14}N- and ^{15}N-bearing forms of DON, respectively). Within most marine heterotrophs, the average ε of N metabolism and release appears to be ~3‰, leading to the rule of thumb, "you are what you eat plus 3‰" [e.g., *DeNiro and Epstein*, 1981; *Minagawa and Wada*, 1984; *Wada et al.*, 1987; *Checkley and Miller*, 1989]. This fractionation upon N release from DON will elevate the δ^{15}N of residual DON relative to the δ^{15}N at which it was produced, consistent with our observations. Peptide hydrolysis may produce simple organic N compounds (i.e., amino acids or short peptides) that are directly and rapidly consumed by phytoplankton. However, NH_4^+ is likely the dominant form of N released and is, of course, also rapidly assimilated.

[30] This model also helps to explain the reduced variability in the concentration and isotopic composition of DON relative to PN_{susp}, even in the case where N is persistently cycling between the two N pools. Typical concentrations of PN_{susp} in the surface ocean are ~0.3 μM [*Altabet*, 1988; *Michaels and Knap*, 1996; *Fujiki et al.*, 2008], whereas [DON] is typically >4 μM. Thus, a net transfer of DON from PN_{susp} would cause a relative concentration change in the DON pool that is >10-fold smaller than those in the PN_{susp} pool, and the same argument yields that the δ^{15}N of the DON pool will be similarly buffered from large changes.

[31] Some of our North Pacific (MP9) data suggest modest but measurable gradients in DON δ^{15}N that are consistent with this explanation for the high δ^{15}N of DON. These data indicate that the highest DON δ^{15}N is found in the surface mixed layer, with ~0.6‰ lower DON δ^{15}N near the deep chlorophyll maximum (Figures 2b and S2). This could indicate net production of DON at the deep chlorophyll maximum, with the δ^{15}N of the total DON pool being pulled toward the PN_{susp} source for the new DON, and net breakdown of DON with isotopic fractionation in the more nutrient-deplete surface mixed layer.

[32] Focusing on the BVAL 32 data set, a number of stations have samples collected at 40 m depth that have ~0.5 μM higher [DON] relative to most of the euphotic zone data, and the δ^{15}N of DON is ~0.5‰ higher in these samples (Figures 4 and S1). This positive correlation does not obviously support our model, but it is not inconsistent with it, either. For example, excess DON may have been produced previously and/or advected in from another region and was undergoing net degradation at the time of sampling. In this case, the δ^{15}N of DON will be higher than at steady state. Obviously, other scenarios are possible, that speak neither for nor against our basic model.

[33] Our explanation for the high δ^{15}N of DON also has implications for the δ^{15}N of PN_{susp}. PN_{susp} δ^{15}N is ~0‰ in the subtropical gyres (−1 to 0‰ at BATS [*Altabet*, 1988] and 0 to 1‰ near Hawaii [*Casciotti et al.*, 2008]), apparently lower than the δ^{15}N of the total fixed N input to the surface ocean, much of which is probably NO_3^- imported from the subsurface with a δ^{15}N of ~2.6‰ in the Sargasso Sea [*Knapp et al.*, 2005] and 4.0‰ near Hawaii [*Casciotti et al.*, 2008] (Table 1).

[34] Although N_2 fixation has been proposed as a mechanism for lowering the δ^{15}N of PN_{susp} [e.g., *Saino and Hattori*, 1987; *Montoya et al.*, 2002; *Mahaffey et al.*, 2003], the conventional explanation for the low-δ^{15}N of PN_{susp} invokes the evidence for excretion of low-δ^{15}N NH_4^+ by zooplankton [*Altabet*, 1988; *Checkley and Miller*, 1989]. From the simplest perspective, just as the excretion of this low-δ^{15}N NH_4^+ works to raise the δ^{15}N of zooplankton relative to their food source, the reassimilation of this low-δ^{15}N NH_4^+ by phytoplankton should cause the δ^{15}N of PN_{susp} to gradually decrease [*Minagawa and Wada*, 1984; *Wada et al.*, 1987; *Fry*, 1988; *Montoya et al.*, 2002]. At the level of generic N fluxes, this is the same explanation that we have applied to DON and its relationship to PN_{susp}: DON is produced by processes with minor isotope fractionation and becomes elevated in ^{15}N by substantial fractionation during the release of low- δ^{15}N ammonium, which is reassimilated by the PN_{susp} pool.

[35] Still, there are problems with this zooplankton-based explanation for the low-δ^{15}N of PN_{susp}. Zooplankton biomass is a very small fraction of PN_{susp} in the euphotic zone [*Madin et al.*, 2001], so that its elevation in δ^{15}N will cause a much smaller δ^{15}N depression in the much larger PN_{susp} pool. However, the δ^{15}N of zooplankton is more similar to the δ^{15}N of the NO_3^- supply from below than is PN_{susp}, indicating a disproportionate depression of PN_{susp} δ^{15}N compared to the elevation of zooplankton δ^{15}N by upper ocean recycling. The PN_{susp} δ^{15}N depression could be caused by the preferential export of zooplankton-related organic material from the upper ocean, and zooplankton fecal pellets are indeed an important mechanism of N export. However, zooplankton fecal pellets are typically only modestly elevated in δ^{15}N relative to their food source [*Altabet and Small*, 1990; *Montoya et al.*, 1992; *Tamelander et al.*, 2006], which derives from PN_{susp} in the case of herbivorous zooplankton. The fecal pellets needed to efficiently export high-δ^{15}N organic matter from the euphotic zone might originate from carnivorous zooplankton. Yet, based on trophic structure and associated energy flow, these zooplankton must be far more rare than herbivorous zooplankton and produce a small fraction of the fecal pellet export. Thus, it is unclear how zooplankton can preferentially export ^{15}N to the degree necessary to explain the very low δ^{15}N of surface ocean PN_{susp}.

[36] The isotope fractionation associated with DON breakdown to simple, phytoplankton-accessible forms of N (most importantly, NH_4^+) provides an alternative mechanism to explain the low δ^{15}N of PN_{susp}. We have demonstrated above that the δ^{15}N of DON added to the background DON pool in the surface ocean is similar to or higher than the NO_3^- supply from the subsurface. Given that N_2 fixation provides some quantity of new N to the subtropical gyres (perhaps as much as 25% at HOT [*Casciotti et al.*, 2008]), this suggests that the N incorporated into the surface ocean DON pool is higher in δ^{15}N than the δ^{15}N of the combined sources of new N to surface waters. This increase in the δ^{15}N of the comparatively large surface ocean DON pool relative to the δ^{15}N of the sources of new N to surface waters needs to be balanced by the accumulation of another surface ocean N pool with a δ^{15}N lower than the δ^{15}N of new N supplied to surface waters; PN_{susp} would appear to be just such a pool.

[37] Despite substantial uncertainties, it is worth quantitatively exploring the potential of DON cycling proposed in Figure 6 to explain the δ^{15}N of PN_{susp}. As described above, [DON] increases by ~0.75 μM from the shallow thermocline into the euphotic zone, while [PN_{susp}] increases by ~0.25 μM, one third as much. Thus, given the DON/PN_{susp} isotope relationship described above, the δ^{15}N depression of PN_{susp} added to the surface ocean relative to the δ^{15}N of the new N supplied to the euphotic zone should be three times greater than the DON δ^{15}N elevation relative to that N supply. Taking our North Atlantic data as a case in point, the DON added to the surface ocean appears to have a δ^{15}N of ~3.9‰, about ~1.3‰ greater than the δ^{15}N of the thermocline NO_3^- supply (~2.6‰). Let us assume for the sake of simplicity that the NO_3^- supply dominates the new N supply in this region (i.e., N_2 fixation is very small relative to it). Following our conceptual model, we predict a δ^{15}N depression for euphotic zone PN_{susp} relative to the NO_3^- supply of 3*1.3‰ = 3.9‰, or a PN_{susp} δ^{15}N of 2.6‰ − 3.9‰ = −1.3‰. While this

prediction matches PN_{susp} δ^{15}N observations [*Altabet*, 1988; *Montoya et al.*, 2002], we would not wish to overstate its significance. The point is simply that DON cycling alone has the capacity to explain the full δ^{15}N depression of euphotic zone PN_{susp}. This leads us to propose that DON-related N cycling is dominantly responsible for the low-δ^{15}N of PN_{susp} of the subtropical ocean. It has been argued previously that the low-δ^{15}N of PN_{susp} indicates N_2 fixation [e.g., *Montoya et al.*, 2002; *Mahaffey et al.*, 2003]; the above calculation shows that this need not be the case. More strongly, the combined isotope data for NO_3^-, DON, PN_{susp}, and the sinking particulate N flux argue that N_2 fixation (and other sources of low-δ^{15}N N) is a minor fraction of annual new N supply in the Sargasso Sea near Bermuda [*Altabet*, 1988; *Knapp et al.*, 2005].

[38] One prediction of our model is that, over an adequately broad area that integrates over the time scale of DON-PN_{susp} cycling, the difference in δ^{15}N between DON and PN_{susp} should reflect the amplitude of the isotope effect for DON breakdown. Applying this approach to data from the Sargasso Sea near Bermuda [*Altabet*, 1988; *Knapp et al.*, 2005] yields a predicted isotope effect of 3.9‰ − −0.2‰ ≈ 4.1‰. However, this value may be too great in that it does not include regions in the Atlantic with higher PN_{susp} δ^{15}N [e.g., *Mahaffey et al.*, 2003]. Given this potential bias, the data are roughly consistent with DON breakdown having the same isotope effect as N metabolism by zooplankton, ~3‰ [*Minagawa and Wada*, 1984; *Wada et al.*, 1987; *Fry*, 1988; *Checkley and Miller*, 1989].

[39] The conceptual model presented above for the controls on bulk surface ocean DON δ^{15}N is as yet incomplete, as it does not address the role of the proportionally large quantity of "background" DON imported from subsurface waters. The low and equivalent gradient in [DON] between the upper 100 m and at 200 m in both the North Atlantic and North Pacific Oceans illustrates that bulk surface ocean DON is dominated by the 3 to 4 μM subsurface (i.e., ≥200 m) DON pool with a δ^{15}N of 4 to 5‰ (Figures 2, S1, and S2 and Table 1) that is seasonally entrained in surface waters [e.g., *Harrison et al.*, 1992; *Hansell and Carlson*, 2001; *Fujiki et al.*, 2008]. We currently calculate subsurface DON δ^{15}N by subtracting NO_3^- from TN, so the δ^{15}N of DON cannot yet be studied throughout the water column, and even the shallow subsurface DON δ^{15}N data have significant uncertainty. Nevertheless, it is worth considering how our conceptual model relates to the subsurface DON pool.

[40] If NH_4^+ is released from DON with substantial isotopic fractionation, then one might expect the δ^{15}N of DON to increase into the subsurface. Given an isotope effect of 3‰ for this degradation and a ~20% decrease in [DON] from the euphotic zone to 200 m, the δ^{15}N of DON at 200 m would be 0.6‰ higher, which is not observed (Figure 2 and Table 1). However, the DON in the thermocline at our sampling sites derives not only from regional downward mixing but also by subduction in distant regions followed by transport along isopycnals. This complicates comparisons of surface to thermocline DON characteristics at any given site. The data in hand may indicate that degradation of DON within the ocean interior occurs by different mechanisms than those operating in the warm, sunlit, biologically active euphotic zone. However, any firm conclusions in this regard await DON isotope measurements in samples from which NO_3^- has been removed.

[41] Quantifying the rate and isotope effect of DON remineralization in the ocean interior is critical for progress in the further use of N isotopes to determine rates of biogeochemical processes in the ocean. For example, the remineralization of low-δ^{15}N DON would correspond to a flux of low-δ^{15}N NO_3^- to the thermocline. In contrast, the eventual remineralization of the residual DON pool would produce high-δ^{15}N NO_3^-. Such effects must be known if we are to robustly interpret NO_3^- δ^{15}N patterns (as well as patterns of the δ^{15}N of other remineralization products) in terms of N_2 fixation, denitrification, NO_3^- assimilation, and N remineralization in the ocean.

4.2. Difference in Bulk DON δ^{15}N Between the North Pacific and North Atlantic

[42] We have focused above on the parallel and similar δ^{15}N elevation in the surface DON pool and shallow subsurface nitrate pool of the North Pacific relative to the Sargasso Sea. However, our measurements of the δ^{15}N of the subsurface NO_3^- supply to the euphotic zone leave open the possibility that the interbasin δ^{15}N difference is slightly greater for nitrate than for DON. The average bulk euphotic zone DON δ^{15}N is ~0.8‰ higher in the North Pacific gyre near Hawaii than in the Sargasso Sea, while the difference in subsurface NO_3^- δ^{15}N is ~1.4‰ (Figure 2 and Table 1). That the magnitude of the difference in DON δ^{15}N between the North Atlantic and North Pacific may not be as great as the difference in subsurface NO_3^- δ^{15}N has several plausible explanations.

[43] First, N_2 fixation and atmospheric deposition have been suggested to contribute a significant fraction of the new N to the euphotic zone of both gyres [*Karl et al.*, 1997; *Dore et al.*, 2002; *Capone et al.*, 2005; *Casciotti et al.*, 2008; *Knapp et al.*, 2008, 2010]. These sources of low-δ^{15}N N would effectively reduce the δ^{15}N difference of the total new N input between the two gyres, an effect that the δ^{15}N of DON should record.

[44] Second, the concentration fields for DON suggest that DON is produced and consumed on the spatial scale of the gyre, if not over a larger area. Much of the North Pacific gyre likely has lower NO_3^- δ^{15}N in the shallow subsurface than where these samples were collected, especially as one moves westward away from the denitrification zones of the eastern tropical Pacific. There may be a similar (but oppositely signed) bias in our estimate of the subsurface NO_3^- δ^{15}N in the North Atlantic gyre, given the geographic limitations of our sampling to date. As a result, we may be overestimating the difference in the δ^{15}N of the NO_3^- supply between these two gyre systems, and thus also overestimating the expected difference in surface ocean DON δ^{15}N.

[45] Third, and related to the previous argument, the [DON] in the shallow subsurface (i.e., at 200 m) is only modestly lower than what is observed in the euphotic zone, indicating that time scales greater than one year are required for remineralization [*Hansell and Carlson*, 2001]. This raises the possibility that, as with DOC, a fraction of the DON observed in the euphotic zone is exchanged over large spatial scales, even possibly between ocean basins. If so,

such transport would mute isotopically distinct inputs to the DON pool occurring in different regions. The uncertainty in what fraction of surface ocean DON is mixed up from the subsurface, and how the isotopic composition of that subsurface DON might vary both within and between ocean basins, highlights the need for a robust method to accurately measure both [DON] and DON δ^{15}N in waters with comparable or higher concentrations of NO_3^- (or other forms of inorganic nitrogen), which would reveal the δ^{15}N of the subsurface DON moving through the ocean's interior.

[46] Given the above potential sources of δ^{15}N decoupling between surface DON and subsurface NO_3^- as measured in a small region, it is remarkable to observe the similarity of the NO_3^-/DON δ^{15}N relationship in the Sargasso Sea and in the North Pacific near Hawaii. Above, we have argued that DON δ^{15}N is higher than the δ^{15}N of the NO_3^- supply and PN_{susp} because of isotope fractionation during its degradation. The magnitude of the few measured isotope effects of relevant chemical reactions span a range of 7‰ (see section 4.1 above). Thus, if DON composition and other environmental parameters vary even slightly between the North Atlantic and North Pacific, one might have predicted differences in net fractionation during degradation of several permil. However, if our conceptual model of DON δ^{15}N is correct, the similarity of the North Atlantic and North Pacific NO_3^-/DON δ^{15}N relationship argues for a net isotope effect of degradation that is similar (to within ~1‰ or less) in the two regions. One potential explanation is that a single specific biochemical reaction (i.e., deamination), occurring with a conserved isotope effect, is responsible for most N release from DON. Alternatively, the conditions for DON breakdown in both regions, including the DON composition, may be very similar, leading to the same association of biochemical reactions, carried out with the same isotope effects, in these two regions.

4.3. Lack of a Signal of N_2 Fixation Events in Bulk DON δ^{15}N

[47] While a signal of N_2 fixation events might have been observed in the DON pool, the lack of such a signal is not surprising when seen in the context of the proposed conceptual model. The potential dynamism of surface ocean [DON] and DON δ^{15}N is inherently dampened by the large fraction of the surface ocean DON pool that appears to persist in the shallow subsurface and thus appears to have a long time constant for production and degradation [e.g., *Hansell and Carlson*, 2001].

[48] In calculations above (section 3.3), we have attempted to identify isotopic changes in the 1 μM DON accumulating in the euphotic zone, but we again find no evidence of a N input with the δ^{15}N characteristic of newly fixed N. However, even this ~1 μM pool of "fresh" surface ocean DON is large in comparison to the amount of N added by a week-long event of rapid N_2 fixation. Again, this result is neither surprising nor very enlightening as to the immediate fate of the newly fixed N. The highest in situ N_2 fixation rate observed in the North Pacific in this data set, ~300 μmol N m^{-2} d^{-1}, represents ~0.003 μM d^{-1} of added N if it is distributed over a ~100 m deep euphotic zone. Over a week, this would lead to the accumulation of ~0.02 μM N, roughly 2% of the ~1 μM DON added to the euphotic zone. Such a fractionally minute input would be unrecognizable in our DON δ^{15}N measurements.

[49] Moreover, our conceptual model for the isotopic elevation of DON predicts that N_2 fixation events will not have an immediate impact on the δ^{15}N of DON. In this model, the δ^{15}N of newly fixed N is similar to that of recycled ammonium returned to the euphotic zone by DON breakdown for subsequent consumption by bacteria and phytoplankton (Figure 6). Of course, N_2 fixation does have a δ^{15}N lower than that of the subsurface NO_3^- supply. The isotopic evidence for this low-δ^{15}N input would only emerge in the DON pool as the δ^{15}N of all the N reservoirs in the surface ocean shift downward in response to the decrease in the δ^{15}N of the total new N input to the surface ocean.

[50] While this is one potential explanation for the difference in surface ocean DON δ^{15}N between the North Atlantic and North Pacific, we again note that this interpretation is limited by the present geographic coverage of subsurface NO_3^- δ^{15}N and surface ocean DON δ^{15}N measurements. As stable isotope techniques are improved and applied to the low latitude marine N cycle, our attention should focus on recognizing the N_2 fixation inputs on seasonal and longer time scales, periods which are adequately long for them to contribute significantly to upper ocean N pools. Finally, in this type of analysis to quantify the significance of N_2 fixation as a source of new N to a region, we cannot focus on only a single N pool but rather must characterize the δ^{15}N of all of the resident fixed N pools as well as the measurable fluxes into and out of the euphotic zone [*Altabet*, 1988; *Knapp et al.*, 2005; *Casciotti et al.*, 2008].

5. Conclusion

[51] Reported here is a survey of bulk oligotrophic surface ocean [DON] and DON δ^{15}N from the North Atlantic and North Pacific Oceans, as well as above the North Australian shelf, and a comparison to shallow subsurface NO_3^- δ^{15}N when the samples were available. A conceptual model (Figure 6) is proposed to explain the δ^{15}N of DON, which is high relative to other oligotrophic surface ocean N pools and fluxes and yet appears responsive to the δ^{15}N of the nitrate supply within a given region. In this model, DON is produced in the surface ocean by the solubilization of PN_{susp} without isotope fractionation, while subsequent breakdown and deamination of DON involves substantial fractionation (roughly 3 to 5‰), producing DON with an elevated δ^{15}N and supplying low- δ^{15}N regenerated N (most prominently NH_4^+) back into the euphotic zone. The deamination of DON is similar to and complements the previously proposed mechanism of low-δ^{15}N NH_4^+ excretion by zooplankton [*Checkley and Miller*, 1989]. As a mechanism to generate the observed low-δ^{15}N PN_{susp} in the low-latitude surface ocean, we argue that DON breakdown is quantitatively more important than zooplankton excretion, based on the relative mass of the surface ocean DON and zooplankton pools. This proposed model of DON deamination effectively incorporates the "microbial loop" into our understanding of surface ocean N isotope dynamics.

[52] While [DON] is similar between the two ocean basins, the δ^{15}N of DON in the surface ocean is different, with North Atlantic DON δ^{15}N ~4‰, and North Pacific

DON δ^{15}N ~5‰. This difference is likely due to the difference in the δ^{15}N of subsurface NO_3^- in each region, which indicates that NO_3^- is the dominant source of new N to the low latitude surface ocean. This is not surprising, especially since DON produced in the upwelling and deep mixing zones adjacent to the gyres may contribute a portion of the DON found in highly stratified, oligotrophic surface waters. At the same time, the similar NO_3^--to-DON δ^{15}N relationship in the North Atlantic and North Pacific, in the context of our conceptual model, requires a remarkably similar amplitude for isotope fractionation during DON breakdown in these two regions.

[53] Neither surface ocean [DON] nor DON δ^{15}N covaried with N_2 fixation rates as measured by others in seawater incubations at the time of sample collection. This too is not surprising, as previous work has suggested that DON integrates over long time scales in surface waters and thus does not respond greatly to short time scale N cycling events (of hours to days) [*Hansell and Carlson*, 2001; *Knapp et al.*, 2005]. This inertia is reflected in and results from the large component of "background" DON that is mixed up from the shallow thermocline into the surface ocean, obscuring the isotopic signature of recently generated surface ocean DON. A better understanding of the response of newly produced surface ocean DON concentration and δ^{15}N to the sources of new N to surface waters awaits methods that can more precisely determine marine [DON] and DON δ^{15}N in the presence of NO_3^- and other forms of inorganic nitrogen.

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