Vol. 65: 35–61, 1990 | MARINE ECOLOGY PROGRESS SERIES
Mar. Ecol. Prog. Ser. | Published July 19

# Natural abundance of $^{15}N$ in particulate nitrogen and zooplankton in the Chesapeake Bay

**J. P. Montoya[1], S. G. Horrigan[2], J. J. McCarthy[1]**

[1] Museum of Comparative Zoology, Harvard University, Cambridge, Massachusetts 02138, USA
[2] Marine Sciences Research Center, SUNY-Stony Brook, Stony Brook, New York 11794, USA

ABSTRACT: Samples of dissolved inorganic nitrogen (DIN), particulate nitrogen (PN), and several species of zooplankton were collected at a series of stations in the main channel of the Chesapeake Bay, USA, during cruises in spring and fall 1984. The spatial and temporal variation in the natural abundance of $^{15}N$ ($\delta^{15}N$) in each of these pools, in combination with measurements of the concentrations of DIN, PN, plant pigments, and the rates of biologically-mediated transformations of nitrogen, provide a number of insights into the dynamics of the nitrogen cycle in the Chesapeake Bay. During both spring and fall, $\delta^{15}N$ of surface layer PN showed no consistent Bay-wide pattern of distribution. Instead, the overall gradient of DIN concentrations along the axis of the Bay appears to be less important than local processes in determining the distribution of $^{15}N$ in PN. The relationship between $\delta^{15}N$ of PN and $\delta^{15}N$ of dissolved pools indicated that phytoplankton uptake was the dominant process acting on DIN in spring, but that microbially-mediated transformations of nitrogen dominated in fall. During both seasons, $\delta^{15}N$ of particulate and dissolved pools suggested that phytoplankton consume both $NO_3^-$ and $NH_4^+$ roughly in proportion to concentration. The $\delta^{15}N$ of the zooplankton species sampled generally increased with trophic level. The $\delta^{15}N$ of the copepod *Acartia tonsa* was higher than that of PN by 4.2 ± 2.3‰ ($\bar{x}$ ± SD) in spring and 3.3 ± 1.0 ‰ ($\bar{x}$ ± SD) in fall. Similarly, $\delta^{15}N$ of the ctenophore *Mnemiopsis leidyi* was higher than that of *A. tonsa* by 2.0 ± 2.6‰ ($\bar{x}$ ± SD) in spring and 3.3 ± 1.0‰ ($\bar{x}$ ± SD) in fall. A reversal of the usual relationship between *A. tonsa* and *M. leidyi* occurred near the southern end of the Bay during spring, where $\delta^{15}N$ of the copepod was greater than that of the ctenophore by as much as 4.9‰. In general, spatial variability of $\delta^{15}N$ of all 3 of these trophic levels (PN, copepods, and ctenophores) was greater in spring than in all, suggesting that phyto- and zooplankton have a greater direct influence on the estuarine nitrogen cycle during spring. A comparison of the 2 transects conducted on each cruise demonstrates that $\delta^{15}N$ of the PN and *A. tonsa*, but not that of *M. leidyi*, can change markedly on a time scale of roughly a week. Such changes clearly indicate that repeated sampling may be essential in studies of the natural abundance of $^{15}N$ in dynamic planktonic systems such as that in the Chesapeake Bay.

## INTRODUCTION

The natural abundance of $^{15}N$ has been used as an in situ tracer of the movement of nitrogen in a number of recent field studies (Heaton 1986, Owens 1987, Peterson & Fry 1987 all provide recent reviews of this topic). The utility of $^{15}N$ measurements in such studies arises from the small, but measurable, differences in $^{15}N$ content which are characteristic of different pools of nitrogen. In many situations, the $^{15}N$ isotopic signature provides a sensitive indicator of source/sink relationships between the pools, and simple linear mixing models may allow the quantification of the contribution of different sources to a single pool of nitrogen. Since samples for $^{15}N$ natural abundance measurements can be collected with relatively few manipulations, this approach can provide a useful counterpart to traditional studies of nitrogen transformations using bottle incubations with tracer-level additions of $^{15}N$-labelled substrates.

Although the 2 isotopes of nitrogen, $^{14}N$ and $^{15}N$, are nearly identical in their chemical behavior, they may differ slightly in the rate at which they undergo reaction. This phenomenon, called isotopic fractionation, is typical of reaction sequences in which a bond to a nitrogen atom is formed or broken as part of the rate-limiting step. Under such conditions, the heavy isotope generally reacts more slowly than the light isotope, leading to the formation of product which is slightly depleted in $^{15}N$ relative to the available substrate pool. The magnitude of this fractionation effect can be quan-


0171-8630/90/0065/0035/$ 03.00

tified as the ratio of the rate constants for reaction of the light ($^{14}k$) and heavy ($^{15}k$) isotopes:

$$\alpha = \frac{^{14}k}{^{15}k} \quad (1)$$

Since most fractionation effects are quite small, the per mil enrichment factor, which is equal to the instantaneous difference in $\delta^{15}N$ (see Eq. 4) between the available substrate and the product formed, is often used in place of $\alpha$:

$$\varepsilon = (\alpha - 1) \quad 1000 \quad (2)$$

In practice, the calculation for $\alpha$ or $\varepsilon$ requires a knowledge of the isotopic enrichment of the substrate and product pools, as well as the extent of the reaction. In field studies, where information on the mechanism and extent of a reaction may be difficult to obtain, the magnitude of the fractionation effect is often qualitatively estimated using the observed difference between the $\delta^{15}N$ values of the product and substrate pools for a reaction:

$$D = \delta^{15}N_{product} - \delta^{15}N_{substrate} \quad (3)$$

Although isotopic fractionation may complicate the use of simple mixing models in elucudating source-sink relationships among pools of nitrogen, the alteration of isotopic ratios by isotopic fractionation may be a useful indicator of the nature and extent of reactions occurring in the field. For example, Wada et al. (1975) have used the observed $\delta^{15}N$ of $NO_3^-$ in the ocean and estimates of the isotopic fractionation associated with denitrification to arrive at an estimate of the oceanic contribution to the global rate of denitrification. Similarly, Yoshida (1988) has used isotopic fractionation factors measured in the laboratory to argue that $N_2O$ is formed from $NO_2^-$ rather than directly from $NH_4^+$ during nitrification in the eastern tropical North Pacific.

A complex example of isotopic fractionation occurs in food webs. In the laboratory, animals reared and maintained on diets of known isotopic composition typically have a higher $\delta^{15}N$ than their food, though interspecific and individual differences in the $\delta^{15}N$ of animals raised on the same diet may be comparable to the difference between an animal and its food (DeNiro & Epstein 1981, Macko et al. 1982).

Nevertheless, studies in a variety of terrestrial and aquatic ecosystems, conducted largely within the last decade, have revealed a general pattern of increase in $\delta^{15}N$ with trophic level. For example, this pattern has been observed in copepods, euphausiids, chaetognaths, and fish from the Bering Sea and the North Pacific (Miyake & Wada 1967, Minagawa & Wada 1984); *Neocalanus robustior* and chaetognaths from the North Pacific Central Gyre and *Calanus pacificus* and chaetognaths from the Southern California Bight (Mullin et al. 1984); *Acartia tonsa* and 2 species of *Temora* from the Gulf of Mexico (Checkley & Entzeroth 1985); 2 species of benthic amphipods from the Gulf of Mexico (Macko et al. 1982); a variety of planktonic and benthic species from Georges Bank (Fry 1988); and a variety of intertidal invertebrates and fish from the coast of Japan (Minagawa & Wada 1984). The physiological bases of this trophic level effect are not well understood, but the net increase in $\delta^{15}N$ which accompanies the transfer of nitrogen between trophic levels appears to be relatively invariant. Minagawa & Wada (1984) have used data on the $\delta^{15}N$ of 29 animal species from a wide variety of terrestrial and aquatic habitats to estimate the mean trophic level effect to be $3.4 \pm 1.1$ ‰ ($\bar{x} \pm SD$). The apparent constancy of this biological concentration of $^{15}N$ suggests that the $\delta^{15}N$ of heterotrophs may be a useful indicator of average trophic level, if the $\delta^{15}N$ of the primary producers in an ecosystem is known. In practice, the $\delta^{15}N$ of the primary producers may not be an easily measured quantity, since differences in the form of inorganic nitrogen utillized and in the physiology of nitrogen uptake and assimilation may lead to differences in $\delta^{15}N$ between plant species. Such interspecific differences, as well as the spatial and temporal variations in the $\delta^{15}N$ of primary producers and heterotrophs, deserve further study.

The variety of biogeochemical processes which occur in estuaries and the generally high levels of dissolved nutrients and biomass which characterize most estuaries make them convenient sites for basic studies of the distribution of $^{15}N$ in aquatic ecosystems. The natural abundance of $^{15}N$ has been used in studies of the nitrogen cycle in a number of estuarine ecosystems. For example, Mariotti et al. (1984) studied the seasonal and spatial patterns of variation in the $\delta^{15}N$ of the dissolved and particulate pools of nitrogen in the Scheldt Estuary in Belgium and The Netherlands. In winter, the $\delta^{15}N$ of particulate nitrogen in the Scheldt is correlated with salinity, suggesting that $^{15}N$ content is a good indicator of the relative contributions of terrestrial and marine sources to the particulate nitrogen in the estuary. In summer, the distribution of $^{15}N$ in the dissolved pools ($NH_4^+$ and $NO_3^-$) changes dramatically in the middle portion of the estuary, reflecting the importance of the conversion of $NH_4^+$ to $NO_3^-$ by microbial nitrification. The $\delta^{15}N$ of the particulate nitrogen also shows large spatial variations during summer, with a pronounced maximum in the region of intense nitrification. Similarly, Owens (1985) has used the spatial variations of $\delta^{15}N$ in particulate nitrogen in the Tamar Estuary in Britain to infer the biological processes of importance in different parts of the estuary. In this system, the $\delta^{15}N$ of suspended particles is highest near the upper end of the estuary, in an area where the net nontidal movement of water promotes the retention of detritus and seston, generating a turbidity maximum. The high $\delta^{15}N$ of

particulate matter in the turbidity maximum probably results from isotopic fractionation during the degradation of organic matter. Downstream from the turbidity maximum, the $\delta^{15}N$ of particulate nitrogen proves to be a good index of the relative contribution of phytoplankton and detritus to the total pool of particulate nitrogen. More recently, Wada et al. (1987a) used the $\delta^{15}N$ of particulate nitrogen and sediments as indicators of the important transformations of nitrogen in the Otsuchi River in Japan, and to estimate the terrestrial contribution to sediments in different parts of Otsuchi Bay. The most extensive study to date of the $\delta^{15}N$ of particulate nitrogen has been conducted in the Delaware River and Bay (USA) by Cifuentes et al. (1988). In this system, the $\delta^{15}N$ of suspended particles shows pronounced seasonal changes driven by biological processes. For example, in early spring, low values of $\delta^{15}N$ (ca 5 ‰) in the middle portion of the estuary are associated with isotopic fractionation during phytoplankton uptake of $NH_4^+$. Later in spring, the $\delta^{15}N$ of suspended particles reaches a maximum of 18 ‰ as a result of the uptake of the isotopically enriched residual $NH_4^+$. Finally, in winter, the $\delta^{15}N$ of the suspended particles reflects the mixture of phytoplankton and detrital nitrogen in different parts of the estuary.

The nitrogen cycle in the Chesapeake Bay, USA, has been studied by a number of workers in recent years, and the gross spatial and temporal patterns of variation in the major reservoirs of nitrogen in the Bay have been described by Carpenter et al. (1969), McCarthy et al. (1975, 1977), and Taft et al. (1978). The high levels of biomass and dissolved inorganic nitrogen which characterize the Bay facilitate experimental studies of the transformation of nitrogen in the water column, and simplify the task of collecting material for isotopic analysis. During spring and fall 1984, samples of the major pools of dissolved inorganic nitrogen, particulate nitrogen, and the common zooplankton species were collected at a series of stations in the main channel of the Bay in conjunction with a field study of nitrogen transformations in the water column (Horrigan et al. 1990b). A suite of standard chemical analyses were performed at each station, and experimental measurements of a number of biologically mediated processes were conducted at a subset of these stations. In combination with these ancillary data, measurements of the isotopic composition of nitrogen can provide insights into the nature and relative importance of different pathways in the estuarine nitrogen cycle. The rate measurements and the implications of the natural abundance measurements of the dissolved pools of nitrogen have been discussed elsewhere (Horrigan et al. 1990a,b). In the following sections of this paper, the natural abundance of $^{15}N$ in the particulate nitrogen and zooplankton will be discussed in the context of these other findings.

## MATERIALS AND METHODS

Samples for this study were collected during cruises in spring (8 to 17 June) and fall (27 September to 5 October) 1984. The general cruise plan and station protocol have been described in detail by Horrigan et al. (1990a,b), but aspects relevant to this study are briefly described below.

During each cruise, samples were collected at a series of stations forming a transect along the main channel of the Bay from near Baltimore to the mouth of the Bay (Fig. 1). A main channel transect of the Bay was conducted at the start and end of each cruise to allow evaluation of short-term (within-cruise) as well as seasonal (between-cruise) changes. At each station, water samples were collected from above (bottle depth = 2 to 3 m) and below (bottle depth = 8 to 31 m) the pycnocline using a rosette equipped with 10 l Niskin bottles. Several bottles were filled at each depth, and their contents were combined to meet the sample requirements of the various experiments and analyses. In addition to salinity and temperature, the concentrations of $NO_2^-$, $NO_3^-$, $NH_4^+$, dissolved $O_2$, and phytoplankton pigments at each depth were routinely measured using standard methods (Horrigan et al. 1990b). In addition, a number of experiments were conducted to quantify the rates of various biological processes at a subset of these stations. These experiments are described in detail elsewhere (Horrigan et al. 1990b). All samples were collected during the day, and experiments were all conducted around local noon to minimize the possible influence of diurnal variations in plankton metabolism.

At most transect stations, samples of dissolved inorganic nitrogen (DIN), particulate nitrogen (PN), and zooplankton were collected for isotopic analysis. Methods for isotopic analysis of the dissolved pools of $NH_4^+$ and ($NO_3^-$ + $NO_2^-$) have been described elsewhere (Horrigan et al. 1990a). To isolate samples of whole PN ($PN_{whl}$), seawater was screened through 102 µm Nitex mesh to remove large zooplankton, then filtered under gentle vacuum (≤ 25 cm Hg vacuum) onto precombusted (440 °C for 20 to 30 min) 25 mm Whatman GF/F filters. Samples of the small size fraction of PN ($PN_{<10}$) were prepared by passing seawater through a second screen of 10 µm Nitex mesh before filtration onto GF/F filters. The filters containing the PN samples were then placed in plastic envelopes (RPS Plastine film envelopes), dried at 60 °C, and stored over desiccant for later isotopic analysis. At selected stations, the filtrate from each depth was collected and frozen for later isolation and isotopic analysis of the dissolved pools (Horrigan et al. 1990a). Although our methods allowed us to isolate the dissolved pools and zooplankton, our samples of bulk PN included detritus

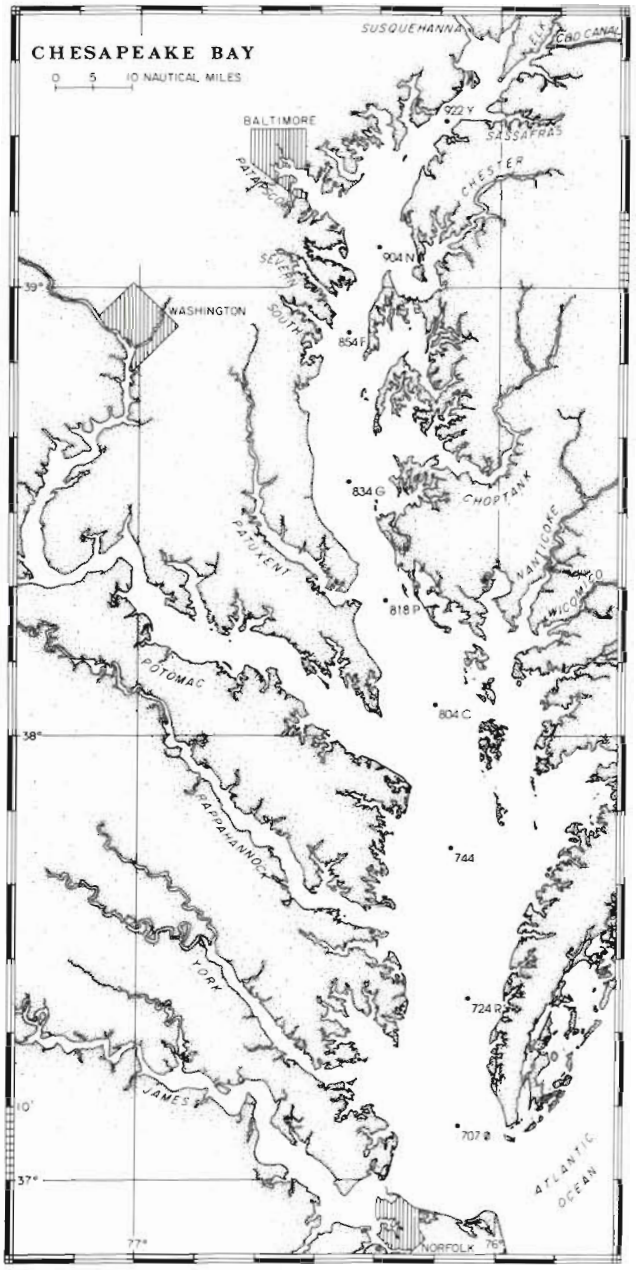


Fig 1 Location of experimental stations in the Chesapeake Bay, USA Samples were also collected at locations in the main channel between those marked, at stations separated by ca 5' of latitude. Station numbers are based on latitude for example, Stns 922 and 724 are located 9 22' and 7°24' north of the 30th parallel respectively

and a portion of the microbial and microzooplankton populations in addition to phytoplankton.

Zooplankton were collected using a 0.5 m diameter net fitted with a 220 µm mesh and a nonfiltering cod end Several vertical tows were carried out at each station, and the resulting samples were combined before sorting Large gelatinous zooplankton, where present, were removed immediately by gently passing the concentrated plankton sample through a coarse strainer Representative specimens were rinsed several times in filtered surface water, then placed on large (45 mm) precombusted GF/F filters in petri dishes, dried at 60°C, and stored in plastic envelopes over desiccant. All of these gelatinous zooplankton released large amounts of fluid which was absorbed by the filter as the sample dried. Samples of the ctenophore *Mnemiopsis leidyi* were obtained at most stations during both cruises. Specimens of another ctenophore species, *Beroe ovata*, and an unidentified scyphozoan medusa were obtained at a subset of these stations. Smaller zooplankton were sorted with a large bore pipette in the shipboard laboratory under dim light. The animals were gently transferred from the concentrated sample through 3 rinses in filtered Bay surface water, then placed on a precombusted 45 mm GF/C filter, dried at 60°C, and stored in a plastic envelope over desiccant. *Acartia tonsa* was the most common crustacean zooplankter during these cruises, and an attempt was made to obtain a sample of it at each station. Approximately 50 individual *A. tonsa* were needed to meet the mass requirements of the isotopic analysis. Samples of the larger copepod *Centropages typicus* were obtained at a number of stations; ca 20 individuals of this species were needed for isotopic analysis. In addition to the other zooplankton, chaetognaths were collected at several stations near the southern end of the Bay.

All samples were converted to $N_2$ gas for isotopic analysis using a Dumas combustion system, and the analyses were performed using a double inlet, dual collecter mass spectrometer (VG Micromass 602E). The sample preparation and analysis system was designed for handling relatively small samples (1 to 4 µmol N) and is described in detail by Nevins et al. (1985). The precision of the isotopic measurement varies with sample size, but is of the order of ± 0.15‰ (± SD) for replicate standards in the size range typical of the samples discussed here. Replicate analyses of natural samples were performed where possible, and provided an estimate of the precision of the entire sample collection and handling protocol.

All isotopic abundances will be presented using the $\delta^{15}N$ notation.

$$\delta^{15}N = \left(\frac{S}{R} - 1\right) \times 1000 \qquad (4)$$

where S and R represent the isotope ratios ($^{15}N/^{14}N$) in the sample and a reference compound, respectively. Atmospheric dinitrogen is isotopically homogeneous (Junk & Svec 1958, Mariotti 1983, 1984), and is commonly used as a reference compound. All analyses reported here were performed using a reference gas prepared from atmosphere (Nevins et al. 1985), and all

results are reported as per mil (‰) deviations from the isotopic composition of atmospheric dinitrogen. The notation used to represent the $\delta^{15}N$ of the pools of nitrogen sampled for this study is shown in Table 1. In general, '$\delta^{15}$' prefixed to a pool name denotes the $\delta^{15}N$

Table 1 Definition of symbols and abbreviations used in the text

| Symbol | Definition |
|---|---|
| $PN_{whl}$ | Whole particulate nitrogen (< 110 μm) |
| $PN_{<10}$ | Small size fraction of PN (< 10 μm) |
| $\delta^{15}NH_4^+$ | $\delta^{15}N$ of $NH_4^+$ |
| $\delta^{15}(NO_3^- + NO_2^-)$ | $\delta^{15}N$ of the combined pool of ($NO_3^- + NO_2^-$) |
| $\overline{\delta^{15}DIN}$ | Weighted mean of $\delta^{15}NH_4^+$ and $\delta^{15}(NO_3^- + NO_2^-)$ |
| $\delta^{15}PN_{whl}$ | $\delta^{15}N$ of PN < 110 μm |
| $\delta^{15}PN_{<10}$ | $\delta^{15}N$ of PN < 10 μm |
| $\delta^{15}N_{Acartia}$ | $\delta^{15}N$ of *Acartia tonsa* (copepod) |
| $\delta^{15}N_{Mnemiopsis}$ | $\delta^{15}N$ of *Mnemiopsis leidyi* (ctenophore) |
| $\delta^{15}N_{scyphozoa}$ | $\delta^{15}N$ of scyphozoan medusae |
| $\delta^{15}N_{Beroe}$ | $\delta^{15}N$ of *Beroe ovata* (ctenophore) |
| $\delta^{15}N_{Centropages}$ | $\delta^{15}N$ of *Centropages typicus* (copepod) |
| $\delta^{15}N_{chaetognath}$ | $\delta^{15}N$ of chaetognaths |
| $\Delta^{15}(PN_{whl} - NH_4^+)$ | $\delta^{15}PN_{whl} - \delta^{15}NH_4^+$ |
| $\Delta^{15}(PN_{<10} - NH_4^+)$ | $\delta^{15}PN_{<10} - \delta^{15}NH_4^+$ |
| $\Delta^{15}(PN_{whl} - NO_3^-)$ | $\delta^{15}PN_{whl} - \delta^{15}(NO_3^- + NO_2^-)$ |
| $\Delta^{15}(PN_{<10} - NO_3^-)$ | $\delta^{15}PN_{<10} - \delta^{15}(NO_3^- + NO_2^-)$ |
| $\Delta^{15}(cop - PN_{whl})$ | $\delta^{15}N_{Acartia} - \delta^{15}PN_{whl}$ |
| $\Delta^{15}(cop - PN_{<10})$ | $\delta^{15}N_{Acartia} - \delta^{15}PN_{<10}$ |
| $\Delta^{15}(cte - PN_{whl})$ | $\delta^{15}N_{Mnemiopsis} - \delta^{15}PN_{whl}$ |
| $\Delta^{15}(cte - PN_{<10})$ | $\delta^{15}N_{Mnemiopsis} - \delta^{15}PN_{<10}$ |
| $\Delta^{15}(cte - cop)$ | $\delta^{15}N_{Mnemiopsis} - \delta^{15}N_{Acartia}$ |

of a given pool of nitrogen, and '$\Delta^{15}(X-Y)$' represents the difference $\delta^{15}X - \delta^{15}Y$, where X and Y are different pools of nitrogen. The different zooplankton species analyzed are indicated by subscripted generic names. Finally, $\overline{\delta^{15}DIN}$ represents the concentration-weighted mean of $\delta^{15}NH_4^+$ and $\delta^{15}(NO_3^- + NO_2^-)$:

$$\overline{\delta^{15}DIN} = \frac{\{[NH_4^+] \times \delta^{15}NH_4^+\} + \{([NO_3^-] + [NO_2^-]) \times \delta^{15}(NO_3^- + NO_2^-)\}}{[NH_4^+] + [NO_3^-] + [NO_2^-]} \quad (5)$$

## RESULTS

### Spring cruise

#### General

The spatial distribution of the major dissolved species of nitrogen during this study has been described in detail elsewhere (Horrigan et al. 1990b), and will be presented here only in summary form. During the spring cruise, the surface waters of the Bay contained high concentrations of $NO_3^-$ and variable, but generally low, concentrations of $NO_2^-$ and $NH_4^+$. The concentration of $NO_3^-$ was highest at the north end of the Bay (up to 60 μmol $l^{-1}$) and decreased to values below 1 μmol $l^{-1}$ near the mouth of the Bay, showing a significant correlation with salinity ($r = -0.960$, $n = 46$, $p < 0.01$). In much of the Bay, $NO_3^-$ concentrations departed from a conservative mixing line, indicating consumption of $NO_3^-$ (Horrigan et al. 1990a).

The surface concentration of $NO_2^-$ varied between 0.6 and 1.0 μmol $l^{-1}$ in the northern part of the Bay, and rose to a maximum of ca 2.0 μmol $l^{-1}$ at Stn 853C. For the Bay as a whole, $NO_2^-$ concentrations showed a significant correlation with salinity ($r = -0.703$, $n = 38$, $p < 0.01$), with the greatest departures from a linear relationship occurring at the northern end of the Bay. Surface layer concentrations of $NH_4^+$ were as high as 4 μmol $l^{-1}$ at the northern end of the Bay and generally decreased toward the south. $NH_4^+$ concentrations were significantly correlated with salinity in the surface layer ($r = -0.555$, $n = 19$, $p < 0.01$).

Below the pycnocline, the concentration of $NH_4^+$ was high throughout the Bay (up to 30 μmol $l^{-1}$), and the concentration of $NO_2^-$ (up to 4 μmol $l^{-1}$) was elevated in the vicinity of Stn 834G. Nitrate concentrations were highest at the northern end of the Bay (up to 25 μmol $l^{-1}$), and varied between the limit of detection and ca 10 μmol $l^{-1}$ in the rest of the Bay. The concentration of $O_2$ was low (≤ 10 % saturated) below the pycnocline in the northern half of the Bay (Stns 804C to 904N) throughout this cruise, though the spatial extent of the low-$O_2$ water mass was somewhat greater on the second transect (Horrigan et al. 1990b).

#### Variability between replicate samples

All the data available from this cruise, including those from stations that were not part of the main-channel transects, were used to evaluate the magnitude of the variation between independent isotopic analyses of replicate samples collected at the same time and place (Table 2). In most cases, replicate samples were analyzed within a span of several weeks, though some replicate analyses were separated by several months to a year. The number of replicates processed varied between stations and pools of nitrogen. For example, at least 3 subsamples of *Mnemiopsis leidyi* from 12 stations, and duplicate samples from 19 other stations were analyzed. In contrast, there was sufficient material for duplicate analyses of *Acartia tonsa* at only 7 stations, and for more than 3 analyses at only 2 stations.

Table 2. Reproducibility of isotopic measurements performed on samples collected at the same time and place during the spring cruise but analyzed separately. The range and sample standard deviation (SD) were calculated for each station where replicate samples were obtained. Mean range and mean SD represent the unweighted average of these quantities over the N stations

| Sample | Mean range | Mean SD | n |
|---|---|---|---|
| $\delta^{15}PN_{whl}$ | 0.5 ‰ | 0.3 ‰ | 12 |
| $\delta^{15}N_{Acartia}$ | 1.0 ‰ | 0.6 ‰ | 9 |
| $\delta^{15}N_{Mnemiopsis}$ | 1.2 ‰ | 0.6 ‰ | 31 |
| $\delta^{15}N_{scyphozoa}$ | 1.2 ‰ | 0.8 ‰ | 6 |

For each set of samples from a single station, the range and standard deviation of the replicate analyses were used to estimate the composite variation associated with natural variability in the population, sample collection, and isotopic analysis. The mean value of each of these quantities was then calculated using all the data from this cruise. The average range in $\delta^{15}N$ spanned by replicate analyses of whole PN from 12 stations was 0.5‰ (mean SD = 0.3‰). The variability associated with zooplankton was somewhat greater, with average ranges of 1.0‰ for 9 sets of *Acartia tonsa* replicates, 1.2‰ for 31 sets of *Mnemiopsis leidyi* replicates, and 1.2‰ for 6 sets of scyphozoan medusae.

## First transect (8 to 14 June)

The first, downbay transect of this cruise was the most detailed of the 4 transects, lasting 7 d. A number of stations were sampled more than once, usually on successive days. Results from this transect are shown in Fig. 2 and summarized in the upper panel of Fig. 6.

**$\delta^{15}$PN measurements.** During this transect, the $\delta^{15}N$ of the whole PN ($\delta^{15}PN_{whl}$) in the surface layer of the Bay varied between 6.2 and 10.5‰, with little obvious trend along the north-south axis of the Bay (Fig. 2B). Repeated visits to several stations during this transect yielded values of $\delta^{15}PN_{whl}$ which typically differed by less than 1‰ (e.g. Stns 818P, 744A, and 724R), though samples from 2 visits to Stn 804C (10 and 12 June) differed by 1.5‰. The $\delta^{15}N$ of surface PN was less variable than the $\delta^{15}N$ of the major DIN pools (Fig. 6). In general, the $^{15}N$ content of the PN was lower than that of the DIN (Fig. 2A, B, Table 3), but at 2 stations (918P and 904N), the $\delta^{15}N$ of the PN was markedly higher than that of the $NH_4^+$ and ($NO_3^-$ + $NO_2^-$) pools. For the transect as a whole, $\delta^{15}PN_{whl}$ was not signifi-

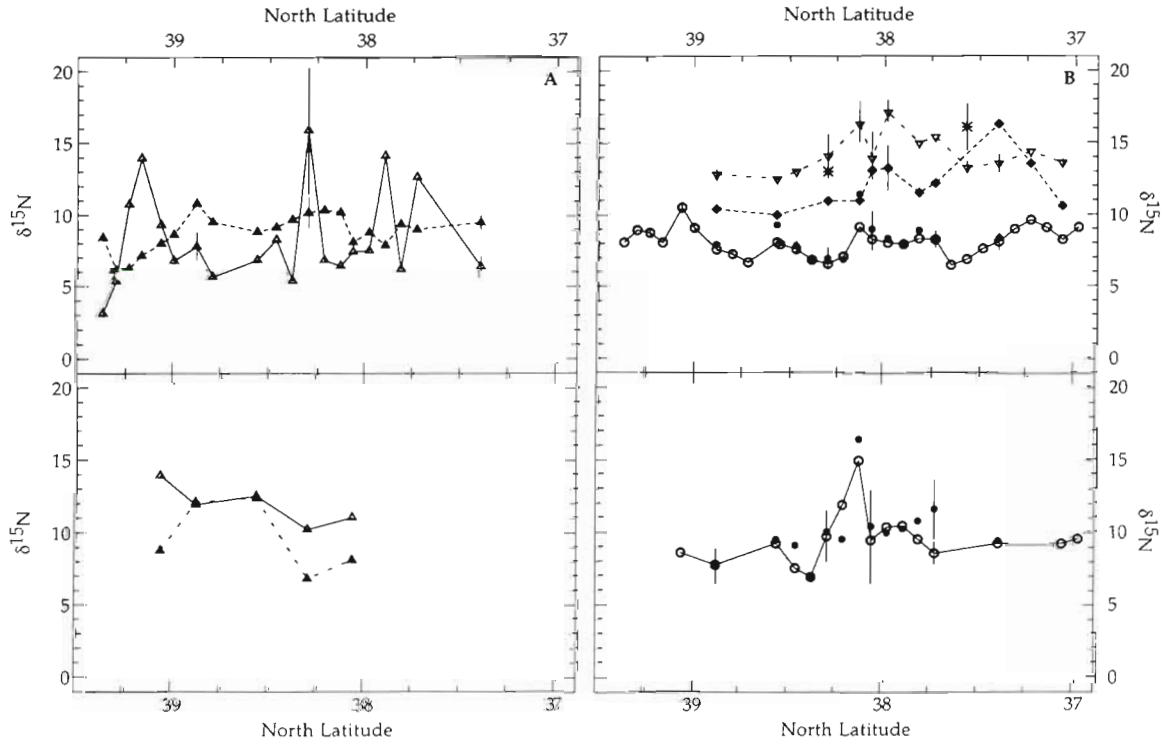


Fig. 2. $\delta^{15}N$ of the particulate and dissolved pools of nitrogen during the first transect of the spring cruise (8 to 14 June). Upper portion of each panel: data from the surface layer; lower portion: data from below the pycnocline. At stations where replicate samples were obtained, the mean $\delta^{15}N$ is plotted, with vertical bars representing the range of values observed. (A) $\delta^{15}N$ of $NH_4^+$ (△) and ($NO_3^-$ + $NO_2^-$) (▲); (B) $\delta^{15}N$ of $PN_{whl}$ (○), $PN_{<10}$ (●), *Acartia tonsa* (◆), *Mneniopsis leidyi* (▽), and scyphozoans (✱)

Table 3. Summary of differences in $\delta^{15}N$ between particulate and dissolved pools of nitrogen during the spring cruise. Differences were calculated for samples collected at the same station, then averaged over an entire transect

| $\Delta^{15}N$ (by transect) | Depth | Mean (‰) | SD | Minimum (‰) | Maximum (‰) | n |
|---|---|---|---|---|---|---|
| First transect | | | | | | |
| $\Delta^{15}(PN_{whl} - NH_4^+)$ | Surf | −0.6 | 4.2 | −13.3 | 4.9 | 21 |
| | Deep | −4.0 | 1.2 | −5.4 | −2.3 | 5 |
| $\Delta^{15}(PN_{whl} - NO_3^-)$ | Surf | −0.8 | 1.9 | −4.4 | 2.8 | 21 |
| | Deep | −1.7 | 2.2 | −4.4 | 1.1 | 5 |
| $\Delta^{15}(PN_{<10} - NH_4^+)$ | Surf | −1.1 | 4.8 | −14.0 | 5.0 | 14 |
| | Deep | −2.8 | 1.4 | −4.2 | −0.8 | 4 |
| $\Delta^{15}(PN_{<10} - NO_3^-)$ | Surf | −1.4 | 1.7 | −5.1 | 1.2 | 14 |
| | Deep | −1.2 | 3.0 | −4.4 | 2.6 | 4 |
| Second transect | | | | | | |
| $\delta^{15}(PN_{whl} - NH_4^+)$ | Surf | −2.8 | 2.5 | −5.8 | 1.1 | 7 |
| $\delta^{15}(PN_{whl} - NO_3^-)$ | Surf | −0.4 | 1.8 | −2.5 | 2.0 | 10 |
| $\delta^{15}(PN_{<10} - NH_4^+)$ | Surf | −2.1 | 2.6 | −4.7 | 1.2 | 4 |
| $\delta^{15}(PN_{<10} - NO_3^-)$ | Surf | −1.1 | 1.4 | −2.4 | 1.3 | 6 |

cantly correlated with either $\delta^{15}NH_4^+$ or $\delta^{15}(NO_3^- + NO_2^-)$. In contrast, $\delta^{15}PN_{whl}$ was significantly correlated with $\overline{\delta^{15}DIN}$, the concentration-weighted mean $\delta^{15}N$ of the $NH_4^+$ and $(NO_3^- + NO_2^-)$ pools. These correlations are summarized in Table 4.

The $\delta^{15}N$ of the small size fraction of PN ($\delta^{15}PN_{<10}$) in the surface layer was highly correlated with that of the whole PN (Table 4). The mean difference between size fractions was 0.38‰, which was smaller than the mean range for replicate measurements of $\delta^{15}PN_{whl}$. Like the whole PN, the small size fraction showed no significant correlation with the $\delta^{15}N$ of either form of dissolved inorganic nitrogen, but was significantly correlated with $\overline{\delta^{15}DIN}$ (Table 4).

The $\delta^{15}N$ of whole PN collected below the pycnocline varied between 6.4 and 14.9‰ (Fig. 2B). At most stations on this transect, the deep values of $\delta^{15}PN_{whl}$ were similar to or greater than the $\delta^{15}N$ of PN collected in the surface layer. The greatest differences between the surface and deep layers occurred between Stns 818P and 744R, where the values of $\delta^{15}PN_{whl}$ below the pycnocline were as much as 5.8‰ greater than the corresponding surface values. The surface and deep values of $\delta^{15}PN_{whl}$ were not significantly correlated on this transect. In addition, the difference in $\delta^{15}PN_{whl}$ showed no significant association with the variation in DIN concentration, salinity, or density across the pycnocline. At the 5 stations at which the 3 pools were sampled, $\delta^{15}PN_{whl}$ was always lower than $\delta^{15}NH_4^+$, and usually lower than $\delta^{15}(NO_3^- + NO_2^-)$ (Table 3). The $\delta^{15}N$ of the deep PN showed no significant correlation with the $\delta^{15}N$ of either pool of DIN or their weighted mean (Table 5), though the small number of stations available for this comparison makes it unlikely that any but the strongest correlations would be significant.

Below the pycnocline, the $\delta^{15}N$ of the small size fraction of PN varied between 6.9 and 16.3‰ (Fig. 2B), and was highly correlated with $\delta^{15}PN_{whl}$ (Table 5). A comparison of the 2 size fractions (paired-samples t-test) showed no significant difference in $\delta^{15}N$ between them ($p > 0.05$). Like the $\delta^{15}N$ of whole PN, $\delta^{15}PN_{<10}$ showed no significant correlation with the $\delta^{15}N$ of the deep pools of DIN. The deep values of $\delta^{15}PN_{<10}$ were always similar to or higher than their corresponding surface values, with differences as great as 5.1‰ (Stn 808D, Fig. 2B). Despite these differences, the surface and deep values of $\delta^{15}PN_{<10}$ were significantly correlated on this transect ($r = 0.767$, $n = 15$, $p < 0.01$). The difference between surface and deep values of $\delta^{15}PN_{<10}$ was not significantly correlated with the difference in salinity, density, or DIN concentration between layers.

**$\delta^{15}N$ of zooplankton.** The $\delta^{15}N$ of the copepod *Acartia tonsa*, $\delta^{15}N_{Acartia}$, ranged between 10.0 and 16.3‰ on this transect, and was greater than the $\delta^{15}N$ of the PN at all stations where both pools were sampled (Fig. 2B). The mean difference in $\delta^{15}N$ between the copepods and the whole PN, $\Delta^{15}N(cop - PN_{whl})$, was 4.0‰ (Table 6). The $\delta^{15}N$ of *Acartia* increased from the north end of the transect to Stn 724R, and was highly correlated with salinity in this portion of the Bay (Table 4). At Stn 724R, $\delta^{15}N_{Acartia}$ exceeded the $\delta^{15}N$ of the ctenophore *Mnemiopsis leidyi*. South of this station, $\delta^{15}N_{Acartia}$ decreased to values around 10‰ (Fig. 2B). For the entire transect, the correlation between $\delta^{15}N_{Acartia}$ and salinity was not significant. $\delta^{15}N_{Acartia}$ was also not significantly correlated with either $\delta^{15}PN_{whl}$ or $\delta^{15}PN_{<10}$ (Table 4).

The $\delta^{15}N$ of the ctenophore *Mnemiopsis leidyi* increased from 12.5‰ at the northern end of the Bay to

Table 4. Correlation matrix for the $\delta^{15}N$ of the surface PN and zooplankton samples from the first transect of the spring cruise. Number of observations is shown in parentheses beneath each correlation coefficient

| | $\delta^{15}PN_{whl}$ (‰) | $\delta^{15}PN_{<10}$ (‰) | $\delta^{15}N_{Acartia}$ (‰) | $\delta^{15}N_{Mnemiopsis}$ (‰) |
|---|---|---|---|---|
| Salinity | 0.164 (35) | 0.218 (18) | 0.370[a] (12) | 0.033[b] (15) |
| $[NO_3^-]$ | −0.006 (35) | −0.138 (17) | −0.479 (11) | −0.092 (14) |
| $[NO_2^-]$ | −0.235 (26) | −0.131 (16) | −0.069 (12) | 0.115 (15) |
| $[NH_4^+]$ | 0.676 (7) | −0.156 (6) | 0.045 (6) | 0.997•• (6) |
| $\delta^{15}(NO_3^- + NO_2^-)$ | −0.429 (21) | −0.156 (14) | −0.037 (9) | −0.130 (9) |
| $\delta^{15}NH_4^+$ | −0.185 (21) | −0.431 (14) | −0.293 (9) | −0.115 (9) |
| $\overline{\delta^{15}DIN}$ | −0.513• (20) | −0.558• (13) | −0.355 (8) | −0.267 (8) |
| $\delta^{15}PN_{whl}$ | 1.000 (35) | 0.776•• (18) | 0.361 (12) | 0.268 (15) |
| $\delta^{15}PN_{<10}$ | | 1.000 (18) | −0.083 (10) | 0.373 (11) |
| $\delta^{15}N_{Acartia}$ | | | 1.000 (12) | 0.111 (12) |
| $\delta^{15}N_{Mnemiopsis}$ | | | | 1.000 (15) |

• $p < 0.05$; •• $p < 0.01$

[a] $\delta^{15}N_{Acartia}$ is significantly correlated with salinity if the 2 southernmost stations are eliminated ($r = 0.871$, $n = 10$, $p < 0.01$)

[b] $\delta^{15}N_{Mnemiopsis}$ is significantly correlated with salinity if stations south of 734U (inclusive) are eliminated ($r = 0.777$, $n = 10$, $p < 0.01$)

17.9‰ at Stn 759A, then declined to values of 13 to 14‰ at the southern end of the Bay (Fig. 2B). For stations north of 734U, $\delta^{15}N_{Mnemiopsis}$ was significantly correlated with salinity (Table 4), but not with $\delta^{15}PN_{whl}$, $\delta^{15}PN_{<10}$, or $\delta^{15}N_{Acartia}$. For the whole transect, the difference between the $\delta^{15}N$ of the ctenophores and the whole PN, $\Delta^{15}N(cte - PN_{whl})$, ranged from 4.3 to 9.1‰, with a mean of 6.3‰ (Table 6). $\delta^{15}N_{Mnemiopsis}$ was not significantly correlated with either $\delta^{15}PN_{whl}$ or $\delta^{15}PN_{<10}$ (Table 4). The difference in $\delta^{15}N$ between the ctenophores and the copepods, $\Delta^{15}N(cte - cop)$, was quite variable. In the part of the Bay extending north from Stn 744A, the $\delta^{15}N$ of the ctenophores was distinctly higher than that of the copepods ($\bar{x}$ = 3.1‰, Table 6). At Stn 724R, $\delta^{15}N_{Mnemiopsis}$ reached a local minimum of 13.0‰, which was 3.3‰ lower than $\delta^{15}N_{Acartia}$ (Fig. 2B). Further south, $\delta^{15}N_{Mnemipsis}$ returned to values around 14‰, and was once again greater than $\delta^{15}N_{Acartia}$. Over the entire transect, the mean value of $\Delta^{15}N(cte - cop)$ was 2.4‰ (Table 6).

Samples of large scyphozoan medusae were collected at 2 stations on this transect (818P and 734U). The $\delta^{15}N$ of these samples ($\delta^{15}N_{scyphozoa}$) varied between 12.5 and 17.7‰, spanning a range similar to that of $\delta^{15}N_{Mnemiopsis}$. At Stn 818P, the mean values of $\delta^{15}N_{Mnemiopsis}$ ($\bar{x} \pm SD = 13.8 \pm 0.8$‰, $n = 4$) and $\delta^{15}N_{scyphozoa}$ ($\bar{x} \pm SD = 13.0 \pm 0.8$‰, $n = 3$) were quite similar. In contrast, $\delta^{15}N_{scyphozoa}$ was higher than $\delta^{15}N_{Mnemiopsis}$ at Stn 734U.

### Second transect (15 to 17 June)

The second, northward transect of the Bay was completed in only 3 d. Results from this transect are shown in Fig. 3. The lower panel of Fig. 4 summarizes the range and variability in the $\delta^{15}N$ of different pools of nitrogen for the Bay as a whole.

**$\delta^{15}$PN measurements.** During this transect, surface values of $\delta^{15}PN_{whl}$ ranged between 6.4 and 9.6‰, with a mean of 8.2 ± 0.9‰ ($\bar{x} \pm SD$, $n = 12$), which was not significantly different from the mean on the first tran-

Table 5. Correlation matrix for the $\delta^{15}N$ of the deep PN from the spring cruise. Number of observations is shown in parentheses beneath each correlation coefficient

| | Downbay Transect | | Upbay Transect | |
|---|---|---|---|---|
| | $\delta^{15}N_{whl}$ (‰) | $\delta^{15}PN_{<10}$ (‰) | $\delta^{15}PN_{whl}$ (‰) | $\delta^{15}PN_{<10}$ (‰) |
| Salinity | −0.026 (19) | −0.123 (16) | 0.542 (11) | 0.689 (8) |
| $[NO_3^-]$ | −0.132 (9) | 0.391 (6) | 0.110 (11) | 0.041 (8) |
| $[NO_2^-]$ | −0.008 (18) | −0.014 (15) | −0.451 (11) | −0.249 (8) |
| $[NH_4^+]$ | 0.050 (7) | 0.082 (6) | −0.696• (10) | −0.700 (7) |
| $\delta^{15}(NO_3^- + NO_2^-)$ | 0.451 (5) | −0.111 (4) | nd[a] | nd |
| $\delta^{15}NH_4^+$ | 0.569 (5) | −0.048 (4) | nd | nd |
| $\overline{\delta^{15}DIN}$ | 0.533 (5) | 0.111 (4) | nd | nd |
| $\delta^{15}PN_{whl}$ | 1.000 (19) | 0.801•• (16) | 1.000 (11) | 0.849•• (8) |
| $\delta^{15}PN_{<10}$ | | 1.000 (16) | | 1.000 (8) |

• $p < 0.05$; •• $p < 0.01$
nd: no $\delta^{15}DIN$ data are available for the second transect

Table 6. Summary of differences in $\delta^{15}N$ between different pools of planktonic nitrogen during the spring cruise. Differences were calculated for samples collected at the same station and time, then averaged over an entire transect

| $\Delta^{15}N$ | Mean (‰) | SD | Minimum (‰) | Maximum (‰) | n |
|---|---|---|---|---|---|
| First transect | | | | | |
| $\Delta^{15}(cop - PN_{whl})$ | 4.0 | 1.7 | 1.8 | 7.6 | 12 |
| $\Delta^{15}(cop - PN_{<10})$ | 3.5 | 2.4 | −0.5 | 8.0 | 10 |
| $\Delta^{15}(cte - PN_{whl})$ | 6.3 | 1.4 | 4.3 | 9.1 | 15 |
| $\Delta^{15}(cte - PN_{<10})$ | 5.9 | 1.6 | 3.2 | 8.7 | 11 |
| $\Delta^{15}(cte - cop)$[a] | 2.4 | 2.2 | −3.3 | 5.3 | 12 |
| | (3.1) | (1.2) | (0.8) | (5.3) | (9) |
| Second transect | | | | | |
| $\Delta^{15}(cop - PN_{whl})$ | 4.5 | 3.5 | 1.2 | 10.4 | 6 |
| $\Delta^{15}(cop - PN_{<10})$ | 6.3 | 3.1 | 3.0 | 10.3 | 4 |
| $\Delta^{15}(cte - PN_{whl})$ | 5.7 | 1.9 | 3.4 | 9.7 | 9 |
| $\Delta^{15}(cte - PN_{<10})$ | 6.4 | 1.9 | 4.9 | 10.0 | 6 |
| $\Delta^{15}(cte - cop)$[a] | 1.1 | 3.3 | −4.9 | 4.6 | 6 |
| | (2.2) | (1.7) | (−0.2) | (4.6) | (5) |

[a] Values calculated excluding stations south of 744A shown in parentheses

sect. South of Stn 845F, there was little difference between the values of $\delta^{15}PN_{whl}$ measured on the 2 transects. At Stns 845F and 853C, however, the value of $\delta^{15}PN_{whl}$ was ca 2‰ higher on the second transect. In contrast, at Stns 904N and 922Y, $\delta^{15}PN_{whl}$ was ca 1.5‰ lower on the second transect. At all stations for which data on the $\delta^{15}N$ of DIN are available, $\delta^{15}PN_{whl}$ was lower than either $\delta^{15}NH_4^+$ or $\delta^{15}(NO_3^- + NO_2^-)$ (Fig. 3, Table 3). The $\delta^{15}N$ of whole PN was not significantly correlated with $\delta^{15}NH_4^+$, $\delta^{15}(NO_3^- + NO_2^-)$, or $\overline{\delta^{15}DIN}$ on this transect (Table 7).

The surface values of $\delta^{15}PN_{<10}$ ranged from 6.9 to

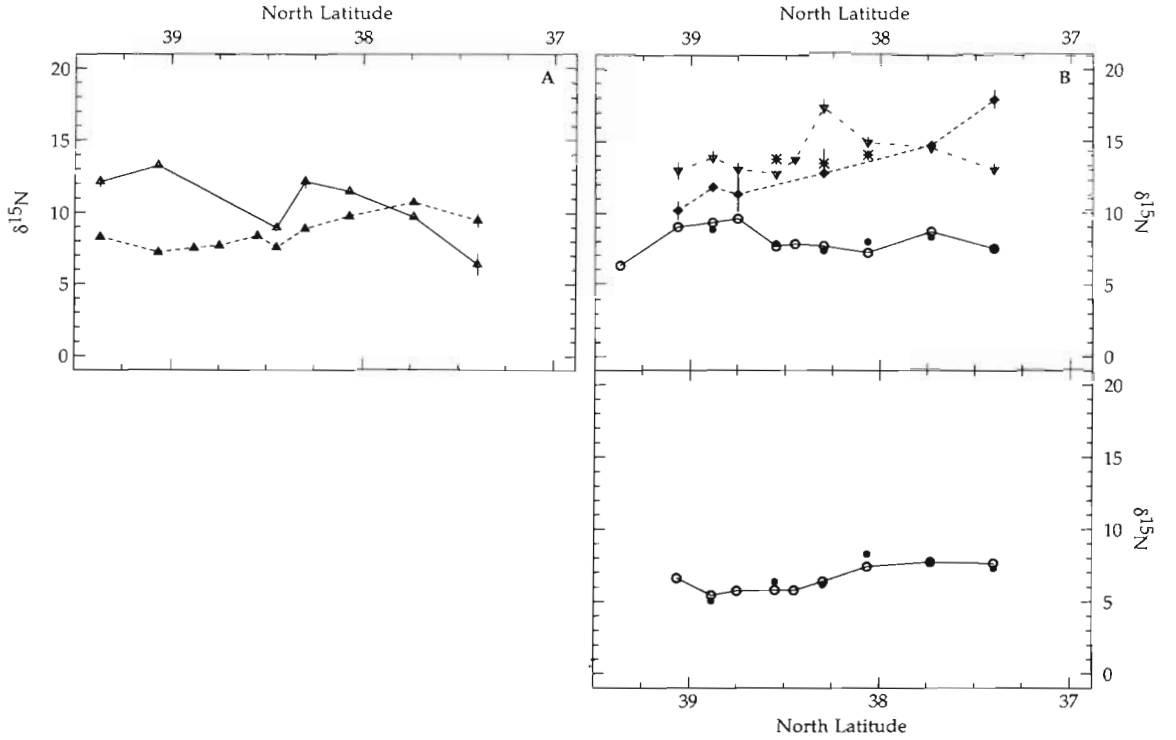


Fig. 3. $\delta^{15}N$ of the particulate and dissolved pools of nitrogen during the second transect of the spring cruise (15 to 17 June). Upper portion of each panel: data from the surface layer; lower portion: data from below the pycnocline (no data available for (A)). At stations where replicate samples were obtained, the mean $\delta^{15}$ N is plotted, with vertical bars representing the range of values observed. (A) $\delta^{15}N$ of $NH_4^+$ (△) and ($NO_3^-$ + $NO_2^-$) (▲); (B) $\delta^{15}N$ of $PN_{whl}$ (○), $PN_{<10}$ (●), *Acartia tonsa* (◆), *Mnemiopsis leidyi* (▽), and scyphozoans (✳)

8.9 ‰ (Fig. 3B), and were not significantly correlated with $\delta^{15}PN_{whl}$ (Table 7). A paired samples t-test showed no significant difference between the $\delta^{15}N$ of the 2 size fractions. The $\delta^{15}N$ of the small size fraction of PN was not significantly associated with the $\delta^{15}N$ of either dissolved pool of nitrogen, or their weighted mean ($\delta^{15}DIN$).

The $\delta^{15}N$ of whole PN collected below the pycnocline on this transect ranged from 5.4 to 7.7 ‰, which was appreciably lower than the range of values obtained from the first transect (compare Figs. 2B and 3B). The greatest difference between surface and deep values of $\delta^{15}PN_{whl}$ occurred between Stns 818P and 904N; $\delta^{15}PN_{whl}$ was lower below the pycnocline, with a maximum difference of ca 3.9 ‰ at Stns 845F and 853C. The cross-pycnocline differences in $\delta^{15}PN_{whl}$ showed no significant association with the differences in salinity, density, [$NO_3^-$], or [$NH_4^+$]. In contrast, the cross-pycnocline differences in $\delta^{15}PN_{whl}$ and [$NO_3^-$] were significantly correlated ($r = 0.877$, $n = 9$, $p < 0.01$). Below the pycnocline, the values of $\delta^{15}PN_{<10}$ were very similar to $\delta^{15}PN_{whl}$, with a maximum difference between the 2 size fractions of 0.8 ‰; a paired samples t-test ($df = 5$) revealed no significant difference between size fractions. The difference between surface and deep values of $\delta^{15}PN_{<10}$ showed no correlation with the difference between surface and deep salinities, densities, or with the difference in concentration of $NO_2^-$ or $NH_4^+$ across the pycnocline. The difference in $\delta^{15}PN_{<10}$ across the pycnocline was significantly correlated with the difference in [$NO_3^-$] ($r = 0.827$, $n = 7$, $p < 0.05$). The $\delta^{15}N$ of the dissolved pools of nitrogen below the pycnocline was not measured on this transect.

**$\delta^{15}N$ of zooplankton.** The values of $\delta^{15}N_{Acartia}$ from this transect (range: 10.2 to 18.6 ‰) are higher than those from the first transect at all stations sampled on both occasions. The difference between transects ranged from 1.4 ‰ at Stn 853C (sampled on 9 and 17 June) to 2.5 ‰ at Stn 744A (sampled on 13 and 15 June). $\delta^{15}N_{Acartia}$ differed by 1.6 ‰ between 2 visits to Stn 724R separated by only 1 d (14 and 15 June). $\delta^{15}N_{Acartia}$ was highly correlated with the salinity of the surface water on this transect (Table 7), following the pattern found on the earlier transect. $\delta^{15}N_{Acartia}$ showed a significant negative correlation with $\delta^{15}PN_{whl}$, but not $\delta^{15}PN_{<10}$ (Table 7). The difference between $\delta^{15}N_{Acartia}$ and both $\delta^{15}PN_{whl}$ and $\delta^{15}PN_{<10}$ was somewhat greater on this transect than during the first transect (Table 6).

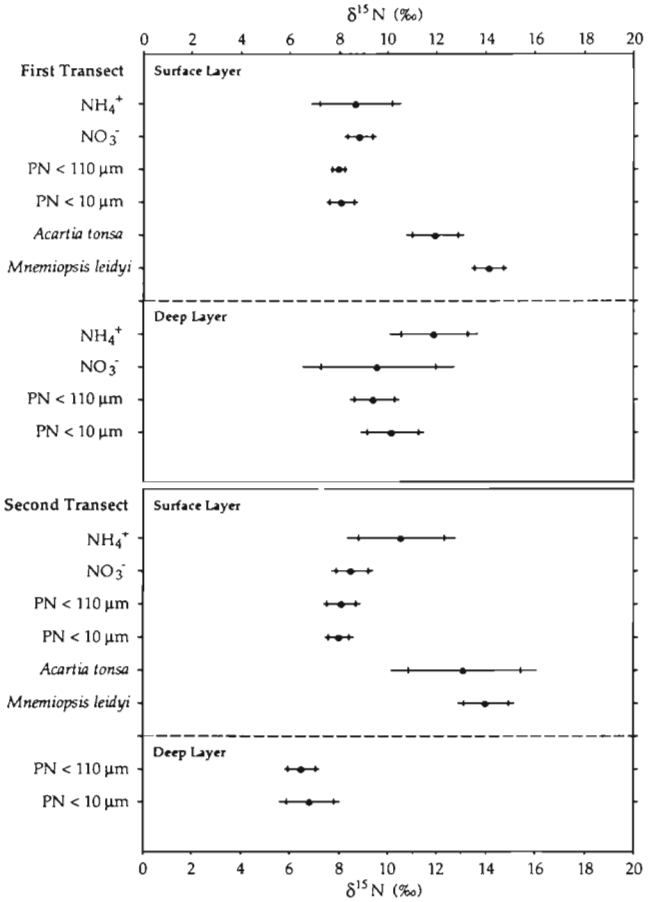


Fig. 4. Summary plots of $\delta^{15}N$ of the major dissolved and planktonic pools of nitrogen during the spring cruise. (•) Mean $\delta^{15}N$ of each pool of nitrogen. The ends of the horizontal line through each circle and the vertical cross-bars show the 95 % and 90 % confidence intervals about the mean, respectively. Upper panel summarizes the data collected during the first transect (8 to 14 June); lower panel summarizes data from the second transect (15 to 17 June) of the cruise

The $\delta^{15}N$ of the ctenophores did not vary systematically between transects. The range of values on the second transect (12.8 to 18.0 ‰) was similar to that from the first one, though the location of the highest values was somewhat further north at the end of the cruise (Stn 818P). The largest difference between transects was an increase of 3.5 ‰ for samples taken at Stn 818P on 11 and 16 June. $\delta^{15}N_{Mnemiopsis}$ was not significantly correlated with $\delta^{15}PN_{whl}$, $\delta^{15}PN_{<10}$, or $\delta^{15}N_{Acartia}$ (Table 7).

Samples of scyphozoan medusae were obtained at 3 stations on this transect. At Stn 833F, $\delta^{15}N_{scyphozoa}$ was 1.0 ‰ greater than $\delta^{15}N_{Mnemiopsis}$, but $\delta^{15}N_{scyphozoa}$ was lower than $\delta^{15}N_{Mnemiopsis}$ at the other 2 stations sampled (818P and 804C). At Stn 818P, the mean $\delta^{15}N$ of the medusae collected on the 2 transects differed by only 0.5 ‰.

## Fall cruise

### General

The fall cruise was characterized by much lower concentrations of $NO_3^-$ throughout the Bay. In the surface layer, the concentration of $NO_3^-$ reached 45 µmol $l^{-1}$ in the northern end of the Bay, but fell rapidly toward the south, reaching values undetectable with normal colorimetric methods by Stn 843 and remaining low throughout the rest of the Bay. Surface concentrations of $NO_2^-$ as high as 2.5 µmol $l^{-1}$ occurred in the northern part of the Bay, but concentrations approached the limit of detection at the mouth of the Bay. Ammonium was the major component of the surface DIN pool in much of the Bay, with concentrations as high as 20 µmol $l^{-1}$. The southern end of the Bay, however, was characterized by low concentrations of all 3 major forms of DIN. On this cruise, the 2 transects of the Bay (27 to 29 Sep and 3 to 5 Oct) were separated by several days, during which an intense storm (on 1 Oct) contributed to vertical mixing of the Bay. Following the storm, the concentrations of $NH_4^+$ and $NO_2^-$ in the surface layer were higher throughout much of the Bay, and the rates of a variety of microbially mediated transformations of nitrogen increased markedly (Horrigan et al. 1990a,b).

The distribution of $NO_3^-$ and $NH_4^+$ below the pycnocline was generally similar to that in the surface layer. In contrast, the concentration of $NO_2^-$ below the pycnocline was highest near Stn 843, where the deep concentrations were higher than the surface values. Elsewhere, $NO_2^-$ concentrations tended to be lower below the pycnocline than above. During the first transect of the Bay (27 to 29 Sep), $O_2$ concentrations as low as 2 to 4 % of saturation occurred in the deep water at 2 northern stations (Stns 853C and 904N). In contrast, during the second transect of the Bay (3 to 5 Oct), $O_2$ concentrations below the pycnocline never dropped below 56 % of saturation.

### Variability between replicate samples

The variability associated with sample collection and analysis was quantified using the mean range and standard deviation associated with replicate analyses (Table 8). For this cruise, the variability of replicate measurements of $\delta^{15}PN_{whl}$ was very similar to that for the spring cruise. In contrast to the spring cruise, the variability among replicates of the more abundant zooplankton species was lower than for the PN. The mean range associated with 21 sets of measurements of $\delta^{15}N_{Acartia}$ was only 0.3 ‰ (mean SD = 0.2 ‰), while the mean range for $\delta^{15}N_{Mnemiopsis}$ was 0.4 ‰ (mean SD = 0.2 ‰, n = 28). Samples of another ctenophore species,

Table 7. Correlation matrix for the $\delta^{15}N$ of the surface PN and zooplankton samples from the second transect of the spring cruise. Number of observations is shown in parentheses beneath each correlation coefficient

| | $\delta^{15}PN_{whl}$ (‰) | $\delta^{15}PN_{<10}$ (‰) | $\delta^{15}N_{Acartia}$ (‰) | $\delta^{15}N_{Mnemiopsis}$ (‰) |
|---|---|---|---|---|
| Salinity | 0.128 (12) | −0.783* (8) | 0.718* (8) | −0.120 (11) |
| $[NO_3^-]$ | −0.207 (12) | 0.776* (8) | −0.845* (8) | 0.096 (11) |
| $[NO_2^-]$ | 0.261 (12) | 0.851** (8) | −0.553 (8) | 0.276 (11) |
| $[NH_4^+]$ | −0.462 (12) | 0.144 (8) | −0.671 (8) | 0.427 (11) |
| $\delta^{15}(NO_3^- + NO_2^-)$ | −0.319 (10) | −0.255 (6) | 0.763 (6) | 0.369 (9) |
| $\delta^{15}NH_4^+$ | 0.062 (7) | 0.047 (4) | −0.983* (4) | 0.398 (6) |
| $\overline{\delta^{15}DIN}$ | −0.005 (7) | 0.981 (4) | 0.640 (4) | 0.333 (6) |
| $\delta^{15}PN_{whl}$ | 1.000 (12) | 0.415 (8) | −0.732* (8) | −0.317 (11) |
| $\delta^{15}PN_{<10}$ | | 1.000 (8) | −0.501 (6) | 0.004 (8) |
| $\delta^{15}N_{Acartia}$ | | | 1.000 (8) | −0.087 (8) |
| $\delta^{15}N_{Mnemiopsis}$ | | | | 1.000 (11) |

* $p < 0.05$; ** $p < 0.01$

Table 8. Reproducibility of isotopic measurements performed on samples collected at the same time and place during the fall cruise but analyzed separately. Range and sample standard deviation (SD) were calculated for each station where replicate samples were obtained. Mean range and mean SD represent the unweighted average of these quantities over the n stations

| Sample | Mean range | Mean SD | n |
|---|---|---|---|
| $\delta^{15}PN_{whl}$ | 0.4 ‰ | 0.3 ‰ | 32 |
| $\delta^{15}N_{Acartia}$ | 0.3 ‰ | 0.2 ‰ | 21 |
| $\delta^{15}N_{Mnemiopsis}$ | 0.4 ‰ | 0.2 ‰ | 28 |
| $\delta^{15}N_{scyphozoa}$ | 0.4 ‰ | 0.3 ‰ | 2 |
| $\delta^{15}N_{Centropages}$ | 0.4 ‰ | 0.3 ‰ | 3 |
| $\delta^{15}N_{Beroe}$ | 0.6 ‰ | 0.3 ‰ | 5 |

*Beroe ovata*, were collected at several stations; the mean range associated with replicate samples of this zooplankter was 0.6 ‰ (mean SD = 0.3 ‰, n = 5).

### First transect (27 to 28 September)

The first, southbound transect of the Bay was completed in only 2 d. Results from this transect are shown in Fig. 5. The variation in $\delta^{15}N$ of the different pools of nitrogen is summarized in the upper panel of Fig. 7.

**$\delta^{15}$PN measurements.** On this transect, the $\delta^{15}N$ of whole PN in the surface layer showed no significant association with salinity or DIN concentrations. The highest values of $\delta^{15}PN_{whl}$ (8.7 to 9.6 ‰) occurred between Stns 818P and 833F. The lowest value of this transect was 5.0 ‰, from the southernmost station sampled (724R). With the exception of this station, $\delta^{15}PN_{whl}$ showed relatively little spatial variation on this transect, with a range of only 2.5 ‰ (7.1 to 9.6 ‰, Fig. 5B). At all stations sampled, $\delta^{15}PN_{whl}$ was markedly lower than $\delta^{15}NH_4^+$ and similar to or lower than $\delta^{15}(NO_3^- + NO_2^-)$ (Fig. 5, Table 9). North of Stn 813R, the mean value of $\Delta^{15}(PN_{whl} - NH_4^+)$ was −7.1 ‰ (SD = 0.9 ‰, n = 8); from Stn 813R southward, the mean difference was −2.9 ‰ (SD = 0.6 ‰, n = 4). In the southern part of the Bay, $\delta^{15}PN_{whl}$ appeared to vary closely with $\delta^{15}NH_4^+$ (Fig 5) but $\delta^{15}PN_{whl}$ showed no significant correlation with either $\delta^{15}NH_4^+$ or $\delta^{15}(NO_3^- + NO_2^-)$ (Table 10). In contrast, $\delta^{15}PN_{whl}$ was significantly correlated with $\overline{\delta^{15}DIN}$, the concentration-weighted mean $\delta^{15}N$ of the dissolved pools (Table 10).

The $\delta^{15}N$ of the small size fraction of surface PN

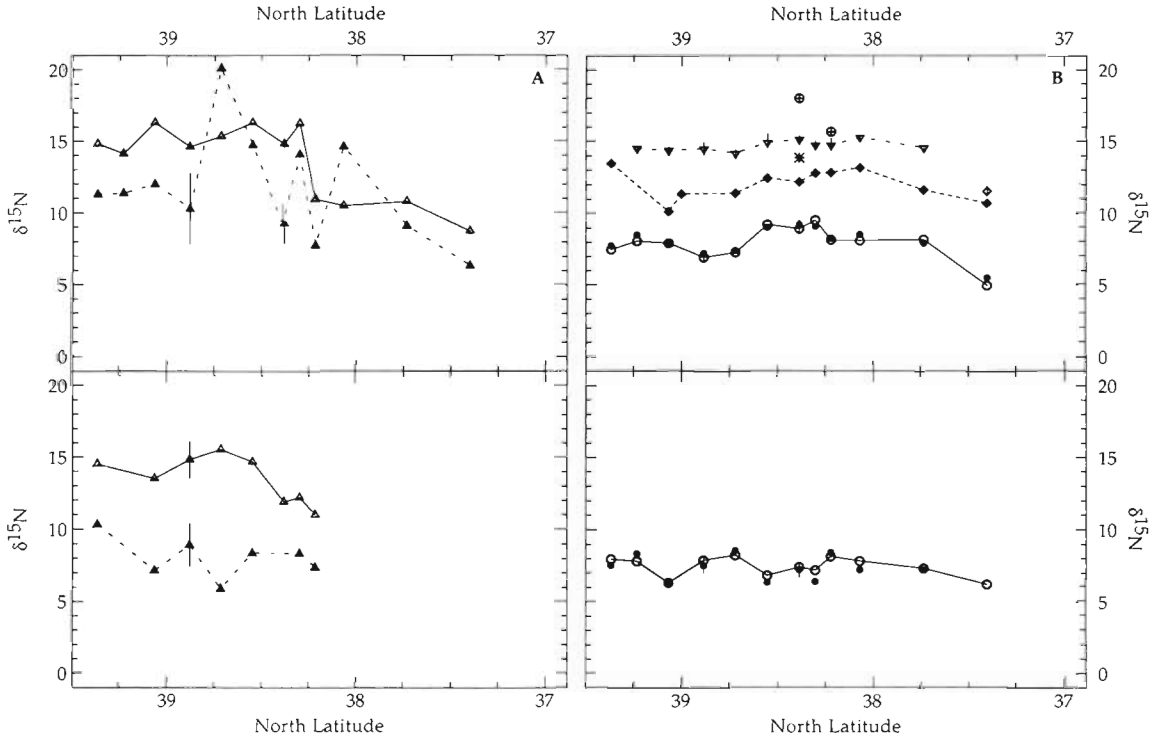


Fig. 5. $\delta^{15}N$ of the particulate and dissolved pools of nitrogen during the first transect of the fall cruise (27 to 28 September). Upper portion of each panel: data from the surface layer; lower portion: data from below the pycnocline. At stations where replicate samples were obtained, the mean $\delta^{15}N$ is plotted, with vertical bars representing the range of values observed. (A) $\delta^{15}N$ of $NH_4^+$ (△) and ($NO_3^-$ + $NO_2^-$) (▲); (B) $\delta^{15}N$ of $PN_{whl}$ (○), $PN_{<10}$ (●), *Acartia tonsa* (◆), *Mnemiopsis leidyi* (▽), *Beroe ovata* (⊕), *Centropages typicus* (◇), and scyphozoans (∗)

Table 9. Summary of differences in $\delta^{15}N$ between particulate and dissolved pools of nitrogen during the fall cruise. Differences were calculated for samples collected at the same station, then averaged over an entire transect

| $\Delta^{15}N$ (by transect) | Depth | Mean (‰) | SD | Minimum (‰) | Maximum (‰) | n |
|---|---|---|---|---|---|---|
| First transect | | | | | | |
| $\Delta^{15}(PN_{whl} - NH_4^+)$ | Surf | −5.9 | 2.1 | −8.4 | −2.4 | 14 |
| | Deep | −6.1 | 1.7 | −8.2 | −2.8 | 9 |
| $\Delta^{15}(PN_{whl} - NO_3^-)$ | Surf | −3.6 | 3.5 | −12.8 | 0.8 | 14 |
| | Deep | −0.6 | 1.7 | −2.5 | 2.4 | 8 |
| $\Delta^{15}(PN_{<10} - NH_4^+)$ | Surf | −5.7 | 2.2 | −8.3 | −1.9 | 14 |
| | Deep | −6.4 | 1.8 | −8.3 | −2.5 | 9 |
| $\Delta^{15}(PN_{<10} - NH_3^-)$ | Surf | −3.4 | 3.6 | −12.7 | 1.0 | 14 |
| | Deep | −0.9 | 1.9 | −2.8 | 2.7 | 8 |
| Second transect | | | | | | |
| $\Delta^{15}(PN_{whl} - NH_4^+)$ | Surf | −9.2 | 3.1 | −12.4 | −1.5 | 10 |
| | Deep | −7.0 | 2.1 | −9.5 | −3.0 | 8 |
| $\Delta^{15}(PN_{whl} - NO_3^-)$ | Surf | −1.8 | 2.2 | −6.1 | 0.7 | 10 |
| | Deep | 0.5 | 1.8 | −2.7 | 2.8 | 8 |
| $\Delta^{15}(PN_{<10} - NH_4^+)$ | Surf | −9.1 | 3.4 | −12.8 | −1.5 | 10 |
| | Deep | −6.9 | 1.9 | −9.3 | −3.5 | 8 |
| $\Delta^{15}(PN_{<10} - NO_3^-)$ | Surf | −1.8 | 2.1 | −5.6 | 0.7 | 10 |
| | Deep | 0.6 | 2.1 | −2.8 | 3.3 | 8 |

Table 10. Correlation matrix for the $\delta^{15}N$ of the surface PN and zooplankton samples from the first transect of the fall cruise. Number of observations is shown in parentheses beneath each correlation coefficient

| | $\delta^{15}PN_{whl}$ (‰) | $\delta^{15}PN_{<10}$ (‰) | $\delta^{15}N_{Acartia}$ (‰) | $\delta^{15}N_{Mnemiopsis}$ (‰) |
|---|---|---|---|---|
| Salinity | −0.245 (14) | −0.289 (14) | −0.431 (11) | 0.398 (12) |
| $[NO_3^-]$ | −0.133 (14) | −0.088 (14) | 0.274 (11) | −0.441 (12) |
| $[NO_2^-]$ | 0.269 (14) | 0.290 (14) | 0.116 (11) | −0.132 (12) |
| $[NH_4^+]$ | −0.258 (14) | −0.255 (14) | −0.578 (11) | −0.574 (12) |
| $\delta^{15}(NO_3^- + NO_2^-)$ | 0.295 (14) | 0.254 (14) | 0.102 (11) | −0.214 (12) |
| $\delta^{15}NH_4^+$ | 0.509 (14) | 0.476 (14) | 0.034 (11) | −0.258 (12) |
| $\overline{\delta^{15}DIN}$ | 0.556• (14) | 0.504 (14) | −0.002 (11) | −0.173 (12) |
| $\delta^{15}PN_{whl}$ | 1.000 (14) | 0.975•• (14) | 0.463 (11) | 0.621• (12) |
| $\delta^{15}PN_{<10}$ | | 1.000 (14) | 0.501 (11) | 0.748•• (12) |
| $\delta^{15}N_{Acartia}$ | | | 1.000 (11) | 0.691• (9) |
| $\delta^{15}N_{Mnemiopsis}$ | | | | 1.000 (12) |

• $p < 0.05$; •• $p < 0.01$

varied between 5.5 and 9.6‰ (Fig 5B). The mean difference between size fractions was 0.2‰, which was similar in magnitude to the variability in $\delta^{15}PN_{whl}$ (Table 8). Like the whole PN, the small size fraction showed no significant association with the $\delta^{15}N$ of either the $NH_4^+$ or $(NO_3^- + NO_2^-)$ pools (Table 10). Although the correlation between $\delta^{15}PN_{<10}$ and $\overline{\delta^{15}DIN}$ was stronger, it was consistent with the null hypothesis of no significant association between the 2 variables.

The $\delta^{15}N$ of whole PN collected below the pycnocline ranged from 6.2 to 8.2‰, and showed little correlation with the surface values of $\delta^{15}PN_{whl}$ ($r = 0.14$, $n = 15$). The difference between surface and deep values of $\delta^{15}PN_{whl}$ showed no consistent spatial pattern: the difference between layers (deep − surface) ranged from −2.4 (Stn 833F) to 1.3‰ (Stn 724R), with a mean for the whole transect of 0.2‰. The largest differences occurred between Stn 818P and 833F, where a local minimum in the deep $\delta^{15}PN_{whl}$ co-occurred with a local maximum in the surface values of $\delta^{15}PN_{whl}$. The mean difference between surface and deep values of $\delta^{15}PN_{whl}$ was not significantly associated with the difference in salinity, density, or $[NO_3^-]$ across the pycnocline. In contrast, the correlations between the cross-pycnocline difference in $\delta^{15}PN_{whl}$ and the difference in $[NH_4^+]$ ($r = -0.726$, $n = 15$, $p < 0.01$) and $[NO_2^-]$ ($r = 0.526$, $n = 15$, $p < 0.05$) were both significant. Below the pycnocline, $\delta^{15}PN_{whl}$ was significantly correlated with salinity, but showed no significant association with the concentration or $\delta^{15}N$ of DIN (Table 11). At all 8 stations where $\delta^{15}NH_4^+$ was measured, $\delta^{15}PN_{whl}$ was lower than $\delta^{15}NH_4^+$ (Figs. 5 and 7).

In the deep layer, $\delta^{15}PN_{<10}$ varied between 6.3 and 8.6‰, and showed a strong correlation with $\delta^{15}PN_{whl}$ (Table 11). The mean difference between size fractions was not significantly different from zero (paired samples t-test, $p > 0.05$). In the deep layer, $\delta^{15}PN_{<10}$ was not significantly correlated with any of the chemical or physical variables measured. The difference between surface and deep values of $\delta^{15}PN_{<10}$ was significantly correlated with the difference between surface and deep concentrations of $NO_2^-$ ($r = 0.592$, $n = 14$, $p < 0.05$) and $NH_4^+$ ($r = -0.643$, $n = 14$, $p < 0.05$).

**$\delta^{15}N$ of zooplankton.** The $^{15}N$ enrichment of the copepod *Acartia tonsa* was consistently greater than that of the PN on this transect, with an average difference between $\delta^{15}N_{Acartia}$ and $\delta^{15}PN_{whl}$ of 4.0‰ (Table 12). The highest value of $\delta^{15}N_{Acartia}$ from this transect

Table 11 Correlation matrix for the $\delta^{15}N$ of the deep PN from the fall cruise. Number of observations is shown in parentheses beneath each correlation coefficient

| | Downbay transect | | Upbay transect | |
|---|---|---|---|---|
| | $\delta^{15}N_{whl}$ (‰) | $\delta^{15}PN_{<10}$ (‰) | $\delta^{15}PN_{whl}$ (‰) | $\delta^{15}PN_{<10}$ (‰) |
| Salinity | −0.573• | −0.428 | −0.824•• | −0.780•• |
| | (14) | (13) | (10) | (10) |
| $[NO_3^-]$ | 0.286 | 0.258 | 0.768•• | 0.506 |
| | (14) | (13) | (10) | (10) |
| $[NO_2^-]$ | 0.394 | 0.191 | 0.594 | 0.732• |
| | (14) | (13) | (10) | (10) |
| $[NH_4^+]$ | −0.192 | −0.339 | 0.198 | 0.443 |
| | (14) | (13) | (10) | (10) |
| $\delta^{15}(NO_3^- + NO_2^-)$ | 0.028 | −0.085 | 0.392 | 0.187 |
| | (8) | (8) | (8) | (8) |
| $\delta^{15}NH_4^+$ | 0.159 | 0.228 | 0.542 | 0.641 |
| | (9) | (9) | (8) | (8) |
| $\overline{\delta^{15}DIN}$ | −0.156 | −0.023 | 0.517 | 0.608 |
| | (8) | (4) | (8) | (8) |
| $\delta^{15}PN_{whl}$ | 1.000 | 0.836•• | 1.000 | 0.913•• |
| | (14) | (13) | (10) | (10) |
| $\delta^{15}PN_{<10}$ | | 1.000 | | 1.000 |
| | | (13) | | (10) |

• $p<0.05$; •• $p<0.01$

Table 12. Summary of differences in $\delta^{15}N$ between different pools of planktonic nitrogen during the fall cruise. Differences were calculated for samples collected at the same station and time, then averaged over an entire transect

| $\Delta^{15}N$ | Mean (‰) | SD | Minimum (‰) | Maximum (‰) | n |
|---|---|---|---|---|---|
| First transect | | | | | |
| $\Delta^{15}$(cop − $PN_{whl}$) | 4.0 | 1.2 | 2.2 | 6.0 | 11 |
| $\Delta^{15}$(cop − $PN_{<10}$) | 3.9 | 1.1 | 2.1 | 5.7 | 11 |
| $\Delta^{15}$(cte − $PN_{whl}$) | 6.5 | 0.7 | 5.2 | 7.7 | 12 |
| $\Delta^{15}$(cte − $PN_{<10}$) | 6.4 | 0.6 | 5.6 | 7.4 | 12 |
| $\Delta^{15}$(cte − cop) | 2.7 | 0.7 | 1.9 | 4.2 | 9 |
| Second transect | | | | | |
| $\Delta^{15}$(cop − $PN_{whl}$) | 3.6 | 0.5 | 0.8 | 4.8 | 8 |
| $\Delta^{15}$(cop − $PN_{<10}$) | 3.2 | 1.4 | 0.8 | 4.5 | 8 |
| $\Delta^{15}$(cte − $PN_{whl}$) | 7.3 | 2.1 | 3.0 | 9.5 | 7 |
| $\Delta^{15}$(cte − $PN_{<10}$) | 7.6 | 1.2 | 5.9 | 9.6 | 7 |
| $\Delta^{15}$(cte − cop) | 4.5 | 1.5 | 3.2 | 6.9 | 5 |

(13.5 ‰) occurred at the northernmost station sampled (922Y). The minimum value of $\delta^{15}N_{Acartia}$ (10.2 ‰) occurred at Stn 904N, with generally higher values to the south of this station forming a broad local maximum of around 13 ‰ in the mid-Bay. At the southern end of the transect, $\delta^{15}N_{Acartia}$ decreased to values around 11 ‰. There was no significant correlation between $\delta^{15}N_{Acartia}$ and salinity, DIN concentrations, or the $\delta^{15}N$ of either size fraction of PN (Table 10).

The $\delta^{15}N$ of the ctenophore *Mnemiopsis leidyi* showed little spatial variation on this transect. $\delta^{15}N_{Mnemiopsis}$ varied between 14.2 and 15.3 ‰ (Fig. 5B), with a mean of 14.7 ± 0.4 ‰ ($\bar{x}$ ± SD, n = 10). The difference between $\delta^{15}N_{Mnemiopsis}$ and $\delta^{15}PN_{whl}$, which was largely a function of the variation in $\delta^{15}PN_{whl}$, averaged 6.5 ‰ on this transect (Table 12). At every station where both zooplankton species were sampled, $\delta^{15}N_{Mnemiopsis}$ was markedly higher than $\delta^{15}N_{Acartia}$, with a mean difference of 2.7 ‰ (Table 12).

Samples of the ctenophore *Beroe ovata* were obtained

at 2 stations in the mid-Bay (813R and 823). At both stations, $\delta^{15}N_{Beroe}$ was higher than $\delta^{15}N_{Mnemiopsis}$. At Stn 823, a large scyphozoan medusa was also collected, for which $\delta^{15}N_{scyphozoa}$ (13.9 ‰) was approximately midway between $\delta^{15}N_{Mnemiopsis}$ (15.2 ‰) and $\delta^{15}N_{Acartia}$ (12.2 ‰). Finally, at the southernmost station on this transect (724R), the large copepod *Centropages typicus* was abundant. $\delta^{15}N_{Centropages}$ (11.6 ‰) at this station was slightly higher than $\delta^{15}N_{Acartia}$ (10.7 ‰) (Fig. 5B).

### Second transect (3 to 5 October)

The second, northbound transect of the Bay lasted from 3 to 5 October, and began 2 d after an intense storm contributed to cross-pycnocline mixing of DIN and $O_2$ (Horrigan et al. 1990a,b). The spatial trends in $\delta^{15}N$ of the dissolved and particulate pools are shown in Fig. 6. The lower panel of Fig. 7 summarizes the distribution of $\delta^{15}N$ values in the planktonic and dissolved pools.

**$\delta^{15}$PN measurements.** The surface values of $\delta^{15}PN_{whl}$ on this transect ranged from 4.8 to 10.5 ‰, which was similar to the range obtained on the first transect (Fig. 5B). At most stations in the mid-Bay, however, $\delta^{15}PN_{whl}$ was distinctly lower on the second transect; between Stns 744A and 833F, $\delta^{15}PN_{whl}$ decreased by 2.0 to 3.8 ‰. At 2 stations at the northern and southern ends of the Bay, $\delta^{15}PN_{whl}$ increased between transects: the $\delta^{15}N$ of whole PN increased by 2.6 ‰ at Stns 904N and 724R. At all stations on this transect, $\delta^{15}PN_{whl}$ was lower than $\delta^{15}NH_4^+$, and similar to or lower than $\delta^{15}(NO_3^- + NO_2^-)$ (Fig. 6A, B, Table 9). $\delta^{15}PN_{whl}$ was not significantly correlated with salinity, DIN concentrations, or the $\delta^{15}N$ of either pool of DIN (Table 13).

The $\delta^{15}N$ of the small size fraction of PN in the surface layer was similar to and significantly correlated with that of the whole PN (Fig. 5B, Table 13). The mean difference between $\delta^{15}PN_{<10}$ and $\delta^{15}PN_{whl}$ was only 0.1 ‰. The 2 size fractions differed appreciably at only 2 stations on this transect: at Stn 904N, $\delta^{15}PN_{<10}$ was 2.9 ‰ lower than $\delta^{15}PN_{whl}$, while at Stn 707O, the small size fraction was 1.6 ‰ higher in $\delta^{15}N$ than the whole PN. Although $\delta^{15}PN_{<10}$ showed no significant correlation with salinity or the $\delta^{15}N$ of the DIN pools, $\delta^{15}PN_{<10}$ and $[NO_3^-]$ were significantly correlated in the surface layer (Table 13).

Below the pycnocline, the $\delta^{15}N$ of $PN_{whl}$ ranged

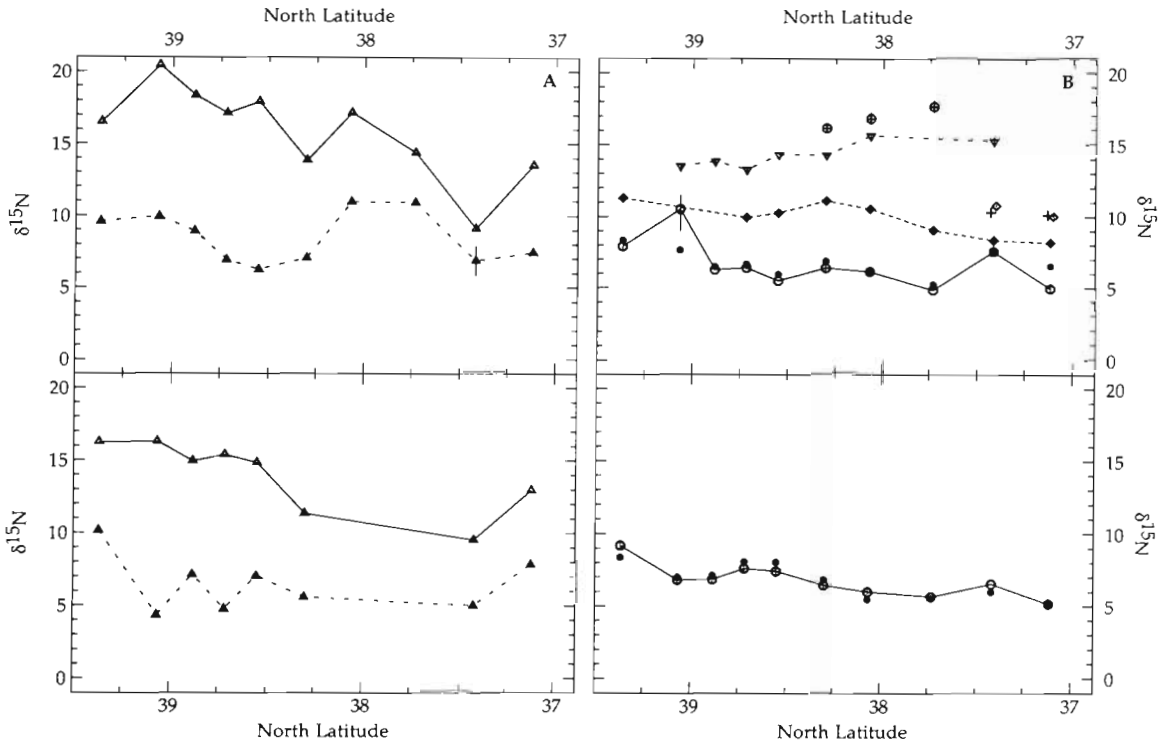


Fig. 6. $\delta^{15}N$ of the particulate and dissolved pools of nitrogen during the second transect of the fall cruise (3 to 5 October). Upper portion of each panel: data from the surface layer; lower portion shows data from below the pycnocline. At stations where replicate samples were obtained, the mean $\delta^{15}N$ is plotted, with vertical bars representing the range of values observed. (A) $\delta^{15}N$ of $NH_4^+$ (○) and $(NO_3^- + NO_2^-)$ (▲); (B) $\delta^{15}N$ of $PN_{whl}$ (□), $PN_{<10}$ (●), *Acartia tonsa* (◆), *Mnemiopsis leidyi* (▽), *Beroe ovata* (⊕), *Centropages typicus* (◇), and chaetognaths (+)

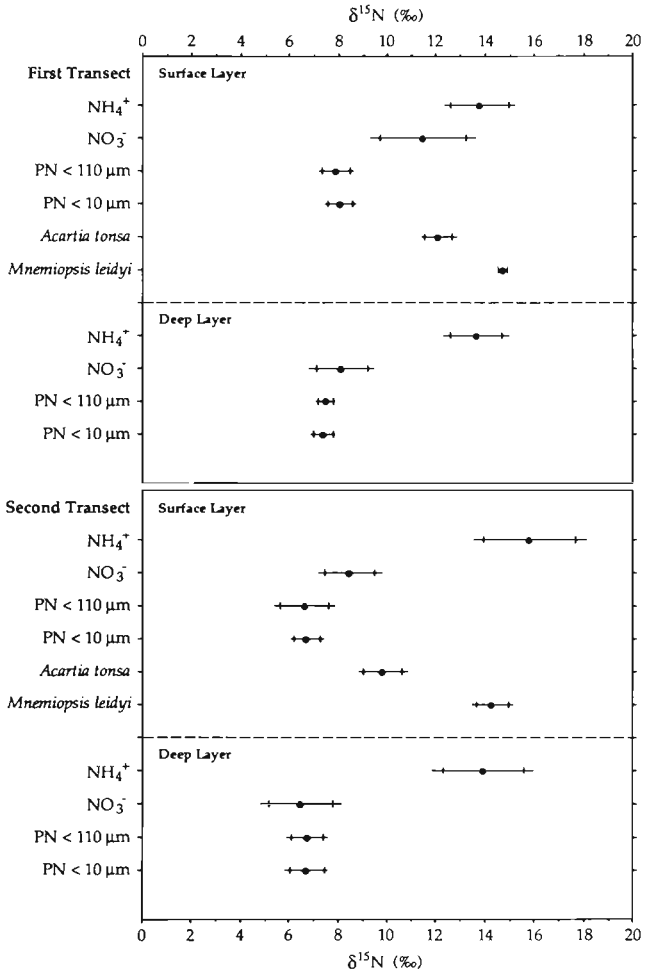


Fig. 7. Summary plots showing the $\delta^{15}N$ of the major dissolved and planktonic pools of nitrogen during the fall cruise. (•) Mean $\delta^{15}N$ of each pool of nitrogen. The ends of the horizontal line through each circle and the vertical cross-bars show the 95 % and 90 % confidence intervals about the mean, respectively. Upper panel summarizes the data collected during the first transect (27 to 28 September); lower panel summarizes data from the second transect (3 to 5 October) of the cruise

between 5.2 and 9.2 ‰, and showed a significant correlation with salinity (Table 11). Although the range of values was similar on the 2 transects of this cruise, $\delta^{15}PN_{whl}$ decreased between transects at 5 of the 8 stations sampled on the second transect; the decrease in $\delta^{15}PN_{whl}$ was largest at Stns 804C (1.8 ‰) and 744A (2.3 ‰). The surface and deep values of $\delta^{15}PN_{whl}$ showed some marked differences in the northern half of this transect. In this portion of the Bay, the deep values of $\delta^{15}PN_{whl}$ differed from surface values by as much as +1.9 ‰ (Stn 833F) and −3.8 ‰ (Stn 904N). In the southern half of the Bay, surface and deep values of $\delta^{15}PN_{whl}$ were similar. For the transect as a whole, the difference between surface and deep values of $\delta^{15}PN_{whl}$ was significantly correlated with the difference in $[NH_4^+]$ across the pycnocline ($r = -0.656$, $n = 10$, $p < 0.05$), but not with the differences in salinity, density, $[NO_3^-]$, or $[NO_2^-]$ between layers.

The small size fraction of PN below the pycnocline was very similar in $\delta^{15}N$ to $PN_{whl}$; over the whole transect, the mean difference between the 2 size fractions was less than 0.1 ‰. In the deep layer, $\delta^{15}PN_{<10}$ and $\delta^{15}PN_{whl}$ were highly correlated, as were $\delta^{15}PN_{<10}$ and salinity (Table 11). The difference between $\delta^{15}PN_{<10}$ in the surface and deep layers was not significant for the transect as a whole (paired samples t-test). The difference in $\delta^{15}PN_{<10}$ across the pycnocline was significantly correlated with the difference in $[NH_4^+]$ between the layers ($r = -0.722$, $n = 10$, $p < 0.05$).

**$\delta^{15}N$ of zooplankton.** The $\delta^{15}N$ of *Acartia tonsa* decreased at all stations sampled on both transects. The smallest change, at Stn 843F, was 1.5 ‰; elsewhere, $\delta^{15}N_{Acartia}$ declined by as much as 2.6 ‰ (Stn 804C) between the first and second transects of this cruise. The general spatial pattern for $\delta^{15}N_{Acartia}$ was similar to the one found in the first transect: the highest value occurred at the northernmost station (922Y), and $\delta^{15}N_{Acartia}$ reached a local maximum in the mid-Bay. The general trend toward lower values in the south led to a significant correlation with salinity (Table 13). There was no significant association between $\delta^{15}N_{Acartia}$ and the $\delta^{15}N$ of either size fraction of PN. Despite the decrease in $\delta^{15}N_{Acartia}$ throughout the Bay, the difference between $\delta^{15}N_{Acartia}$ and the 2 size fractions of PN was not very different on the 2 transects (Table 12).

The $\delta^{15}N$ of the ctenophore *Mnemiopsis leidyi* changed relatively little between transects. $\delta^{15}N_{Mnemiopsis}$ decreased at 5 of the 6 stations sampled on both transects, though the largest difference was only 0.9 ‰. The mean difference between $\delta^{15}N_{Mnemiopsis}$ and the $\delta^{15}N$ of both PN and *Acartia tonsa* was somewhat greater on this transect because of the larger decrease in $\delta^{15}N$ of the other 2 pools. $\delta^{15}N_{Mnemiopsis}$ was not significantly correlated with the $\delta^{15}N$ of any of the other planktonic pools measured on this transect (Table 13).

Samples of *Beroe ovata* were obtained at 3 stations on this transect. At 2 of these stations (818P and 823), $\delta^{15}N_{Beroe}$ was distinctly higher than $\delta^{15}N_{Mnemiopsis}$; *Mnemiopsis leidyi* was not collected at the third station (744A), which gave the highest value of $\delta^{15}N_{Beroe}$ (17.7 ‰). The copepod *Centropages typicus* was sampled at the 2 southernmost stations of this transect (707O and 724R); at both stations, $\delta^{15}N_{Centropages}$ was much higher than $\delta^{15}N_{Acartia}$. At Stn 724R, $\delta^{15}N_{Centropages}$ decreased by 0.9 ‰ between transects. Finally, 2 samples of chaetognaths were collected at the southern end of this transect; at both stations, $\delta^{15}N_{chaetognath}$ was very similar to $\delta^{15}N_{Centropages}$.

Table 13. Correlation matrix for the $\delta^{15}N$ of the surface PN and zooplankton samples from the second transect of the fall cruise. Number of observations is shown in parentheses beneath each correlation coefficient

| | $\delta^{15}PN_{whl}$ (‰) | $\delta^{15}PN_{<10}$ (‰) | $\delta^{15}N_{Acartia}$ (‰) | $\delta^{15}N_{Mnemiopsis}$ (‰) |
|---|---|---|---|---|
| Salinity | −0.498 (10) | −0.508 (10) | −0.809* (8) | 0.685 (7) |
| $[NO_3^-]$ | 0.407 (10) | 0.677* (10) | 0.524 (8) | −0.708 (7) |
| $[NO_2^-]$ | 0.534 (10) | 0.203 (10) | 0.786* (8) | −0.743 (7) |
| $[NH_4^+]$ | 0.045 (10) | −0.202 (10) | 0.374 (8) | −0.835* (7) |
| $\delta^{15}(NO_3^- + NO_2^-)$ | 0.176 (10) | −0.126 (10) | 0.176 (8) | 0.210 (7) |
| $\delta^{15}NH_4^+$ | 0.308 (10) | −0.056 (10) | 0.632 (8) | −0.555 (7) |
| $\overline{\delta^{15}DIN}$ | −0.197 (10) | −0.638 (10) | 0.169 (8) | −0.282 (7) |
| $\delta^{15}PN_{whl}$ | 1.000 (10) | 0.769** (10) | 0.374 (8) | −0.271 (7) |
| $\delta^{15}PN_{<10}$ | | 1.000 (10) | 0.236 (8) | −0.180 (7) |
| $\delta^{15}N_{Acartia}$ | | | 1.000 (8) | −0.210 (7) |
| $\delta^{15}N_{Mnemiopsis}$ | | | | 1.000 (7) |

* $p < 0.05$; ** $p < 0.01$

## DISCUSSION

Most previous investigations of the natural abundance of $^{15}N$ in aquatic systems have been directed toward either the study of the distribution of $^{15}N$ in the dissolved and particulate forms of nitrogen (Mariotti et al. 1984, Owens 1985, Altabet & McCarthy 1986, Wada et al. 1987a, Cifuentes et al. 1988 are some recent examples), or the distribution of $^{15}N$ in food webs (Macko et al. 1982, Mullin et al. 1984, Checkley & Entzeroth 1985, Wada et al. 1987b, Fry 1988 for example). In this study, samples of the dissolved and particulate pools of nitrogen as well as several species of zooplankton were collected at a series of stations spanning the length of the Chesapeake Bay. This sampling scheme permits an evaluation of the distribution of $^{15}N$ in the planktonic food web in the Bay, as well as the spatial variation in the $\delta^{15}N$ of 3 trophic levels of plankton. The 2 transects of the Bay conducted on each cruise (spring and fall) were separated by several days, providing a measure of the variability of $\delta^{15}N$ in these trophic levels on a time scale of days as well as seasons. In the following sections of this paper, the precision of the various isotopic analyses will be treated first, followed by a discussion of the general spatial patterns of $\delta^{15}N$ in Chesapeake Bay plankton, and finally, the patterns of temporal change within and between cruises.

### Variability between replicate $\delta^{15}N$ analyses of plankton

This data set is one of the first to allow quantitative estimates of the degree of variation which exists between replicate portions of a single sample of plankton. The difficulty and expense of sample collection and processing for isotopic analysis has contributed to the small number of samples analyzed in most studies, and the variability associated with replicate analyses of standards is commonly used to estimate the precision of the entire sample collection and handling procedure. This provides no information on the degree of natural variation among replicate samples from the same system, which makes the interpretation of differences between samples difficult at best. In this study, the

mean range and standard deviation of replicate analyses provided an indication of the amount of variation inherent in samples of plankton from the Chesapeake Bay.

The variability in replicate measurements of $\delta^{15}PN_{whl}$ was roughly twice the variability associated with replicate standards, and was quite similar during the 2 cruises (Tables 2 and 8). In the spring, the variation between replicate samples of zooplankton was greater, and appeared to increase somewhat with trophic level. This may reflect either a greater internal heterogeneity in larger, more complex organisms, or greater variability between such individuals. Although both of these explanations may apply to the large gelatinous zooplankton, neither seems likely to explain the variability in $\delta^{15}N$ analyses of *Acartia tonsa*, since each analysis represents the nitrogen from roughly 50 individual copepods.

In the fall, the variation associated with $\delta^{15}N_{Acartia}$ and $\delta^{15}N_{Mnemiopsis}$ was somewhat less than that associated with $\delta^{15}PN_{whl}$. In addition, there was little difference in variability between these and other trophic levels of the zooplankton. The lower variability associated with the zooplankton collected on this cruise may reflect a real seasonal difference in isotopic heterogeneity in these animals, though the possibility that experience in sorting and handling the animals may have contributed to greater homogeneity between subsamples on the second cruise cannot be wholly eliminated. This seems unlikely to be a complete explanation since all the zooplankton sorting and preparation was conducted by a single investigator, and there was no apparent trend in variability during either cruise, as would be expected if experience in the sorting procedure were related to replication quality.

Taking all these data into consideration, the overall precision of the measurements of the $\delta^{15}N$ of PN reported here is approximately $\pm 0.3$ ‰ ($\pm$ SD). It is more difficult to estimate the precision of the isotopic analyses of zooplankton because of the large difference between the 2 cruises. For the spring samples, the precision ($\pm$ SD) of the $\delta^{15}N$ measurements of *Acartia tonsa* and *Mnemiopsis leidyi* are around $\pm 0.6$ ‰, which differs substantially from the precision of ca $\pm 0.2$ ‰ for the fall samples of these 2 species.

### General spatial patterns in $\delta^{15}N$ of PN

At the beginning of this study, a useful working hypothesis was that the $\delta^{15}N$ of the major planktonic pools of nitrogen would change in a regular manner down the length of the Bay, reflecting the overall north-south gradient in the availability of nitrogenous nutrients. The major sink for $NO_3^-$ in the Bay is uptake by phytoplankton, and the major source of $NH_4^+$ is local remineralization of planktonic biomass (McCarthy et al. 1977, Taft et al. 1978). In combination with the net movement of surface water toward the south, these 2 processes lead to a southward increase in the extent of biological processing of the nitrogen in the Bay. Since isotopic fractionation is known to occur in the uptake of $NO_3^-$ by phytoplankton as well as during the remineralization of particulate nitrogen (Wada & Hattori 1978), it seemed likely that the spatial variation in $\delta^{15}PN_{whl}$ would reflect the cumulative effect of isotopic fractionation on the dissolved and particulate pools of nitrogen.

The $\delta^{15}N$ of the surface PN does not show any such clear patterns of variation (Figs. 2, 3, 5 and 6), suggesting that, during the 2 sampling periods, processes occurring on a relatively small scale were more important than those associated with the overall distribution of nitrogenous nutrients in the Bay. This may not be true at times when the rate of estuarine flushing is greater. Evidence for the small spatial scale of variation in the $\delta^{15}N$ of PN comes from the spring cruise (Fig. 2): $\delta^{15}PN_{whl}$ differed by as much as 3 ‰ between stations separated by only 3 min of latitude. In addition, the $\delta^{15}N$ of surface PN collected on the first transect of the spring cruise showed a number of distinct local maxima and minima distributed down the length of the Bay with no obvious relationship to salinity or nutrient concentrations. The fall cruise was characterized by relatively little variation in $\delta^{15}PN_{whl}$; during the first transect, the range of $\delta^{15}N$ values was only 2.5 ‰ over most of the Bay, though values in the mid-Bay did tend to be higher than those elsewhere (Fig. 5A). The second transect showed a wider range of values of $\delta^{15}PN_{whl}$, though much of this increased spatial variation resulted from a marked decrease in the $^{15}N$ content of whole PN in the mid-Bay between transects (compare Figs. 5 and 6).

The $\delta^{15}N$ of PN below the pycnocline also showed no consistent pattern of spatial variation. The range of $\delta^{15}N$ values in whole PN collected at depth was greater in spring than in fall, and only the fall samples showed a significant correlation with salinity. These patterns suggest that the large-scale gradients in chemical and physical properties in the Bay exert a somewhat greater influence on the $\delta^{15}N$ of PN at depth in fall than in spring. This may reflect the greater spatial heterogeneity in biological activity in the Bay during spring (Horrigan et al. 1990b), and the strong influence of localized blooms of phytoplankton in the surface layer on the $\delta^{15}N$ of PN both above and below the pycnocline (see below).

In general, the surface and deep values of $\delta^{15}PN_{whl}$ showed no consistent relationship. The first transect of the spring cruise was characterized by 3 local maxima

in $\delta^{15}PN_{whl}$ below the pycnocline. Two of these maxima (Stns 834G and 808D) coincided with local maxima in $\delta^{15}PN_{whl}$ in the surface layer, suggesting that variations in the $\delta^{15}N$ of the whole PN in the 2 layers are not entirely independent during this season. During the first transect in the fall, the opposite pattern occurred: local maxima in deep $\delta^{15}PN_{whl}$ occurred with local minima in surface $\delta^{15}PN_{whl}$. It is interesting to note that, in this case, the surface maximum in $\delta^{15}PN_{whl}$ occurred in the same section of the Bay as a local maximum in chlorophyll *a* concentration (Horrigan et al. 1990b). The high values of $\delta^{15}PN_{whl}$ below the pycnocline at Stns 843F and 853C also coincided with a local maximum in the concentration of chlorophyll *a* below the pycnocline. This pattern is intriguing, since it suggests that the phytoplankton may have had a relatively high $\delta^{15}N$ on this transect. Unfortunately, the elemental composition data available for this transect are not sufficiently detailed to show whether the PN at stations with high chlorophyll *a* concentrations also contained unusually large amounts of detritus of high $\delta^{15}N$. An additional complication is that high concentrations of chlorophyll *a* below the pycnocline probably result from sedimentation out of the surface layer, rather than active growth at depth. In this case, the local elevation in $\delta^{15}PN_{whl}$ may simply represent the alteration of $\delta^{15}N$ by isotopic fractionation during the decomposition of the sinking phytoplankton.

The 2 size fractions of surface PN were not significantly different during either cruise, though a number of stations on the first transect of the spring cruise showed clear differences between size fractions below the pycnocline. At these stations, the small size fraction of PN was higher in $\delta^{15}N$ by up to 4.4 ‰, though most such differences were on the order of 1 to 2 ‰. None of the other 3 other transects showed similarly large differences between size fractions collected in either the surface or deep layer of the Bay. This suggests that, in general, the small size fraction of PN is not dramatically different from the whole PN in isotopic composition or in its seasonal pattern of variation in $\delta^{15}N$. In the remainder of this discussion, the relationship between $\delta^{15}PN_{whl}$ and a variety of other variables will be described in some detail. In most cases, the same relationships also apply to the small size fraction of PN.

### Relationship between $\delta^{15}PN$ and $\delta^{15}DIN$

At most stations on both cruises, $\delta^{15}PN_{whl}$ was lower than the $\delta^{15}N$ of one or both of the DIN pools analyzed (Figs. 4 and 7). This is consistent with the usual effect of isotopic fractionation during uptake of inorganic nitrogen, which should result in preferential uptake of the lighter isotope. At 3 stations during the spring cruise, $\delta^{15}PN_{whl}$ was higher than the corresponding values of $\delta^{15}NH_4^+$ and $\delta^{15}(NO_3^- + NO_2^-)$. At Stn 900B, the difference between $\delta^{15}PN_{whl}$ and the $\delta^{15}N$ of the DIN pools was small enough (0.4 ‰) to be within the range of analytic error. In contrast, at Stns 904N and 918P, the magnitude of the difference (1.1 and 2.8 ‰, respectively) was well beyond the limits of analytical uncertainty. This elevation in $\delta^{15}N$ of PN relative to that of the nitrogenous nutrients probably reflects either the utilization of some nitrogen source other than the DIN pools assayed, or the presence of unusual amounts or types of detritus or microheterotrophs in the PN. The available data do not allow a full evaluation of these possibilities, though comparison of primary production rates and nitrogen uptake rates measured in experiments with $^{15}N$-labelled substrates suggest that most of the phytoplankton nitrogen demand in this portion of the Bay was met by uptake of $NH_4^+$, with smaller contributions from the $NO_3^-$ and $NO_2^-$ pools (Horrigan et al. 1990b).

The magnitude of the difference between $\delta^{15}PN$ and the $\delta^{15}N$ of the 2 DIN pools at the rest of the stations was consistent with previously reported fractionation factors for the uptake of DIN. For example, the difference between the $\delta^{15}N$ of either size fraction of PN and $\delta^{15}NH_4^+$ was never greater than 13.3 ‰, and the difference between $\delta^{15}PN$ and $\delta^{15}(NO_3^- + NO_2^-)$ was never greater than 12.8 ‰. Laboratory estimates of the isotopic fractionation factor ($\alpha$) for the uptake of $NO_3^-$ range between 1.0002 and 1.0230 (Wada & Hattori 1978, Wada 1980, Montoya & McCarthy unpubl.), while most estimates of $\alpha$ for the uptake of $NH_4^+$ range between 1.0000 and 1.0096 (Wada 1980). In general, $\alpha$ varies between species of phytoplankton and with growth rate and culture conditions within a single species. The expected difference in $\delta^{15}N$ between the substrate and product pools ($\delta^{15}N_{substrate} - \delta^{15}PN$) associated with this range of fractionation factors is roughly 2 to 23 ‰ for uptake of $NO_3^-$, and 0.0 to 9.6 ‰ for uptake of $NH_4^+$, which is similar to the range of differences actually observed in the Bay.

One of the most interesting contrasts between the 2 cruises was in the relationship between $\delta^{15}PN_{whl}$ and the $\delta^{15}N$ of the dissolved pools. $\delta^{15}PN_{whl}$ showed no significant association with either $\delta^{15}NH_4^+$ or $\delta^{15}(NO_3^- + NO_2^-)$ on any of the 4 transects, but was significantly correlated with $\delta^{15}DIN$ on the first transect of each cruise. The absence of a significant association between $\delta^{15}PN_{whl}$ and $\delta^{15}DIN$ on the other 2 transects is not surprising. On the second transect of the spring cruise, estimates of both $\delta^{15}NH_4^+$ and $\delta^{15}(NO_3^- + NO_2^-)$ are available for only 7 stations, making standard tests of significance of the correlation coefficient very weak. In the fall, the second transect of the Bay occurred a few days after an intense storm had contri-

buted to mixing of nutrients and $O_2$ across the pycnocline. Following the storm, the rates of a number of microbially-mediated transformations of nitrogen were markedly enhanced, leading to alterations in the $\delta^{15}N$ of the DIN (Horrigan et al. 1990a). The effects of this storm will be discussed in greater detail below.

The association between $\delta^{15}PN_{whl}$ and $\overline{\delta^{15}DIN}$ suggests that both $NH_4^+$ and $NO_3^-$ make an important contribution to the phytoplankton nitrogen demand both in the spring and the fall, and that the contribution of each pool is roughly proportional to pool size. This pattern was not anticipated, and is different from the DIN uptake rates measured using $^{15}N$-labelled substrates at a subset of the stations visited during these cruises. The results of these experiments suggest that $NH_4^+$ was taken up preferentially during both seasons, and $NO_2^-$ was taken up preferentially in the spring (Horrigan et al. 1990b). This general pattern of utilization of more reduced substrates in preference to $NO_3^-$ is in keeping with the results of previous research on the relative preference of phytoplankton for DIN in the Bay and elsewhere (e.g. McCarthy et al. 1977, McCarthy 1980). The correlation between $\delta^{15}PN_{whl}$ and $\overline{\delta^{15}DIN}$, however, suggests that the phytoplankton, over time scales longer than a typical bottle incubation, may utilize the major pools of nitrogen roughly in proportion to availability. This relationship between the $\delta^{15}N$ of the particulate and dissolved pools of nitrogen deserves further study, and a more extensive comparison of natural abundance measurements of PN and DIN samples collected at the time of DIN uptake experiments may help resolve the apparent contradiction between nutrient preferences inferred from standard uptake experiments and these $\delta^{15}N$ data.

The sign of the correlation between $\delta^{15}PN_{whl}$ and $\overline{\delta^{15}DIN}$ also provides useful insights into the nitrogen cycle in the Bay. On the first transect of the spring cruise, $\delta^{15}PN_{whl}$ and $\overline{\delta^{15}DIN}$ were negatively correlated, which is consistent with the effect of isotopic fractionation on the $\delta^{15}N$ of 2 pools which are related as product and reactant. That is, this pattern suggests that the major determinant of the $\delta^{15}N$ of both PN and DIN was phytoplankton uptake of DIN. Horrigan et al. (1990a) have previously reported that $\delta^{15}(NO_3^- + NO_2^-)$ was negatively correlated with the concentration of $NO_3^-$ on this transect, a relationship which allowed an estimate of the fractionation factor for the consumption of $NO_3^-$. The value of this fractionation factor ($\alpha = 1.0070$) was similar to laboratory estimates of the fractionation factor for $NO_3^-$ uptake by phytoplankton (Wada & Hattori 1978, Wada 1980, Montoya & McCarthy unpubl.), lending support to previous suggestions that phytoplankton uptake is the major sink for $NO_3^-$ in the Bay (McCarthy et al. 1977), as well as to the suggestion that the uptake of DIN by phytoplankton is the primary determinant of the $\delta^{15}N$ of DIN during this season.

In contrast, $\delta^{15}PN_{whl}$ and $\overline{\delta^{15}DIN}$ showed a positive correlation in the surface layer during the first transect of the fall cruise. A positive correlation between the $\delta^{15}N$ of the substrate and product pools for a reaction suggests that the $\delta^{15}N$ of the substrate pool is determined by factors other than the reaction, and that the product pool simply reflects this external influence upon the $\delta^{15}N$ of the substrate. That is, these data indicate that phytoplankton uptake was not the primary determinant of $\overline{\delta^{15}DIN}$ during the fall. At this time of year, the major pool of DIN in most of the Bay was $NH_4^+$ (Horrigan et al. 1990b), and other natural abundance data and rate measurements from this cruise suggest that $\delta^{15}NH_4^+$ was strongly affected by microbially-mediated oxidation of $NH_4^+$, both during the summer and into the fall (Horrigan et al. 1990a,b). The $\delta^{15}N$ of surface PN then reflected these changes in $\delta^{15}NH_4^+$, once allowance is made for the isotopic fractionation associated with $NH_4^+$ uptake by phytoplankton (Montoya et al. unpubl.).

In summary, the relationship between $\delta^{15}PN_{whl}$ and the $\delta^{15}N$ of the dissolved pools of nitrogen suggests that the nitrogen cycle in the Bay as a whole is dominated by phytoplankton-mediated processes in the spring, and by microbially-mediated processes in the fall. Because phytoplankton biomass and production are not uniformly distributed in the Bay (e.g. Horrigan et al. 1990b), one likely consequence of the springtime dominance of phytoplankton is an increase in the overall spatial heterogeneity of the $\delta^{15}N$ of both the particulate and dissolved pools. This may help explain the complex pattern of local maxima and minima in the $\delta^{15}N$ of these pools during the spring cruise. This is quite different from the rather uniform values of $\delta^{15}PN_{whl}$ which characterized the Bay in the fall, when microbial transformations of nitrogen exerted a dominant influence on the $\delta^{15}N$ of the dissolved and, indirectly, the particulate pools of nitrogen.

### Cross-pycnocline differences in $\delta^{15}PN$

During the spring cruise, the surface and deep values of $\delta^{15}PN_{whl}$ did not show any consistent relationship. For example, during the first transect, the magnitude of the difference between layers was not significantly correlated with the cross-pycnocline difference in any of the chemical or physical quantities measured. In general, the deep values of $\delta^{15}PN_{whl}$ were similar to or higher than surface values, which is consistent with the expected effect of remineralization and decomposition on particles sinking below the pycnocline (Miyake & Wada 1971, Wada 1980, Altabet & McCarthy 1986).

During this transect, a number of stations in the northern half of the Bay were characterized by very high surface concentrations of chlorophyll *a* as well as high rates of primary production, and much of the deep water in the Bay was low in dissolved $O_2$. Both of these observations are consistent with the hypothesis that isotopic fractionation during the remineralization of PN sinking out of the surface layer is responsible for the elevated $\delta^{15}N$ found at depth. This could also account for some of the variability in the deep values of $\delta^{15}PN_{whl}$, since the magnitude of the flux and the extent of remineralization were unknown and would depend upon local conditions.

In contrast, the cross-pycnocline differences in $\delta^{15}PN_{whl}$ and $[NO_3^-]$ showed a significant positive correlation on the second transect of the Bay in the spring. This correlation resulted from the notable difference (up to 3.9‰) between surface and deep values of $\delta^{15}PN_{whl}$ in the northern portion of the Bay where surface $NO_3^-$ concentrations were high. Further south, the surface and deep values of $\delta^{15}PN_{whl}$ were very similar. The portion of the Bay characterized by the largest differences between surface and deep values of $\delta^{15}PN_{whl}$ was centered about Stn 853C. Ancillary data suggest that the pronounced difference between surface and deep values of $\delta^{15}PN_{whl}$ in this portion of the Bay may reflect the sedimentation of phytoplankton biomass across the pycnocline (see below).

In the fall, the difference in $\delta^{15}PN_{whl}$ between surface and deep layers of the Bay was correlated with the difference in $[NH_4^+]$ between layers. This correlation was significant on both transects, and for both size fractions of PN. In the southern half of the Bay, there was little difference between surface and deep values of $\delta^{15}PN$, but notable differences with depth occurred north of Stn 818P. During this transect, the deep water in the northern half of the Bay was characterized by low concentrations of $O_2$ and high concentrations of $NH_4^+$. At all stations where $[NH_4^+]$ below the pycnocline was markedly higher than in the surface layer, the deep values of $\delta^{15}PN_{whl}$ were lower than surface values. During this cruise, the rates of microbially-mediated transformations of nitrogen below the pycnocline were high (Horrigan et al. 1990b), so the low $\delta^{15}PN_{whl}$ values associated with high $[NH_4^+]$ at depth may reflect the presence of a large, metabolically-active population of bacterioplankton.

### $\delta^{15}N$ of zooplankton: general patterns

The zooplankton collected during this study include samples of animals that feed primarily as herbivores (*Acartia tonsa*) and carnivores (*Mnemiopsis leidyi*, *Beroe ovata*, the scyphozoan medusae, and the chaetognaths), allowing an assessment of the patterns of variation in the $\delta^{15}N$ of 2 trophic levels in addition to the primary producers. The $\delta^{15}N$ of the zooplankton in the Bay largely confirmed the trophic level effect reported previously (De Niro & Epstein 1981, Macko et al. 1982, Minagawa & Wada 1984, Checkley & Entzeroth 1985, Wada et al. 1987b), with mean differences between trophic levels of ca 2 to 4‰ (Tables 6 and 12, Figs. 4 and 7). Surprisingly, there was no consistent correlation between the $\delta^{15}N$ of either species of zooplankton and $\delta^{15}PN_{whl}$, or between $\delta^{15}N_{Mnemiopsis}$ and $\delta^{15}N_{Acartia}$ (Tables 4, 7, 10, and 13). The absence of a correlation with $\delta^{15}PN_{whl}$ may reflect spatial changes in the quality of PN: a variety of evidence suggests that detrital nitrogen derived from plankton is typically more enriched in $^{15}N$ than phytoplankton (Wada 1980, Altabet & McCarthy 1986), while detritus of terrestrial origin in typically low in $\delta^{15}N$ (Mariotti et al. 1984, Owens 1985, Wada et al. 1987a), so spatial variations in the nature and the extent of the detrital contribution to PN could lead to variable differences between $\delta^{15}PN_{whl}$ and the $\delta^{15}N$ of the fraction of PN actually used by higher trophic levels. Since the ratio of chlorophyll *a* to PN in the surface layer was relatively invariant on all 4 transects (Horrigan et al. 1990b), this does not seem likely.

Another possible explanation is that the time scales of change in the $\delta^{15}N$ of the 3 trophic levels sampled may be different enough to obscure the relationship between the $\delta^{15}N$ of an animal and that of its food. Such a difference in characteristic times could arise naturally from the great range of generation times (hours to weeks) represented in the sample set of phytoplankton, copepods, and gelatinous zooplankton. In this context, the important point is that dissimilar time scales for change in the $\delta^{15}N$ of different trophic levels will contribute to the variability in $\Delta\delta^{15}N$ between the trophic levels unless the $\delta^{15}N$ of the primary producers at the base of the food web is constant. During both cruises, $\delta^{15}PN_{whl}$ changed appreciably between transects at some (spring) or all (fall) of the stations sampled, suggesting that at least part of the lack of association between the $\delta^{15}N$ of different trophic levels may be due to differences in generation time, and the resulting differences in the time scale of change in $\delta^{15}N$. This issue is discussed in greater detail below in connection with the general patterns of temporal variability in $\delta^{15}N$.

A third possibility is that the spatial variations in the $\delta^{15}N$ of food are less important in determining the $\delta^{15}N$ of a consumer than are other aspects of the biology of the consumer itself. For example, during both transects of the spring cruise, the $\delta^{15}N$ of both *Acartia tonsa* and *Mnemiopsis leidyi* increased with salinity in the northern part of the Bay. This trend led to highly significant

correlations between the $\delta^{15}N$ of each of the 2 zooplankton species and salinity in this portion of the Bay. In contrast, the $\delta^{15}N$ of the surface PN showed no trend with salinity. Both species of zooplankton departed from this pattern in the southern part of the Bay, and showed decreasing or constant values of $\delta^{15}N$ with increasing salinity. One consequence of this pattern was a reversal of the usual trophic level separation in $\delta^{15}N$ at the southern end of the Bay. At Stn 724R, $\delta^{15}N_{Acartia}$ was consistently higher than $\delta^{15}N_{Mnemiopsis}$, with a maximum difference of almost 5 ‰. This pattern was unexpected, and may reflect: (1) the consumption of significant amounts of PN by the ctenophores, which would lead to a lower $\delta^{15}N$ than a purely carnivorous diet; (2) carnivorous feeding by copepods, which would lead to a higher $\delta^{15}N$ than a strictly herbivorous diet; or (3) a fundamental change in the magnitude of the isotopic fractionation effect in either the ctenophores or the copepods. Although $\delta^{15}N$ measurements alone do not clearly indicate which of these possible explanations may be important, Deason & Smayda (1982) have shown that *M. leidyi* is not able to graze effectively on phytoplankton. Furthermore, the smaller range of values of $\delta^{15}N_{Mnemiopsis}$ and the relative constancy of the difference in $\delta^{15}N$ between the ctenophores and the PN both suggest that the change is in copepod feeding or isotopic fractionation patterns rather than in the behavior or physiology of the ctenophores. Lonsdale et al. (1979) have documented carnivorous feeding in adult *A. tonsa*, and a greater dependence on animal food at the southern end of the Bay could lead to a significant elevation of $\delta^{15}N_{Acartia}$ relative to $\delta^{15}PN_{whl}$.

In the fall, the 2 major groups of zooplankton and the PN showed a relatively constant separation in $\delta^{15}N$. For the Bay as a whole, there was no overlap in $\delta^{15}N$ between *Acartia tonsa* and $PN_{whl}$ or between *A. tonsa* and *Mnemiopsis leidyi*. In both cases, the mean difference in $\delta^{15}N$ between trophic levels was similar to the mean of 3.4 ‰ reported by other researchers (DeNiro & Epstein 1981, Macko et al. 1982, Minagawa & Wada 1984, Checkley & Entzeroth 1985, Fry 1988). Although the $\delta^{15}N$ of the PN and *A. tonsa* changed markedly throughout the Bay between transects on this cruise, the mean difference between the 2 trophic levels was largely unchanged. This suggests that the changes in $\delta^{15}N_{Acartia}$ occurred as the copepods fed on and incorporated PN of changing $\delta^{15}N$. The magnitude of the change in $\delta^{15}N$ of the 2 trophic levels can be used to estimate the turnover time for nitrogen in the copepods, and this approach yields values very similar to the generation time of *A. tonsa* reared in the laboratory (Montoya et al. unpubl.).

Although only a small number of specimens of other zooplankton species were analyzed, it is worth noting several general points about their $\delta^{15}N$ relative to the data for other zooplankton reported above. The large scyphozoan medusae collected on both cruises covered a range of $\delta^{15}N$ values similar to that of the ctenophore *Mnemiopsis leidyi*, suggesting that they feed at the same average trophic level. At any single station, however, $\delta^{15}N_{scyphozoa}$ might differ from $\delta^{15}N_{Mnemiopsis}$ by as much as 3.9 ‰, which indicates that the 2 species may at times have different feeding strategies. In contrast, samples of the ctenophore *Beroe ovata* from the fall cruise were consistently higher in $\delta^{15}N$ than *M. leidyi* collected at the same station. This pattern is consistent with the trophic biology of *B. ovata*, which feeds on other ctenophores, including *M. leidyi* (Reeve & Walter 1978, and references therein). Chaetognaths from the 2 stations on the fall cruise were also analyzed; in both cases, $\delta^{15}N_{chaetognath}$ was about 2 ‰ greater than $\delta^{15}N_{Acartia}$, a difference in keeping with the predatory feeding behavior of chaetognaths. The $\delta^{15}N$ of *Centropages typicus* was very similar to that of the chaetognaths, suggesting that this large copepod may also be feeding on crustacean zooplankton.

Taken together, these data suggest that the zooplankton in the Bay as a whole are characterized by greater isotopic heterogeneity in the spring than in the fall. This is reflected in the larger spread of replicate analyses of zooplankton collected in the spring, and in the greater overall spatial variability in the $\delta^{15}N$ of zooplankton at that time of year. This seasonal difference is consistent with the greater spatial variability in $\delta^{15}PN_{whl}$ during the spring, which in turn reflects the dominant influence of phytoplankton uptake on the DIN pools during that season.

### Temporal patterns in the $\delta^{15}N$ of plankton

The sampling strategy followed in this study allows an evaluation of changes in the $\delta^{15}N$ of plankton on 2 different time scales: between cruises and between transects. In general, between-transect differences were as great as between-cruise differences in $\delta^{15}N$ for plankton collected at any given station. The best example of the magnitude of change that can occur on relatively short time scales comes from the fall cruise, during which a storm contributed to the vertical mixing of nutrients and $O_2$ in the water column (Horrigan et al. 1990b). This storm occurred in the interval between the 2 transects of the Bay, which differed markedly in the $\delta^{15}N$ of both surface PN and *Acartia tonsa* (Figs. 5 and 6). Over a 1 wk period, the $\delta^{15}N$ of surface PN decreased by as much as 3.8 ‰ in the mid-Bay, though stations at the northern and southern ends of the Bay showed increases in $\delta^{15}PN_{whl}$ of 2.6 ‰. The decrease in $\delta^{15}PN_{whl}$ between transects reflected the uptake of $NH_4^+$ by phytoplankton, and yielded an

estimate of the isotopic fractionation factor for $NH_4^+$ uptake (Montoya et al. unpubl.). Most importantly in this context, these changes were of the same magnitude as the differences between seasons. The implications of these rapid changes in $\delta^{15}N$ during the fall cruise will be discussed in greater detail elsewhere (Montoya et al. unpubl.).

In contrast, the $\delta^{15}N$ of PN below the pycnocline was largely unchanged between transects of the fall cruise. At Stns 744A and 804C, however, $\delta^{15}PN_{whl}$ decreased by 1.7 and 1.8‰, respectively. These changes could not be accounted for by simple mixing of the surface and deep pools of PN, since the surface values of $\delta^{15}PN_{whl}$ at these stations were higher than deep values on both transects. At both stations, the concentration of chlorophyll *a* was lower, and the ratio of pheopigments to chlorophyll *a* was higher on the second transect. As noted above, $\delta^{15}PN_{whl}$ and chlorophyll *a* tended to covary on this cruise, suggesting that the phytoplankton component of PN may have been relatively high in $\delta^{15}N$. The decrease in both $\delta^{15}N$ and chlorophyll *a* at these 2 stations is consistent with this suggestion.

During the spring cruise, there was no obvious Bay-wide trend in the surface values of $\delta^{15}PN_{whl}$ with time. Most of the changes between transects were similar in magnitude to the differences between samples collected on successive days at several stations during the first transect of the cruise. The largest change between transects occurred in the northern part of the Bay, where $\delta^{15}PN_{whl}$ increased in the region of Stns 853C and 845F. This increase in $\delta^{15}PN_{whl}$ in the surface layer was associated with a decrease in the surface concentration of chlorophyll *a* (Horrigan et al. 1990b), and a decrease in $\delta^{15}PN_{whl}$ at depth. These observations suggest that the sinking of phytoplankton biomass of relatively low $\delta^{15}N$ out of the surface layer may have contributed to the changes in $\delta^{15}PN_{whl}$ both above and below the pycnocline at these stations. If this interpretation is correct, then the contribution of phytoplankton to $\delta^{15}PN_{whl}$ was very different during the 2 cruises: the phytoplankton component of $PH_{whl}$ was relatively low in $\delta^{15}N$ in the spring, and relatively high in $\delta^{15}N$ in the fall. This difference may be related to the generally higher values of $\delta^{15}(NO_3^- + NO_2^-)$ and $\delta^{15}NH_4^+$ which characterized the Bay in the fall (compare Figs. 4 and 7). Although the average values of $\delta^{15}PN_{whl}$ were similar on the first 3 transects of the Bay (the 2 in the spring and the first transect of the fall cruise), the higher $\delta^{15}N$ of the DIN pools during the fall cruise may have contributed to a relatively high $\delta^{15}N$ in the biologically active component of whole PN. Cifuentes et al. (1988) have reported such a seasonal cycle in the $\delta^{15}N$ of PN in the Delaware River and Bay.

Elsewhere in the Bay, $\delta^{15}PN_{whl}$ at depth decreased between transects of the spring cruise, though these changes were not associated with similar changes in surface samples. The extent of anoxia in deep water was greater on the second transect, and experiments conducted between the 2 transects showed high rates of bacterial production and $NH_4^+$ uptake by particles below the pycnocline (Horrigan et al. 1990b). These observations suggest that at least part of the change in $\delta^{15}PN_{whl}$ in the deep layer resulted from bacterial production and isotopic fractionation during $NH_4^+$ uptake.

The $\delta^{15}N$ of *Acartia tonsa* showed clear changes between transects both in the spring and the fall. In the spring, only 4 stations yielded samples of *A. tonsa* on both transects, and $\delta^{15}N_{Acartia}$ increased at all of these stations by 1.5 to 2.5‰. At the northernmost of the 4 stations, the surface value of $\delta^{15}PN_{whl}$ increased by 1.8‰ between transects, but the other stations showed little change in $\delta^{15}PN_{whl}$. At all of these stations, the surface concentration of chlorophyll *a* decreased between transects. The magnitude of the change in pigment concentrations was greatest in the northern part of the Bay, where a prominent bloom around Stn 853C on the first transect had declined greatly by the second transect. These pigment concentration changes suggest that the quantity, and perhaps the quality, of the particulate food available to the copepods changed between the first and second transects. A shift in diet toward greater dependence on zooplankton (Lonsdale et al. 1979) could also have contributed to the increase in $\delta^{15}N_{Acartia}$ during this cruise.

In the fall, $\delta^{15}N_{Acartia}$ decreased between transects throughout the Bay, with changes as great as 2.6‰. These decreases were consistent with the concurrent decline in $\delta^{15}PN_{whl}$, since a decrease in the $\delta^{15}N$ of phytoplankton should ultimately lead to a decrease in the $\delta^{15}N$ of grazers. The relationship between the change in $\delta^{15}N$ of the 2 trophic levels yielded an estimate of the turnover time for nitrogen in copepods very similar to literature values for the generation time of *Acartia tonsa* (Montoya et al. unpubl.).

The ctenophore *Mnemiopsis leidyi* did not show dramatic changes in $\delta^{15}N$ between transects of either cruise. In the spring, both transects showed a mid-Bay maximum in $\delta^{15}N$, though the location of the peak value of $\delta^{15}N_{Mnemiopsis}$ was somewhat farther north on the second transect. This shift may simply be an artifact of the relatively sparse sample set from the second transect. During the fall cruise, $\delta^{15}N_{Mnemiopsis}$ decreased slightly at 5 of the 6 stations sampled on both transects. During both cruises, the between-transect changes in $\delta^{15}N_{Mnemiopsis}$ were much smaller than the changes in $\delta^{15}PN_{whl}$ and $\delta^{15}N_{Acartia}$. This difference in the magnitude of temporal variation between trophic levels probably results from the much larger size of the ctenophores, and the longer turnover time for body nitrogen associated with greater size.

The magnitude and rapidity of some of the changes in $\delta^{15}N$ during this study clearly indicate that temporal variability on relatively short time scales must be considered in interpreting $^{15}N$ natural abundance data. In practical terms, this means that, in ecosystems as dynamic as the Chesapeake Bay, repeated sampling through time may be necessary to determine the average behavior of the system. Another benefit of repeated sampling is that changes in $\delta^{15}N$ are often as informative as average values since the magnitude and direction of a change in $\delta^{15}N$ can provide information about the nature and extent of biologically-mediated transformations of nitrogen (Horrigan et al. 1990a, Montoya et al. unpubl.). In addition, a knowledge of the relative rates of change associated with different pools of nitrogen in an ecosystem may allow some reconstruction of the time course of change in $\delta^{15}N$ from samples of pools with different response times. For example, these data suggest that the $\delta^{15}N$ of ctenophores is less variable through time than $\delta^{15}N_{Acartia}$, which, in turn, is less variable than $\delta^{15}PN_{whl}$. This raises the possibility that the value of $\delta^{15}N_{Mnemiopsis}$ might provide an estimate of the average value of $\delta^{15}N_{Acartia}$ over some characteristic time preceding the time of sample collection. Similarly, the instantaneous value of $\delta^{15}N_{Acartia}$ might be a good indicator of the mean value of $\delta^{15}PN_{whl}$ over another, shorter, characteristic time. This sort of analysis will require a better understanding of the relationship between the $\delta^{15}N$ of a consumer and that of its food, but could help reduce the need for repeated sampling of dynamic systems.

### Whole-bay temporal trends in $\delta^{15}N$

Although short-term changes in $\delta^{15}N$ at a station can indicate the nature of local processes affecting the $^{15}N$ content of different planktonic pools of nitrogen, changes on a larger spatial scale may be easiest to find in the distribution of $\delta^{15}N$ values from an entire transect. For example, a comparison of the values of surface $\delta^{15}PN_{whl}$ from the 4 transects of this study suggests that the overall distributions of $\delta^{15}N$ values from the 2 transects of the spring cruise and the first transect of the fall cruise were quite similar, but that the final transect of the fall cruise was significantly different from the other 3 (Figs. 4 and 7). The major form of DIN available in the surface layer in much of the Bay was $NO_3^-$ in the spring and $NH_4^+$ in the fall. This difference reflects the important contribution of $NH_4^+$ produced by remineralization below the pycnocline to the nutrition of surface layer phytoplankton during the summer and autumn (Taft et al. 1978, Taft et al. 1980, Officer et al. 1984). The well-developed pycnocline and strong vertical gradients in dissolved nutrients and $O_2$ present during the first 3 transects of this study all suggest that vertical mixing was strongly inhibited. In contrast, the storm which passed over the Bay between transects of the fall cruise contributed to a significant mixing of the surface and deep waters of the Bay, an increase in the concentration of $NH_4^+$ in much of the Bay, and a concomitant increase in the rate of uptake of $NH_4^+$ by phytoplankton (Horrigan et al. 1990b). These observations all suggest that the availability of $NH_4^+$, and the resulting opportunities for isotopic fractionation during the uptake of $NH_4^+$ by phytoplankton, exert a major influence on the $\delta^{15}N$ of surface PN in the Bay as a whole.

In contrast, data from below the pycnocline show that the first transect of the spring cruise was the outlier in the set, with notably higher values of $\delta^{15}N$ than any of the other 3 transects (Figs. 4 and 7). During this transect, several stations were characterized by very high concentrations of chlorophyll *a* along with high rates of primary production in the surface layer. A variety of ancillary data suggest that the decomposition of material produced by phytoplankton growth in the surface layer contributed to high rates of $NH_4^+$ remineralization below the pycnocline (Horrigan et al. 1990b). The elevated values of $\delta^{15}PN_{whl}$ at depth reflect the isotopic fractionation associated with the decomposition of PN sinking out of the surface layer (Miyake & Wada 1971, Wada 1980). Thus, the high values of $\delta^{15}PN_{whl}$ below the pycnocline were an indirect result of the high levels of biomass and primary production in the surface layer during this transect.

## CONCLUSIONS

Measurements of the stable isotope content of plankton in the Chesapeake Bay have yielded a number of insights into the nitrogen cycle in the Bay. The $\delta^{15}N$ of PN reflects the isotopic enrichment of the DIN consumed by phytoplankton, and the relationship between $\delta^{15}PN_{whl}$ and the $\delta^{15}N$ of the dissolved pools can provide an estimate of the relative importance of phytoplankton uptake of DIN in comparison to other sinks for DIN. These results indicated that the phytoplankton utilize $NH_4^+$ and ($NO_3^- + NO_2^-$) roughly in proportion to availability. In spring, phytoplankton uptake was the major influence on the $\delta^{15}N$ of the DIN pool, while microbially-mediated processes were more important in fall. With one notable exception, the $\delta^{15}N$ of the zooplankton showed the usual increase with trophic level, and the average separation in $\delta^{15}N$ between trophic levels in the Bay is similar to values reported from other ecosystems. The only departure from this pattern occurred during the spring cruise at the southern end of the Bay, where $\delta^{15}N_{Acartia}$ was higher than

$\delta^{15}N_{Mnemiopsis}$. A variety of data suggest that this inversion of the usual relationship between $\delta^{15}N_{Acartia}$ and $\delta^{15}N_{Mnemiopsis}$ may be due to changes in either the feeding habits or the isotopic fractionation factor associated with feeding in *Acartia tonsa*.

The $\delta^{15}N$ of PN and *Acartia tonsa* both can change markedly on a time scale of roughly a week (between transects). The rapidity and magnitude of some of these changes, and the varying degree of spatial and temporal heterogeneity in the $\delta^{15}N$ of the plankton clearly indicate that intensive sampling may be essential in studies of $^{15}N$ in dynamic systems like the Chesapeake Bay.

*Acknowledgements.* We thank Ms C. R. Adler, Ms A. R. Michelson, and Mr R. Loftus for assistance in collecting the samples, Mr J. L. Nevins for assistance in all phases of sample collection and analysis, and the captain and crew of the RV 'Warfield' for their assistance and cooperation. The comments and suggestions of Drs M. A. Altabet, R. Goericke, R. J. Etter, and 2 anonymous reviewers were invaluable in helping us to clarify and streamline this manuscript. This work was supported by NSF grants OCE-82-14932 and OCE-86-14199.

## LITERATURE CITED

Altabet, M. A., McCarthy, J. J. (1986). Vertical patterns in $^{15}N$ natural abundance in PON from the surface waters of warm-core rings. J. mar. Res. 44: 185–201

Carpenter, J. H., Pritchard, D. W., Whaley, R. C. (1969). Observations of eutrophication and nutrient cycles in some coastal plain estuaries. In: Eutrophication: causes, consequences, correctives. National Academy of Sciences, Washington, D.C., p. 210–211

Checkley, D. M., Entzeroth, L. C. (1985). Elemental and isotopic fractionation of carbon and nitrogen by marine, planktonic copepods and implications to the marine nitrogen cycle. J. Plankton Res. 7: 553–568

Cifuentes, L. A., Sharp, J. H., Fogel, M. L. (1988). Stable carbon and nitrogen isotope biogeochemistry in the Delaware estuary. Limnol. Oceanogr 33: 1102–1115

Deason, E. E., Smayda, T J. (1982). Experimental evaluation of herbivory in the ctenophore *Mnemiopsis leidyi* relevant to ctenophore-zooplankton-phytoplankton interactions in Narragansett Bay, Rhode Island, USA. J. Plankton Res. 4: 220–236

DeNiro, M. J., Epstein, S. (1981). Influence of diet on the distribution of nitrogen isotopes in animals. Geochim. Cosmochim. Acta 45: 341–351

Fry, B. (1988). Food web structure on Georges Bank from stable C, N, and S isotopic compositions. Limnol. Oceanogr. 33: 1182–1190

Heaton, T. H. E. (1986). Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere: a review. Chem. Geol. (Isot. Geosci. Sect.) 59: 87–102

Horrigan, S. G., Montoya, J. P., Nevins, J. L., McCarthy, J. J. (1990a). Natural isotopic composition of dissolved inorganic nitrogen in the Chesapeake Bay. Estuar. coast. Shelf Sci. (in press)

Horrigan, S. G., Montoya, J. P., Nevins, J. L., McCarthy, J. J., Ducklow, H. W., Goericke, R., Malone, T (1990b). Nitrogenous nutrient transformations in the spring and fall in the Chesapeake Bay. Estuar. coast. Shelf Sci. (in press)

Junk, G., Svec, H. J. (1958). The absolute abundance of the nitrogen isotopes in the atmosphere and compressed gas from various sources. Geochim. Cosmochim. Acta 14: 234–243

Lonsdale, D. J., Heinle, D. R., Siegfried, C. (1979). Carnivorous feeding behavior of the adult calanoid copepod *Acartia tonsa* Dana. J. exp. mar Biol. Ecol. 36: 235–248

Macko, S. A., Lee, W. Y., Parker, P. L. (1982). Nitrogen and carbon isotope fractionation by two species of marine amphipods: laboratory and field studies. J. exp. mar Biol. Ecol. 63: 145–149

Mariotti, A. (1983). Atmospheric nitrogen as a reliable standard for natural $^{15}N$ abundance measurements. Nature, Lond. 303: 685–687

Mariotti, A. (1984). Natural $^{15}N$ abundance measurements and atmospheric nitrogen standard calibration. Nature, Lond. 311 251–252

Mariotti, A., Lancelot, C., Billen, G. (1984). Natural isotopic composition of nitrogen as a tracer of origin for suspended organic matter in the Scheldt estuary. Geochim. Cosmochim. Acta 48: 549–555

McCarthy, J. J. (1980). Nitrogen. In: I. Morris (ed.) The physiological ecology of phytoplankton. Blackwell, Oxford, p. 191–234

McCarthy, J. J., Taylor, W. R., Taft, J. L. (1975). The dynamics of nitrogen and phosphorus cycling in the open waters of the Chesapeake Bay. In: Church, T M. (ed.) Marine chemistry in the coastal environment. ACS, Washington, D.C., p. 664–681

McCarthy, J. J., Taylor, R. W., Taft, J. L. (1977). Nitrogenous nutrition of the plankton in the Chesapeake Bay. 1. Nutrient availability and phytoplankton preferences. Limnol. Oceanogr. 22: 996–1011

Minagawa, M., Wada, E. (1984). Stepwise enrichment of $^{15}N$ along food chains: further evidence and the relation between $\delta^{15}N$ and animal age. Geochim. Cosmochim. Acta 48: 1135–1140

Miyake, Y., Wada, E. (1967). The abundance ratio of $^{15}N/^{14}N$ in marine environments. Rec. oceanogr. Wks Japan 9: 37–53

Miyake, Y., Wada, E. (1971). The isotope effect on the nitrogen in biochemical oxidation-reduction reactions. Rec. oceanogr. Wks Japan 11: 1–6

Mullin, M. M., Rau, G. H., Eppley, R. W (1984). Stable nitrogen isotopes in zooplankton: Some geographic and temporal variations in the North Pacific. Limnol. Oceanogr. 29: 1267–1273

Nevins, J. L., Altabet, M. A., McCarthy, J. J. (1985). Nitrogen isotope analysis of small samples: sample preparation and calibration. Analyt. Chem. 57 2143–2145

Officer, C. B., Biggs, R. B., Taft, J. L., Cronin, L. E., Tyler, M. A., Boynton, W. B. (1984). Chesapeake Bay anoxia: origin, development, and significance. Science 223: 22–27

Owens, N. J. P. (1985). Variations in the natural abundance of $^{15}N$ in estuarine suspended particulate matter: a specific indicator of biological processing. Estuar. coast. Shelf Sci. 20: 505–510

Owens, N. J. P. (1987). Natural variations in $^{15}N$ in the marine environment. Adv. mar. Biol. 24: 390–451

Peterson, B. J., Fry, B. (1987). Stable isotopes in ecosystem studies. Ann. Rev. Ecol. Syst. 18: 293–320

Reeve, M. R., Walter, M. A. (1978). Nutritional ecology of ctenophores – a review of recent research. In: Russell, R. S., Yonge, M. (eds.) Advances in marine biology. Academic Press, New York, p. 249–287

Taft, J. L., Elliott. A. J., Taylor, W R. (1978). Box model

analysis of Chesapeake Bay ammonium and nitrate fluxes. In: Wiley, M. L. (ed.) Estuarine interactions. Academic Press, New York, p. 115–130

Taft, J. L., Taylor, W R., Hartwig, E. O., Loftus, R. (1980). Seasonal oxygen depletion in Chesapeake Bay. Estuaries 3: 242–247

Wada, E. (1980). Nitrogen isotope fractionation and its significance in biogeochemical processes occurring in marine environments. In: Goldberg, E., Horibe, Y., Saruhashi, K. (eds.) Isotope marine chemistry. Uchida Rokakuho Co., Tokyo, p. 375–398

Wada, E., Hattori, A. (1978). Nitrogen isotope effects in the assimilation of inorganic nitrogenous compounds. Geomicrobiol. J. 1: 85–101

Wada, E., Kadonaga, T., Matsuo, S. (1975). $^{15}N$ abundance in nitrogen of naturally occurring substances and global assessment of denitrification from isotopic viewpoint. Geochem. J. 9: 139–148

Wada, E., Minagawa, M., Mizutani, H., Tsuji, T., Imaizumi, R., Karasawa, K. (1987a). Biogeochemical studies on the transport of organic matter along the Otsuchi River watershed, Japan. Estuar. coast. Shelf Sci. 25: 321–336

Wada, E., Terazaki, M., Kobaya, Y., Nemoto, T (1987b). $^{15}N$ and $^{13}C$ abundances in the Antarctic Ocean with emphasis on biogeochemical structure of the food web. Deep Sea Res. 34: 829–841

Yoshida, N. (1988). $^{15}N$-depleted $N_2O$ as a product of nitrification. Nature, Lond. 335: 528–529

*This article was presented by Dr M. R. Lewis, Washington, D.C., USA*

*Manuscript first received: November 3, 1989*
*Revised version accepted: March 9, 1990*