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## Vertical patterns in <sup>15</sup>N natural abundance in PON from the surface waters of warm-core rings

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#### ABSTRACT

The natural abundance of <sup>15</sup>N in PON from the upper 200 m of 4 warm-core rings and the Sargasso Sea was measured. Minima in the  $\delta^{15}N$  of PON often occurred near the depth at which NO<sub>3</sub><sup>-</sup> was first detectable. Frequently, maxima in PON concentration and minima in C/N ratio also co-occurred in this region. The average value for the  $\delta^{15}N$  of PON below the top of the nitracline was almost always greater than that above the top of the nitracline. The observed vertical pattern for the  $\delta^{15}N$  of PON is most likely the result of isotopic fractionation in the processes of NO<sub>3</sub><sup>-</sup> uptake by phytoplankton at the base of the euphotic zone and the degradation of PON below the euphotic zone. Variations in the strength and coherence of this vertical pattern appear to occur in response to both rapid physical modification of the water column and the trophic status of the euphotic zone.

#### 1. Introduction

Naturally occurring variations in the abundance of <sup>15</sup>N (by convention  $\delta^{15}N$ ; Hoering, 1955) have been used to investigate a variety of processes within the marine nitrogen cycle. Cline and Kaplan (1975) used the  $\delta^{15}N$  of NO<sub>3</sub><sup>-</sup> to investigate denitrification in the O<sub>2</sub> minimum region of the Eastern Tropical Pacific. Sweeney and Kaplan (1980) estimated the terrestrial contribution of nitrogen to coastal marine sediments based on the difference in  $\delta^{15}N$  between terrestrial and marine sources. Saino and Hattori (1980) observed an increase in the  $\delta^{15}N$  of suspended particulate organic nitrogen (PON) with depth in the Indian ocean and concluded that this was a result of the progressive decomposition of this material with depth. These studies led us

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to pursue an intensive study of the distribution of <sup>15</sup>N natural abundance in warm-core rings. One objective was to assess the utility of this approach for studying the nitrogen cycle of the near-surface open ocean.

Altabet and McCarthy (1985) have discussed the advantages of using <sup>15</sup>N natural abundance as an *in situ* tracer of the marine nitrogen cycle. A principal advantage of this method is that variations in  $\delta^{15}N$  will occur on the temporal/spatial scales of the most important processes affecting the nitrogen pools examined. With respect to PON in the upper ocean, it was hypothesized that the principal factors determining the  $\delta^{15}N$  of PON in the euphotic zone are the vertical processes which transport nitrogen into and out of the euphotic zone.

The importance of vertical processes to the chemical and biological cycles of the open ocean has been widely recognized. Attention has been drawn to the relationships that exist between the vertical flux of nutrients into the euphotic zone, primary production, and the downward flux of particles (Eppley and Peterson; 1979; Deuser and Ross; 1980; Eppley *et al.*, 1983). Since the availability of nitrogen in the open ocean is considered to be the limiting factor for phytoplankton growth (Eppley *et al.*, 1973), it is specifically the upward flux of this element that regulates primary production and thus also the downward flux of particulates. Dugdale and Goering (1967) made reference to  $NO_3^-$  as the source of this 'new' nitrogen to the euphotic zone. Eppley and Peterson (1979) expanded upon this concept to stress the necessity for the upward flux of  $NO_3^-$  into the euphotic zone to balance the downward flux of particulate organic nitrogen (PON) in order to maintain the observed levels of biomass and primary production of the oligotrophic open ocean.

These important vertical fluxes are associated with large gradients in related properties in the upper 200 m of the ocean. The flux of  $NO_3^-$  is dependent upon both the vertical  $NO_3^-$  gradient and upward physical transport processes (advection and turbulant diffusion). Typically, under oligotrophic conditions,  $NO_3^-$  concentrations are detectable only near the base of the euphotic zone and continue to increase with depth down to at least 700 m in the subtropical gyres. The top of this 'nitracline,' near the base of the euphotic zone, is a region where the  $NO_3^-$  gradient is usually the largest. The vertical flux of  $NO_3^-$  in this region must, on average, balance the uptake of  $NO_3^-$  by phytoplankton.

Cullen and Eppley (1981), presenting their own data, and also reviewing previously published data for the vertical distribution of chlorophyll, noted the persistent co-occurrence of the top of the nitracline with a chlorophyll maximum that is usually at the base of the euphotic zone. Cullen and Eppley (1981) comment, however, that in different regions the chlorophyll maximum is the product of different processes. In some instances, such as during upwelling conditions, it may represent a biomass or primary productivity maximum. In other regions, such as in the oligotrophic central gyres, it can be the result of an increase in chlorophyll per phytoplankton cell, representing an adaptation to low light levels at depth. McCarthy and Altabet (1984) note that, in any case, the co-occurrence of the chlorophyll maximum, the top of the nitracline, and other features with the base of the euphotic zone underscores the significance of this boundary region for the pelagic ecosystem. These co-occurrences suggest that the base of the euphotic zone is an important boundary region with regard to nitrogen dynamics. In a vertical profile of  $\delta^{15}$ N in suspended PON from the Indian Ocean, a minimum was observed at the top of the nitracline (Saino and Hattori, 1980). The scarcity of data of similar type, however, does not permit an evaluation of the generality of this pattern.

The principal questions addressed in this paper are: Is there a persistent vertical pattern in the  $\delta^{15}N$  of PON in the upper 200 m? If a general pattern exists, can it be explained in terms of current views regarding nitrogen cycling in the ocean? A total of 33 vertical profiles for the  $\delta^{15}N$  of suspended PON were obtained as part of the Warm Core Rings Program. Synoptic data for  $NO_3^-$  concentration, the concentration of particulate organic nitrogen (PON), and the carbon to nitrogen (C/N) ratio of suspended particulate organic matter (POM) were also generated for comparison with the <sup>15</sup>N natural abundance data. Samples were taken from four different warm-core rings and the Sargasso Sea. There were considerable differences among the regions studied in the depth of the euphotic zone, PON concentration in the euphotic zone, degree of stratification, and other parameters that are indicative of variations in the magnitude and pattern of nitrogen cycling. A detailed analysis of  $\delta^{15}N$  data collected in several different regimes is presented as an evaluation of the usefulness of this approach to the study of nitrogen dynamics in the upper ocean.

#### 2. Methods

All samples were collected using General Oceanics Go-Flo bottles. Samples from Ring 81-D were collected using 5-liter bottles, all others with 30-liter bottles. After retrieval, the Go-Flo bottles were drained immediately into 60-liter vats. It was necessary to trip more than one bottle at a given depth to provide enough material for all of the companion studies in the Warm Core Ring Program. Sub-sampling occurred immediately after the vats were filled.

PON samples for  $\delta^{15}N$  analysis were prepared by filtering 4 to 6 liters of water through 2.5 cm Whatman GF/F glass fiber filters which were precombusted at 500 degrees C. Filters were dried and stored in tightly stoppered glass vials. N<sub>2</sub> gas for mass spectrometric analysis was prepared from samples by an *in vacuo* Dumas combustion technique. <sup>15</sup>N natural abundance measurements were performed using a VG Micromass 602E mass spectrometer. Details of the sample preparation methodology are presented elsewhere (Nevins *et al.*, 1985). Precision for the  $\delta^{15}N$  determination was  $\pm$  0.1 per mil. All values for  $\delta^{15}N$  presented are relative to the <sup>15</sup>N/<sup>14</sup>N ratio of atmospheric N<sub>2</sub>.

Samples for PON and POC determination were collected similarly to those for  $\delta^{15}N$  analysis. A Perkin-Elmer Model 240 B Elemental Analyser was used to determine



Figure 1. Map of station positions and the approximate locations of the warm-core rings at the time the stations were made. Stations 5–10 were made during the first transect across Ring 82-B. Stations 11–18 were made during the second transect across Ring 82-B. Note the change in ring location between these two transects. Stations 27 and 28 were made before Ring 82-H separated from the Gulf Stream and appear to be outside the ring boundary when in fact they were at the center of the meander. Station numbers are cross-referenced with station names in Table 1.

PON and POC. In some instances, PON concentration was calculated based on the mass spectrometer signal strength.  $NO_3^-$  concentration data are from Fox *et al.* (1983) and Fox *et al.* (1984 a, b, c, and d).

#### 3. Results

Samples were collected from four different warm-core rings (Rings 81-D, 82-B, 82-E, and 82-H) and the Sargasso Sea. Station locations and the position of these warm-core rings at the time of sampling are shown in Figure 1. Table 1 cross-references the profile numbers shown in Figure 1 with the station names. The primary characteristics of these warm-core rings and associated waters have been discussed previously (Altabet and McCarthy, 1985).

Figure 2 shows two representative profiles for the  $\delta^{15}N$  of PON, PON concentration,  $NO_3^-$  concentration, and C/N ratio for Ring 82-B in June. Subsurface maxima in PON concentration, minima for the  $\delta^{15}N$  of PON, and minima in C/N ratio are evident in or near the region where the  $NO_3^-$  gradient is sharpest at the top of the nitracline. For both profiles there is a discernable increase in the  $\delta^{15}N$  of PON below the top of nitracline co-occurring with decreasing PON concentration. The second station (KN095 624.07) appears to exhibit a subsurface peak in the  $\delta^{15}N$  of PON within this region. This peak occurs in a depth interval where C/N ratio increases with depth.

Table 1. Station operation list cross-reference to profile number (see Fig. 1). Average  $\delta^{15}N$  values were weighted by PON concentration. Y—yes, N—No, LM—local minimum, nd—no data

		Ave. δ <sup>15</sup> N above the	Ave. $\delta^{15}N$ below the	δ <sup>15</sup> min. near the	PON max near the	C/N min. near the
Station	Profile	top of the	top of the	top of the	top of the	top of the
Operation	No.	nitracline	nitracline	nitracline?	nitracline?	nitracline?
Ring 81-D						
All 110 926.03	1	4.6	8.3	Ν	N	Ν
All 110 927.03	2	11.0	8.1	LM	Ν	Ν
All 110 927.09	3	5.2	8.9	LM	N	N
All 110 1002.14	4	4.6	4.3	Ν	Y	
Ring 82-B						
1st Transect						
KN095 616.02	5	8.3	11.5	Y	Ν	Y
KN095 616.04	6	6.9	11.4	Y	Y	Y
KN095 616.06	7	6.1	17.2	LM	Y	Y
KN095 616.08	8	7.5	13.3	Y	Y	Y
KN095 617.01	9	6.1	9.6	Y	Υ	Y
KN095 617.03	10	4.6	6.5	Y	Y	Y
Ring 82-B						
2nd Transect						
KN095 623.01	11	10.1	16.9	Y	Y	Y
KN095 623.03	12	10.2	13.3	Y	Y	Y
KN095 623.06	13	8.9	13.3	Ν	Y	N
KN095 624.01	14	8.5	14.2	Y	Y	Y
KN095 624.03	15	5.1	11.6	Y	Υ	Y
KN095 624.07	16			LM	Y	Y
KN095 625.01	17	6.4	11.6	Y	Y	Y
KN095 625.03	18	5.0	12.5	Y	Y	Y
Ring 82-E						
KN097 818.04	19	5.3	8.0	Y	Y	Y
KN097 818.07	20	4.7	9.3	Y	Y	Y
KN097 818.10	21	3.0	14.2	Y	Y	Y
KN097 819.01	22	4.3	8.5	Y	Y	Ν
KN097 819.04	23	3.4	8.3	Y	Y	Y
KN097 819.07	24	4.9	10.1	Y	Y	Y
KN097 820.01	25	3.8	7.6	Y	Y	Y
KN097 820.11	26	2.6	5.0	Y	Y	nd
Ring 82-H						
KN098 1001.08	27	6.3	7.7	LM	nd	nd
KN098 1003.07	28	7.5	11.6	LM	nd	nd
KN098 1009.02	29	4.6	7.1	Y	nd	ndi
KN098 1012.05	30	5.9	8.6	Y	Y	N
KN098 1005.07	31	2.7	6.6	Y	nd	nd
Sargasso Sea						
KN093 501.15	32	4.1	13.6	Y	N	nd
KN097 813.01	33	4.4	nd	nd	nd	nd



Figure 2. Profiles for NO<sub>3</sub><sup>-</sup> ( $\Xi$ ), the  $\delta^{15}$ N of PON ( $\odot$ ), PON concentration ( $\Box$ ), and C/N ratio ( $\triangle$ ) for stations KN095 617.01 (#9) and KN095 624.07 (#16).

For Ring 82-E, representative profiles are shown in Figure 3. At both stations, a minimum in the  $\delta^{15}N$  of PON occurred at or near the top of the nitracline. The NO<sub>3</sub><sup>-</sup> profile for station KN097 820.11 is unusual, possessing a maximum at the top of the nitracline. Such a feature was also observed for other stations in Ring 82-E. Horizontal intrusions of water from outside the ring at the depth corresponding to the top of the nitracline may have produced the observed maxima. Nevertheless, the  $\delta^{15}N$  minimum again occurs near the depth at which NO<sub>3</sub><sup>-</sup> is first detectable. Also, as in the case of Ring 82-B, maxima in PON occur at or just above the minima in  $\delta^{15}N$  of PON. A minimum in the C/N ratio is also associated with this feature in station KN097 819.04. C/N data are not available for station KN097 820.11. The increase in  $\delta^{15}N$  below the top of the nitracline, forming a subsurface maximum in the case of KN097



Figure 3. Profiles for NO<sub>3</sub><sup>-</sup> ( $\underline{X}$ ), the  $\delta^{15}$ N of PON (O), and PON ( $\Box$ ) concentration for stations KN097 819.04 (#23) and KN097 820.11 (#26) with data for C/N ratio for KN097 819.04 ( $\triangle$ ).

819.04, follows the same pattern as in Ring 82-B, in that it co-occurs with decreasing PON concentrations and increasing C/N ratio. The high data density for station KN097 820.11 clearly demonstrates the association of the  $\delta^{15}$ N minimum with the region where the NO<sub>3</sub><sup>-</sup> gradient is largest. However, there is only a slight maximum in PON. Additional structure in the vertical profile for the  $\delta^{15}$ N of PON is apparent at this station.

Representative profiles for the  $\delta^{15}N$  of PON, NO<sub>3</sub><sup>-</sup> concentration, C/N ratio, and PON concentration from Ring 82-H are presented in Figure 4. At the time station KN098 1001.08 was made, Ring 82-H was detaching from the Gulf Stream and was actually the center of a meander. Station KN098 1012.05 was made near the center of Ring 82-H after it had detached from the Gulf Stream.



Figure 4. Profiles for NO<sub>3</sub><sup>-</sup> ( $\Xi$ ), the  $\delta^{15}$ N of PON ( $\odot$ ), PON concentration ( $\Box$ ), and C/N ratio ( $\triangle$ ) for stations KN098 1001.08 (#27) and KN098 1012.05 (#30).

Similar vertical patterns for the  $\delta^{15}$ N of PON are found in this ring when compared to the other rings, though they are not as pronounced. For station KN098 1001.08, there is a local minimum associated with the top of nitracline. For station KN098 1012.05, a  $\delta^{15}$ N minimum and a PON maximum reside above the top of the nitracline.

Figure 5 presents data for two representative stations from Ring 81-D. Station AII 110 926.03 was a ring center station and station AII 110 927.09 was made in the high velocity region of the ring at its edge. Except for an increase in the  $\delta^{15}N$  of PON in the lower portion of the profile, the vertical features observed in the other warm-core rings studied are not apparent. These stations were made at a time during which Ring 81-D was undergoing rapid change due to both storm activity and interaction with the Gulf Stream (Joyce *et al.*, 1984).



Figure 5. Profiles for NO<sub>3</sub><sup>-</sup> ( $\Xi$ ), the  $\delta^{15}$ N of PON ( $\odot$ ), PON concentration ( $\Box$ ), and C/N ratio ( $\triangle$ ) for stations AII 110 926.03 (#1) and AII 110 927.09 (#3).

Profiles for two Sargasso Sea stations are presented in Figure 6. Station KN093 501.15 was occupied May 1, 1982 and exhibits the general pattern of a minimum in the  $\delta^{15}N$  of PON associated with the top of the nitracline with an increase below this depth. In this case, the deep maximum in  $\delta^{15}N$  is especially sharp. PON concentrations were higher than what is considered typical for the Sargasso Sea (unpublished data), coinciding with an atypically shallow nitracline. Additionally, stratification in the upper 100 m was weak, suggesting that at this time the water column was in transition from winter to summer-time conditions. Station KN097 813.02, which was occupied in mid-August of that year, shows very little variation in the  $\delta^{15}N$  of PON with depth. Evidently, the top of the nitracline occurred below the greatest depth sampled.

Table 1 presents a summary of results for each station where sampling occurred in the upper 200 m. The average  $\delta^{15}$ N values were weighted by the PON concentration at



Figure 6. Profiles for NO<sub>3</sub><sup>-</sup> ( $\Xi$ ), the  $\delta^{15}$ N of PON ( $\odot$ ), and PON concentration ( $\Box$ ), for stations KN093 501.15 (#32) and KN097 813.01 (#33) with data for C/N ratio for KN097 813.01 ( $\triangle$ ).

each depth sampled. The product of  $\delta^{15}N$  and PON concentration was calculated for each depth and summed over the depth interval of interest. This value was divided by the sum of PON concentrations over the same depth interval.

#### 4. Discussion

It is apparent that there are vertical patterns in the  $\delta^{15}N$  of PON that persist from station to station over a wide range of hydrographic areas. These features may be indicative of vertical processes within the nitrogen cycle common to all these regions inasmuch as  $\delta^{15}N$  values are influenced by these processes.

Most pervasive is the increase in the  $\delta^{15}N$  of PON below the upper portion of the nitracline to values higher than those for the euphotic zone (see Table 1). Saino and

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Hattori (1980) observed an increase in the  $\delta^{15}N$  of suspended PON with depth below the euphotic zone. They concluded that isotopic fractionation in the process of particle degradation led to higher  $\delta^{15}N$  values for PON with depth below the euphotic zone. Presumably, the bacteria and microheterotrophs that degrade particles preferentially remineralize <sup>14</sup>N relative to <sup>15</sup>N, leading to a progressive increase in the  $\delta^{15}$ N of the particles as they undergo degradation. Though the remineralization of PON to dissolved forms of nitrogen occurs both above and below the euphotic depth, within the euphotic zone these forms are quickly assimilated back into particulate form, and the pool size of dissolved inorganic nitrogen is small compared to the pool of suspended PON. As a result, it is expected that the recycling of nitrogen between autotrophs and heterotrophs would have only a negligible effect on the  $\delta^{15}N$  of PON within the euphotic zone. Below the euphotic zone, nitrogen remineralized into dissolved forms is not assimilated back into the particulate fraction due to insufficient light for photosynthesis. Accordingly, isotopic fractionation in the process of remineralization would cause an increase in the  $\delta^{15}$ N of the remaining PON. Based on the present data, it appears that in stratified waters, the vertical distribution of  $\delta^{15}$ N in PON reflects the fact that the top of the nitracline represents a boundary below which degradation occurs faster than the autotrophic assimilation of the products of degradation. This conclusion is further supported by the frequent occurrence of a rapid decrease in PON concentration below the top of the nitracline. Similarly, an increase in the C/N ratio below this depth provides further evidence that the PON below the top of the nitracline has undergone progressive degradation with depth.

In theory, a relationship should exist between the degree to which PON has been degraded and the observed increase in  $\delta^{15}$ N. This relationship is given for the general case of nitrogen transformation from a nitrogen pool 'A' to a pool 'B' by the following equation adapted from Hoering and Ford (1960):

$$\Delta \delta^{15} \mathbf{N}_{(A-B)} = \ln F \cdot (1/\beta - 1) \cdot 1000.$$
 (1)

The following approximation was used:

$$\Delta \delta^{15} \mathbf{N}_{(A-B)} \simeq \ln \frac{{}^{15} \mathbf{N} / {}^{14} \mathbf{N} (A)}{{}^{15} \mathbf{N} / {}^{14} \mathbf{N} (B)} \cdot 1000$$

since the difference in isotopic ratios is very small compared to unity:

$$\ln \frac{{}^{15}\text{N}/{}^{14}\text{N}(A)}{{}^{15}\text{N}/{}^{14}\text{N}(B)} \simeq \frac{{}^{15}\text{N}/{}^{14}\text{N}(A)}{{}^{15}\text{N}/{}^{14}\text{N}(B)} - 1$$

 $\beta$  is the isotopic fractionation factor, F is the fraction of the nitrogen source remaining, and  $\Delta \delta^{15}$ N is the associated change in  $\delta^{15}$ N.

The use of Eq. 1 assumes a single step degradation process for which a single  $\beta$  exists and assumes that degradation is the only process controlling PON concentration below the top of the nitracline. For each station, F is calculated using the PON concentration



Figure 7.  $\Delta \delta^{15}$ N vs. 1n F. See text for explanation.

of the PON maximum and the PON concentration at the depth where the  $\delta^{15}N$  of PON reaches its maximum value:

$$F = 1 - \frac{\text{PON at PON maximum}}{\text{PON at }\delta^{15}\text{N maximum}}.$$
 (2)

The value of  $\Delta \delta^{15}$ N is the difference between the maximal  $\delta^{15}$ N value and the minimal  $\delta^{15}$ N value associated with the PON maximum. Figure 7 presents a plot of 1n F vs.  $\Delta \delta^{15}$ N. There is a trend toward a greater range in  $\Delta \delta^{15}$ N with decreasing 1n F suggesting that the most advanced degree of degradation can result in larger  $\delta^{15}$ N values. The large degree of scatter and lack of a linear relationship, though, indicate that the assumptions listed above are too simplistic. Furthermore, the variation among stations within a ring is as large or larger than the variation between rings. These findings imply that processes in addition to particle decomposition control the concentration of PON below the euphotic zone. Turbulent vertical mixing will also result in deviations from Eq. 1. Even if degradation were the only process affecting the concentration of PON below the euphotic zone, the data would be consistent with the complex nature of particle degradation. A varying isotopic fractionation factor is probably associated with variations in both the chemical composition of the PON and the species composition of the community of microheterotrophs responsible for decomposition.

A minimum in the  $\delta^{15}N$  of PON near the top of the nitracline is another persistent feature of the data set (see Table 1). Of 33 profiles, 23 had the lowest  $\delta^{15}N$  values for that profile associated with the top of the nitracline. An additional 6 had local minima in the  $\delta^{15}N$  of PON near the top of the nitracline. Of the 3 stations which showed no minima in  $\delta^{15}N$  at the top of the nitracline, one was the Sargasso Sea station for which no samples were taken within the nitracline. The other two were made in Ring 81-D at the time it was undergoing rapid changes; there was both intense storm activity and interaction with the Gulf Stream (Joyce *et al.*, 1984). Of 28 stations for which PON concentration was measured across the top of the nitracline, 23 had maxima associated with the  $\delta^{15}N$  minima. Of 25 stations for which there are C/N data, 19 had C/N minima associated with the  $\delta^{15}N$  minima. The average value for the C/N value for these minima is 8.1, somewhat higher than the Redfield ratio of 7. It appears that across a wide variety of hydrographic regimes, the base of the euphotic zone is a distinct region in terms of nitrogen dynamics which is reflected in the  $\delta^{15}N$  of PON. It is likely that phytoplankton growing in this region are primarily light limited and depend heavily on NO<sub>3</sub><sup>-</sup> as a nitrogen source. NO<sub>3</sub><sup>-</sup> uptake (unpublished data) was usually highest at the base of the euphotic zone at most of these stations.

In the open ocean, where other sources of new nitrogen are relatively insignificant,  $NO_3^-$  is the primary nitrogen source for the formation of 'new' PON in the euphotic zone (Eppley and Peterson, 1979). The principal sinks for euphotic zone PON are the removal of large, fast sinking particles and the turbulent mixing of small particles through the base of the euphotic zone. The PON maximum most likely represents a region of net production for PON due to the localization of phytoplankton  $NO_3^-$  uptake at this depth. PON produced at the base of the euphotic zone is redistributed both upward and downward by turbulent mixing. C/N ratios approaching that of the Redfield ratio suggest that this region at the top of the nitracline is both one in which phytoplankton are nitrogen sufficient and for which there is a minimum of highly degraded detritus. The co-occurrence of maxima in chlorophyll *a* and ATP (G. Hitchcock and C. Langdon respectively, personal communications) with maxima for PON is a further indication that the PON maximum is also a maximum for biologically active material.

The presence of a  $\delta^{15}$ N minimum at the top of the nitracline may best be explained as a result of isotopic fractionation in the uptake of  $NO_3^-$  by phytoplankton. Wada and Hattori (1978) measured fractionation factors as high as 1.015 for laboratory cultures of diatoms. Altabet and McCarthy (1985) approximated a fractionation factor of 1.004 for NO<sub>3</sub><sup>-</sup> uptake in Ring 82-B in April. Isotopic fractionation in the uptake and assimilation of  $NO_3^-$  by phytoplankton within the upper portion of the nitracline would result in lower values for the  $\delta^{15}N$  of PON. Such fractionation would also result in an increase in the  $\delta^{15}$ N of the remaining NO<sub>3</sub><sup>-</sup> such that there would be an inverse relationship between NO<sub>3</sub><sup>-</sup> concentration and the  $\delta^{15}$ N of NO<sub>3</sub><sup>-</sup> in the euphotic zone. Such a relationship has been observed for the Subarctic Pacific Ocean (Wada, 1980; unpublished data, this laboratory). Phytoplankton higher up in the euphotic zone would take up this 'heavier' NO<sub>3</sub><sup>-</sup>, resulting in higher values for the  $\delta^{15}N$  of PON toward the surface. It is clear that isotopic fractionation in the degradation of PON below the euphotic zone is required to create an actual minimum in the  $\delta^{15}N$  of PON at the top of the nitracline. A mathematical model of these processes has been successful in simulating the observed vertical features (Altabet et al., 1986).

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Figure 8. Average  $\delta^{15}N$  vs. the minimum value for  $\delta^{15}N$  for each profile.

In Figure 8, the minimum  $\delta^{15}N$  value is plotted against the average  $\delta^{15}N$  value for each station. A linear regression shows that the slope of a line fitted to the points is not significantly different from 1 (0.82, S.E. = 0.53) and the Y-intercept is +2.8 per mil (S.E. = 0.13). The regression itself was significant at P < .001 using the F test. The value of the  $\delta^{15}N$  minimum appears to be approximately 2.8 per mil lower than the average value for the  $\delta^{15}N$  of euphotic zone PON. The difference between the minimum in  $\delta^{15}N$  and the average value would be determined in part by the fractionation factor associated with NO<sub>3</sub><sup>-</sup> uptake by phytoplankton. The consistent difference between the  $\delta^{15}N$  minimum and the average  $\delta^{15}N$  suggest that the fractionation factor for NO<sub>3</sub><sup>-</sup> uptake is similar for most of the stations surveyed. There are other factors which must be taken into account in order to assume actual fractionation factors. Examples are the rate of turbulent mixing and the depth at which degradation occurs more rapidly than autotrophic nitrogen assimilation.

While there is a general vertical pattern for the  $\delta^{15}N$  of PON from ring to ring, there also appear to be specific regional differences in the coherence and amplitude of that pattern. Implicit thus far in the analysis of the present data have been two assumptions: first, that horizontal processes are not significant in determining the vertical profiles for the  $\delta^{15}N$  of PON; second, that the systems examined are in a near steady state condition. The profiles for Ring 81-D appear to be very noisy, showing large variations between each depth interval sampled. Similarly, the profiles for PON and C/N ratio do not show maxima or minima, respectively, associated with the top of nitracline. There is evidence that near-surface Slope Water from outside the ring was transported directly into the core region of the ring (Joyce *et al.*, 1984). If the Slope Water carried PON with a distinct  $\delta^{15}N$  value the observed pattern may be explained if the two water masses had not mixed completely with one another. Similarly, departures from the general pattern at the edges of a ring may be due to the interleaving of waters across the ring boundary. Non-steady state conditions caused by horizontal advection may also disrupt what appears to be the typical vertical pattern for the  $\delta^{15}N$  of PON.

Another difference between rings is in the strength of the features themselves. In Ring 82-H, the  $\delta^{15}N$  minimum is not as well defined as in the other rings. A more uniform vertical profile for the  $\delta^{15}N$  of PON seems to be associated with more oligotrophic conditions. An extreme case of this is found for station KN097 813.01. The top of the nitracline must have been at a depth greater than 160 m for this station. The  $\delta^{15}$ N of PON for this station varied by no more than 1 per mil. Data for station KN093 501.15 demonstrate that this is not a feature common to the Sargasso Sea. Instead, this station has a vertical pattern for the  $\delta^{15}N$  of PON similar to stations in Rings 82-B and 82-E. It has been suggested that station KN093 501.15 was made in the remnant of cold-core ring (O. Brown, pers. comm.). In any case, these differences in the strength of the vertical pattern may be due, in part, to the influence of nitrogen dynamics on the composition of the PON. It has been observed that a greater percentage of the PON is made up of detrital material under oligotrophic conditions (Holligan et al., 1984). If detrital material is relatively refractory compared to the living component of the PON, a large background of detritus mixed evenly throughout the euphotic zone would tend to damp out much of the vertical structure observed for more eutrophic regimes. The higher C/N ratios for station KN097 813.01 and for those in Ring 82-II support this hypothesis.

In conclusion, the observed vertical patterns for the  $\delta^{15}N$  of PON, the concentration of PON, NO<sub>3</sub><sup>-</sup> concentration, and C/N ratio can be explained by current paradigms regarding the vertical fluxes of nitrogen into and out of the euphotic zone. Inter-ring differences in the coherence and magnitude of the generalized pattern suggest differences in the nitrogen dynamics of rings of various ages and histories. Further work is needed, however, to understand all the structure found in the vertical profiles for the  $\delta^{15}N$  of PON.

Acknowledgments. We thank J. Nevins, J. Montoya, and C. Adler for assistance in collecting and analyzing samples. This work was carried out as part of the Gulf Stream Warm Core Rings Program. It was supported by N.S.F. grant OCE 80-22990 and dissertation improvement award OCE 83-14013.

#### REFERENCES

Altabet, M. A. and J. J. McCarthy. 1985. Temporal and spatial variations in the natural abundance of <sup>15</sup>N in PON from a warm-core ring. Deep-Sea Res., 32, 755-772.

- Altabet, M. A., A. R. Robinson and L. J. Walstad. 1986. A model for the vertical flux of nitrogen in the upper-ocean: Simulating the alteration of isotopic ratios. J. Mar. Res., 44, 203-225.
- Cline, J. D. and I. R. Kaplan. 1975. Isotopic fractionation of dissolved nitrate during denitrification in the Eastern Tropical North Pacific Ocean. Mar. Chem., 3, 271–299.
- Cullen, J. J. and R. W. Eppley. 1981. Chlorophyll maximum layers of the Southern California Bight and possible mechanisms of their formation and maintenance. Oceanol. Acta, 4, 23-32.
- Deuser W. and E. Ross. 1980. Seasonal change in the flux of organic carbon to the deep Sargasso Sea. Nature, 283, 364–365.
- Dugdale, R. C. and J. J. Goering. 1967. Uptake of new and regenerated forms of nitrogen in primary productivity. Limnol. Oceanogr., 12, 196-206.
- Eppley, R. W. and B. J. Peterson. 1979. Particulate organic matter flux and planktonic new production in the deep ocean. Nature, 282, 677–680.
- Eppley, R. W., E. H. Renger and P. R. Betzer. 1983. The residence time of particulate organic carbon in the surface layer of the ocean. Deep-Sea Res., 30, 311-323.
- Eppley, R. W., E. H. Renger and W. G. Harrison. 1979. Nitrate and phytoplankton production in southern California coastal waters. Limnol. Oceanogr., 24, 483–494.
- Eppley, R. W., E. H. Renger, E. L. Venrick and M. M. Mullin. 1973. A study of plankton dynamics and nutrient cycling in the central gyre of the North Pacific Ocean. Limnol. Oceanogr., 18, 534-551.
- Fox, M. F., P. F. Bates and D. R. Kester. 1983. Nutrient data for warm-core ring 81-D from R/V Atlantis II cruise 110. University of Rhode Island, Graduate School of Oceanography, Technical Report 83-3, Narragansett, RI.

— 1984a. Nutrient data for warm-core ring 82-B from R/V Knorr cruise 93. University of Rhode Island, Graduate School of Oceanography, Technical Report 84-1, Narragansett, RI.

- ----- 1984b. Nutrient data for warm-core ring 82-B from R/V Knorr cruise 95. University of Rhode Island, Graduate School of Oceanography, Technical Report 84-2, Narragansett, RI.
- 1984c. Nutrient data for warm-core rings 82-B and 82-E from R/V Knorr cruise 97. University of Rhode Island, Graduate School of Oceanography, Technical Report 84-3, Narragansett, RI.
- —— 1984d. Nutrient data for warm-core ring 82-H from R/V Knorr cruise 98. University of Rhode Island, Graduate School of Oceanography, Technical Report 84-4, Narragansett, RI.
- Hoering, T. 1955. Variations in the nitrogen-15 abundance in naturally occurring substances. Science, 122, 1233-1234.
- Hoering, T. and H. T. Ford. 1960. The isotope effect in the fixation of nitrogen by *Azotobacter*. J. Amer. Chem. Soc., 82, 376-378.
- Holligan, P. M., R. P. Harris, R. C. Newell, D. S. Harbour, R. N. Head, E. A. S. Linley, M. I. Lucas, P. R. G. Tranter and C. M. Weekley. 1984. Vertical distribution and partitioning of organic carbon in mixed, frontal, and stratified waters of the English Channel. Mar. Ecol. Prog. Ser., 14, 111-127.
- Joyce, T., R. Backus, K. Baker, P. Blackwelder, O. Brown, T. Cowles, R. Evans, G. Fryxell, D. Mountain, D. Olson, R. Schlitz, R. Schmitt, P. Smith, R. Smith and P. Wiebe. 1984. Rapid evolution of a Gulf Stream warm-core ring. Nature, 308, 837–840.
- McCarthy, J. J. and M. A. Altabet. 1984. Patchiness in nutrient supply: Implications for phytoplankton ecology, *in* Trophic Interactions within Aquatic Ecosystems, D. G. Meyers and J. R. Strickler, eds., Westview Press, Washington, DC.
- Nevins, J. L., M. A. Altabet and J. J. McCarthy. 1985. Nitrogen isotope ratio analysis of small samples: Sample preparation and calibration. Anal. Chem., 57, 2143–2145.

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- Saino, T. and A. Hattori. 1980. <sup>15</sup>N natural abundance in oceanic suspended particulate matter. Nature, 283, 752–754.
- Sweeney, R. E. and I. R. Kaplan. 1980. Natural abundances of <sup>15</sup>N as a source indicator for near-shore marine sedimentary and dissolved nitrogen. Mar. Chem., 9, 81–94.
- Wada, E. 1980. Nitrogen isotope fractionation and its significance in biogeochemical processes in marine environments, *in* Isotope Marine Chemistry, E. D. Goldberg, Y. Horibe and K. Saruhashi, eds., Uchida Rokakuho Publishing Co. Ltd., Tokyo, 375–398.
- Wada, E. and A. Hattori. 1978. Nitrogen isotope effects in the assimilation of inorganic nitrogenous compounds by marine diatoms. Geomicrobiol. J., 1, 85-101.