

Isotopic composition of suspended particulate nitrogen ($\delta^{15}\text{N}_{\text{sus}}$) in surface waters of the Atlantic Ocean from 50°N to 50°S

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[1] Isotopic composition of suspended particulate nitrogen ($\delta^{15}\text{N}_{\text{sus}}$) has been studied in near-surface waters along a transect extending from 50°N to 50°S in the Atlantic Ocean. The $\delta^{15}\text{N}_{\text{sus}}$ values ranged from -0.8 to $+5.4\text{‰}$ and showed a significant correlation with depth of nitracline ($\delta^{15}\text{N}_{\text{sus}} = -0.047 \times D_{\text{NO}_3} + 5.706$; $R^2 = 0.81$, $n = 15$) in nutrients-depleted regions (45°N–40°S). This inverse relationship implied that higher uptake of new NO_3^- during mesotrophic conditions, characterized by shallower D_{NO_3} , derived relatively enriched $\delta^{15}\text{N}_{\text{sus}}$. On the other hand, lower ^{15}N signature of the remineralized NH_4^+ would be mainly imprinted on particulate nitrogen pool in the oligotrophic regions characterized by deep D_{NO_3} . The observed inverse $\delta^{15}\text{N}_{\text{sus}}-D_{\text{NO}_3}$ relationship can be modeled by a simple isotopic mass balance equation concerning with the N utilizability of phytoplankton (in terms of f -ratio). The model results that the variations in $\delta^{15}\text{N}_{\text{sus}}$ reflect the regional differences in nitrogen cycle in the upper ocean. In the region between equator and 15°N, where N_2 -fixing cyanobacteria (*Trichodesmium* spp.) were found, the measured $\delta^{15}\text{N}_{\text{sus}}$ values were about 2‰ lower than those expected from the regression with the D_{NO_3} , indicating that over 38% of the suspended particulate nitrogen came through N_2 -fixation in this region. Regional variations in $\delta^{15}\text{N}_{\text{sus}}$ in surface waters also correlated with those in water column productivity implying that the $\delta^{15}\text{N}_{\text{sus}}$ signature can provide an estimate of in situ algal production.

INDEX TERMS: 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); 4845 Oceanography: Biological and Chemical: Nutrients and nutrient cycling; 4853 Oceanography: Biological and Chemical: Photosynthesis; 4870 Oceanography: Biological and Chemical: Stable isotopes; **KEYWORDS:** stable nitrogen isotope, nutrient cycling, N_2 fixation, primary production, Atlantic Ocean

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1. Introduction

[2] Relative abundance of stable isotopes of nitrogen ($^{15}\text{N}/^{14}\text{N}$ ratio conventionally expressed as per mil departure, $\delta^{15}\text{N}$, from that of atmospheric N_2) in marine organic and inorganic pools has been found to vary significantly over a range of spatial and temporal scales [Saino and Hattori, 1980; Owens, 1987; Wada and Hattori, 1991; Altabet, 1996; Rau et al., 1998]. These variations are caused by mass-dependent isotopic fractionations associated with various biogeochemical transformations that constitute the nitrogen cycle. As each pathway leaves its characteristic isotopic signatures on the products and the reactants, the

^{15}N signal can provide information potentially on the mechanisms as well as rates of these transformations.

[3] The primary biological transformation of nitrogen in ecosystems in the upper ocean is utilization of dissolved forms of inorganic nitrogen (such as, NO_3^- , NH_4^+ , and episodically N_2) by phytoplankton. The availability of nitrogen often limits primary production in marine systems, creating a tight linkage between the marine C and N cycles. Isotopic fractionation associated with particulate nitrogen (PN) formation governs isotopic signature in the PN, and hence the $\delta^{15}\text{N}$ of suspended PN ($\delta^{15}\text{N}_{\text{sus}}$) would record the N availability in the euphotic zone (EZ) [Wada and Hattori, 1991], while significant isotopic differences between N substrates (e.g., 5–6‰ for $\delta^{15}\text{N}$ of NO_3^- , 0‰ for N_2) could allow to estimate the utilizability of these sources by algal populations from the variations in $\delta^{15}\text{N}_{\text{sus}}$ [Altabet and McCarthy, 1985; Altabet, 1988; Karl et al., 1997]. Although these ^{15}N characteristics of the organic nitrogen could be altered by the subsequent particle transformation processes such as metabolism, diagenesis, and trophic transfer in the water column and seafloor [Wada, 1980; Saino and Hattori, 1980, 1987], the application of sedimentary $\delta^{15}\text{N}$ has been expected to reconstruct the N cycles in the paleocean.

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Numerous attempts have been made to interpret $\delta^{15}\text{N}_{\text{sus}}$ and discuss its potential utility as natural tracer of nitrogen biogeochemistry in the marine environments [reviewed by Wada and Hattori, 1991].

[4] Several studies [Saino and Hattori, 1985; Rau et al., 1991; Altabet and Francois, 1994a; Altabet, 1996] have revealed negative correlation between the $\delta^{15}\text{N}_{\text{sus}}$ and the concentration of NO_3^- in near-surface waters of several eutrophic regions where NO_3^- is the major nitrogen source for phytoplankton growth. Variations in $\delta^{15}\text{N}_{\text{sus}}$ have been explained by a model based on the Rayleigh fractionation kinetics assuming a closed-system. These results have been taken to imply that the ^{15}N signal in PN could be used as an index of nutrient availability and utilization. Consequently, $\delta^{15}\text{N}$ records in sediments have been used to reconstruct paleo-nutrient conditions and biological productivity [Calvert et al., 1992; Francois et al., 1992, 1993; Altabet and Francois, 1994b; Farrell et al., 1995]. However, other studies have shown that the fractionation factor differs from one species to another and is also dependent on physiology and growth rate [Montoya and McCarthy, 1995; Pennock et al., 1996; Waser et al., 1998] and this should be taken into account while interpreting the data. Rau et al. [1998] applied the accumulated product equation to a large $\delta^{15}\text{N}_{\text{sus}}$ data set generated from the Monterey Bay and found poor fits, and suggested that the assumption of a closed system may not be strictly valid.

[5] Saino and Hattori [1980] argued that in the oligotrophic regions where primary productivity is mostly supported by regenerated NH_4^+ , the isotopic values of both the regenerated NH_4^+ and suspended PN should be close to that of oceanic NO_3^- (5–7‰) since all forms of inorganic nitrogen are taken up and regenerated within the upper layer quickly enough to prevent any isotopic fractionation. However, in areas that are affected by N_2 -fixation, lower $\delta^{15}\text{N}$ value should be expected because this process adds lighter nitrogen (–2 to 0‰) to the combined nitrogen pool. Based on this logic, the ^{15}N signal of PN has been used to quantify the extent of N_2 -fixation in the subtropical Pacific using a simple two-source model [Karl et al., 1997]. On the other hand, Altabet [1988] suggested that the low $\delta^{15}\text{N}$ value of the suspended PN in the EZ of the Sargasso Sea was caused by the preferential removal of ^{15}N -enriched nitrogen by the sinking matter leaving the suspended matter relatively depleted in this isotope. Consistent with this interpretation, Checkley and Miller [1989] found that the NH_4^+ excreted by zooplankton was depleted in ^{15}N and so the PN formed from this nitrogen source should have low $\delta^{15}\text{N}$ values. Thus the source of light nitrogen in the oligotrophic waters is still being debated.

[6] The Atlantic Meridional Transect (AMT) Programme investigates biological processes in the Atlantic Ocean over broad spatial scales (50°N–50°S) [Robins and Aiken, 1996] and is well suited, due to its wide geographical coverage, for evaluating the spatial variation in ^{15}N signal in the suspended PN pool in near-surface waters of the Atlantic Ocean. The cruise track spanning over 13,500 km crosses a wide range of physical and biogeochemical provinces, including temperate, tropical, and subtropical regions, that are characterized by a variety of ecosystem dynamics and

biogeochemical fluxes. A compilation of results undertaken during the AMT cruises has been provided by Aiken and Bale [2000]. Large spatial variations in biogeochemical properties were recorded during these cruises (these data are made available via the Internet; <http://www.pml.ac.uk/amt/index.html>). For example, the biomass and community structure of phytoplankton and bacteria as well as primary productivity varied dramatically along the track depending on the hydrographic setting [Zubkov et al., 1998, 2000; Marañón and Holligan, 1999; Aiken et al., 2000; Gibb et al., 2000; Marañón et al., 2000]. We aim here (1) to determine the large scale distribution in nitrogen isotopic composition of suspended particles in surface waters of the Atlantic Ocean during September–October, 1996, and (2) to discuss on the factors that contribute to the variability in $\delta^{15}\text{N}_{\text{sus}}$, taking into account a wide range of hydrographic settings and types of planktonic communities (in turn characterized by contrasting trophic structures). Finally, we will examine the relationship between primary productivity and $\delta^{15}\text{N}_{\text{sus}}$ with a view to the potential for the application of ^{15}N signatures as past and present oceanographic tool.

2. Materials and Methods

[7] This study is based on sampling undertaken along the “AMT-3” cruise track (Figure 1) on board the RRS *James Clark Ross* during September–October, 1996. All samples were collected underway from the ship’s non-toxic seawater supply that drew water from 7 m below the sea surface.

[8] In order to isolate the suspended particulate matter, about 15 liters of water were filtered through precombusted GF/F filters (Whatman; 47 mm diameter) and the filters were stored frozen until isotopic analysis. In the shore laboratory, the filters were exposed to HCl fumes overnight and then vacuum dried. The N_2 produced by the Dumas combustion method in sealed quartz tubes [Minagawa et al., 1985] was purified cryogenically on a vacuum line. Isotopic measurements were made using a Finnigan MAT 252 mass spectrometer. The concentrations of particulate organic carbon (POC) and PN were estimated through manometric measurements of the amounts of gases (CO_2 and N_2 , respectively) produced.

[9] About 200 mL of sample was filtered through GF/F filter for chlorophyll *a* (Chl *a*) analysis. The pigment was extracted with *N,N*-dimethylformamide (DMF) at –20°C in the dark, and measured following a non-acidification method using a Turner Designs 10-AU fluorometer [Welschmeyer, 1994].

[10] Continuous vertical profiles of temperature and salinity were obtained with a Neil Brown Mark IIIB CTD (conductivity–temperature–depth) system. Inorganic nutrients were measured colorimetrically using a Technicon AAI Autoanalyser.

3. Results

3.1. Hydrography and Nutrients

[11] As the AMT-3 cruise track covered a large latitudinal range, it facilitated sampling of all the major biogeochemical provinces. This is demonstrated by the distribution of

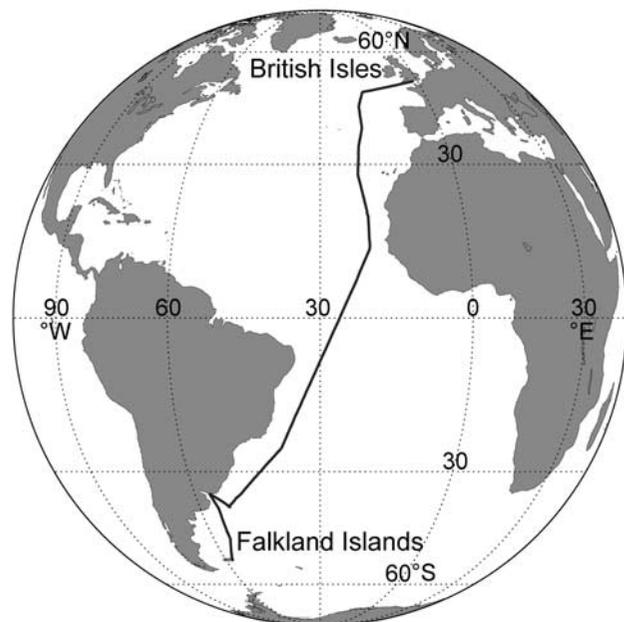


Figure 1. Cruise track for the Atlantic Meridional Transect (AMT)-3.

temperature (Figure 2). Mixed-layer temperature increased from $\sim 17^{\circ}\text{C}$ at the northern end of the transect to 23°C at 35°N as the thermal stratification predominated. Surface temperature was relatively uniform ($23\text{--}25^{\circ}\text{C}$) in the northern subtropical gyre, but an outcropping of the isotherms occurred around 20°N due to upwelling off Mauritania. South of this latitude to about 15°S , the thermocline gradually deepened and the mixed-layer depth in the southern subtropical gyre was greater than that in the northern subtropical gyre. Surface temperature fell rapidly from $>17^{\circ}\text{C}$ to $<8^{\circ}\text{C}$ across the South Subtropical Convergence (SSC) located between 35°S and 45°S .

[12] The combined nitrate and nitrite (hereafter nitrate) concentrations were below detection limit ($<0.05\ \mu\text{M}$) in the surface mixed layer along the transect except in the temperate regions (Figure 3). NO_3^- concentrations rose rapidly across the SSC. The location of the nitracline, defined as the depth where nitrate concentration exceeded $1\ \mu\text{M}$, followed closely that of the thermocline indicating that the upward

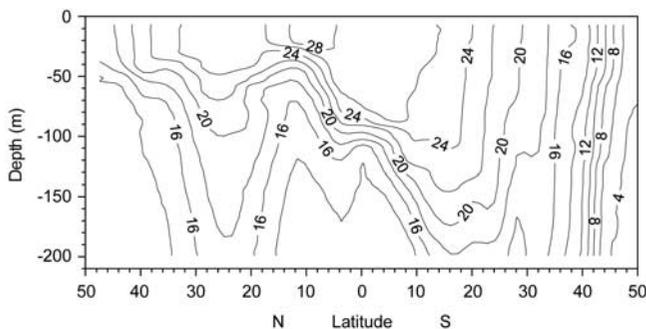


Figure 2. Latitudinal distribution of temperature ($^{\circ}\text{C}$) during AMT-3 (from *Marañón et al., Deep Sea Res., Part I, 47, 825–857, 2000*, with permission).

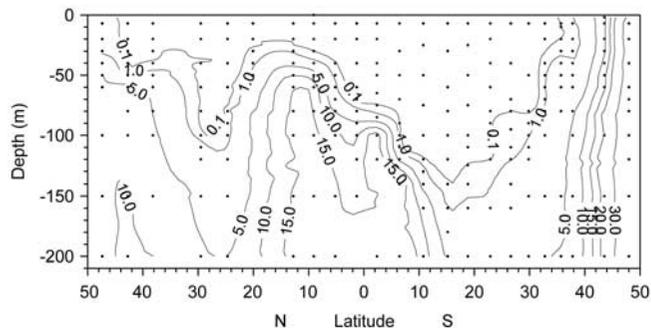


Figure 3. Latitudinal distribution of the concentration of nitrate plus nitrite (μM) during AMT-3 (from *Marañón et al., Deep Sea Res., Part I, 47, 825–857, 2000*, with permission).

supply of nutrients was controlled by the physical structure of the water column.

3.2. Chl *a* and PN Concentrations

[13] Concentrations of Chl *a* and PN in surface water exhibited excellent correlation with each other (Figure 4). Both parameters varied widely along the transect (over 10-fold for Chl *a* and eightfold for PN). Maximal concentrations (Chl *a* $> 0.4\ \mu\text{g L}^{-1}$ and PN $> 0.6\ \mu\text{mol N L}^{-1}$) were found in temperate waters toward both ends of the transect, probably reflecting an increased supply of nutrients to the euphotic layer due to enhanced vertical mixing. In the northern hemisphere, this situation corresponds to the boundary region (around 48°N) between European Continental Shelf Water and North Atlantic Drift provinces [*Hooker et al., 2000*], and in southern hemisphere, it is close to the edge of the SSC. Similarly, substantial peak found around 20°N , could be related to the shoaling of thermocline in this region, a feature noticed on other AMT cruises as well [*Aiken et al., 2000; Gibb et al., 2000; Marañón et al., 2000; Zubkov et al., 2000*]. Elsewhere, the concentrations of both Chl *a* and PN were low and relatively constant (Chl *a* $< 0.1\ \mu\text{g L}^{-1}$ and PN $< 0.3\ \mu\text{mol N L}^{-1}$), typical of the oligotrophic central gyres.

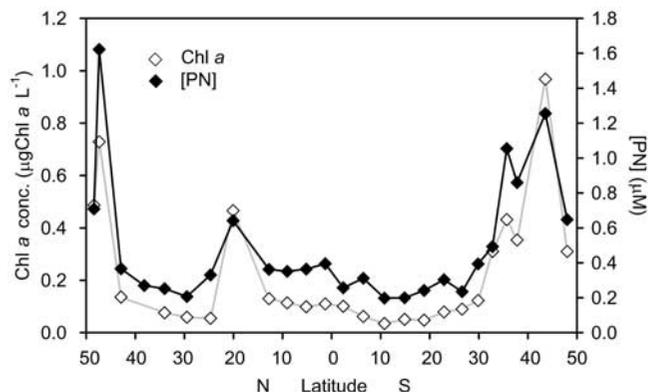


Figure 4. Latitudinal distributions of the concentrations of Chl *a* ($\mu\text{g Chl } a\ \text{L}^{-1}$) and PN (μM) in surface waters.

[14] The latitudinal distribution of primary productivity estimated by the ^{14}C technique mirrored those of Chl *a* and PN [Marañón and Holligan, 1999]. Analysis of phytoplankton compositions along this transect revealed the dominance of diatoms in the high-productivity temperate and upwelling areas whereas cyanobacteria (mainly *Prochlorococcus* spp.) and small flagellates dominate in the low-productivity regions [Zubkov et al., 1998; Marañón et al., 2000].

3.3. $\delta^{15}\text{N}$ of Suspended PN

[15] The $\delta^{15}\text{N}_{\text{sus}}$ values in surface waters ranged between -0.8 and $+5.4\text{‰}$ (Figure 5). Relatively high values (averaging 4‰) were found in the northern temperate region (50° – 43°N) and decreased toward south to 0‰ in the northern subtropical gyre. Even lower values (-0.8‰) were measured in the southern subtropical gyre. However, the region located between two gyres was characterized by elevated $\delta^{15}\text{N}_{\text{sus}}$ levels (up to 5‰), especially close to 20°N latitude where the thermocline shoaled. While approaching SSC from north, the $\delta^{15}\text{N}_{\text{sus}}$ first increased to the maximal value of 5.4‰ and then decreased rapidly by 5‰ toward the southern end of the transect. Thus the lowest values of $\delta^{15}\text{N}$ generally occurred within the two subtropical gyres while the highest values were seen in temperate waters (except low values in south of SSC) and in the areas affected by upwelling. Although the variability of $\delta^{15}\text{N}_{\text{sus}}$ was larger than that of PN concentration in the equatorial and subtropical regions, the distribution of $\delta^{15}\text{N}_{\text{sus}}$ seemed to reflect the changes in the water column structure.

4. Discussion

4.1. Regional $\delta^{15}\text{N}_{\text{sus}}$ Variability

[16] The $\delta^{15}\text{N}$ of bulk PN analyzed would reflect both the autotrophic particle formation and the subsequent heterotrophic processes. In the latter, the diagenetic fractionation potentially contributes to the enriched ^{15}N signal. However, no such relationship between the $\delta^{15}\text{N}_{\text{sus}}$ and C/N is evident in our data ($R^2 = 0.01$, $n = 23$), when it is assumed that C/N varied systematically with the degree of diagenesis [Waples and Sloan, 1980]. In this section, therefore, we shall discuss the observed changes in the $\delta^{15}\text{N}_{\text{sus}}$ with the assumption that it would be determined predominantly during the algal production. Based on ambient NO_3^- concentrations, three patterns of $\delta^{15}\text{N}_{\text{sus}}$ distribution could be discerned from our data.

[17] First, in the eutrophic region south of SSC, the $\delta^{15}\text{N}_{\text{sus}}$ values decreased from 5.4 to 0.2‰ where NO_3^- concentrations increased abruptly from <0.1 to $35\ \mu\text{M}$. The PN and Chl *a* concentrations also increased toward the southern end of the transect, indicating that the supply of NO_3^- mainly regulated primary production in this area. Phytoplankton biomass in this region was dominated by large diatoms that are thought to sink relatively faster out of the EZ via aggregation or grazing, implying high turnover rate of the suspended PN [Smetacek, 1985; Alldredge et al., 1995]. In such a case, the observed decrease in $\delta^{15}\text{N}$ probably resulted from the preferential uptake of $^{14}\text{NO}_3^-$ relative to $^{15}\text{NO}_3^-$ by phytoplankton (due to the difference in the reaction rates between isotopes) under the NO_3^- -replete conditions. This negative co-variation of $\delta^{15}\text{N}_{\text{sus}}$ with $[\text{NO}_3^-]$ reflects the relationship between $\delta^{15}\text{N}$ of newly

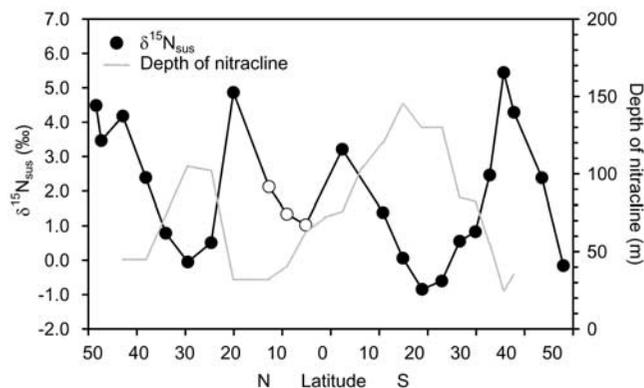


Figure 5. Latitudinal distributions of $\delta^{15}\text{N}_{\text{sus}}$ (‰) and the depth of nitracline (m). The open symbols correspond to samples from the stations at 15°N – 0°N where *Tricodesmium* was detected in significant numbers.

formed PN and the partial depletion of NO_3^- due to phytoplankton utilization, which is governed by Rayleigh fractionation kinetics [Wada and Hattori, 1976, 1978; Saino and Hattori, 1985]. In the vicinity of frontal systems, where $[\text{NO}_3^-]$ varied dramatically, Albet and Francois [1994a, 1994b] found the distinct horizontal changes in $\delta^{15}\text{N}$ for near surface PN and core top sediments and proposed the possibility of the reconstruction of paleo-nutrient levels from the sediment $\delta^{15}\text{N}$. Using the Rayleigh fractionation model they computed the fractionation factor during NO_3^- uptake (ϵ_p) to be 6‰ .

[18] Second, in the mesotrophic regions, where surface NO_3^- is depleted below the level of detection, a shallow nitracline ensures steady NO_3^- supply into the EZ. This subsurface NO_3^- supply sustains the high biomass and growth rate of algae in surface waters in the northern part of our study region, in the divergence zone around 20°N , and around the northern limit of the SSC at about 35°S [Marañón et al., 2000]. The $\delta^{15}\text{N}_{\text{sus}}$ values in these regions were found to be relatively high (4 – 6‰) and comparable to the isotopic composition of NO_3^- in deep waters [5 – 6‰ ; Liu and Kaplan, 1989; Sigman et al., 1997; Tanaka and Saino, 2002]. This suggested that all NO_3^- supplied from deep were consumed so quickly by algae in the EZ that its original ^{15}N signal would be reflected in the $\delta^{15}\text{N}_{\text{sus}}$ [Albet and McCarthy, 1985; Wada and Hattori, 1991]. However, it should be noted that in the upper mixed layer regenerated nitrogen, mainly as NH_4^+ , also contributes to PN formation as indicated by the fact that *f*-ratios over 0.5 have rarely been observed in such mesotrophic regions [Planas et al., 1999; Rees et al., 1999; Donald et al., 2001]. The regenerated NH_4^+ , in general, does not accumulate, but it is quickly taken up in open ocean. This also indicates no partial utilization of NH_4^+ by phytoplankton and, consequently, the $\delta^{15}\text{N}$ signature of NH_4^+ would be imprinted on PN formed from NH_4^+ . Therefore, our results imply that the isotopic composition of NH_4^+ in these regions is also close to that of NO_3^- . We consider the variation in $\delta^{15}\text{N}$ of NH_4^+ later on.

[19] Third, in the oligotrophic subtropical gyres, where deep (100 – $145\ \text{m}$) nitraclines, and the lowest (-2 to 1‰) $\delta^{15}\text{N}_{\text{sus}}$ values were observed among all regions studied here. The concentrations of PN and Chl *a* as well as algal

productivity were also low in these nutrient-impoverted environments where the remineralized NH_4^+ is believed to sustain most of the primary production [Eppley, 1981; Dugdale and Wilkerson, 1992; Harrison et al., 1996]. Similar to the mesotrophic region, there would be no partial utilization of dissolved nitrogenous nutrients and, therefore, the isotopic composition of suspended PN is expected to be determined mainly by that of remineralized NH_4^+ . The observed low $\delta^{15}\text{N}_{\text{sus}}$ values in the oligotrophic central gyres may thus reflect the lighter isotopic composition of NH_4^+ , but this would contradict the above speculations on the $\delta^{15}\text{N}$ signature of regenerated NH_4^+ in the mesotrophic regions.

[20] Recycled nitrogen in the form of NH_4^+ and urea within the EZ mainly comes from excretion by zooplankton and heterotrophs. Checkley and Entzeroth [1985] and Checkley and Miller [1986] reported that NH_4^+ excreted by zooplankton was ^{15}N -depleted relative to their bodies and fecal pellets. Their findings were consistent with the ^{15}N enrichment with trophic levels [DeNiro and Epstein, 1981; Minagawa and Wada, 1984]. While the particles such as fecal pellets enriched in $\delta^{15}\text{N}$ rapidly sink out of the EZ, the regenerated NH_4^+ depleted in $\delta^{15}\text{N}$ is utilized by algae subsequently. This mode of nitrogen cycling implies that the NH_4^+ recycled within the EZ sustains for longer period and becomes more depleted in $\delta^{15}\text{N}$ through the regeneration/uptake processes with ^{15}N loss by sinking. Since the efficiency of N recycling varies among the ecosystems [King, 1987], the regional difference in the trophic structure may reflect the ^{15}N signal of regenerated NH_4^+ . For example, under oligotrophic conditions nitrogen flows in the ecosystem through a long and complex food chain, of which picophytoplankton form the base. Such an N cycle is expected to undergo an efficient removal of ^{15}N from the EZ and results in NH_4^+ depleted in ^{15}N through regeneration, compared with the other conditions (meso- and eutrophic regions). This can account for the regional differences in $\delta^{15}\text{N}$ of NH_4^+ recycled within the EZ. Recycling of NH_4^+ as well as the supply of new NO_3^- would control $\delta^{15}\text{N}_{\text{sus}}$. However, it should be pointed out that the dissolved organic nitrogen (DON) as another N pool exists in the upper ocean. The recent studies have reported high production rate and downward DON flux in the oligotrophic surface waters driven by its concentration gradient [Bronk et al., 1994; Vidal et al., 1999]. Benner et al. [1997] found the isotopic composition of the surface DON comparable or somewhat higher than $\delta^{15}\text{N}$ of new NO_3^- . They implied that DON pool might also exert the role of ^{15}N removal from the EZ, and contribute to low $\delta^{15}\text{N}$ of combined N pool (NH_4^+ and suspended PN) like the sinking PN. Further studies will be needed to clarify this phenomenon. In the following discussion, an attempt is made to evaluate the significance of these processes.

4.2. Factors Controlling $\delta^{15}\text{N}_{\text{sus}}$ in Surface Waters

4.2.1. Relationship Between $\delta^{15}\text{N}_{\text{sus}}$ and Nitracline Depth

[21] As stated earlier, elevated $\delta^{15}\text{N}_{\text{sus}}$ may occur when NO_3^- supplied into the EZ from the thermocline represents a major nitrogen source for phytoplankton growth. However, its concentration is kept at near-zero levels due to complete utilization. On the other hand, phytoplankton preferentially

incorporate $^{14}\text{NO}_3^-$ relative to $^{15}\text{NO}_3^-$ due to the isotopic fractionation during NO_3^- uptake and have lowered $\delta^{15}\text{N}$ values under NO_3^- replete conditions when NO_3^- utilization is incomplete [Miyake and Wada, 1967]. Thus, the supply of new NO_3^- from the subsurface waters and the extent of its utilization should determine the isotopic composition of organic matter synthesized by the phytoplankton. In order to explore this relationship in the our study region, we plotted the nitracline depth (D_{NO_3}) versus the $\delta^{15}\text{N}_{\text{sus}}$ in Figure 6 assuming that the depth of the nitracline serves as a surrogate for the rate of NO_3^- supply into the EZ from below the mixed layer [e.g., Herbland and Voituriez, 1979; Cleveland et al., 1989; Malone et al., 1993; Marañón and Holligan, 1999; Marañón et al., 2000]. A significant negative relationship ($R^2 = 0.66$) was observed and the correlation was improved further ($R^2 = 0.81$) when samples from 0 to 15°N, where the N_2 -fixing cyanobacteria were found in significant numbers [Marañón et al., 2000; Tyrrell et al., in preparation], were excluded from the analysis. Similar inverse relationships between the photosynthetic parameters and the nitracline depth have also been observed by Marañón and Holligan [1999] and Marañón et al. [2000] using data collected during the same cruise. These results are consistent with that the injection rate of relatively ^{15}N -rich NO_3^- from the thermocline to the EZ not only controls the phytoplankton productivity, but also exerts a major control over the isotopic composition of suspended PN pool in surface waters over large parts of the Atlantic Ocean.

[22] We have incorporated this relationship into the isotopic mass balance equation [Altabet, 1988]

$$\delta^{15}\text{N}_{\text{phyto.}} = f_{\text{new N}} \times \delta^{15}\text{N}_{\text{new N}} + (1 - f_{\text{new N}}) \times \delta^{15}\text{N}_{\text{regen. N}} \quad (1)$$

where $f_{\text{new N}}$ (dimensionless) is the ratio of new nitrogen from NO_3^- to total nitrogen utilized by phytoplankton for the PN synthesis and $\delta^{15}\text{N}_{\text{phyto.}}$, $\delta^{15}\text{N}_{\text{new N}}$, and $\delta^{15}\text{N}_{\text{regen. N}}$ (‰) are the isotopic compositions of phytoplankton, new NO_3^- , and regenerated NH_4^+ , respectively. We assume that the relative index for new NO_3^- supply rate, V_{NO_3} (dimensionless), varies in inverse proportion to D_{NO_3} (m) and that it controls the degree of new NO_3^- utilization, $f_{\text{new N}}$:

$$\begin{aligned} V_{\text{NO}_3} &= a/D_{\text{NO}_3} \quad (0 < a) \\ f_{\text{new N}} &= bV_{\text{NO}_3} = A/D_{\text{NO}_3} \quad (0 < b, 0 < A = ab \leq D_{\text{NO}_3}) \end{aligned} \quad (2)$$

where a , A (m), and b (dimensionless) denote the constants. As stated above, the trophic structure in the EZ generally depends on the ambient nutrient levels, i.e., oligotrophic waters where new NO_3^- supply is lower and smaller phytoplankton dominate are characterized by a longer and more complex food chain, while the food chain is shorter and simpler in nutrient-rich systems with large primary producers [Lalli and Parsons, 1994]. Then we assume the average number of trophic transfers in the EZ is related inversely to V_{NO_3} or positively to D_{NO_3} , with a constant c (dimensionless) or d (m), respectively:

$$\text{No. trophic steps} = c/V_{\text{NO}_3} = dD_{\text{NO}_3} \quad (c > 0, d = c/a > 0) \quad (3)$$

Moreover, the trophic structure also regulates the dynamics of nitrogen isotopes. We assume that the $\delta^{15}\text{N}_{\text{regen. N}}$ varies

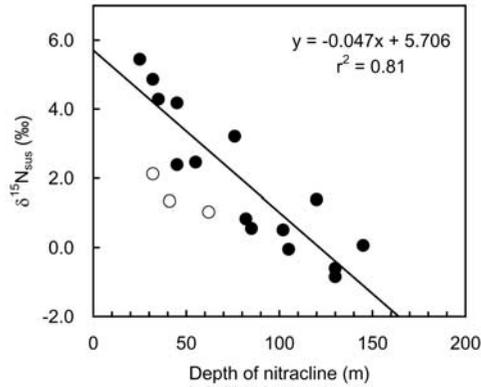


Figure 6. Correlation between the depth of nitracline and $\delta^{15}\text{N}_{\text{sus}}$ in the surface waters. The regression excludes the data from the stations at 15°N – 0°N (open circles).

depending on the number of trophic transfers. i.e., the more complex is the trophic structure the more depleted is the regenerated NH_4^+ in ^{15}N relative to new NO_3^-

$$\begin{aligned} \delta^{15}\text{N}_{\text{regen. N}} &= \delta^{15}\text{N}_{\text{new N}} - e \times (\text{No. trophic steps}) \\ &= \delta^{15}\text{N}_{\text{new N}} - B D_{\text{NO}_3} \quad (e > 0, B = ed > 0) \end{aligned} \quad (4)$$

where e (‰) and B (‰ m^{-1}) are constants. By combining equations (1), (2), and (4) we get

$$\delta^{15}\text{N}_{\text{phyto.}} = -B D_{\text{NO}_3} + (\delta^{15}\text{N}_{\text{new N}} + AB) \quad (5)$$

Equation (5) reveals a negative linear relationship between $\delta^{15}\text{N}_{\text{phyto.}}$ and nitracline depth, which is consistent with our results if we assume that the isotopic composition of suspended PN reflects that of phytoplankton. Taking the $\delta^{15}\text{N}_{\text{new N}}$ as 5.0‰, we computed the values of constants A and B from the slope and intercept of the regression line in Figure 6 as 15 and 0.047, respectively. Based on these values the f -ratio and $\delta^{15}\text{N}_{\text{regen. N}}$ were estimated to be 0.11 and -1.6 ‰, respectively, in the subtropical gyre ($D_{\text{NO}_3} = 140$ m) and 0.38 and $+3.1$ ‰ in the mesotrophic region ($D_{\text{NO}_3} = 40$ m). These estimates of the f -ratio agree well with the literature values from the Atlantic Ocean (Table 1) and so it is reasonable to believe that the regional variability in the computed $\delta^{15}\text{N}_{\text{regen. N}}$ values are realistic.

[23] In the above treatment it has been assumed that the $\delta^{15}\text{N}$ of source NO_3^- remained constant (5‰) all along the AMT transect. It is obvious from (5) that a variable isotopic composition of NO_3^- can bring about changes in the isotopic composition of phytoplankton. However, studies conducted in various oceanic areas have revealed that except in regions that experience intense denitrification (e.g., the eastern tropical North and South Pacific Ocean and the Arabian Sea), where a preferential loss of $^{14}\text{NO}_3^-$ causes ^{15}N enrichment in the residual NO_3^- [Cline and Kaplan, 1975; Brandes et al., 1998], the $\delta^{15}\text{N}$ of NO_3^- in subsurface waters is quite constant at 5–6‰ [Liu and Kaplan, 1989; Sigman et al., 1997; Tanaka and Saino, 2002]. The open Atlantic Ocean, however, does not experience denitrification in the water column [Gruber and

Sarmiento, 1997], and therefore our assumption of constant $\delta^{15}\text{N}$ of source NO_3^- is not unreasonable.

4.2.2. Influence of N_2 -Fixation on $\delta^{15}\text{N}_{\text{sus}}$

[24] The $\delta^{15}\text{N}$ of NO_3^- in the ocean is generally higher than that of atmospheric N_2 by 5–6‰. Moreover, biological fixation of N_2 involves little isotopic fractionation and the N_2 -fixer, cyanobacteria *Trichodesmium*, has been reported to exhibit low $\delta^{15}\text{N}$ values of -2 to 0 ‰ [Minagawa and Wada, 1986; Wada and Hattori, 1991]. Therefore, this process tends to lower the $\delta^{15}\text{N}$ of the combined nitrogen pool. In the latitudinal range 0° – 15°N , where the abundance of N_2 -fixing organisms increased significantly [Marañón et al. 2000], the $\delta^{15}\text{N}$ values of suspended PN were, on average, 2‰ lower than the values expected from the regression between $\delta^{15}\text{N}_{\text{sus}}$ and nitracline depth (Figure 6 and Table 2). We have used the magnitude of this departure to quantify the contribution (r) from N_2 -fixation using the relationship:

$$\delta^{15}\text{N}_{\text{sus}} = (1 - r) \times \delta^{15}\text{N}_{\text{phyto.}} + r \times \delta^{15}\text{N}_{\text{cyano.}} \quad (6)$$

The $\delta^{15}\text{N}_{\text{phyto.}}$ is estimated from the regression line between $\delta^{15}\text{N}_{\text{sus}}$ and nitracline depth and $\delta^{15}\text{N}_{\text{cyano.}}$ is the isotopic composition of N_2 -fixing cyanobacteria. The averaged contribution of N_2 -fixation to the suspended PN pool works out to be $38 \pm 13\%$ when we use a value of -2 ‰ for $\delta^{15}\text{N}_{\text{cyano.}}$ (Table 2). If the isotopic composition of cyanobacteria is taken to be the same as that of atmospheric N_2 , this contribution would be even larger ($59 \pm 15\%$). Tyrrell et al. (in preparation) have also estimated that atmospheric N_2 fixed in this region 0 – 15°N accounts, on average, for 20% of the total new N input into the EZ, which would correspond to a lower contribution ($\sim 10\%$) to total N uptake if we assume an f -ratio of 0.5. It is quite likely that the nitrogen derived from N_2 -fixation is accumulated and recycled in the upper layer. Carpenter et al. [1999] observed low values of $\delta^{15}\text{N}$ in both suspended PN and zooplankton in the tropical Atlantic where the extensive bloom of an N_2 -fixing cyanobacteria associated with diatoms were found. They suggested that the isotopic signature of N_2 -fixation might propagate rapidly through the food web, as results the nitrogen pool would be isotopically light due to the recycling of recently fixed nitrogen. Since the N_2 -fixers observed in

Table 1. Compilation of f -Ratios Observed in the Tropical and Subtropical Atlantic Ocean^a

| Region | f -Ratio | Source |
|---|------------------|-----------------------|
| Gulf Stream | 0.17–0.2 | Glibert et al. [1988] |
| Sargasso Sea | 0.04–0.08 | Glibert et al. [1988] |
| 30° – 47°S , 48° – 38°W | 0.16–0.24 | Metzler et al. [1997] |
| 28.5°S , 23°W | 0.21–0.30 | Lewis et al. [1986] |
| 0° – 4°S | 0.33–0.45 | Le Bouteiller [1986] |
| North subtropical gyre | 0.18 | Planas et al. [1999] |
| Equatorial Atlantic | 0.24 | Planas et al. [1999] |
| South subtropical gyre | 0.12 | Planas et al. [1999] |
| North subtropical gyre, 38° – 24°N | 0.21 (0.14–0.33) | This study |
| Equatorial Atlantic, 21°N – 7°S | 0.30 (0.14–0.47) | This study |
| South subtropical gyre, 10° – 33°S | 0.16 (0.10–0.27) | This study |

^a This table was compiled largely from the study of Planas et al. [1999].

Table 2. The Contribution of N₂ Fixed to PN Pool in Surface Waters at North Tropical Atlantic

| Station | Latitude, °N | Nitracline Depth, m | $\delta^{15}\text{N}_{\text{sus}}$, ‰ | $\delta^{15}\text{N}_{\text{phyto.}}^{\text{a}}$, ‰ | Contribution of N ₂ Fixed to PN Pool, % | | |
|---------|--------------|------------------------|--|--|--|-------------|-------------|
| | | | | | $\delta^{15}\text{N}_{\text{cyano.} = 0}$, ‰ | = 1, ‰ | = 2 (‰), ‰ |
| 9 | 12.75 | 32 | 2.1 | 4.2 | 49.4 ± 14.4 | 39.9 ± 13.1 | 33.5 ± 11.7 |
| 10 | 9.05 | 41 | 1.3 | 3.8 | 64.5 ± 11.6 | 51.0 ± 11.8 | 42.2 ± 11.1 |
| 11 | 5.17 | 62 | 1.0 | 2.8 | 63.2 ± 18.4 | 46.5 ± 17.4 | 36.8 ± 15.2 |
| Average | | | | | 59.0 ± 14.8 | 45.8 ± 14.4 | 37.5 ± 12.7 |

^aHere $\delta^{15}\text{N}_{\text{phyto.}}$ was estimated from the regression line between $\delta^{15}\text{N}_{\text{sus}}$ and nitracline depth (see text).

this study were free-living and the particles produced would be small with slow sinking rates, an effective nitrogen recycling could be expected in systems with substantial N₂-fixation.

[25] The uncertainty (over 10%, Table 2) in estimating fixed N₂ contribution (r) was directly derived from the standard error ($\pm 0.9\%$) associated with the determination of $\delta^{15}\text{N}_{\text{phyto.}}$ in (6) using the $\delta^{15}\text{N}_{\text{sus}}$ versus D_{NO_3} regression as the reference relationship for non-active sites of N₂-fixation. The dispersions of the source data for this regression may be partially attributed to the influences of the episodic events such as the N₂-fixation preceding our observation and the incomplete utilization of NO₃⁻ by algae. The former would derive the ¹⁵N depleted PN and shift the $\delta^{15}\text{N}_{\text{phyto.}}$ regression to D_{NO_3} below. This, thus, gives rise to the underestimation of both $\delta^{15}\text{N}_{\text{phyto.}}$ and r . On the other hand, the latter would leave nano-molar levels of NO₃⁻, which is isotopically very heavy (e.g., $\delta^{15}\text{N} > 10\%$ when $[\text{NO}_3^-] < 1\text{--}3 \mu\text{M}$ —*Rau et al.*, 1998; *Tanaka and Saino*, 2002), in the EZ and, its enriched ¹⁵N signal would be imprinted in the PN formed consequently. As a result, both the estimated $\delta^{15}\text{N}_{\text{phyto.}}$ values and r to be overestimated. However, there is no conclusive evidence to evaluate these deductions on the uncertainty associated with the estimation of the contribution of N₂-fixation. All in all, our ¹⁵N analysis indicates that biological fixation of atmospheric nitrogen contributes significantly to the suspended PN pool in the region between 0 and 15°N, where N₂-fixers have been found, and that the fixed N is actively recycled within the upper layer. Thus our results support the view that N₂-fixation can be an important contributor to biological productivity rates in nutrient-impooverished surface waters [*Liu et al.*, 1996; *Brandes et al.*, 1998; *Marañón et al.*, 2000].

4.3. $\delta^{15}\text{N}$ as a Proxy of Present and Past Biological Production

[26] Our results clearly demonstrate that $\delta^{15}\text{N}_{\text{sus}}$ in the surface waters of the Atlantic Ocean varies over a range of 6‰ in response to regional changes in nutrient conditions. We conclude that the availability of both new and recycled nitrogen controls the isotopic composition of suspended PN in nutrient-depleted systems. Since both the biological productivity and the isotopic composition of suspended PN are controlled by the availability of nutrients, we explored the possibility of using the $\delta^{15}\text{N}_{\text{sus}}$ signal as a proxy of algal production. For this purpose we combined our isotopic data with the productivity data of *Marañón et al.* [2000]. A significant positive correlation ($R^2 = 0.60$) was found between these parameters (Figure 7). However, this

correlation existed only in regions where NO₃⁻ depletion occurred in surface waters. The correlation coefficient became smaller ($R^2 = 0.49$) when data from eutrophic regions were included because the isotopic fractionation disturbed the relationships. The isotopic data thus lend support to the view that the supply of new NO₃⁻, from below the surface mixed layer, dominantly controls the primary productivity along the AMT track. Thus, a higher NO₃⁻ supply resulted in a higher biological production and a greater contribution of isotopically heavier NO₃⁻ to the suspended PN pool. Conversely, lower NO₃⁻ supply caused lower biological production that was fueled mostly by isotopically light regenerated NH₄⁺ lowering the $\delta^{15}\text{N}_{\text{sus}}$. This implies that the $\delta^{15}\text{N}_{\text{sus}}$ can provide an estimate of in situ algal production.

[27] With respect to the utility of $\delta^{15}\text{N}$ records in sediments as a proxy for reconstruction of surface nutrient levels and algal production in the past [*Altabet and Francois*, 1994b; *Farrell et al.*, 1995], an important issue to be addressed is how well the $\delta^{15}\text{N}$ of sinking matter records the diverse nutrient regimes. Our results show that $\delta^{15}\text{N}_{\text{sus}}$ is closely tied to the nutrient supply and if, as stated earlier, the isotopic composition of sinking and suspended matter may differ substantially and variedly depending upon complex factors related to the trophic structure, the relationship between the $\delta^{15}\text{N}$ of sinking particles (and hence of sedimentary nitrogen) on the one hand and biological productivity or surface nutrient levels on the other may not be straightforward. This is especially so when we also take into

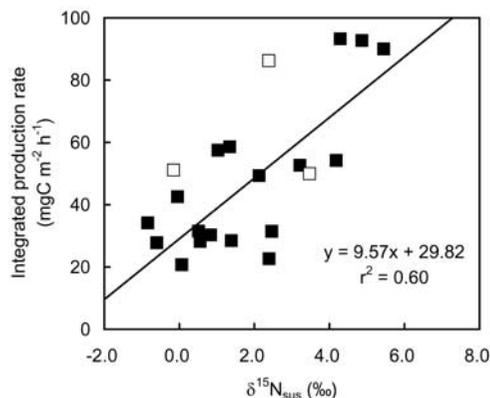


Figure 7. Correlation between the $\delta^{15}\text{N}_{\text{sus}}$ and the integrated production rate. The regression excludes the data from the temperate stations (open squares). The data on algal production are obtained from the work of *Marañón et al.* [2000].

account inputs from N₂-fixation. Hence the application of $\delta^{15}\text{N}$ signal as a paleoceanographic tool needs further validation through collection of data from various biogeochemical regimes.

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