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Isotopic characterization of atmospheric nitrogen inputs as sources of enhanced primary production in coastal Atlantic Ocean waters

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Abstract Current estimates indicate that atmospheric nitrogen deposition is responsible for 26 to over 70% of “new” nitrogen (N) input to North Carolina estuaries and coastal waters. Concentrations of N in coastal rainfall events in a 2-yr period (August 1990 to 1992) ranged from 0.7 to 144 μM for NO_3^- and 0.5 to 164 μM for NH_4^+ . The $\delta^{15}\text{N}$ values of the NO_3^- and the NH_4^+ were determined in 15 rain events. NH_4^+ values averaged -3.13‰ (range: -12.5 to $+3.6$), while NO_3^- plus dissolved organic N fractions had an average $\delta^{15}\text{N}$ of $+1.0\text{‰}$ (range: -2.0 to $+4.7$). The uptake of this isotopically light N into particulate N, in parallel with primary productivity and biomass (as chlorophyll *a*) determinations, was examined in microcosm and mesocosm bioassays. As phytoplankton productivity and biomass increased with added rainwater N, the $\delta^{15}\text{N}$ of particulate N decreased. To investigate the effects of significant atmospheric N loading with stable isotope tracers, we measured the $\delta^{15}\text{N}$ of the $> 1 \mu\text{m}$ fraction from surrounding coastal waters. Owing to the episodic nature of atmospheric deposition and the great variation in N loading with each event, a simple assessment of the atmospheric contribution was not possible. During a period in which rainfall inputs were significant and frequent (August 1992), $\delta^{15}\text{N}$ values were several ‰ more negative than during periods of drought (Fall 1990). These experiments and observations emphasize the contribution of atmospheric nitrogen deposition to “new” production in coastal waters.

Introduction

Coastal oceans and estuaries receive a significant fraction of their external or “new” nitrogen (N) loading from atmospheric sources of natural and anthropogenic origin. Current estimates range from 20 to over 50% (Correll and Ford 1982; Duce 1986, 1991; Soderlund 1987; Loye-Pilot et al. 1990; Prado-Fiedler 1990; Fisher and Oppenheimer 1991). Even surface waters of remote open ocean regions are now under the influence of continentally derived, atmospheric N enrichment (Menzel and Speath 1962; Jickells et al. 1982; Prospero and Savoie 1989; Duce et al. 1991; Owens et al. 1992). From a N budget perspective, atmospheric N deposition is expected to be most significant in estuaries, coastal oceans, and continentally bound seas “downwind” of large emission sources (Rodhe et al. 1980; Galloway et al. 1984; Derwent and Nodop 1986). Anthropogenic atmospheric N emissions have increased and will continue to do so as urban, agricultural, and industrial sources proliferate in both highly developed and developing countries (Stensland 1980; Bribblecombe and Stedman 1982; Placit et al. 1986; Rodhe and Rood 1986).

Accelerating atmospheric N inputs to coastal waters may be linked to enhanced primary production in coastal waters, because production in these waters is frequently N limited and hence sensitive to N enrichment (Dugdale 1967; Ryther and Dunstan 1971; Boynton et al. 1982; D’Elia et al. 1986; Howarth 1988; Fisher et al. 1992; Paerl 1993). Nitrogen-enriched rainfall has been shown to stimulate primary production in N depleted waters, such as those off the North Carolina Atlantic coast (Paerl 1985; Paerl et al. 1990; Willey and Cahoon 1991; Willey and Paerl 1993). The dominant, biologically available, inorganic atmospheric N species include NO_3^- and NH_4^+ (Duce 1986; GESAMP 1989; Duce et al. 1991). In addition, atmospheric deposition contains significant amounts organic N, trace concentrations of PO_4^{3-} , and metals, most notably Fe (GESAMP 1989; Duce et al. 1991). In light of recent findings that Fe and perhaps other trace metals may play a role as limiting nutrients in certain regions of the world’s

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oceans (Bruland et al. 1991; Martin et al. 1991), the possibility exists that components of atmospheric deposition in addition to N may be responsible for the observed stimulation of coastal primary production.

We investigated N isotope tracers at the natural abundance level ($\delta^{15}\text{N}$) to test whether the nitrogen in atmospheric deposition is responsible for enhanced primary production. The effectiveness of natural abundance level tracers depends on many parameters that must be understood before the technique can be generally applied. First, atmospheric nitrogen sources must have distinct, if not unique, isotopic signatures relative to other major nitrogen sources. Second, it is well known that during uptake and biosynthesis, numerous isotope fractionations occur in nitrogen metabolism by phytoplankton and bacteria (Fogel and Cifuentes 1993). Knowledge concerning the possibility and extent of these fractionations is therefore critical. Third, there must be sufficient amounts of nitrogen compounds added to the system, such that uptake of the atmospheric N deposition can be detected. Finally, a basic understanding of phytoplankton production and trophic fate is needed to understand the mechanism of nitrogen transfer.

The $\delta^{15}\text{N}$ of ammonium (NH_4^+) and nitrogen oxides (NO_x) in rainwater has been measured primarily in Europe and South Africa (Heaton 1986). Isotopic compositions in atmospheric N emissions varied with sources and their location. Nitrogen emissions in the North Carolina, USA coastal area could originate from local municipalities (NO_x from vehicles) and agricultural practices (e.g. NH_3 volatilization) or they could be transported for some distance to the coast from midwestern industrial sites (Stensland 1980; Galloway et al. 1984; Luke and Dickerson 1987). Showers et al. (1990) published a study on the $\delta^{15}\text{N}$ of dissolved nitrogen nutrients in the Neuse River, which enter this coastal region, so that comparisons of their results with our measurements of $\delta^{15}\text{N}$ in rainwater should answer the first concern.

Nitrogen is a limiting nutrient in North Carolina coastal waters throughout much of the year (Thayer 1974; Paerl 1985; Paerl et al. 1990; Rudek et al. 1991), and concentrations of both NH_4^+ and NO_3^- rarely exceed a few μM (Rudek 1992). At these concentrations, microorganisms actively transport NH_4^+ across their cell membranes (Kleiner 1981). Experiments with phytoplankton and bacteria (Pennock et al. 1988; Hoch et al. 1992; Fogel and Cifuentes 1993) at these low concentrations show very little fractionation (less than 4‰). Isotopic fractionation of NO_3^- can also be significant (Pennock et al. 1988); however, in situations where all the NO_3^- is taken up by phytoplankton, there is no possibility for this fractionation to be expressed.

Rainfall amounts and nutrient levels of each rainfall event have been measured at the Institute of Marine Sciences (IMS), Morehead City, North Carolina, for the past five years (Paerl et al. 1990). Many of these rainfall events contain sufficient amounts of N for isotopic analyses ($>3 \mu\text{M N-NH}_4^+$; $>10 \mu\text{M N-NO}_3^-$). Utilizing an array of microcosm and mesocosm bioassays in combination with stable N isotope determinations, we characterized N sources and their fate in North Carolina coastal waters.

Methods and materials

Estimating atmospherically derived "new" N inputs

Major "new" nitrogen inputs, including atmospheric contributions based on the U. S. Environmental Protection Agency's Research Atmospheric Deposition Model (RADM), were estimated for coastal North Carolina, USA waters (U.S. EPA, Air Quality Laboratory, Research Triangle Park, NC). The RADM-based average daily atmospheric deposition (wet and dry) estimate was $1161.5 \mu\text{g N m}^{-2} \text{d}^{-1}$ for the North Carolina coastal region near Morehead City (Fig. 1). The dominant local source of terrigenous input in this region is the Newport River (Fig. 1), which drains nearby Coastal Plain agricultural and municipal wastewater discharges. No significant industrial N sources exist in this area. Newport River daily discharge into coastal waters is well characterized (Kirby-Smith and Costlow 1989). The remaining "new" N sources include upwelled and advective inputs originating from continental slope and deeper waters east of the Gulf Stream (Atkinson 1985) and N_2 fixation. Nitrogen fixation is largely associated with infrequent near-shore blooms of the planktonic cyanobacterium *Trichodesmium* sp.; it is estimated to contribute no more than 5% to total "new" N inputs (Paerl et al. 1987; Paerl et al. 1993). Groundwater seepage may also contribute to the N budget, but at present its relative contribution is unknown. Because advective and N_2 fixation inputs are very small, they had little impact on the "new" N input calculations. Infrared AVHRR satellite imagery, capable of detecting temperature differences between riverine discharge plumes and coastal surface waters, was used to delineate the minimal (225 km^2) and maximal (1600 km^2) aerial extent of Newport River discharge into coastal Atlantic shelf waters off Morehead City, North Carolina.

For the Albemarle-Pamlico estuarine system (collectively referred to as Pamlico Sound in Fig. 1), terrigenous (runoff) and point source N inputs via major tributaries have been documented (Stanley 1989; Dodd et al. 1992). For the purpose of N budget calculations, these input sources were combined. No reliable estimate of groundwater N input exists, but it is considered to be small ($<10\%$) relative to surface inputs (Dodd et al. 1992). In this system N_2 fixation also accounts for less than 5% of "new" N inputs (Paerl et al. 1987). We utilized the RADM-based coastal North Carolina atmospheric N deposition estimates for this estuarine system as well.

Sampling sites and procedures

Rainwater containing both wet and dry deposition was routinely collected following storm events. The collection site was located on the IMS roof, well clear of trees and other obstructions potentially influencing deposition rates and nutrient content. An Aerochem Model 301 automated wet/dry sampler was utilized for collecting wet and dry deposition on which pH and nutrient determinations were made. Following storm events, rain collection buckets were cleaned by rinsing with 0.1 N HCl, followed by exhaustive rinses with 18 mega Ω deionized water. Bucket samples were analyzed for soluble nutrients ($\text{NO}_3^-/\text{NO}_2^-$, NH_4^+ , PO_4^{3-}) using high sensitivity colorimetric techniques outlined in Strickland and Parsons (1972). pH was analyzed using a Fisher, high sensitivity pencil electrode. pH calibrations prior to December 1990 were based on high ionic strength standards. Subsequent samples were calibrated against a set of Orion low ionic strength buffers. All pH measurements were triplicated, with the mean reported here.

Bulk rainwater samples for bioassay purposes were collected on the IMS roof in cleaned (as outlined above) polyethylene 20-liter pans which were positioned on an elevated stand near the wet/dry collector. Following rainfall events, bulk samples were transferred to cleaned polyethylene carboys for use in bioassays. On some occasions, carboys were stored frozen at -20°C for several weeks for later use in bioassays. If samples were stored, they were re-analyzed for nutrient content just prior to bioassay use.

Near-surface seawater samples were collected from three sites (Fig. 1) for subsequent nutrient and particulate nitrogen (PN) $\delta^{15}\text{N}$ analyses. Sampling sites included: (1) Bogue Sound, a euhaline ti-

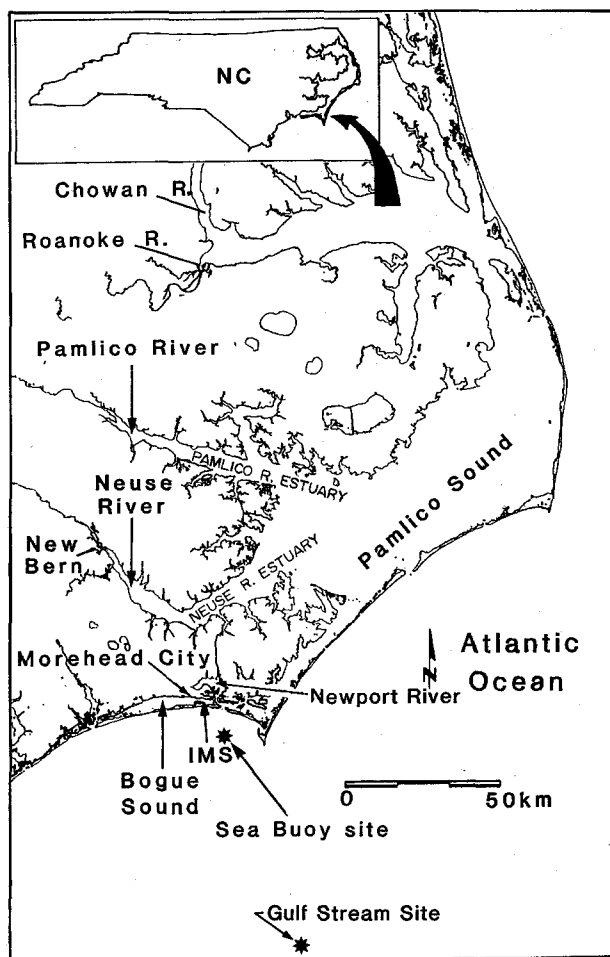


Fig. 1 Map of coastal North Carolina, including Atlantic coastal waters adjacent to Bogue Sound and the Institute of Marine Sciences (IMS) in Morehead City. Major rivers and estuaries shown, including the local Newport River Estuary (mouth of the Newport River) and the Albemarle-Pamlico Sound system (referred to here as Pamlico Sound) which is delineated by the Outer Banks. The near-shore Sea Buoy and off-shore Gulf Stream collection sites are marked (*).

dal sound on which IMS is located; (2) a coastal Atlantic Ocean location 7 km due south of Beaufort Inlet, termed the "Seabuooy"; and (3) a Gulf Stream location 40 km south of Beaufort Inlet (Fig. 1). All samples were collected with either cleaned polyethylene buckets or carboys and dispensed in cleaned Nalgene 1 to 2 liter polyethylene bottles for transport on ice to IMS for filtration.

Examining the trophic fate and production impacts of atmospheric nitrogen deposition

In order to investigate direct impacts of atmospheric N deposition on in situ primary production, arrays of microcosms and mesocosms were deployed using N-depleted coastal water derived from Bogue Sound (Fig. 1). During high tide, sets of ≈670-liter cylindrical (1 m diameter, 1.3 m deep) translucent fiberglass "hydrocorral" mesocosms or 3-liter polyethylene "Cubitainer" microcosm bioassay vessels were filled with Atlantic Ocean water. Both sets of vessels were maintained in a 150 m², 1.2 m deep outdoor concrete pond system (flushed with Bogue Sound water), ensuring natural irradiance and temperature conditions. Mesocosms remained open to the atmosphere and were circulated by bubbling with air. This facilitated gas exchange and complete vertical mixing, typifying shallow, near-shore coastal waters (Rudek et al. 1991; Rudek 1992). Cubitainers

were suspended in the pond, agitated twice daily and covered with a layer of neutral density screening to avoid photoinhibition of phytoplankton (Rudek et al. 1991; Paerl et al. 1990). We used in situ ¹⁴C primary productivity and chlorophyll *a* measurements to assess the impacts of atmospheric nitrogen input, at natural rainfall dilution levels (Paerl et al. 1990), as well as a range of nutrients known to stimulate primary production of North Carolina estuarine and coastal phytoplankton assemblages (Mallin et al. 1991; Rudek et al. 1991). Specific details on bioassay methods are in Paerl (1987), Paerl et al. (1990) and Rudek et al. (1991).

Rainwater and individual, as well as combined, nutrient additions were made in triplicate to bioassays. Rainwater was added at 1 to 10% of bioassay volumes; dilutions were based on salinity changes in natural surface waters immediately after rainfall events. Nutrient additions included N-NO₃⁻ (as NaNO₃: 0.1 to 6 μM) and P-PO₄³⁻ (as KH₂PO₄: 0.1 to 3 μM). The δ¹⁵N of the NaNO₃ was +0.9‰. Bioassays were sampled 1, 2, 5 and 8 d after initiation. Inorganic N (NO_x⁻ and NH₄⁺) and P (PO₄³⁻) content of rainwater and receiving coastal waters were determined by high-sensitivity colorimetric techniques (Jones 1984; Strickland and Parsons 1972).

Microalgal primary production was determined by collecting subsamples at intervals given above, dispensing samples in triplicate clear and single dark 125-ml Pyrex primary productivity bottles, and adding 7 μCi of ¹⁴C-NaHCO₃ (58 μCi μmol⁻¹ specific activity; ICN Inc.). Bottles were then resuspended in the mesocosms or pond (corresponding to the light intensity in microcosms) and incubated for 3 h at mid-day. Samples were filtered onto 25 mm GF/F filters, processed and assayed for ¹⁴C incorporation according to Paerl (1987). Parallel samples were analyzed for chlorophyll *a* (and phaeopigments) and carotenoid accessory pigments by trichromatic spectrophotometric, fluorometric and HPLC photodiode array spectrophotometry techniques (Millie et al. 1994).

Productivity and biomass assays were accompanied by stable N isotope analyses at the natural abundance level of the incorporation of atmospheric vs non-atmospheric sources of nitrogen supporting and stimulating production. For N isotope determinations, particulate material from bioassays was filtered (1 to 2 liters) on a precombusted GF/F filter, dried, and stored at -20 °C in a desiccator until analysis. The filter, cut into strips, was placed in a pre-heated quartz tube with CuO and Cu reagents, evacuated and sealed. The sealed tube was combusted at 900 °C for 1 h, then cooled at a controlled rate. Nitrogen gas was cryogenically separated from CO₂ and H₂O and subsequently analyzed in a double focusing isotope ratio mass spectrometer (modified by Nuclide Corp.). The isotope ratio (δ¹⁵N) is defined as:

$$\delta^{15}\text{N} = \left[\frac{(^{15}\text{N}/^{14}\text{N} \text{ sample})}{(^{15}\text{N}/^{14}\text{N} \text{ standard})} - 1 \right] \times 1000. \quad (1)$$

The standard for δ¹⁵N is air (0.0‰). Replicate analyses of samples yielded a SD of ±0.5‰, whereas for standards the reproducibility was ±0.2‰. For dissolved combined N species, NH₄⁺ was adsorbed on Zeolite (W-85) (Velinsky et al. 1989). Zeolite plus NH₄⁺ were then analyzed as above. Both NO₃⁻ and any dissolved organic N from ≈250 ml rainwater were freeze-dried in a CentriVap (Lab-conco), placed in a quartz tube and analyzed as above. Reproducibility of these analyses was typically ±0.5‰.

Results

Budgetary estimates of the importance of atmospheric nitrogen inputs in estuarine coastal Atlantic Ocean waters

Based on watershed vs atmospheric N input estimates in North Carolina coastal waters, we determined that terrigenous inputs (dominated by Newport River discharge) con-

Table 1 New nitrogen inputs for North Carolina coastal waters. Shown are conservative (small Newport River discharge plume) and liberal (large river discharge plume) scenarios for the extent of atmospheric (atm.) inputs in the Newport River discharge (in Atlantic coastal waters) area. Estimates of atmospheric N loading for the Albemarle-Pamlico (A.-P.) Sound System also given. The Regional Atmospheric Deposition Model estimate for daily atmospheric deposition in North Carolina coastal waters is $1\,161.5\ \mu\text{g N m}^{-2}\text{ d}^{-1}$

Location and treatment	Daily terrigenous N loading (kg N d^{-1})	Size of river discharge plume or surface area	N input from atmospheric sources (%)	
			Direct fall	Total atm. input ^a
Coastal Atlantic:	469.6 ^b			
Conservative		225 km^2	35.75	
Liberal		1 600 km^2	79.8	
Albemarle Sound	26 380 ^b	5 335 km^2	9.6	51.1
Pamlico Sound	28 987 ^c	2 419 km^2	17.6	37.8
A.-P. Sound estuarine system	55 377 ^c	7 754 km^2	14.0	43.8

^a Includes both wet and dry deposition

^b Kirby-Smith and Costlow (1989)

^c Based on Stanley (1989) and Dodd et al. (1992), which includes contributions from watershed atmospheric deposition, calculated at a 77.5% retention rate plus direct fall

Table 2 Dissolved inorganic N (DIN) content and pH of rainfall events greater than 0.5 cm at the Institute of Marine Sciences, Morehead City, North Carolina from August 1990 to 1992. DIN concentrations are in $\mu\text{mol N l}^{-1}$

Date	pH	[NO ₃ ⁻]	[NH ₄ ⁺]	Amount (cm)	Date	pH	[NO ₃ ⁻]	[NH ₄ ⁺]	Amount (cm)
1990					1991				
Aug 09	3.58	47.07	79.68	4.23	Sep 17	4.17	29.92	0.45	0.76
Sep 10	3.41	158.07	101.17	0.51	25	5.03	4.44	0.57	6.70
Oct 24–26	4.60	21.07	7.39	3.98	26	4.94	6.37	2.55	3.28
Nov 06	5.74	42.46	9.14	0.53	Oct 04	4.77	6.00	3.00	2.31
30	4.75	15.46	3.48	1.85	06	4.79	9.88	1.08	6.35
Dec 04	5.40	2.87	5.56	1.43	17	4.84	13.44	17.21	2.92
09	4.65	9.33	3.14	2.49	Nov 11	4.83	18.57	81.21	2.03
21	4.45	20.03	5.32	1.19	Dec 04	5.15	0.68	9.62	5.26
22	4.81	4.29	0.65	0.77	28	5.08	18.84	1.33	3.50
					29	5.44	3.21	2.30	3.68
1991					1992				
Jan 03–04	4.17	31.03	6.06	0.44	Jan 03	5.38	3.74	25.21	10.64
09	4.79	5.37	3.34	4.66	13	4.69	2.69	24.71	2.36
12	4.79	16.00	8.71	1.94	24	4.85	2.78	24.21	1.57
16	5.10	5.96	1.93	2.84	29	5.02	10.43	21.71	1.69
20	5.16	2.16	3.14	3.78	Feb 13	5.20	1.29	6.58	2.26
25	4.74	8.49	2.06	2.27	24	4.76	7.21	72.21	2.34
Mar 05	5.13	6.23	5.44	5.30	Mar 07	4.90	3.21	5.32	4.93
14	4.36	26.91	19.69	1.56	16	4.37	90.03	62.54	0.48
30	5.07	11.42	13.38	2.24	23	4.31	34.18	27.14	1.02
Apr 22	4.79	11.29	4.69	3.71	26	4.74	6.32	20.06	1.68
28	4.91	5.51	2.90	3.23	31	4.46	15.36	18.71	1.12
May 01	4.65	8.93	12.29	0.81	Apr 22	4.32	4.66	13.66	2.49
Jun 03	3.84	82.86	45.14	0.38	25	4.01	1.58	18.84	0.91
17	4.35	13.81	16.07	2.26	May 04	3.65	144.11	108.12	0.38
18	4.22	25.43	6.09	0.56	27	3.86	68.57	164.42	0.94
20	4.62	12.00	3.64	1.68	31	4.52	11.50	5.54	6.73
24	4.29	19.79	57.86	4.41	Jun 05	4.47	12.01	18.76	1.78
Jul 05	4.05	31.14	14.64	4.09	09	4.93	6.84	11.74	3.45
12	4.07	28.21	1.21	0.89	15	4.33	41.44	17.77	0.68
16	4.09	52.56	1.93	0.66	Jul 21	4.66	19.61	0.61	3.02
22	4.06	25.06	12.36	1.98	27	4.66	43.18	28.37	3.02
30	4.93	8.34	7.50	5.33	Aug 03	4.13	59.36	61.62	0.51
Aug 06	4.56	11.29	8.93	2.67	06	3.96	45.47	30.71	3.38
08	4.04	17.27	13.79	2.03	09	4.41	16.50	2.85	5.03
13	4.09	19.49	3.16	2.43	14	4.70	1.56	1.82	2.94
16	4.15	23.81	0.64	1.50	17	4.99	22.61	32.53	11.35
18	4.77	8.45	1.08	2.44	20	4.80	15.89	35.41	4.93
19	5.56	3.27	0.26	2.50					
21	4.39	13.91	1.98	0.91					
23	4.67	9.36	0.54	0.76					
27	4.60	6.41	0.45	4.47					

tribute from 293 to 2088 $\mu\text{g N m}^{-2} \text{d}^{-1}$ to this region. These estimates are based on minimal (i.e., relatively dry periods) vs maximal (i.e., wet, high discharge periods) aerial extent of the Newport River discharge plume in these waters (P. Tester, NOAA/NMFS laboratory, Beaufort, NC). This analysis indicates that atmospheric N deposition accounts for 36 to nearly 80% of regional "new" N input to coastal North Carolina waters (Table 1).

A similar analysis of the relative importance of atmospheric N loading in Pamlico Sound and the greater Albemarle-Pamlico Estuary yields estimates ranging from 38 to 44%, somewhat lower than North Carolina Atlantic coastal waters, but nevertheless a significant fraction (Table 1). The precise contributions of atmospheric deposition to total N input budgets for these systems are debatable, because groundwater inputs have not been adequately incorporated into these calculations. Furthermore, some outwelling of fixed N from salt marshes and upstream wetlands may impact the open estuarine and coastal N budgets, but these contributions are considered to be relatively small (<5%). If we weigh these additional sources fairly heavily (i.e., assigning them 15% of total "new" N inputs), then atmospheric N inputs would decrease proportionately. At most, this would decrease the relative importance of atmospheric deposition as a "new" N source to a range of 26 to 70%. For the Pamlico Sound and Albemarle-Pamlico Estuary, the values would drop to 30 to 40%. Dissolved organic nitrogen (DON) was not included in atmospheric nitrogen deposition estimates, whereas it was included in the estimates of terrigenous N loading. Since a fraction of atmospherically derived DON may constitute an important source of N nutrition for phytoplankton, its omission from current atmospheric nitrogen input calculation could lead to underestimates of biologically available N entering coastal waters.

Nitrogen content of individual storm events and their isotopic compositions

In a 2-yr period from August 1990 to August 1992, there were over 70 rainfall events that contributed significant nitrogen loading to Bogue Sound (Table 2). Coastal rain is highly variable in concentration of nitrogen species, timing, and rainfall amounts. High pH rain events (>5.0) generally contained lower nitrate and ammonium concentrations (often <20 μM), whereas lower pH rain events (<4.0) typically contained concentrations of either nitrate or ammonium >50 μM (Fig. 2). The majority of rain events were intermediate in terms of pH, DIN, and amount. Beyond these general trends, no statistically significant correlations among these parameters were determined. Rainfall amounts and nitrogen loadings varied seasonally with higher pH events occurring during fall and winter, and at lower pH in spring and summer (Fig. 3). On a volume-corrected basis, DIN loadings to the coastal area averaged over 500 $\mu\text{mol DIN m}^{-2} \text{event}^{-1}$ in summer relative to less than 300 $\mu\text{mol DIN m}^{-2} \text{event}^{-1}$ in fall.

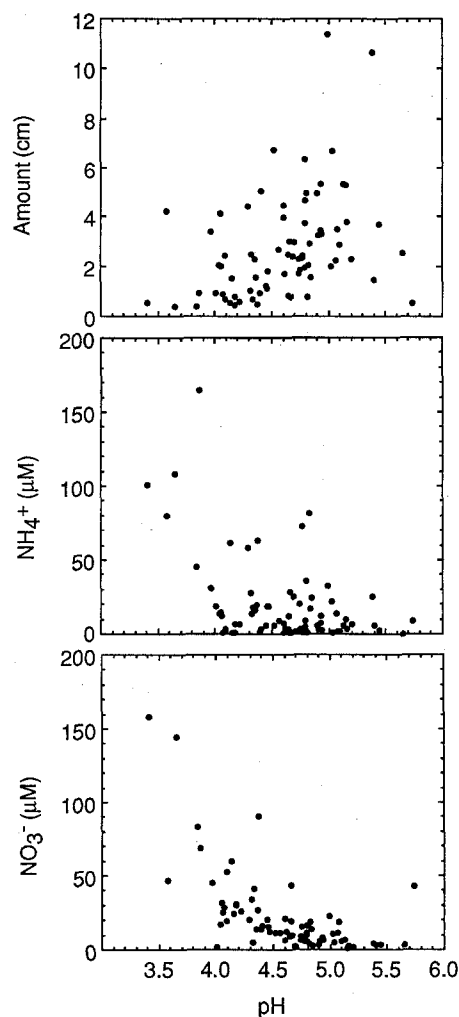


Fig. 2 Relationship of concentrations of the dominant dissolved inorganic nitrogen (DIN) species nitrate and ammonium to pH of rainfall collected at the University of North Carolina's Institute of Marine Sciences, Morehead City, North Carolina, from August 1990 to August 1992

Measurements of NH_4^+ and a combined NO_3^- and DON fraction from 15 of these rainfall events show that $\delta^{15}\text{N}$ values were highly variable (Table 3). In all cases, the isotopic composition of ammonium was more negative than that of coexisting NO_3^- plus DON (Table 3). Similar $\delta^{15}\text{N}$ for inorganic nitrogen species have been measured previously (Heaton 1986). Atmospheric nitrogen originating from combustion (i.e., NO_x from industry or automobiles) has an isotopic composition similar to that of air ($\delta^{15}\text{N} = 0.0$), whereas atmospheric nitrogen derived from agricultural emissions can have NH_4^+ $\delta^{15}\text{N}$ distinct from those of NO_x . In North Carolina, atmospheric nitrogen appears to originate from both combustion and agriculture.

Trophic impacts of atmospheric nitrogen deposition

Microcosm experiments confirmed the incorporation of atmospheric N into particulate N (Figs. 4, 5 and Table 4).

Table 3 Summary of representative rainfall events between August 1990 and October 1991

Date	Amount (cm)	pH ^a	[NO ₃ ⁻] (μM)	δ ¹⁵ N (NO ₃ +DON)	[NH ₄ ⁺] (μM)	δ ¹⁵ N (NH ₄)	[PO ₄ ³⁻] (μM)
1990							
09 Aug	4.23	3.58	47.07	2.2	14.46	-9.5	
10 Sep	0.51	3.41	122.16	-0.4	40.71	-12.5	
14 Sep	0.92	5.14	15.25	-2.0	10.34	-2.0	0.31
21 Dec	1.37	4.45	20.03		5.32	1.2	0.29
1991							
25 Jan	2.27	4.74	8.49		2.06	2.2	7.04
14 Mar	1.56	4.36	26.91	3.8	19.69	3.6	0.16
22 Apr	3.76	4.79	11.29	1.5	4.69	-1.5	0.13
27 Apr	1.27	4.91	5.51	-0.2	2.90	-0.8	0.10
05 Jul	4.09	4.05	31.14	-0.4	14.64	-1.6	0.35
22 Jul	1.98	4.06	25.06	4.7	1.08	-3.9	0.46
30 Jul	5.33	4.93	8.34	1.1	3.11	-5.6	0.53
07 Sep	0.76	4.17	29.92	1.8		-2.8	0.80
25 Sep	6.71	5.03	4.44		0.57	-12.1	0.73
17 Oct	2.92	4.84	13.44	0.6	17.21	-2.8	0.46
1992							
06 Aug	3.38	3.96	45.43	-0.9	30.64	-4.0	0.31

^a pH calibrations prior to December 1990 were based on high ionic strength standards; those following utilized Orion low ionic strength buffers

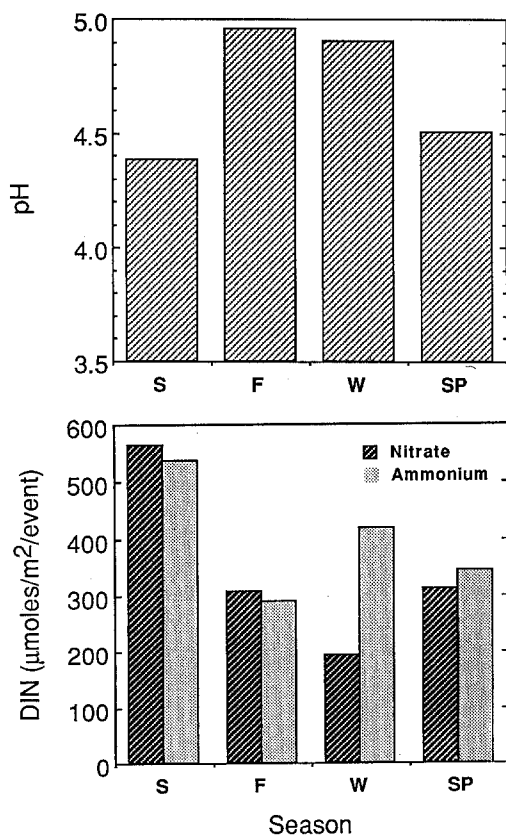


Fig. 3 Seasonal trends in pH and volume-corrected rainfall dissolved inorganic nitrogen (DIN) (ammonium plus nitrate) deposition (per event) at the University of North Carolina's Institute of Marine Sciences from August 1990 to August 1992

Rainwater was first added at relatively high concentrations to demonstrate isotopic incorporation unambiguously. Indeed, δ¹⁵N of PN decreased as a function of the amount of atmospheric N added (Fig. 4). Primary production and chlorophyll *a* concentration increased, with productivity leveling off between 5 and 10% rainwater additions. The 10% rainwater led to approximately 23 μg N l⁻¹ (1.7 μM N) enrichment. These experiments appear to confirm the hypothesis that δ¹⁵N values will decrease markedly with the addition of atmospheric N.

In order to mimic more natural conditions, we conducted a mesocosm experiment in which we examined the differential impacts on primary production, phytoplankton biomass (chlorophyll *a*), and δ¹⁵N signature in response to two distinct rainfall events at natural dilutions (Fig. 5, Table 4). The first was a high-N storm of continental-oceanic mixed origin, whereas the second was a less N-enriched storm of oceanic origin (Fig. 5, Table 4). Both storm events brought substantial amounts of rainfall to the North Carolina coastal area. A marked difference in stimulation of primary production and phytoplankton biomass was observed in response to respective events after 24 h incubation. The storm of mixed origin led to stimulation exceeding controls (no additions) by 53% and additions of rainwater from the oceanic storm by 32%. Even after 48 h, a marked stimulation of productivity was evident in the mixed-rainwater amended mesocosms. Independent, but parallel enrichments with N (as NO₃⁻) as P (as PO₄³⁻) indicated that N was the likely source of biostimulation (Fig. 5). In general, the lowest δ¹⁵N values were found in phytoplankton from rainwater additions receiving the mixed event. Furthermore,

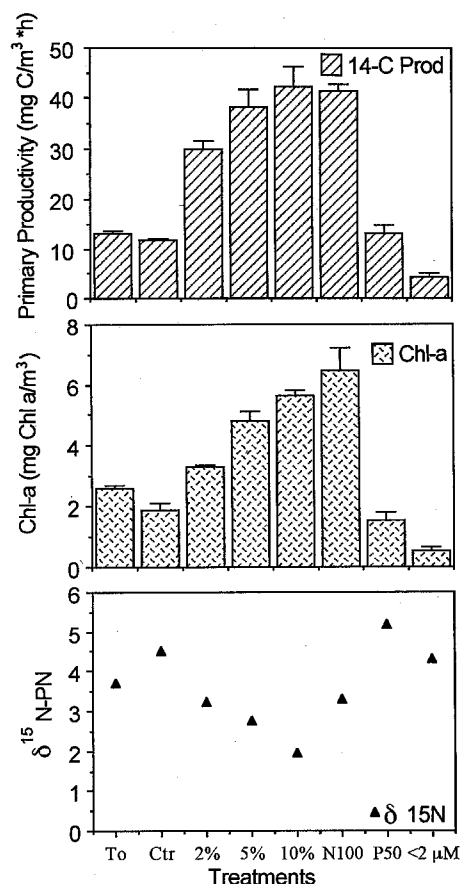


Fig. 4 Primary productivity, chlorophyll *a* production and stable isotope ($\delta^{15}\text{N}$) compositions of North Carolina coastal (Bogue Sound) Atlantic Ocean phytoplankton in response to a 6 August 1992 rainfall event. Rainfall was added in 3.0-liter Cubitainer microcosm bioassays. Error bars are mean of triplicates \pm SE. Samples were collected at the start of the experiment (T_0) and after 48 h incubation outdoors. [Ctr = control (no additions); *N100* = NO_3^- -N at $100 \mu\text{g N l}^{-1}$ ($7.1 \mu\text{M}$); *P50* = PO_4^{3-} -P at $50 \mu\text{g P l}^{-1}$ ($1.6 \mu\text{M}$). $< 2 \mu\text{m}$ is a picoplanktonic fraction which was prepared by size fractionation filtration ($2 \mu\text{m}$ Nuclepore) of Bogue Sound water; this step indicated that a bulk of the primary productivity and N incorporation was by a fraction $> 2 \mu\text{m}$.

depressed $\delta^{15}\text{N}$ values and were accompanied by enhanced rates of primary production in response to atmospheric N additions (Fig. 4 and Table 4).

Particulate nitrogen $\delta^{15}\text{N}$ characteristics of coastal waters

The total range in the $\delta^{15}\text{N}$ of particulate material collected from North Carolina coastal waters over a period of 2 yr varied by 14.3‰ (Table 5). The PN $\delta^{15}\text{N}$ values were not distributed randomly. The most negative isotopic composition was from a midsummer *Trichodesmium* sp. (cyanobacterium) bloom that was shown to fix N_2 (Paerl et al. 1994). The most positive values were measured in samples from the fall of 1990. During August and early September, numerous rainfall events having high inorganic nitrogen

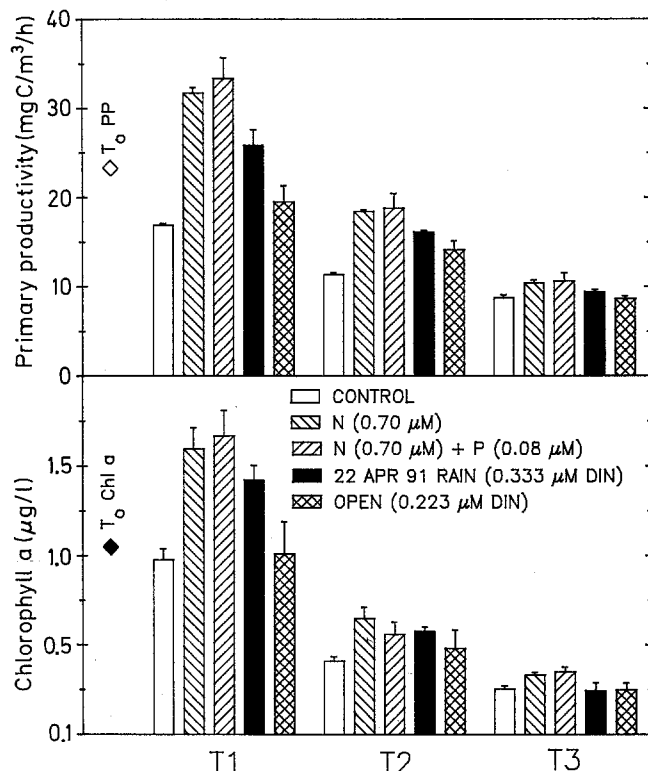


Fig. 5 Mesocosm bioassay showing impact of rainfall on photosynthetic activity and chlorophyll *a* content of Bogue Sound phytoplankton. Treatments, included NO_3^- , NO_3^- plus PO_4^{3-} enrichments, rainfall (collected 22 April 1991) at a dilution of 2.08%, and an "open" treatment (allowing rain to fall directly into a set of mesocosms at the initiation of bioassay, creating a final dilution of 2.65%). Additions of PO_4^{3-} alone showed no enhancement of phytoplankton production in previous micro- and mesocosm experiments; they were consequently not repeated in this experiment. (T_0 symbols chlorophyll *a*; *PP* primary productivity values at the initiation of the bioassay, prior to nutrient and rainwater additions; T_1 - T_3 sampling points of Days 1 to 3 of experiment. Error bars are mean of triplicates \pm SE

(NO_x , NH_4^+) concentrations (Table 2) occurred, but after September 1990, little or no rain fell until a major storm on 24 to 26 October. Following this storm, the isotopic compositions of PN fell by at least 3‰.

From December 1990 to February 1991 there was considerable rainfall, but minimal primary production. During this time, PN $\delta^{15}\text{N}$ values averaged 5.5‰ (SD \pm 0.49; $n=8$) in Bogue Sound and 5.8‰ at the Sea Buoy. An average $\delta^{15}\text{N}$ value for three samples collected 40 km offshore was 4.0‰. These isotopic compositions are typical of marine phytoplankton in coastal and oceanic regions that are not strongly affected by upwelling or sewage-derived N inputs (Altabet and McCarthy 1986; Fry 1988; Goering et al. 1990; Rau et al. 1990).

In summer 1992, the $\delta^{15}\text{N}$ values of PN averaged 4.3‰ (SD \pm 0.76; $n=11$). During this interval, rain storms with substantial nitrogen loadings were frequent (Table 2).

Table 4 Stable N isotope analyses of particulate nitrogen (PN), rainwater NH_4^+ , NO_3^- + dissolved organic nitrogen (DON) and NO_3^- "new" N sources in microcosm and mesocosm bioassays. Results from two bioassays shown. Microcosm assay of 6 August 1992 rainfall of mixed origin (continental plus oceanic). Mesocosm assay of 22 April 1991 (continental plus oceanic) and 27 April 1991 (oceanic) storms, respectively. Percent dilution of rainfall indicated for each treatment. Control is no rain or nutrients added. Concentrations of NH_4^+ and NO_3^- resulting from various treatments given. (na not applicable)

Bioassay Treatment	$[\text{NH}_4^+]$ (μM)	$[\text{NO}_3^-]$ (μM)	$\delta^{15}\text{N-NH}_4^+$ (‰)	$\delta^{15}\text{N-NO}_3^- + \text{DON}$ (‰)	Final $\delta^{15}\text{N-PN}$ (‰)
Microcosm (Initial $\delta^{15}\text{N-PN} = +3.7$)					
Control	0	0	na	na	+4.5
2%	0.31	0.45	-4.0	-0.9	+3.3
5%	1.55	2.25	-4.0	-0.9	+2.8
10%	3.10	4.50	-4.0	-0.9	+2.0
N- NO_3^-	0	7.10	na	+0.9	+3.3
P- PO_4^{3-}	0	0	na	na	+5.2
Mesocosm (Initial $\delta^{15}\text{N-PN} = +6.1$)					
Control	0.0	0.0	na	na	+6.1
2.08% ^a	0.1	0.3	-1.5	+1.5	+4.0
2.65% ^b	0.1	0.1	-0.8	-0.2	+6.0
N- NO_3^-	0.0	0.7	na	+0.9	+6.2
N- $\text{NO}_3^- + \text{PO}_4^{3-}$	0.0	0.7	na	+0.9	+5.8

^a Continental plus oceanic storms

^b Oceanic storms

Table 5 Stable nitrogen isotopic compositions of particulate material from North Carolina coastal waters. Samples collected primarily from three stations: Bogue Sound, Sea Buoy site, and 40 km offshore (see Fig. 1)

Season	Sample	Date	$\delta^{15}\text{N}$
Fall 1990	Bogue Sound	09 Sep	3.4
	Bogue Sound	20 Sep	5.3
	Bogue Sound	17 Oct	10.7
	Bogue Sound	27 Oct	6.1
	Sea Buoy	23 Sept	6.1
	Sea Buoy	27 Sept	5.6
	Sea Buoy	17 Oct	12.8
	Sea Buoy	29 Oct	9.0
Winter 1990-1991	Bogue Sound	22 Dec	6.0
	Bogue Sound	01 Jan	5.5
	Bogue Sound	16 Jan	5.3
	Bogue Sound	17 Jan	5.6
	Bogue Sound	22 Jan	6.1
	Bogue Sound	22 Jan	4.5
	Bogue Sound	23 Jan	5.6
	Bogue Sound	30 Jan	5.3
	Sea Buoy	06 Feb	6.2
	Sea Buoy	30 Jan	5.0
	Sea Buoy	30 Jan	6.2
	40 km offshore	26 Dec	2.4
	40 km offshore	30 Jan	5.0
40 km offshore	06 Feb	4.7	
Spring 1991	Sea Buoy	18 Apr	6.5
	Sea Buoy	22 Apr	7.3
	Sea Buoy	28 Apr	10.0
	Bogue Sound	22 Apr	5.4
Summer 1992	Bogue Sound	11 Aug	3.7
	Bogue Sound	14 Aug	3.3
	Bogue Sound	15 Aug	3.6
	Bogue Sound	16 Aug	4.4
	Bogue Sound	19 Aug	3.8
	Bogue Sound	22 Aug	5.1
	Bogue Sound	26 Aug	4.8
	Bogue Sound	30 Jul	4.8
<i>Trichodesmium</i> sp. bloom		05 Jul	-1.5

Summer rains have the lowest pH values and highest dissolved inorganic N contents (Table 2, Fig. 3). Enhanced atmospheric deposition (i.e., low $\delta^{15}\text{N}$) would lead to a depression in seawater PN $\delta^{15}\text{N}$ values, which was observed. In addition, N_2 fixation could have played a role in lowering the $\delta^{15}\text{N}$ of the PN, much of it taking place during the *Trichodesmium* sp. blooms that occurred at this time (Paerl et al. 1994).

Discussion

In both microcosm and mesocosm rainfall bioassays, per amount of total DIN (DIN: NO_3^- , NO_2^- , NH_4^+), biostimulation appeared to be greater in the rainfall-amended as opposed to N-enriched treatments (Figs. 4 and 5). Moreover, the $\delta^{15}\text{N}$ of particulate material from the 22 April rainfall mesocosm addition was over 1‰ more negative than would be expected given a total concentration of 0.33 M DIN added from the rainwater (Table 4). Nutritive factors in addition to DIN may be involved in the observed enhancement of primary production. One possibility is DON (Timperley et al. 1985; Mopper and Zika 1987), which may comprise a significant fraction (25 to 45%) of atmospheric N deposition (Nowicki and Oviatt 1990; Paerl et al. unpublished). If a portion of the DON component of rainfall can be biologically utilized, additional production responses could result. There is ample evidence that marine phytoplankton can assimilate a variety of "reactive" DON compounds such as amino acids and urea (McCarthy 1972; Paul 1983; Antia et al. 1991; Paerl 1991). Timperley et al. (1985) and Mopper and Zika (1987) found urea and amino acids, respectively, to be significant constituents of rainfall.

Since phosphorus additions failed to stimulate primary production (either over control or in a synergistic manner with N) in this and previous bioassays, it is unlikely that

this nutrient is responsible for the observed enhancement. In fact, the addition of P resulted in more positive $\delta^{15}\text{N}$ values in particulates (Fig. 4, Table 4), possibly indicative of P-stimulated microbial N regeneration. Lastly, trace metal (B, Co, Fe, Mn, Mo, Zn) enrichments in rainfall, which were not present in the N enrichments, may have led to additional stimulation of primary production above the N effect alone but cannot account for $\delta^{15}\text{N}$ changes. Previous examinations of nutrient limitation of these waters, however, strongly discount this possibility, as trace metals combined with N additions failed to enhance primary production above N additions alone (Paerl et al. 1990; Rudek et al. 1991).

In both microcosm and mesocosm experiments, N would have had to be regenerated through remineralization in order to account for the fixation of C and for biomass production (measured C:N values = 7.0 to 8.2). In the microcosm experiment, N was turned over about 1.5 times in 48 h in response to a 10% rainwater addition. With the 2 and 5% rainwater additions, turnover was about two times in 48 h. In unamended controls, N turnover was 20 times per 48 h. In mesocosms, regenerated N in the controls turned over about 30 times in 48 h, which is approximately twice as fast as regeneration under rain-amended conditions. It is not surprising, therefore, that the $\delta^{15}\text{N}$ in controls increased by less than 1‰, owing to small isotope effects in multiple mineralization and uptake cycles. We conclude that, although the amount of rain-based N after dilution in seawater may be relatively low, this amount can profoundly affect N cycling characteristics in these N-depleted waters.

Overall, the nitrogen from atmospheric deposition in North Carolina has $\delta^{15}\text{N}$ values different from the two other nitrogen sources: regenerated and terrestrial. Nitrogen, as NH_4^+ , mineralized from particulate nitrogen by microorganisms, should have an isotopic composition equal to or slightly greater than the $\delta^{15}\text{N}$ of the particulate nitrogen (Fogel and Cifuentes 1993). There is a small negative isotope fractionation in the formation of mineralized NH_4^+ ; however, it is rarely measured in nature owing to rapid uptake of this limiting nutrient (Cifuentes et al. 1989; Hoch 1992). The particulate nitrogen $\delta^{15}\text{N}$ in the area typically ranges from +4.5 to +6.5‰ (Table 5). We would therefore expect regenerated nitrogen to be several ‰ more enriched in ^{15}N ($\delta^{15}\text{N}$ = +6.5 to +8.5) than PN values (Cifuentes et al. 1989). Terrestrial inputs to the region have been measured by Showers et al. (1990). Both NH_4^+ and NO_3^- in rivers had isotopic signatures of +4 to +16‰. Even though fertilizers ($\delta^{15}\text{N}$ = -1 to +1) may constitute the original source of nitrogen to the North Carolina area, owing to nitrification and denitrification in fields and soils prior to their entry into receiving waters, the isotopic compositions of residual nutrients are generally enriched in $\delta^{15}\text{N}$. Therefore, compared to the two dominant inorganic N components from possible regenerated or terrestrial sources, the atmospheric N isotopic compositions show a relative depletion in the heavy isotope of nitrogen.

The $\delta^{15}\text{N}$ of PN levels from other coastal environments heavily influenced by sewage-derived nitrogen are signifi-

cantly more positive than those of North Carolina. The Scheldt Estuary had a PN $\delta^{15}\text{N}$ up to +11‰ during bloom conditions (Mariotti et al. 1984); the PN of phytoplankton from the Santa Barbara Basin on the Pacific and the Delaware estuary on the Atlantic coast were typically >8‰ in summer (Cifuentes et al. 1988; Rau et al. 1990; Fogel and Paerl 1993).

Effects of isotopic fractionation on the $\delta^{15}\text{N}$ of phytoplankton are minimal, as we demonstrated in our experiments with natural populations in micro- and mesocosms. In all cases, nitrogen concentrations were low enough (<7 μM in microcosms and <1 μM in mesocosms), such that all of the nitrogen would have had to be taken up to support the rates of primary production. No unusually negative $\delta^{15}\text{N}$ values were measured.

Taken together, it can be seen that there is natural variability in the isotopic composition of PN in North Carolina coastal waters, but over a period of several weeks, the $\delta^{15}\text{N}$ of PN generally does not change radically. One exception occurred in the fall of 1990, a period of high N rainfall input followed by drought. We cautiously suggest that the PN $\delta^{15}\text{N}$ measured in summer reflects the addition of a nitrogen source having an isotopically light signature, most likely from atmospheric deposition. Confirmation of this observation will require a technique that removes the detrital material from freshly-synthesized organic matter.

On an aerial basis "new" primary production can be estimated from incorporation of atmospheric N sources (NO_x^- , NH_4^+ , but excluding DON), using the Redfield C:N ratio (7:1) to convert atmospheric N inputs to primary producer biomass. Based on annual atmospheric N loading from EPA-RADM projections, field-based atmospheric N flux data (Kirby-Smith and Costlow 1989; Paerl et al. unpublished), and in situ primary productivity measurements (Mallin et al. 1991; Paerl unpublished), we conclude that 10 to 20% of daily primary production in North Carolina coastal Atlantic waters may be atmospherically driven. If we consider episodic inputs from specific rainfall events, recently emphasized as a significant component of oceanic N loading (Owens et al. 1992), daily "new" primary production owing to atmospheric inputs exceeds 20%.

Using stoichiometric calculations and a suite of biotic tracer and response techniques, it has been shown that atmospheric nitrogen sources are of considerable importance in supporting "new" production in N-depleted coastal waters. A lack of consideration of this N source in coastal N budgets would lead to considerable underestimates of "new" production (Legendre and Gosselin 1989). Enhancement of N loading from atmospheric sources can thus be expected to result in changes in oceanic primary production, the overall eutrophication process, and potentially, alterations in N and C flux.

It will be imperative to determine if the observed enhancement of primary production is beneficial or detrimental to these ecosystems. For example, do increasing levels of atmospheric N loading in estuarine and coastal waters play a role in the recently described "epidemic" of toxic and other harmful phytoplankton blooms impacting coastal

waters (Paerl 1988; Smayda 1989, 1990; Smetacek et al. 1991; Schollhorn and Graneli 1993)? Utilization of isotopic signatures in conjunction with bioassays should help elucidate possible links between atmospheric N enrichment, eutrophication, and harmful algal bloom dynamics. This approach should allow studies that measure not only physiological responses of phytoplankton, to include responses of indicator biomolecules (i.e., chlorophyll), the role of the bacterial (regenerative) fraction, and quantification of trophic transfer in waters enriched by atmospheric N.

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