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The role of denitrification in nitrogen removal and carbon mineralization in Mid-Atlantic Bight sediments

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Abstract

Benthic chambers were used to measure in situ fluxes of dissolved gases (N_2 , O_2 , and N_2O) and inorganic nutrients (NO_3^- , NH_4^+ , and PO_4^{3-}) in continental shelf sediments of the Mid-Atlantic Bight during spring through autumn (May–November). Denitrification was determined by the rate of increase in N_2 relative to Ar, measured using membrane-inlet mass spectrometry. Although sediments were a source of recycled (mineralized) inorganic nitrogen (primarily as NH_4^+) and phosphorus, they only supplied $\approx 1\%$ of total nitrogen required by water column primary production. Overall, sediments were a net sink for total nitrogen due to denitrification. On average denitrification removed $1.7 \text{ mmol N m}^{-2} \text{ d}^{-1}$ and was related to sediment oxygen consumption (SOC), suggesting that nitrogen regenerated from organic matter in the sediment and subsequently nitrified was an important nitrate source for benthic denitrifying bacteria. Coupled nitrification–denitrification was estimated to support 91–100% of total denitrification in LEO-15 sediments. Denitrification in these sediments was an important pathway for carbon mineralization, on average accounting for 13% of total mineralization (2–62%). Denitrification was not related to the organic content of the sediment suggesting that quality of organic matter, rather than simply quantity, was important in controlling denitrification in continental shelf sediments. Denitrification, SOC, and nutrient fluxes showed no strong seasonal patterns. The pattern of N_2O flux was related to bottom water N_2O concentration. Nitrous oxide supersaturation during the summer resulted in flux into sediments, whereas near equilibrium N_2O concentrations during the spring and autumn resulted in flux out of sediments. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Continental shelf; Carbon mineralization; Denitrification; Nitrous oxide; Nutrient flux; Sediment oxygen consumption

1. Introduction

Denitrification, the microbially mediated reduction of NO_3^- and NO_2^- to N_2 and N_2O , is an

important nitrogen loss term in oceanic waters. It has been suggested that the nitrogen inventory in the modern ocean is declining as a result of marine denitrification (McElroy, 1983; Codispoti and Christensen, 1985; Christensen, 1994; Codispoti, 1995). Overall, nitrogen loss via marine denitrification may exceed nitrogen inputs to the ocean from terrestrial sources and atmospheric deposition (McElroy, 1983; Liu and Kaplan, 1984; Codispoti and Christensen, 1985). Much of this

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denitrification occurs in sediments of continental margins, which is suggested as one of the largest sink terms in the global ocean nitrogen budget (Liu and Kaplan, 1984; Hattori, 1983; Christensen et al., 1987a; Seitzinger and Giblin, 1996). Denitrification in sediments of continental margins may remove more than half of total nitrogen inputs to oceans (Christensen, 1994). As oceanic primary production is generally limited by nitrogen (Ryther and Dunstan, 1971; Perry and Eppley, 1981), nitrogen removal via denitrification in continental shelf sediments could constrain marine photosynthesis.

In addition to nitrogen removal, denitrification could be an important pathway for carbon mineralization in sediments. Carbon mineralization via denitrification is generally viewed as insignificant in continental shelf sediments (Jahnke et al., 1982; Christensen et al., 1987b) accounting for only 2.5–6% of total carbon mineralization (Rysgaard et al., 1998; Kostka et al., 1999; calculated from Christensen et al. (1987b)). However, results of diagenesis models based on pore water solute concentrations suggested that denitrification was responsible for as much as 20% of carbon mineralization in eastern Canadian continental margin sediments (Boudreau et al., 1998).

Denitrification has been measured in situ via N_2 flux from sediments on the Washington shelf (Devol, 1991; Devol and Christensen, 1993) and the Western Arctic shelf (Devol et al., 1997) with the use of benthic landers. While denitrification has been measured in sediments cores from Massachusetts Bay (Nowicki et al., 1997) based on N_2 flux (Seitzinger et al., 1980), most current estimates of denitrification in North Atlantic shelf sediments are based on indirect approaches such as stoichiometric calculations (Gardner et al., 1993; Enoksson et al., 1990) and pore water solute concentrations (Billen, 1978; Christensen et al., 1987a; van Raaphorst et al., 1990, 1992). A recent improvement in the technique for measuring N_2 flux from sediments is the use of membrane inlet mass spectrometry (MIMS) (Kana et al., 1994). Using this technology, dissolved N_2 concentrations can be measured with high precision, thus permitting accurate measurement of very small changes in dissolved N_2 concentrations. We have

combined the use of MIMS with the use of benthic chambers for the first time to obtain in situ rate measurements of denitrification at 4 sites in the Mid-Atlantic Bight of the western North Atlantic. In the current study we report on fluxes of N_2 , O_2 , N_2O , and nutrients. We explore the importance of coupled nitrification–denitrification for nitrogen removal, and the role of denitrification in sediment carbon mineralization. Finally, we discuss factors that are related to denitrification in these sediments and how these factors might be used to build predictive models for estimating denitrification rates in continental shelf sediments.

2. Methods

2.1. Study site

The Mid-Atlantic Bight National Undersea Research Center has established a long-term ecosystem observatory site (LEO-15) on the continental shelf near the Rutgers University Marine Field Station at Tuckerton, NJ (39°28'N, 74°15'W). The LEO-15 site is centered on the Beach Haven Ridge, a sand ridge in ≈ 15 m of water. Such ridges are found throughout much of the continental shelf of the northwestern Atlantic, and include both sandy and finer grained sediments (McBride and Moslow, 1991). LEO-15 experiences periodic upwelling events driven by southwesterly winds. This upwelling is a common feature of the Mid-Atlantic Bight and likely contributes to high phytoplankton production and pockets of low dissolved oxygen characteristic of sections of the Mid-Atlantic Bight.

Benthic fluxes of dissolved N_2 , O_2 , N_2O , and nutrients were measured at 4 stations at LEO-15 during 1996–1999. Stations 9 and C are located near the southern end of the ridge in ≈ 11 m of water (Fig. 1). Station C2 is located to the southeast of station C in ≈ 17 m of water. Stations 9, C, and C2 are characterized by sandy sediments. Station 32 is located near the northern end of the ridge in ≈ 15 m of water. Station 32 is characterized by finer grained sediments with higher organic content. The benthic community near stations 9 and 32 are dominated by the polychaetes *Gonia-*

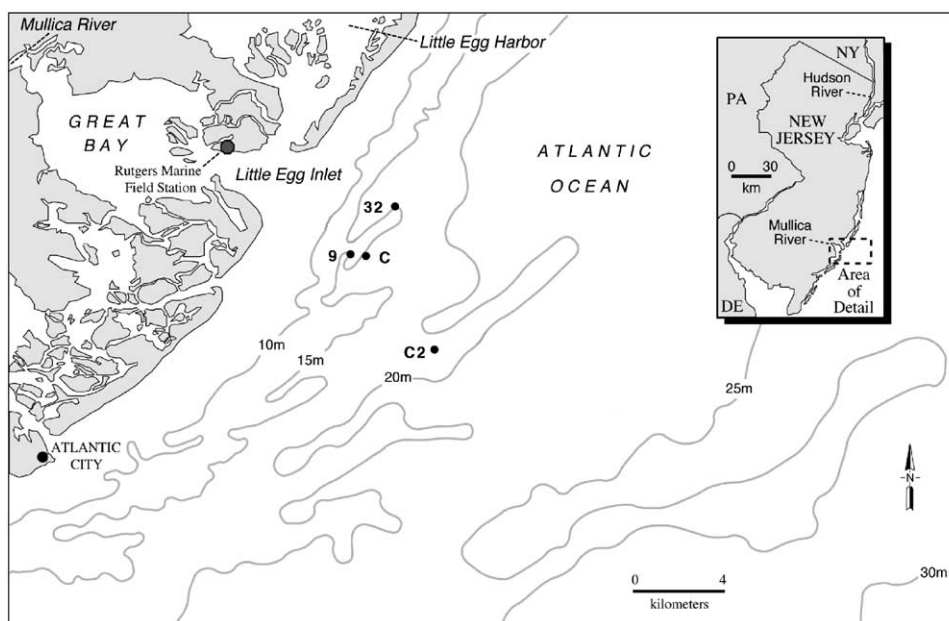


Fig. 1. Study area in the Mid-Atlantic Bight, North Atlantic Ocean (Rutgers Cartography, 1998).

della gracilis, *Spiophanes bombyx*, and *Polygordius* sp., and the bivalve *Tellina agilis* (Boesch et al., 1979). The benthic community near station C is dominated by the polychaetes *S. bombyx* and *G. gracilis*, the amphipods *Pseudunciola obliquua*, *Trichophoxus epistomus*, and the bivalve *Spisula solidissima* (Boesch et al., 1979). Denitrification (N_2 and N_2O fluxes), oxygen consumption, and nutrient fluxes were measured at stations 32 and C in August 1996, at station C2 in October 1996, and at stations 32, C, and 9 in July 1997, June 1998, September 1998, November–December 1998, May 1999, and August 1999 (stations 32 and 9 only). The sampling schedule allowed a picture of the temporal patterns of these processes during late spring through late autumn.

2.2. Benthic flux measurements

Benthic chambers were used to measure fluxes of dissolved N_2 , N_2O , O_2 , and nutrients at each of the 4 stations. Chambers were constructed of acrylic tubing (17 cm diameter \times 25 cm length) capped at one end. The other end was open to the sediments. When deployed, the open ends of

the chambers were gently pressed into the sediments to a depth of ~ 8 cm. The volume above the sediment-water interface was 3.8 l within each chamber. A floating stir bar was fastened to the inside of each chamber top. A sealed PVC housing, which contained a bar magnet mounted to a drive shaft driven by a small DC motor, was mounted on the outside of the chamber top. Rotation of the bar magnet (7 rpm) turned the floating stir bar within the chamber, thereby mixing the chamber water. The chamber top had 2 ports, a sampling port and an inlet port. An empty plastic bag (PVC/PVDC copolymer, Dow Chemical, Inc.) was fastened to the inlet port within the chamber. As water was removed from the sampling port, its volume was replaced by water flowing into the inlet and filling the bag. The filled bag (≈ 600 ml prior to final sampling) was prevented from contacting the stir bar by a small acrylic barrier, and did not interfere with stirring. The bag material is an effective barrier against diffusion of most gases including N_2 , O_2 , and Ar measured in this study (described below). The bag prevented mixing of water inside the chamber with the

surrounding milieu. All bags were leak tested prior to chamber deployment.

At each station three benthic chambers were installed and subsequently sampled by SCUBA divers. At the time of chamber installation, bottom water samples were collected using a Niskin bottle. Bottom water was used to fill clear biological oxygen demand (BOD) bottles (60 ml). Filled BOD bottles were placed on the sediment surface near benthic chambers to serve as controls for processes occurring in the water column. Samples for dissolved N_2 , O_2 , N_2O , and inorganic nutrients (NO_3^- , NH_4^+ , and PO_4^{3-}) were collected by divers in a time series over a 2-day period (generally 1, 4, 7, and 24 h following chamber deployment).

Samples for dissolved N_2 concentration were collected in stainless steel tubes (4 mm internal diameter \times 60 cm) with gas tight plug valves at each end (Nupro SS-4P4T). Divers connected a stainless steel tube to the sampling port of each benthic chamber with a 60 ml syringe connected to the other end of each column. Samples were drawn gently through the stainless steel tubes, filling the tubes and the syringes. Duplicate samples for N_2 were collected at each sampling interval, preserved with $HgCl_2$ (final concentration = 0.25% saturation). Mercuric chloride was introduced by holding sample tubes vertical, and pipetting 40 μ l of saturated $HgCl_2$ solution through the open valve. The small surface area: volume of the sample tube prevented any significant exchange of dissolved gases during the brief time the valve was open. Sample tubes were stored at $\sim 1^\circ C$ above ambient bottom water temperature prior to analysis. We have found that this method prevents the formation of small bubbles as the water volume expands slightly within the rigid sample tube.

Dissolved N_2 concentration was measured using an MIMS system (Kana et al., 1994). Sample tubes were supported vertically and water samples were drawn from the bottom half through a stainless steel capillary using a peristaltic pump with VitonTM tubing (≈ 2 –3 ml of sample were drawn for each analysis). The capillary passed coaxially through a T-shaped glass inlet tube under high vacuum ($\sim 10^{-6}$ mm Hg). Within the inlet tube, the water sample was pushed past a gas permeable silicon membrane. The vacuum degassed the water

sample as it passed the membrane, introducing the gases into a quadrupole mass spectrometer (Balzers PrismaTM). A liquid nitrogen trap was used to freeze out water vapor and carbon dioxide, preventing interference of carbon dioxide with N_2 measurements. Peaks were measured for N_2 and Ar (m/z : 28, 40). Replicate samples generally have a lower % standard deviation among N_2 /Ar measurements ($< 0.05\%$) than among N_2 measurements ($< 0.10\%$). Therefore, increases in N_2 were calculated from the change in N_2 /Ar through time assuming Ar to be constant. The instrument was calibrated using a series of 4 standards, each with a different salinity (0–100 ppt). Standards were prepared by equilibrating water with the atmosphere at a constant temperature. Standards were stirred for a minimum of 48 h, and the stirring rate was slow to prevent entrainment of gas bubbles associated with turbulent mixing. The dissolved gas concentrations in standards (N_2 and Ar) were calculated using the solubility equations of Weiss (1970) for the appropriate temperature and salinity. Standards were interspersed among samples during analysis (one standard after every 3 samples) to ascertain there was no instrument drift, and that precision remained high (i.e. % standard deviation among N_2 /Ar measurements $< 0.05\%$). Denitrification was measured as the increase in dissolved N_2 in chambers through time, calculated by linear regression on all time points for each chamber. Dissolved N_2 concentrations in chambers generally increased linearly over 24 h. Denitrification in the water column was assumed to be negligible since bottom water was well oxygenated.

One syringe sample was immediately filtered on board ship for nutrient analyses (Whatman GF/F). Samples were stored frozen prior to analysis ($-20^\circ C$). Ammonium, nitrate + nitrite (hereafter referred to as nitrate), and soluble reactive phosphorus were measured on a Lachat QuickChem Analyzer (Lachat QuickChem Methods 31-107-06-1-A, 31-107-04-1-A, and 31-115-01-3-A, respectively). Oxygen concentrations were measured from a separate syringe sample using a YSI oxygen meter and electrode (prior to September, 1998) or by micro-Winkler titrations (September, 1998–August, 1999). Nitrous oxide

concentrations were measured from syringe samples at the beginning and end of each chamber incubation. On board ship, syringe samples were gently transferred to serum bottles, stoppered with butyl rubber stoppers, and preserved with HgCl_2 (final concentration = 0.25% saturation). Nitrous oxide was measured following headspace equilibration. Gas samples were injected into a gas chromatograph (Shimadzu GC-8A) equipped with a ^{63}Ni electron capture detector and a $2.44\text{ m} \times 0.318\text{ cm}$ o.d. stainless steel column packed with Poropak Q, 80/100 mesh (N_2 carrier gas flow 30 ml min^{-1}). The total amount of N_2O dissolved in the water and gas phases of the samples was calculated with the N_2O solubility equation of Weiss and Price (1980) for the appropriate temperature and salinity. An N_2O standard series used for instrument calibration was prepared from a 20.5 ppm standard (Matheson Tri-Gas). Standards were interspersed among samples during analysis (one standard after every 5 samples) to ascertain there was no instrument drift. Oxygen, nutrients, and N_2O concentrations were measured in the BOD bottles containing bottom water collected at the beginning of the chamber deployment. These samples were used to correct for water column processes occurring in chambers. Fluxes of oxygen, nutrients, and N_2O were calculated by linear regression as the changes in dissolved concentrations through time. Changes in the concentrations of oxygen and nutrients were generally linear over 24 h. On few occasions the change in dissolved oxygen was non-linear, decreasing more over night than during the day. For these events, separate regression equations were used to calculate sediment oxygen consumption during the night and during the day. Gross primary production was estimated as the difference between dark and light sediment oxygen consumption. Nitrification was estimated as the sum of denitrification (measured via N_2 flux) and nitrate flux, where a positive nitrate flux indicated efflux from sediments.

Chlorophyll was extracted from triplicate sediment samples (<1 g dry weight per sample) in 20 ml buffered acetone. Chlorophyll *a* was quantified by the method of Lorenzen (1967), measuring absorbance at 665 and 750 nm and correcting for

absorbance by phaeopigments (Perkin–Elmer, Inc. Lambda 12 UV/VIS spectrophotometer). Organic content of sediments was determined by percent loss on ignition of triplicate samples (<1 g dry weight per sample) baked at 500°C for 4 h.

3. Results

Between May and late November, bottom water temperatures generally varied by 10°C or less (Table 1). Organic carbon content of sediments (% loss on ignition) was similar at the two sandy sites, 9 and C (0.3–1.0%), and was higher at site 32 with finer grained sediments (1.2–2.1%) (average values from three samples per station by sampling date). While organic carbon content was not measured at site C2, it is a sandy site and most likely had an organic content similar to sites 9 and C.

Over the course of all in situ incubations, N_2 concentration in the chambers increased while O_2 decreased (Fig. 2, represented by chambers at station 9, November, 1998). Concentrations of NO_3^- , NH_4^+ , and PO_4^{3-} generally increased (positive flux out of sediments), although at times there was a flux into the sediments (Table 1).

Denitrification rates did not show a strong seasonal trend (Fig. 3a). At stations C and 9, maximum rates occurred in July, 1997 (2.10 and $2.61\text{ mmol N m}^{-2}\text{ d}^{-1}$, respectively; average values from three chambers per station by sampling date) (Table 1). At station 32, maximum denitrification occurred in September, 1998 ($2.65\text{ mmol N m}^{-2}\text{ d}^{-1}$). Denitrification was lowest at stations 9, C, and 32 in June, 1998 (0.64 , 0.42 , and $0.15\text{ mmol N m}^{-2}\text{ d}^{-1}$ for stations 32, C, and 9, respectively). Denitrification at station C2 was only measured in October, 1996 when the highest mean rate for LEO-15 was recorded ($5.44\text{ mmol N m}^{-2}\text{ d}^{-1}$). Denitrification was not corrected for N_2O flux as N_2O represented a small fraction of total $\text{N}_2 + \text{N}_2\text{O}$ flux from sediments and the N_2O could have been a product of either nitrification or denitrification. No station consistently had the highest rate of denitrification, and average denitrification rates (May–November) were similar among sites (1.69, 1.45, and

Table 1
Flux rates of dissolved gases and nutrients from LEO-15 sediments

	Denitrification (mmol N m ⁻² d ⁻¹)	Net O ₂ consumption (mmol O ₂ m ⁻² d ⁻¹)	Gross primary production (mmol O ₂ m ⁻² d ⁻¹)	PO ₄ ³⁻ flux (mmol P m ⁻² d ⁻¹)	NO ₃ ⁻ flux (mmol N m ⁻² d ⁻¹)	NH ₄ ⁺ flux (mmol N m ⁻² d ⁻¹)
<i>Station 32</i>						
August, 1996	2.29 ± 0 ^a	-18.86 ± 1.46	0	0.55 ± 0.19	0.14 ± 0.05	2.43 ± 0.48
July, 1997	1.26 ± 0.71	-12.33 ± 5.12	0	0.03 ± 0.03	0.02 ± 0.05	1.24 ± 0.83
June, 1998	0.64 ± 0.32	-4.84 ± 0.93	0	0.07 ± 0.07	0.01 ± 0.03	0.52 ± 0.15
September, 1998	2.65 ± 0.90	-35.84 ± 16.38	0	0.16 ± 0.04	-0.01 ± 0.05	1.37 ± 0.72
November, 1998	1.20 ± 0.41	-12.20 ± 6.56	0	0.03 ± 0.02	0.10 ± 0.08	1.14 ± 0.56
May, 1999	1.98 ± 1.53	-15.05 ± 4.22	0	0.07 ± 0.07	0.06 ± 0.03	1.55 ± 0.23
August, 1999	1.81 ± 1.73	-23.74 ± 4.94	0	0.16 ± 0.01	-0.04 ± 0.03	0.62 ± 0.20
<i>Station C</i>						
August, 1996	1.83 ± 0.70	-20.15 ± 13.08	0	1.26 ± 0.26	-0.10 ± 0.13	2.99 ± 1.06
July, 1997	2.10 ± 0.10	-24.09 ± 0.87	0	0.20 ± 0.08	0.16 ± 0.16	1.80 ± 0.41
June, 1998	0.42 ± 0.16	-13.21 ± 10.08	0	0.03 ± 0.02	0.35 ± 0.05	0.60 ± 0.57
September, 1998	0.86 ± 0.56	-31.90 ± 6.94	0	0.02 ± 0.05	0.01 ± 0.06	2.19 ± 1.38
November, 1998	1.40 ± 0.17	-6.89 ± 0.31	0	0.01 ± 0.04	0.23 ± 0.15	-0.15 ± 0.13
May, 1999	2.06 ± 0.67	-15.88 ± 0.17	0	0.03 ± 0.04	0.08 ± 0.06	1.34 ± 0.45
<i>Station 9</i>						
July, 1997	2.61 ± 0.36	-16.72 ± 1.28	0	0.05 ± 0.01	0.21 ± 0.06	0.20 ± 0.04
June, 1998	0.15 ± 0.04	-11.07 ± 6.11	0	0.03 ± 0.01	0.23 ± 0.01	0.39 ± 0.18
September, 1998	1.22 ± 0.56	-24.65 ± 3.59	4.13 ± 3.07	0.01 ± 0.08	-0.01 ± 0.06	1.76 ± 1.56
November, 1998	1.86 ± 0.34	-16.80 ± 3.73	0	0.06 ± 0.04	0.42 ± 0.15	0.88 ± 0.31
May, 1999	1.95 ± 0.59	-8.05 ± 1.17	3.38 ± 6.94	0.02 ± 0.01	0.08 ± 0.02	0.09 ± 0.10
August, 1999	2.22 ± 0.73	-5.74 ± 1.51	0	0.01 ± 0.09	-0.19 ± 0.08	-0.08 ± 0.42
<i>Station C2</i>						
October, 1996	5.44 ± 2.87	-67.65 ± 33.62	0	0.33 ± 0.33	-0.66 ± 0.65	3.29 ± 3.16
<i>LEO-15 average</i>						
August, 1996	2.06 ± 0.33	-19.51 ± 0.91	0	0.91 ± 0.50	0.12 ± 0.03	2.71 ± 0.40
July, 1997	1.99 ± 0.68	-17.71 ± 5.94	0	0.09 ± 0.09	0.13 ± 0.10	1.08 ± 0.81
June, 1998	0.40 ± 0.25	-9.71 ± 4.35	0	0.04 ± 0.02	0.20 ± 0.17	0.50 ± 0.11
September, 1998	1.58 ± 0.95	-30.80 ± 5.68	1.38 ± 2.38	0.06 ± 0.08	-0.01 ± 0.01	1.77 ± 0.41
November, 1998	1.49 ± 0.34	-11.96 ± 4.96	0	0.03 ± 0.03	0.25 ± 0.16	0.62 ± 0.68
May, 1999	2.00 ± 0.06	-12.99 ± 4.30	1.13 ± 2.95	0.04 ± 0.03	0.07 ± 0.01	0.99 ± 0.79
August, 1999	2.02 ± 0.29	-14.74 ± 12.73	0	0.09 ± 0.11	-0.12 ± 0.11	0.27 ± 0.49
Overall average	1.65 ± 0.59	-16.77 ± 7.03	0.36 ± 0.62	0.18 ± 0.32	0.09 ± 0.12	1.13 ± 0.85
	Nitrification (mmol N m ⁻² d ⁻¹)	Bottom water [NO ₃ ⁻] (μM)	% Contribution of water column NO ₃ ⁻ to total denitrification	% Organic carbon	Chl <i>a</i> (μg g ⁻¹)	Temperature (°C)
<i>Station 32</i>						
August, 1996	2.43 ± 0 ^b	1.6	0	—	—	16
July, 1997	1.28 ± 0.72	<0.1	0	1.4	1.6	17
June, 1998	0.65 ± 0.33	0.1	0	1.2	2.9	16
September, 1998	2.64 ± 0.90	0.4	0.4	—	—	18.5
November, 1998	1.30 ± 0.44	0.4	0	1.3	4.6	12.5

Table 1 (continued)

	Denitrification (mmol N m ⁻² d ⁻¹)	Net O ₂ consumption (mmol O ₂ m ⁻² d ⁻¹)	Gross primary production (mmol O ₂ m ⁻² d ⁻¹)	PO ₄ ³⁻ flux (mmol P m ⁻² d ⁻¹)	NO ₃ ⁻ flux (mmol N m ⁻² d ⁻¹)	NH ₄ ⁺ flux (mmol N m ⁻² d ⁻¹)
May, 1999	2.04 ± 1.58	0.2	0	1.8	8.3	12.8
August, 1999	1.77 ± 1.69	1.2	2	2.1	22	14.4
<i>Station C</i>						
August, 1996	1.93 ± 0.74	1.2	0	—	—	16
July, 1997	2.26 ± 0.11	0.2	0	0.7	3.2	17
June, 1998	0.77 ± 0.29	0.2	0	0.8	0.8	16
September, 1998	0.87 ± 0.57	0.3	0	—	—	21.5
November, 1998	1.63 ± 0.20	<0.01	0	0.8	1.7	12.5
May, 1999	2.14 ± 0.70	0.2	0	0.4	4.6	11.6
<i>Station 9</i>						
July, 1997	2.82 ± 0.39	0.1	0	0.4	0.6	17
June, 1998	0.38 ± 0.10	0.2	0	0.3	0.8	16
September, 1998	1.21 ± 0.56	0.3	1	—	—	22
November, 1998	2.28 ± 0.42	0.1	0	1.0	1.8	12.5
May, 1999	2.03 ± 0.61	0.3	0	0.2	1.7	11.6
August, 1999	2.03 ± 0.67	1.3	9	0.3	1.5	14.4
<i>Station C2</i>						
October, 1996	6.10 ± 3.22	6.3	0	—	—	16
<i>LEO-15 average</i>						
August, 1996	2.18 ± 0.35	1.4	0	—	—	16
July, 1997	2.12 ± 0.78	0.1	0	0.8	1.8	17
June, 1998	0.60 ± 0.20	0.2	0	0.8	1.5	16
September, 1998	1.57 ± 0.94	0.3	1	—	—	20.7
November, 1998	1.74 ± 0.50	0.2	0	1.1	2.5	12.5
May, 1999	2.07 ± 0.06	0.2	0	0.8	4.9	12.2
August, 1999	1.90 ± 0.18	1.3	6	1.2	12	14.4
Overall average	1.74 ± 0.55	0.53 ± 0.56	1	0.9	4.5	15.5

^a n = 1.^b n = 1.

—Values not measured.

Positive values indicate efflux from sediments and negative values indicate uptake by sediments. Values listed are mean ± standard deviation for 3 chambers.

1.67 mmol N₂ m⁻² d⁻¹ for stations 32, C, and 9, respectively).

Oxygen uptake by sediments followed no discernible seasonal pattern (Fig. 3b), although uptake was highest in September, 1998 for stations 9, C, and 32. Station 9 had the lowest sediment oxygen demand overall with O₂ uptake ranging between 5.74 mmol O₂ m⁻² d⁻¹ in August, 1999 and 24.65 mmol O₂ m⁻² d⁻¹ in September, 1998 (average values from three chambers per sampling

date) (Table 1). Oxygen uptake at station C ranged between 6.89 mmol O₂ m⁻² d⁻¹ in November, 1998 and 31.90 mmol O₂ m⁻² d⁻¹ in September, 1998. Oxygen uptake at station 32 ranged between 4.84 mmol O₂ m⁻² d⁻¹ in June, 1998 and 35.84 mmol O₂ m⁻² d⁻¹ in September, 1998. Sediment oxygen uptake at station C2 was 67.65 mmol O₂ m⁻² d⁻¹ in October, 1996. Sediment oxygen uptake was correlated with sediment chlorophyll *a* content ($r = 0.538$, $p = 0.047$) and not to sediment

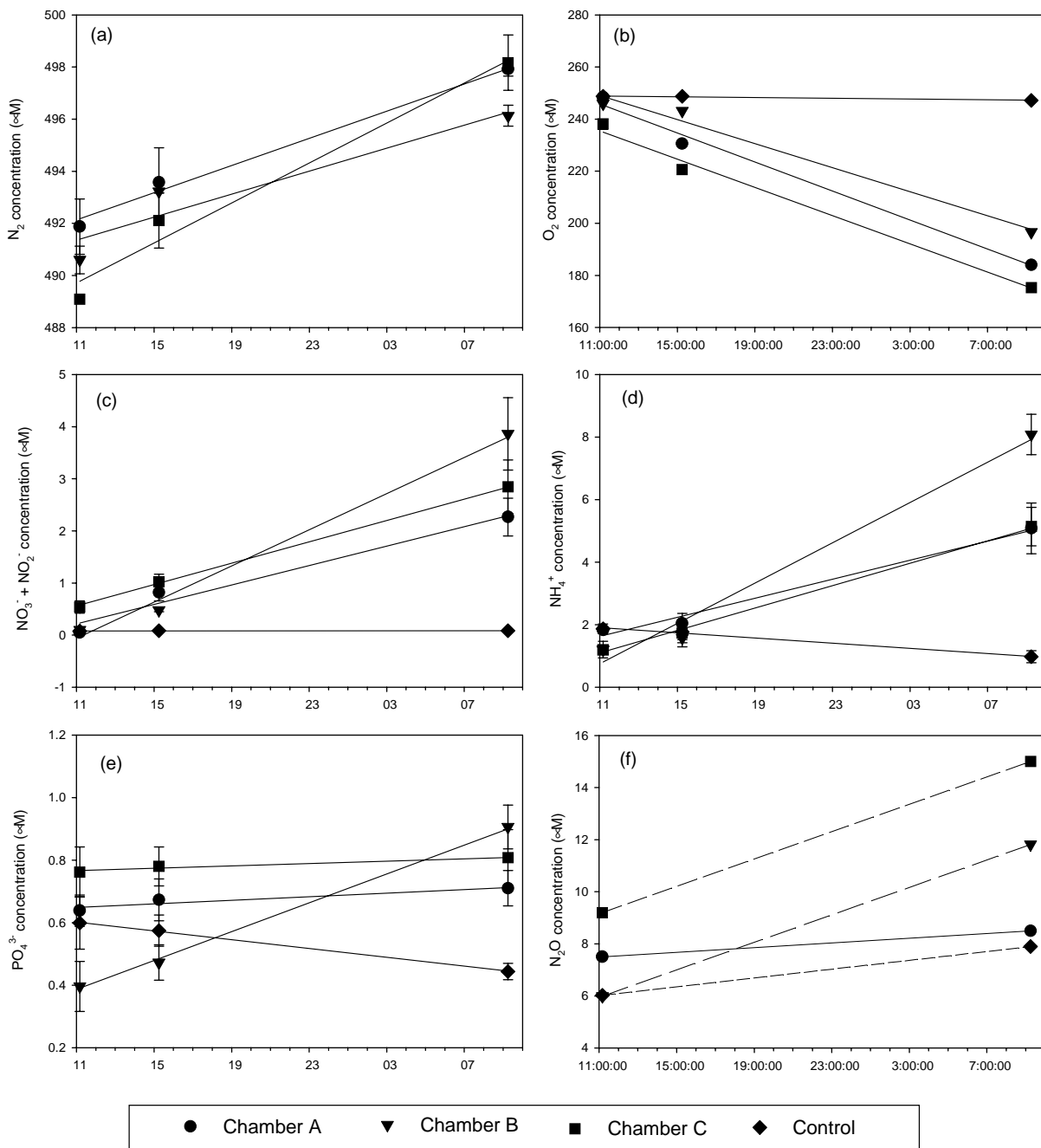


Fig. 2. Changes in the dissolved gas and nutrient concentrations in benthic chamber water over time: (a) N₂, (b) O₂, (c) NO₃⁻ + NO₂⁻, (d) NH₄⁺, (e) PO₄³⁻, and (f) N₂O. Data from station 9, November 9–10, 1998. Error bars for N₂, NO₃⁻ + NO₂⁻, NH₄⁺, and PO₄³⁻ represent the range in values of duplicate samples.

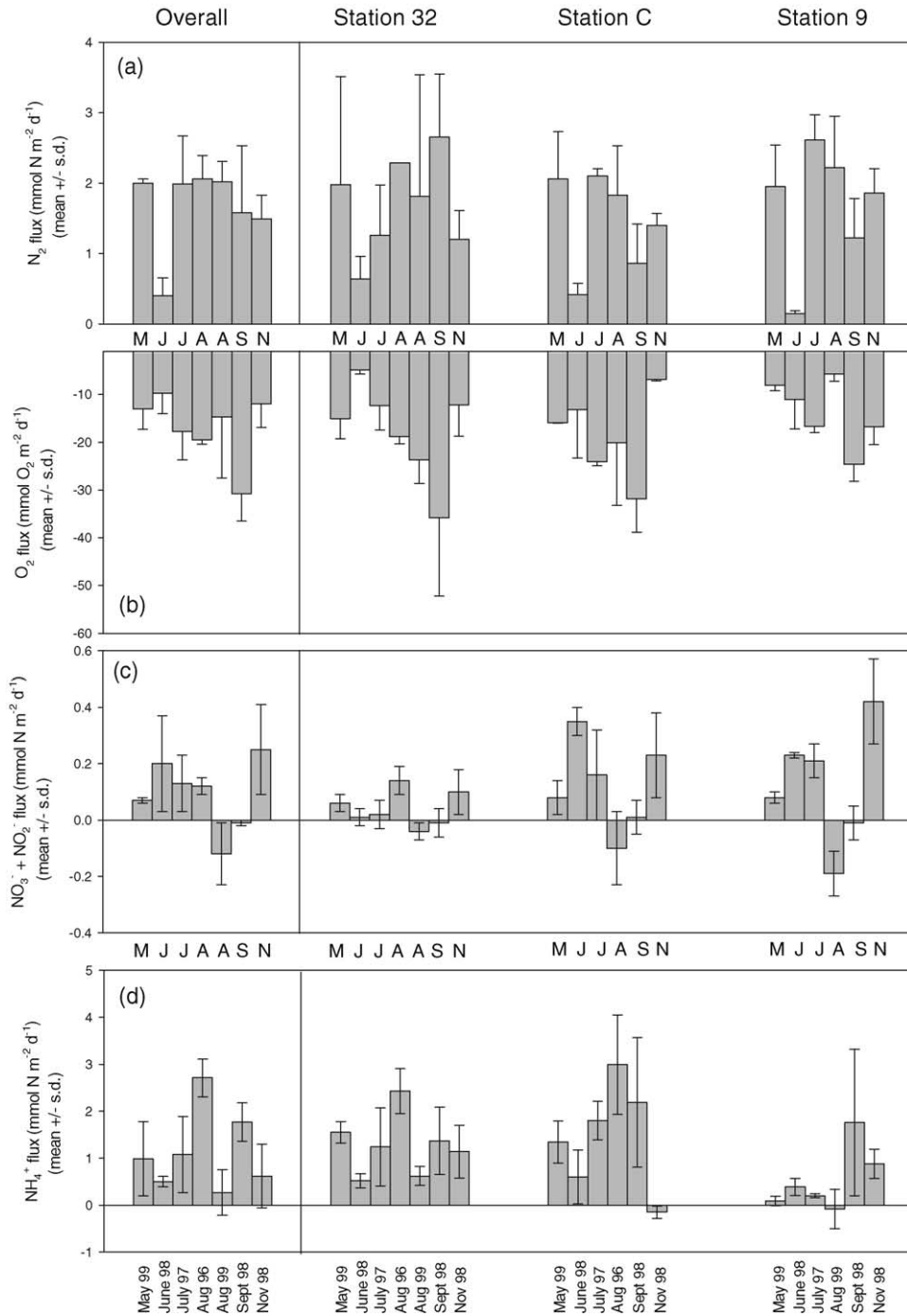


Fig. 3. Benthic flux from LEO-15 sediments: (a) N_2 , (b) O_2 , (c) $\text{NO}_3^- + \text{NO}_2^-$, (d) NH_4^+ . Values are mean \pm standard deviation for three chambers.

organic carbon content or temperature. However, samples were not collected for chlorophyll *a* and organic carbon analyses at all sites and on all dates.

Gross benthic primary production (GPP) was measurable only at station 9 on two dates. Benthic GPP was $4.13 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ in September, 1998 and $3.38 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ in May, 1999 (average values from three chambers). Benthic GPP was not measurable at stations 32, C or C2 on any of the sampling dates (Table 1).

Nitrate flux was out of the sediments on most dates, indicating that denitrification did not consume all nitrate produced within the sediments. There was no discernable seasonal pattern for nitrate flux (Fig. 3c). Nitrate flux was generally greater at the two sandy sediment stations (C and 9) than at the finer grained sediment station (32). Nitrate flux at station 32 was -0.04 to $0.14 \text{ mmol N m}^{-2} \text{ d}^{-1}$ (average values from three chambers per sampling date, negative values denote flux into sediments). On average net flux was directed out of sediments at all times except September, 1998 and August, 1999. However, in both June, 1998 and July, 1997 net flux was into sediments in one of the three chambers. At station C, nitrate flux was 0.01 – $0.35 \text{ mmol N m}^{-2} \text{ d}^{-1}$. Although average flux was out of sediments on all dates, net flux was into sediments in one of the three chambers in August, 1996 and September, 1998. At station 9, nitrate flux was -0.19 – $0.42 \text{ mmol N m}^{-2} \text{ d}^{-1}$. On average, sediments were a sink for nitrate in September, 1998 and August, 1999, although net flux was out of sediments in two of the three chambers in September, 1998.

Ammonium constituted a greater fraction of total inorganic nitrogen flux than nitrate. Ammonium flux was generally out of the sediments with no clear seasonal pattern (Fig. 3d). Ammonium flux at station 32 was 0.52 – $2.43 \text{ mmol N m}^{-2} \text{ d}^{-1}$ (average values from three chambers per sampling date). At station C ammonium flux was -0.15 – $2.99 \text{ mmol N m}^{-2} \text{ d}^{-1}$. Net flux was into sediments only on one date (November, 1998), corresponding with a low oxygen uptake rate ($6.89 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$). Station 9 typically had the lowest ammonium fluxes ranging between -0.08 and $1.76 \text{ mmol N m}^{-2} \text{ d}^{-1}$. Average net flux

was into sediments on only one date (August, 1999), with flux directed out of sediments in one of the three chambers. Net flux was into sediments in one of the three chambers in July, 1997.

Net phosphate flux averaged by station was always out of sediments, although direction of flux was highly variable among chambers within a station. At station 32 phosphate flux was 0.03 – $0.55 \text{ mmol P m}^{-2} \text{ d}^{-1}$ (average values from three chambers per sampling date), with the three highest values being during August (1996 and 1999) and September, 1998. At station C phosphate flux was 0.01 – $1.26 \text{ mmol P m}^{-2} \text{ d}^{-1}$, with fluxes being higher during July, 1997 and August, 1996 than during the other months. At station 9 phosphate flux was relatively small, 0.01 – $0.06 \text{ mmol P m}^{-2} \text{ d}^{-1}$.

Nitrous oxide flux was highly variable, both in magnitude and direction of flux (Fig. 4). Nitrous oxide flux ranged from -3.65 to $4.06 \text{ } \mu\text{mol N m}^{-2} \text{ d}^{-1}$ at station 32, from -3.02 to $2.62 \text{ } \mu\text{mol N m}^{-2} \text{ d}^{-1}$ at station C and from -0.70 to $0.74 \text{ } \mu\text{mol N m}^{-2} \text{ d}^{-1}$ at station 9 (average values from three chambers per station by sampling date, negative value indicates flux into sediments).

4. Discussion

4.1. Nitrogen flux

The average denitrification rate measured in LEO-15 sediments ($1.7 \pm 0.6 \text{ mmol N m}^{-2} \text{ d}^{-1}$ averaged over all stations and all dates) is similar to rates measured via N_2 flux in sediments of the North Pacific shelf off the Washington coast (Devol and Christensen, 1993) and Western Arctic shelf (Devol et al., 1997), and is similar to estimated denitrification rates in sediments of Long Island Sound (calculated from Mackin and Swider, 1989), the Georgia Bight (calculated from Hopkinson et al., 1991), and the Gulf of Mexico (Gardner et al., 1993) based on stoichiometric approaches (Table 2). However, denitrification rates in continental shelf sediments are highly variable, both temporally as indicated in this study, and spatially as indicated by denitrification

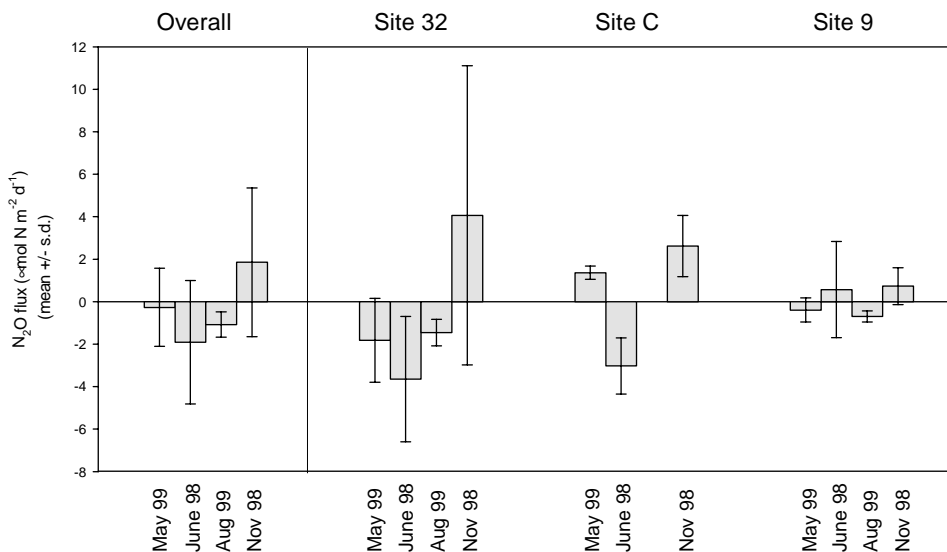


Fig. 4. Nitrous oxide flux in LEO-15 sediments. Values are mean \pm standard deviation for three chambers.

rates estimated in various continental shelf locations (Table 2).

Denitrification at LEO-15 could have contributed to local nitrogen limitation of phytoplankton production by removing mineralized nitrogen rather than returning it to the water column as dissolved inorganic nitrogen (DIN, used here to refer to combined NH_4^+ , NO_3^- , and NO_2^-), as nitrogen appears to limit marine phytoplankton production in the modern ocean (Ryther and Dunstan, 1971; Perry and Eppley, 1981). If we extrapolate our average denitrification rate at LEO-15 ($1.7 \text{ mmol N m}^{-2} \text{ d}^{-1}$) to an annual rate (although no measurements were made between December and April), nitrogen removal by denitrification would have been $621 \text{ mmol N m}^{-2} \text{ yr}^{-1}$. If this mineralized nitrogen were returned to the water column as DIN rather than lost as N_2 , it could have supported an additional $4.1 \text{ mol C m}^{-2} \text{ yr}^{-1}$ of phytoplankton production (assuming a C:N ratio of 6.625:1), increasing production at LEO-15 by 7% based on an annual primary production estimate of $60 \text{ mol C m}^{-2} \text{ yr}^{-1}$ at LEO-15 (MacDonald, 1983). However, given that a nitrogen molecule can be recycled between the water column and sediments numerous times, the amount of nitrogen removed by denitrification if

instead released to the water column as DIN, could translate into an even greater amount of gross primary production.

Although denitrification in LEO-15 sediments removed a quantity of mineralized nitrogen similar to that removed in Washington and Western Arctic shelf sediments, the efficiency of nitrogen removal was lower in LEO-15 sediments than at these other locations. Averaged over all stations and sampling dates, 57% of the total nitrogen mineralized in LEO-15 sediments was lost as N_2 (range 19–100%). A large fraction of mineralized nitrogen (37%) entered the water column as NH_4^+ (range 0–72%), while a small fraction (6%) entered the water column as $\text{NO}_3^- + \text{NO}_2^-$ (range 0–30%). In comparison, 84% of total nitrogen mineralized in Western Arctic shelf sediments was lost as N_2 (range 69–98%), while 9% entered the water column as NH_4^+ (range 0–31%), and 7% entered the water column as $\text{NO}_3^- + \text{NO}_2^-$ (range 0–25%) (calculated from Devol et al., 1997). In Washington shelf sediments, 89% of total nitrogen mineralized in sediments was lost as N_2 (range 70–100%) while 11% entered the water column as NH_4^+ (range 0–30%) (calculated from Devol and Christensen, 1993).

Table 2

Denitrification rates in continental shelf sediments from various regions estimated by a variety of techniques

Location	Denitrification (mmol N m ⁻² d ⁻¹)	Method	References
Mid-Atlantic Bight (LEO-15)	1.7	In situ N ₂ flux	This paper
Washington Shelf	3.2	In situ N ₂ flux	Devol and Christensen (1993)
Arctic Shelf	1.3	In situ N ₂ flux	Devol et al. (1997)
Massachusetts Bay	1.3	N ₂ flux in core incubations	Nowicki et al. (1997)
East China Sea	0.3	Pore water NO ₃ ⁻ profiles	Aller et al. (1985)
North Sea	0.7	Pore water NO ₃ ⁻ profiles	Billen (1978)
Equatorial Africa	0.3	Pore water NO ₃ ⁻ profiles	Bender et al. (1977)
Mexican Shelf	0.1	Pore water NO ₃ ⁻ profiles	Christensen et al. (1987a)
Gulf of Maine	0.1	Pore water NO ₃ ⁻ profiles	Christensen et al. (1987a)
Washington Shelf	0.5	Pore water NO ₃ ⁻ profiles	Christensen et al. (1987b)
North Sea	0.2	Pore water NO ₃ ⁻ profiles	Raaphorst et al. (1990)
Long Island Sound	3.0	Stoichiometric estimate based on DIN deficit, in situ incubations	Calculated from Mackin and Swider (1989)
Georgia Bight	3.2	Stoichiometric estimate based on DIN deficit, in situ incubations	Calculated from Hopkinson et al. (1991)
E. Kattegat ^a	1.0	Stoichiometric estimate based on DIN deficit, in situ incubations	Enoksson et al. (1990)
New York Bight	0.9	Stoichiometric estimate based on DIN deficit, in situ incubations	Calculated from Florek and Rowe (1983)
Gulf of Mexico	1.9	Stoichiometric estimate based on DIN deficit, in situ incubations	Gardner et al. (1993)
Gulf of Mexico	9.9	Stoichiometric estimate based on DIN deficit, in situ incubations	Calculated from Flint and Kamykowski (1984)
Baltic Proper ^b	≤1.8	Modeled estimate based on natural coordinate conservation of nitrogen approach	Shaffer and Rönner (1984)
Baltic Sea ^b	0.5	Whole system nitrogen mass balance model	Wulff (1989)
Gulf of Finland ^b	0.2	Whole system nitrogen mass balance model	Perttilä et al. (1995)
Young Sound	0.2	Isotope pairing	Rysgaard et al. (1998)
Baltic Sea ^a	0.3	Isotope pairing	Tuominen et al. (1998)
Svalbard	0.3	Isotope pairing	Kostka et al. (1999)
North Atlantic Shelf	0.7	Model estimate based on relationship between coupled denitrification and pelagic production	Seitzinger and Giblin (1996)

^a Denitrification in sediments from the Baltic region included as the physical environments in these study sites were similar to those of continental shelves.

^b Estimates based on whole ecosystems include sediment and water column denitrification.

Coastal marine sediments can be an important source of combined nitrogen to the overlying water, releasing ammonium and nitrate following organic matter mineralization. The release of

combined nitrogen from coastal sediments can supply a substantial fraction of the nitrogen demand by phytoplankton in overlying water (Flint and Kamykowski, 1984; Enoksson et al.,

1990). However, sediments were a net sink for combined inorganic nitrogen on the Washington shelf (Christensen et al., 1987b; Devol and Christensen, 1993), the Jordan Basin in the Gulf of Maine (calculated from Christensen et al., 1987a), and the Santa Monica Basin in the California Borderlands (Jahnke, 1990) with nitrate flux into sediments exceeding efflux of ammonium. At LEO-15, sediments generally served as a source of recycled combined DIN, releasing both ammonium and nitrate to the water column. Net DIN flux from LEO-15 sediments was 0.53–2.91 mmol N m⁻² d⁻¹ at station 32, 0.07–3.09 mmol N m⁻² d⁻¹ at station C, and -0.27–1.75 mmol N m⁻² d⁻¹ at station 9. Flux of DIN from sediments averaged across all stations and all dates was 0.27 mmol N m⁻² d⁻¹. If we extrapolate our daily DIN flux to an annual flux (although no measurements were made between December and April), net flux would be 99 mmol N m⁻² yr⁻¹. This net DIN flux could support production of 0.7 mol C m⁻² yr⁻¹ (assuming a C:N ratio of 6.625:1). Given the estimate of primary production at LEO-15 (60 mol C m⁻² yr⁻¹, MacDonald, 1983), the DIN flux from sediments might support ~1% of annual production. Therefore, benthic DIN flux is not a major source of nitrogen for phytoplankton production. Pelagic nutrient regeneration or advection of “new” nitrogen at LEO-15 are likely to be more important sources.

4.2. Coupling of nitrification and denitrification

Denitrification can be supported by nitrate supplied either by diffusion from overlying water (direct denitrification) or by nitrification in the sediments (coupled denitrification; Seitzinger, 1988; Christensen and Rowe, 1984; Risgaard-Petersen et al., 1994). Nitrification is the microbially mediated oxidation of ammonium to nitrite and nitrate. In coastal marine systems, the magnitude of coupled denitrification can be greater than the magnitude of direct denitrification, accounting for 60–100% of total denitrification in a variety of sediment types in continental shelf sediments (calculated from Devol and Christensen, 1993; Devol et al., 1997; Rysgaard et al., 1998). Nitrification rates in LEO-15 sediments were

estimated as the sum of N₂ and NO₃⁻ + NO₂⁻ efflux (as mmol N m⁻² d⁻¹). Denitrification was primarily coupled to nitrification and sediments at LEO-15 rarely consumed nitrate from overlying water. Direct denitrification did not contribute to total denitrification at stations C and C2, and contributed a maximum of 2% and 9% at stations 32 and 9, respectively (Table 1).

4.3. Nitrous oxide flux

Nitrous oxide is a greenhouse gas (Wang et al., 1976) which is also involved in stratospheric ozone depletion (Crutzen, 1970; Hahn and Crutzen, 1982). Most of the atmospheric nitrous oxide is of biogenic origin, and is produced during nitrification and denitrification (Bouwman et al., 1995). Continental shelf regions may be an important source in the global nitrous oxide budget. Support for this comes from both supersaturated nitrous oxide concentrations in the water column in a number of continental shelf regions (reviewed in Bange et al., 1996) and from models (Seitzinger and Kroeze, 1998). However, there are few measurements of nitrous oxide production rates in either sediments or the water column in shelf regions. Nitrous oxide flux in LEO-15 sediments was highly variable and always a small component of the total N flux from the sediments. During summer months at LEO-15 bottom water was supersaturated with N₂O, probably as a result of pelagic nitrification during summer stratification (Fig. 5). During these months, the net flux of N₂O was into the sediments. In November and May the water column was well mixed, as evidenced by temperature and dissolved oxygen profiles (data not shown) and bottom water was not supersaturated with N₂O. As the N₂O concentration increased in the bottom water, flux from sediments decreased or was directed into sediments according to: N₂O flux (μmol N m⁻² d⁻¹) = -0.12 * N₂O concentration (nM) + 1.99; *r* = 0.76, *p* < 0.001. Supersaturation of bottom water with N₂O due to pelagic nitrification, combined with a consumption of N₂O in the sediments by denitrification, may have driven this net flux of N₂O into sediments during summer stratification.

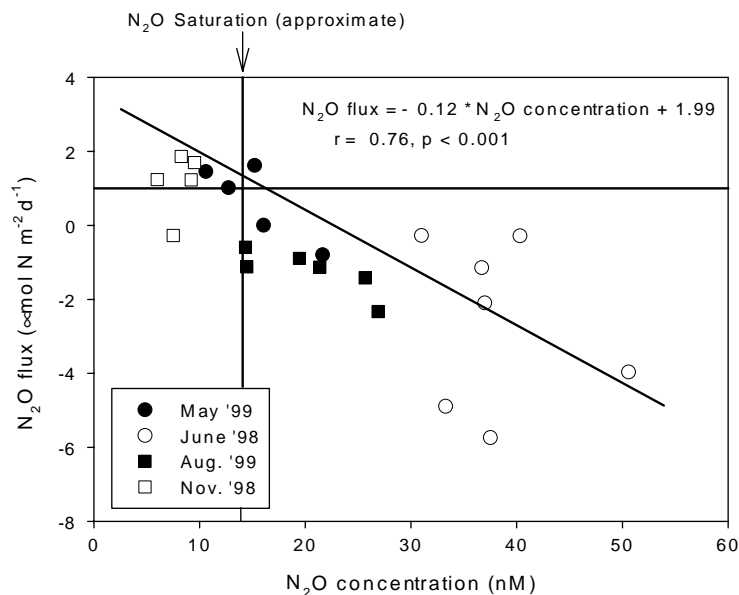


Fig. 5. Relationship between bottom water N₂O concentration and N₂O flux from sediments (negative value indicates flux into sediments). Data are plotted by individual benthic chamber.

4.4. Role of denitrification in carbon mineralization

Sediment nitrification is not only a major source of nitrate for denitrification, but is often an important component of oxygen consumption, accounting for as much as 30% of oxygen demand in estuarine and coastal marine sediments (Seitzinger et al., 1984; Seitzinger and Nixon, 1985; Christensen and Rowe, 1994). On average nitrification accounted for 33% of sediment oxygen demand in Washington shelf sediments (calculated from Devol and Christensen, 1993) and 27% of sediment oxygen demand in Western Arctic sediments (calculated from Devol et al., 1997). At LEO-15 nitrification accounted for 21% of sediment oxygen demand averaged over all stations and dates (range 5 to -71%, Table 3). In addition to nitrification, other sediment processes create an oxygen demand. Principle among these are aerobic respiration, sulfide oxidation, and oxidation of various other reduced chemical species such as Fe²⁺ and Mn²⁺. Oxidized iron, sulfur, and manganese are used as electron acceptors in alternate carbon metabolic pathways. Oxygen

consumption by sediments (by aerobic respiration and oxidation of reduced iron, manganese, and sulfur) can be used to approximate total carbon mineralization, as indicated by Rysgaard et al. (1998) in Arctic Shelf sediments (O₂:CO₂ flux ratio ranged between 0.9 and 1.3 over an annual cycle) and by Giblin et al. (1997) in Boston Harbor sediments (O₂:CO₂ flux ratio ranged between 0.5 and 1.3, averaging close to 1 for the year). Oxygen demand due to nitrification was subtracted from total oxygen demand for LEO-15 sediments. The remaining oxygen demand was assumed to approximate carbon mineralization via all other metabolic pathways, assuming 1 O₂:1 C. Carbon oxidation by denitrification was estimated assuming 106 C:84.8 N according to the equation: (CH₂O)₁₀₆ + 84.8 HNO₃ → 106 CO₂ + 42.4 N₂ + 148.4 H₂O (Richards, 1965). The contribution of denitrification to total carbon mineralization ranged from 10% to 18% at station 32, 3–33% at station C, and 2–62% at station 9 (Table 3). Overall, calculated carbon mineralization averaged 15.35 mmol C m⁻² d⁻¹ with denitrification accounting for 13% of this total. While

Table 3

Relative potential contribution of denitrification and oxygen respiration to carbon oxidation. Carbon oxidation calculated from denitrification rate and sediment oxygen consumption (corrected for nitrification) as described in text

	O ₂ consumption due to nitrification (mmol O ₂ m ⁻² d ⁻¹)	% O ₂ consumption due to nitrification	Total C oxidation (mmol C m ⁻² d ⁻¹)	% of C oxidation by denitrification
<i>Station 32</i>				
August, 1996	4.86	26	16.86	17
July, 1997	2.56	21	11.35	14
June, 1998	1.30	27	4.34	18
September, 1998	5.28	15	33.87	10
November, 1998	2.60	21	11.10	14
May, 1999	4.08	27	13.45	18
August, 1999	3.54	15	22.46	10
<i>Station C</i>				
August, 1996	3.86	19	18.58	12
July, 1997	4.52	19	22.20	12
June, 1998	1.54	12	12.20	4
September, 1998	1.74	5	31.24	3
November, 1998	3.26	47	5.38	33
May, 1999	4.28	27	14.18	18
<i>Station 9</i>				
July, 1997	5.64	34	14.34	23
June, 1998	0.76	7	10.50	2
September, 1998	2.42	10	23.76	6
November, 1998	4.56	27	14.57	16
May, 1999	4.06	50	6.43	38
August, 1999	4.06	71	4.46	62
<i>Station C2</i>				
October, 1996	12.20	18	62.25	11
<i>LEO-15 average</i>				
August, 1996	4.36	22	17.73	15
October, 1996	12.20	18	62.25	11
July, 1997	4.24	24	15.96	16
June, 1998	1.20	12	9.01	6
September, 1998	3.14	10	29.64	7
November, 1998	3.48	29	10.34	18
May, 1999	4.14	32	11.35	22
August, 1999‡	3.80	26	13.47	19
Overall	3.48	21	15.35	13

carbon mineralization via denitrification may be insignificant in some continental shelf sediments (Rysgaard et al., 1998; Kostka et al., 1999, calculated from Christensen et al., 1987b), denitrification appeared to play a significant role in carbon mineralization at LEO-15. However, the

relative contribution of denitrification to total carbon mineralization was highly variable among stations and sampling dates. The reasons for this variability are not yet known. Chamber measurements provide snapshots in time rather than a dynamic view of processes occurring in marine

sediments. The dynamics of denitrification and carbon mineralization need to be studied in greater detail for this variability in the importance of denitrification to be understood.

4.5. *Relating denitrification to sediment oxygen consumption*

While denitrification in continental shelf sediments can have an important local effect on phytoplankton production by reducing nitrogen availability, shelf denitrification can also contribute to the broader pattern of nitrogen limitation in the open ocean as denitrification is a major sink in the global nitrogen budget (Hattori, 1983; Christensen et al., 1987a; Seitzinger and Giblin, 1996). Estimated denitrification in North Atlantic shelf sediments (Seitzinger and Giblin, 1996) exceeds known nitrogen inputs to shelf sediments including export from estuaries and large rivers (Nixon et al., 1996), biological N_2 fixation (Nixon et al., 1996), and atmospheric deposition (Nixon et al., 1996 based on Prospero et al., 1996). Onwelling of nitrate-rich slope water likely supplies 50% or more of the nitrogen required by estimated denitrification in North Atlantic Shelf sediments (Seitzinger and Giblin, 1996). Hence denitrification in shelf sediments of the North Atlantic (and presumably other regions) reduces the oceanic nitrogen inventory, despite the temporal and spatial disconnection from the open ocean. To quantify the importance of denitrification in shelf sediments as a sink in the global ocean nitrogen budget, it is necessary to obtain an accurate global estimate of denitrification in continental shelf sediments. Denitrification in shelf sediments has been measured in few locations, primarily in various regions of the North Atlantic (Table 2), and denitrification in continental shelf sediments is highly variable making estimates specific to place and time. It would be impractical to measure denitrification with the temporal and spatial coverage necessary for extrapolation to the global shelf area. A more efficient approach will be development of robust relationships between denitrification and variables more easily measured with extensive spatial coverage.

Currently, the only spatially explicit model for estimating denitrification in shelf sediments is one developed and applied to the North Atlantic shelf (Seitzinger and Giblin, 1996). Nitrifying bacteria consume oxygen and use the ammonium regenerated by organic matter decomposition as a substrate, oxidizing it to nitrite and nitrate. In these 2 ways sediment oxygen consumption is related to nitrification, and therefore to coupled denitrification. Coupled denitrification was related to sediment oxygen consumption averaged over numerous locations in continental shelf sediments (Seitzinger and Giblin, 1996; coupled denitrification ($\text{mmol N m}^{-2} \text{d}^{-1}$) = $0.116 * \text{sediment oxygen consumption}$ ($\text{mmol O}_2 \text{m}^{-2} \text{d}^{-1}$); $r = 0.80$). Although denitrification coupled with nitrification was not related to sediment oxygen consumption in LEO-15 sediments ($r = 0.286$, $p = 0.236$, $n = 20$), the data values from LEO-15 are similar to previous studies, plotting within the same cluster of data points (Fig. 6). We have added data from LEO-15 (averages from all stations) as well as from the North Arctic shelf (Devol et al., 1997) and recalculated the regression statistics. Data were corrected for nitrate flux into sediments (i.e. direct denitrification). The inclusion of these data substantially increases the number of data points in this relationship that are based on N_2 flux measurements. They do not significantly alter the relationship, although they do increase the scatter somewhat (Fig. 6; coupled denitrification ($\text{mmol N m}^{-2} \text{d}^{-1}$) = $0.105 * \text{sediment oxygen consumption}$ ($\text{mmol O}_2 \text{m}^{-2} \text{d}^{-1}$); $r = 0.76$). The inclusion of Arctic shelf data (Devol et al., 1997) and LEO-15 data gives greater geographical coverage of continental shelf regions, extending from the Arctic to the sub-tropics (Gulf of Mexico), and supports the application of this model to estimate denitrification rates from sediment oxygen consumption in geographically diverse shelf regions. However, including additional factors may help strengthen the prediction of denitrification.

4.6. *Estimating denitrification in various continental shelf regions*

In the model of Seitzinger and Giblin (1996) primary production in continental shelf waters of

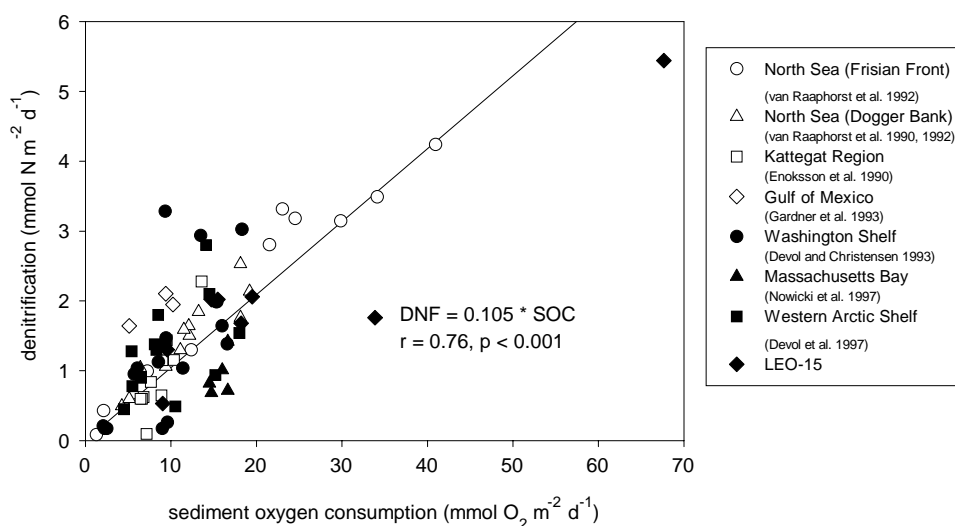


Fig. 6. Denitrification coupled with nitrification versus sediment oxygen consumption. Adapted from Seitzinger and Giblin (1996). Open symbols represent indirect estimates of denitrification (stoichiometric approaches), and closed symbols represent direct measurements of denitrification (N_2 production). LEO-15 data are plotted for each sampling period as the average for all three stations.

the North Atlantic was used to estimate sediment denitrification, assuming that $\approx 16\%$ of phytoplankton production is mineralized in sediments and that coupled denitrification is related to sediment oxygen demand according to the following equation: coupled denitrification ($\text{mmol N m}^{-2} \text{d}^{-1}$) = $0.019 \times$ phytoplankton production ($\text{mmol C m}^{-2} \text{d}^{-1}$) (based on the synthesis of available literature). Estimated denitrification for the shelf region between Nova Scotia and Cape Hatteras is $1.4 \text{ mmol N m}^{-2} \text{d}^{-1}$ (Seitzinger and Giblin, 1996) based on an average primary production rate of $\sim 26 \text{ mol C m}^{-2} \text{yr}^{-1}$ (O'Reilly and Busch, 1984). This is an average estimate for the entire shelf area to the shelf break, and agrees fairly well with the average denitrification rate at LEO-15 ($1.7 \text{ mmol N m}^{-2} \text{d}^{-1}$).

Given the poor distribution in spatial coverage for current denitrification estimates relative to the global shelf area, it is not possible to test the performance of the Seitzinger and Giblin (1996) model in most continental shelf locations. However, the model represents a sensible approach to estimating denitrification in large areas of continental shelf sediments, as primary production

can be estimated with extensive spatial coverage, particularly using satellite imagery. Future efforts toward estimating denitrification in continental shelf sediments globally will require further development of this or similar models for estimating denitrification, and improved temporal and spatial coverage of denitrification measurements for model testing. Toward improving coverage of denitrification measurements, the use of benthic chambers in situ may offer the most realistic estimates of biogeochemical processes in continental shelf sediments. However, the use of chambers does have recognized limitations. Pore water advection driven by current flow over rough sediment surfaces (Huettel and Gust, 1992; Huettel et al., 1996; Marinelli et al., 1998) and turbulent mixing of surficial sediments (Gehlen et al., 1995; Lohse et al., 1996) can affect solute mass transfer leading to an underestimate of actual solute mass transfer in benthic chambers. Consideration of this and other potential methodological constraints should guide how we proceed with improving coverage of site-specific denitrification rates in continental shelf sediments and in how we develop

and test models for estimating denitrification in shelf sediments.

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References

- Aller, R.C., Mackin, J.E., Ullman, W.J., Wang, C.-H., Tsai, S.-M., Jin, J.-C., Sui, Y.-N., Hong, J.Z., 1985. Early chemical diagenesis, sediment-water exchange, and storage of reactive organic matter near the mouth of the Changjiang, East China Sea. *Continental Shelf Research* 4 (1/2), 227–251.
- Bange, H.W., Rapsomanikis, S., Andreae, M.O., 1996. Nitrous oxide in coastal waters. *Global Biogeochemical Cycles* 10, 197–207.
- Bender, M.L., Fanning, K.A., Froelich, P.N., Heath, G.R., Maynard, V., 1977. Interstitial nitrate profiles and oxidation of sedimentary organic matter in the eastern equatorial Atlantic. *Science* 198, 605–609.
- Billen, G., 1978. A budget of nitrogen recycling in North Sea sediments off the Belgian coast. *Estuarine Coastal and Marine Science* 7, 127–146.
- Boesch, D.F., Hartzband, D.J., Ellison, R.J., 1979. Middle Atlantic outer continental shelf environmental studies, Vol. 11B. Chemical and biological benchmark studies. BLM Report No. BLM/YL/ES-79/03, Washington, DC, 301pp. (Chapter 6).
- Boudreau, B.P., Mucci, A., Sundby, B., Luther, G.W., Silverberg, N., 1998. Comparative diagenesis at three sites on the Canadian continental margin. *Journal of Marine Research* 56 (6), 1259–1284.
- Bouwman, A.F., van der Hoek, K.W., Olivier, J.G.J., 1995. Uncertainties in the global sources distribution of nitrous oxide. *Journal of Geophysical Research* 100, 2785–2800.
- Christensen, J.P., 1994. Carbon export from continental shelves, denitrification and atmospheric carbon dioxide. *Continental Shelf Research* 14 (5), 547–576.
- Christensen, J.P., Rowe, G.T., 1984. Nitrification and oxygen consumption in northwest Atlantic deep-sea sediments. *Journal of Marine Research* 42, 1099–1116.
- Christensen, J.P., Murray, J.W., Devol, A.H., Codispoti, L.A., 1987a. Denitrification in continental shelf sediments has major impact on the oceanic nitrogen budget. *Global Biogeochemical Cycles* 1 (2), 97–116.
- Christensen, J.P., Smethie Jr., W.H., Devol, A.H., 1987b. Benthic nutrient regeneration and denitrification on the Washington continental shelf. *Deep-Sea Research* 34 (5/6), 1027–1047.
- Codispoti, L.A., 1995. Is the ocean losing nitrate? *Nature* 376, 724.
- Codispoti, L.A., Christensen, J.P., 1985. Nitrification, denitrification, and nitrous oxide cycling in the eastern tropical South Pacific Ocean. *Marine Chemistry* 16, 277–300.
- Crutzen, P.J., 1970. The influence of nitrogen oxides on the atmospheric ozone content. *Quarterly Journal of Royal Meteorological Society* 96, 320–325.
- Devol, A.H., 1991. Direct measurement of nitrogen gas fluxes from continental shelf sediments. *Nature* 349, 319–321.
- Devol, A.H., Christensen, J.P., 1993. Benthic fluxes and nitrogen cycling in sediments of the continental margin of the eastern North Pacific. *Journal of Marine Research* 51, 345–372.
- Devol, A.H., Codispoti, L.A., Christensen, J.P., 1997. Summer and winter denitrification rates in western Arctic shelf sediments. *Continental Shelf Research* 17 (9), 1029–1050.
- Enoksson, V., Sörensson, F., Granéli, W., 1990. Nitrogen transformations in the Kattegat. *Ambio* 19 (3), 159–166.
- Flint, R.W., Kamykowski, D., 1984. Benthic nutrient regeneration in South Texas coastal waters. *Estuarine Coastal and Shelf Science* 18, 221–230.
- Florek, R.J., Rowe, G.T., 1983. Oxygen consumption and dissolved inorganic nutrient production in marine coastal and shelf sediments of the Middle Atlantic Bight. *International Revue ges. Hydrobiologia* 68 (1), 73–112.
- Gardner, W.S., Briones, E.E., Kaegi, E.C., Rowe, G.T., 1993. Ammonium excretion by benthic invertebrates and sediment-water nitrogen flux in the Gulf of Mexico near the Mississippi River outflow. *Estuaries* 16 (4), 799–808.
- Gehlen, M., Malschaert, J.F.P., van Raaphorst, W., 1995. Spatial and temporal variability of benthic silica fluxes in the southeastern North Sea. *Continental Shelf Research* 15 (13), 1675–1696.
- Giblin, A.E., Hopkinson, C.S., Tucker, J., 1997. Benthic metabolism and nutrient cycling in Boston Harbor, Massachusetts. *Estuaries* 20 (2), 346–364.
- Hahn, J., Crutzen, P.J., 1982. The role of fixed nitrogen in atmosphere photochemistry. *Philosophical Transactions of Royal Society of London, Series B* 296, 521–541.
- Hattori, A., 1983. Denitrification and dissimilatory nitrate reduction. In: Carpenter, E.J., Capone, D.G. (Eds.), *Nitrogen in the Marine Environment*. Academic Press, New York, pp. 191–232.
- Hopkinson Jr., C.S., Fallon, R.D., Jansson, B.-O., Schubauer, J.P., 1991. Community metabolism and nutrient cycling at

- Gray's Reef, a hard bottom habitat in the Georgia Bight. *Marine Ecology Progress Series* 73, 105–120.
- Huettel, M., Gust, G., 1992. Solute release mechanisms from confined sediment cores in stirred benthic chambers and flume flows. *Marine Ecology Progress Series* 82, 187–197.
- Huettel, M., Ziebis, W., Forster, S., 1996. Flow-induced uptake of particulate matter in permeable sediments. *Limnology and Oceanography* 41 (2), 309–322.
- Jahnke, R.A., 1990. Early diagenesis and recycling of biogenic debris at the seafloor, Santa Monica Basin, California. *Journal of Marine Research* 48, 413–436.
- Jahnke, R.A., Emerson, S.R., Murray, J.W., 1982. A model of oxygen reduction, denitrification, and organic matter mineralization in marine sediments. *Limnology and Oceanography* 27, 610–623.
- Kana, T.M., Darkangelo, C., Hunt, M.D., Oldham, J.B., Bennett, G.E., Cornwell, J.C., 1994. A membrane inlet mass spectrometer for rapid high precision determination of N₂, O₂, and Ar in environmental water samples. *Analytical Chemistry* 66, 4166–4170.
- Kostka, J.E., Thamdrup, B., Glud, R.N., Canfield, D.E., 1999. Rates and pathways of carbon oxidation in permanently cold Arctic sediments. *Marine Ecology Progress Series* 180, 7–21.
- Liu, K.-K., Kaplan, I.R., 1984. Denitrification rates and availability of organic matter in marine environments. *Earth and Planetary Science Letters* 68, 88–100.
- Lohse, L., Epping, E.H., Helder, W., van Raaphorst, W., 1996. Oxygen pore water profiles in continental shelf sediments of the North Sea: turbulent versus molecular diffusion. *Marine Ecology Progress Series* 145, 63–75.
- Lorenzen, C.J., 1967. Determination of chlorophyll and phaeopigments: Spectrophotometric determinations. *Water Resources Bulletin* 14, 190–194.
- MacDonald, W.B., 1983. Coastal–estuarine phytoplankton production and nitrogen utilization. Ph.D. Thesis, Department of Ecology, Rutgers University.
- Mackin, J.E., Swider, K.T., 1989. Organic matter decomposition pathways and oxygen consumption in coastal marine sediments. *Journal of Marine Research* 47, 681–716.
- Marinelli, R.L., Jahnke, R.A., Craven, D.B., Nelson, J.R., Eckman, J.E., 1998. Sediment nutrient dynamics on the South Atlantic Bight continental shelf. *Limnology and Oceanography* 43 (6), 1305–1320.
- McBride, R., Moslow, R., 1991. Origin, evolution, and distribution of shoreface sand ridges, Atlantic inner shelf, USA. *Marine Geology* 97, 57–85.
- McElroy, M.B., 1983. Marine biological controls on atmospheric CO₂ and climate. *Nature* 302, 328–329.
- Nixon, S.W., et al., 1996. The fate of nitrogen and phosphorus at the land–sea margin of the North Atlantic Ocean. *Biogeochemistry* 35, 141–180.
- Nowicki, B.L., Requintina, E., van Keuren, D., Kelly, J.R., 1997. Nitrogen losses through sediment denitrification in Boston Harbor and Massachusetts Bay. *Estuaries* 20, 626–639.
- O'Reilly, J.E., Busch, D.A., 1984. Phytoplankton primary production on the northwestern Atlantic shelf. *Rapp. P.-V. Reun. Cons. Int. Explor. Mer* 183, 255–268.
- Perry, M.J., Eppley, R.W., 1981. Phosphate uptake by phytoplankton in the central North Pacific Ocean. *Deep-Sea Research* 28A, 39–49.
- Perttilä, M., Niemistö, L., Mäkelä, K., 1995. Distribution, development, and total amounts of nutrients in the Gulf of Finland. *Estuarine, Coastal and Shelf Science* 41, 345–360.
- Prospero, J.M., et al., 1996. Atmospheric deposition of nutrients to the North Atlantic Basin. *Biogeochemistry* 35, 27–73.
- Raaphorst, W.van, Kloosterhuis, H.T., Cramer, A., Bakker, K.J.M., 1990. Nutrient early diagenesis in the sandy sediments of the Dogger Bank area, North Sea: pore water results. *Netherlands Journal of Sea Research* 26 (1), 25–52.
- Raaphorst, W.van, Kloosterhuis, H.T., Berghuis, E.M., Gieles, A.J.M., Malschaert, J.F.P., van Noort, G.J., 1992. Nitrogen cycling in two types of sediments of the southern North Sea (Frisian Front, Broad Fourteens): field data and mesocosm results. *Netherlands Journal of Sea Research* 28, 293–316.
- Richards, F.A., 1965. Anoxic basins and fjords. In: Riley, J.P., Skirrow, G. (Eds.), *Chemical Oceanography*. Academic Press, London, pp. 611–645.
- Risgaard-Petersen, N., Rysgaard, S., Nielsen, L.P., Revsbech, N.P., 1994. Diurnal variation of denitrification and nitrification in sediments colonized by benthic microphytes. *Limnology and Oceanography* 39, 573–579.
- Rysgaard, S., Thamdrup, B., Risgaard-Petersen, N., Fossing, H., Berg, P., Christensen, P.B., Dalsgaard, T., 1998. Seasonal carbon and nutrient mineralization in a high-Arctic coastal marine sediment, Young Sound, Northeast Greenland. *Marine Ecology Progress Series* 175, 261–276.
- Ryther, J.H., Dunstan, W.M., 1971. Nitrogen, phosphorus, and eutrophication in the coastal marine environment. *Science* 171, 1008–1013.
- Seitzinger, S.P., 1988. Denitrification in freshwater and coastal marine ecosystems: ecological and geochemical significance. *Limnology and Oceanography* 33, 702–724.
- Seitzinger, S.P., Giblin, A.E., 1996. Estimating denitrification in North Atlantic continental shelf sediments. *Biogeochemistry* 35, 235–260.
- Seitzinger, S.P., Kroeze, C., 1998. Global distribution of nitrous oxide production and N inputs in the freshwater and coastal marine ecosystems. *Global Biogeochemical Cycles* 12 (1), 93–113.
- Seitzinger, S.P., Nixon, S.W., 1985. Eutrophication and the rate of denitrification and N₂O production in coastal marine sediments. *Limnology and Oceanography* 30 (6), 1332–1339.
- Seitzinger, S., Nixon, S., Pilson, M.E.Q., Burke, S., 1980. Denitrification and N₂O production in near-shore marine sediments. *Geochimica and Cosmochimica Acta* 44, 1853–1860.
- Seitzinger, S.P., Nixon, S.W., Pilson, M.E.Q., 1984. Denitrification and nitrous oxide production in a coastal marine ecosystem. *Limnology and Oceanography* 29 (1), 73–83.

- Shaffer, G., Rönner, U., 1984. Denitrification in the Baltic proper deep water. *Deep-Sea Research* 31 (3), 197–220.
- Tuominen, L., Heinanen, A., Kuparinen, J., Nielsen, L.P., 1998. Spatial and temporal variability of denitrification in the sediments of the northern Baltic Proper. *Marine Ecology Progress Series* 172, 13–24.
- Wang, W.C., Yung, Y.L., Lacin, A.A., Mo, J., Hanson, J.E., 1976. Greenhouse effects due to man-made perturbations of trace gases. *Science* 194, 685–690.
- Weiss, R.F., 1970. The solubility of nitrogen, oxygen, and argon in water and seawater. *Deep-Sea Research* 17, 721–735.
- Weiss, R.F., Price, B.A., 1980. Nitrous oxide solubility in water and seawater. *Marine Chemistry* 8, 347–359.
- Wulff, F., 1989. A time-dependent budget model for nutrients in the Baltic Sea. *Global Biogeochemical Cycles* 3 (1), 63–78.