

Estimating denitrification in North Atlantic continental shelf sediments

SYBIL P. SEITZINGER¹ & ANNE E. GIBLIN²

¹*Institute of Marine and Coastal Sciences, Rutgers/NOAA CMER Program, Rutgers University, New Brunswick, NJ 08903-0231 (Fax: 908-932-1792);* ²*Ecosystems Center, Marine Biological Laboratory, Woods Hole, MA 02543 (Fax: 508-457-1548)*

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Abstract. A model of coupled nitrification/denitrification was developed for continental shelf sediments to estimate the spatial distribution of denitrification throughout shelf regions in the North Atlantic basin. Using data from a wide range of continental shelf regions, we found a linear relationship between denitrification and sediment oxygen uptake. This relationship was applied to specific continental shelf regions by combining it with a second regression relating sediment oxygen uptake to primary production in the overlying water. The combined equation was: denitrification ($\text{mmol N m}^{-2} \text{d}^{-1}$) = $0.019 \times$ phytoplankton production ($\text{mmol C m}^{-2} \text{d}^{-1}$). This relationship suggests that approximately 13% of the N incorporated into phytoplankton in shelf waters is eventually denitrified in the sediments via coupled nitrification/denitrification, assuming a C:N ratio of 6.625:1 for phytoplankton. The model calculated denitrification rates compare favorably with rates reported for several shelf regions in the North Atlantic.

The model-predicted average denitrification rate for continental shelf sediments in the North Atlantic Basin is $0.69 \text{ mmol N m}^{-2} \text{d}^{-1}$. Denitrification rates (per unit area) predicted by the model are highest for the continental shelf region in the western North Atlantic between Cape Hatteras and South Florida and lowest for Hudson Bay, the Baffin Island region, and Greenland. Within latitudinal belts, average denitrification rates were lowest in the high latitudes, intermediate in the tropics and highest in the mid-latitudes. Although denitrification rates per unit area are lowest in the high latitudes, the total N removal by denitrification ($53 \times 10^{10} \text{ mol N y}^{-1}$) is similar to that in the mid-latitudes ($60 \times 10^{10} \text{ mol N y}^{-1}$) due to the large area of continental shelf in the high latitudes. The Gulf of St. Lawrence/Grand Banks area and the North Sea are responsible for seventy-five percent of the denitrification in the high latitude region. N removal by denitrification in the western North Atlantic ($96 \times 10^{10} \text{ mol N y}^{-1}$) is two times greater than in the eastern North Atlantic ($47 \times 10^{10} \text{ mol N y}^{-1}$). This is primarily due to differences in the area of continental shelf in the two regions, as the average denitrification rate per unit area is similar in the western and eastern North Atlantic.

We calculate that a total of $143 \times 10^{10} \text{ mol N y}^{-1}$ is removed via coupled nitrification/denitrification on the North Atlantic continental shelf. This estimate is expected to underestimate total sediment denitrification because it does not include direct denitrification of nitrate from the overlying water. The rate of coupled nitrification/denitrification calculated is greater than the nitrogen inputs from atmospheric deposition and river sources combined, and suggests that onwelling of nutrient rich slope water is a major source of N for denitrification in shelf regions. For the two regions where N inputs to a shelf region from onwelling have been measured, onwelling appears to be able to balance the denitrification loss.

Introduction

A number of studies have suggested that denitrification is a major sink for fixed nitrogen in the oceans (e.g., Bender et al. 1977; Christensen et al. 1987a, b; Christensen 1994; Codispoti & Christensen 1989; Devol & Christensen 1993; Lui & Kaplan 1984). Recent studies suggest that denitrification losses in the oceans are on the order of 9.2×10^{12} mol N y^{-1} which exceed known oceanic nitrogen inputs (Christensen 1994). More than half of this denitrification (4.8×10^{12} mol N y^{-1}) takes place in sediments, with the remainder in pelagic oxygen minimum zones (Christensen 1994).

Although sediments are commonly thought of as sources of inorganic nitrogen to the overlying water through regeneration, they also serve as a sink for both externally supplied and regenerated nitrogen via denitrification (Seitzinger 1988). Denitrification is the reductive respiration of nitrate or nitrite to N_2 or N_2O , and is carried out by a diverse group of bacteria under anaerobic conditions. Sediments are ideal sites for denitrification because they generally are anaerobic a few mm below the surface (Revsbech et al. 1980; Archer & Devol 1992). Nitrate can be supplied to the sediments either directly from the overlying water (direct denitrification) or through nitrification in the sediments of ammonia released during the decomposition of organic matter (coupled nitrification/denitrification) (Seitzinger 1988; Devol & Christensen 1993).

Studies have indicated that most of the denitrification taking place in marine sediments occurs on the continental shelf (Christensen et al. 1987a; Christensen 1994). Estimates of the amount of N removed on the continental shelf are on the order of 3.6×10^{12} mol N y^{-1} , which accounts for more than 50% of the total nitrogen inputs to the oceans (Christensen et al. 1987a). In contrast, estuarine areas remove about 0.9×10^{12} mol N y^{-1} (Seitzinger 1988) and deep sea sediments remove about 0.5×10^{12} mol N y^{-1} (Christensen 1994). However, in spite of the apparent importance of denitrification on continental shelves to the oceanic N budget there have been very few measurements of denitrification in shelf sediments. Direct measurements of denitrification (N_2 production) in continental shelf sediments are limited to the northwest coast of the U.S. (Devol 1991; Devol & Christensen 1993). Estimates of denitrification have been made in other shelf regions using indirect methods including models of pore water solute profiles (Billen 1978; Christensen 1989; Raaphorst et al. 1992), acetylene block measurements (Haines et al. 1981; Raaphorst et al. 1992; Law & Owens 1990; Lohse et al. 1993), $^{15}NO_3^-$ additions to sediment slurries (Koike & Hattori 1979), and stoichiometric calculations (Florek & Rowe 1983; Gardner et al. 1993).

Because of the paucity of direct measurements of denitrification, estimates of global rates of denitrification in shelf sediments generally have been based

on the application of a single rate to all shelf areas. For example, Christensen et al. (1987 a) estimated that 3.6×10^{12} mol N y^{-1} are removed by denitrification in continental shelf sediments by applying an average nitrate consumption rate that he calculated for continental shelf plus some slope sediments to the global shelf area.

In this paper we estimate the denitrification rate of continental shelf sediments in the North Atlantic. We have focused on the importance of denitrification from coupled nitrification/denitrification because newer studies on shelf sediments have shown that this is an important (Devol & Christensen 1993) and in many cases, the major (Raaphorst et al. 1990; Kelly & Nowicki 1993; Lohse et al. 1993) mechanism by which denitrification occurs in shelf sediments. Like other studies we have had to extrapolate from a very few rate measurements to large areas. However, in this study we have attempted to examine how denitrification may change spatially throughout the North Atlantic shelf by examining the link between denitrification in the sediments and primary production in the overlying water.

Approach and data sources

To estimate the large scale spatial distribution of the denitrification N sink in various continental shelf regions throughout the North Atlantic basin, we assumed that coupled nitrification/denitrification is directly related to carbon oxidation, as measured by oxygen uptake, in shelf sediments. The relationship between denitrification and sediment oxygen consumption has been demonstrated in a wide variety of estuarine and freshwater sediments (Seitzinger 1987 & 1990). Denitrification and sediment oxygen consumption also are related in Washington shelf sediments (Devol & Christensen 1993). Using data from a wide range of continental shelf regions, we developed a relationship between denitrification rates and sediment oxygen consumption rates. We used denitrification rates that were either measured directly (N_2 production) or that were calculated stoichiometrically, as described below. Then, because there still were numerous continental shelf regions with no measured oxygen uptake data, we developed a relationship between sediment oxygen uptake and primary production in the overlying waters. Finally, denitrification rates for shelf areas throughout the North Atlantic were calculated based on: 1) the primary production rate for each region, 2) the derived relationship between denitrification and primary production, and 3) the shelf area for each region.

Denitrification versus O₂ uptake

For continental shelf sediments, a relationship between sediment oxygen consumption and denitrification coupled to sediment nitrification was developed using two types of data. The first type was data from continental shelf studies in which denitrification was measured directly (N_2 flux) in conjunction with sediment oxygen consumption. These included *in situ* measurements made during summer at twelve locations on the Washington continental shelf (Devol & Christensen 1993) and laboratory measurements using cores from five locations in Massachusetts Bay (Kelly & Nowicki 1993; Giblin et al. 1994). For the above studies, we subtracted direct denitrification (which was equated to measured nitrate influx from the overlying water) from the total N_2 flux, to obtain denitrification rates coupled to sediment nitrification. The second type of data included continental shelf studies in which sediment O_2 consumption and DIN (ammonia, nitrate, and nitrite) fluxes were measured simultaneously. In those studies we estimated denitrification rates based on stoichiometric calculations of the DIN deficit (Nixon et al. 1976; Giblin et al. 1992; Gardner et al. 1993). The DIN deficit was calculated as the difference between the predicted and measured DIN effluxes. Predicted DIN effluxes were estimated based on measurements of oxygen consumption rates and an assumed Redfield O:N ratio of 6.625 ($O_2:N$). Denitrification was equated to the DIN deficit, based on the assumption that any mineralized N not released as DIN from the sediments was denitrified. The data include sandy and finer grained sediments with sites ranging in depth from 16 to 106 m. Data for the North Sea include summer measurements at eleven locations (Raaphorst et al. 1990) and measurements over an annual cycle at two other locations (Raaphorst et al. 1992). Data from four stations in the Kattegatt were means of seven sampling events over an annual cycle (Enoksson et al. 1990). Gulf of Mexico data were from two studies: one summer study at four locations (Gardner et al. 1993) and the other a single location on four dates between July and January (Flint & Kamykowski 1984).

The validity of the stoichiometric approach for continental shelf sediments is indicated in studies which have both types of data available. In Washington shelf sediments there was a strong linear relationship between direct measurements of denitrification (N_2 production) and denitrification rates estimated from stoichiometry (slope = 0.98; $r = 0.82$) (data from Devol and Christensen 1993; N_2 flux adjusted for contribution of nitrate from the overlying water). In Massachusetts Bay, the annual denitrification rate measured directly (N_2 flux) compared well with the rate calculated from stoichiometry at various stations, although for individual dates there was sometimes considerable scatter between the measured and calculated rates (Giblin et al. 1993, 1994).

A linear relationship between denitrification and sediment oxygen consumption was found for continental shelf sediments ($r = 0.80$; significant at 0.001 level) (Figure 1):

$$\text{DNF}_c = 0.116 * \text{SOD} \quad (1)$$

where DNF_c equals denitrification coupled to sediment nitrification ($\text{mmol N as N}_2 \text{ m}^{-2} \text{ d}^{-1}$) and SOD equals sediment oxygen consumption ($\text{mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$). The regression line was fit through the origin, based on the assumption that no coupled denitrification/nitrification will occur if there is no oxygen consumption. The slope of the line for the relationship between denitrification and sediment oxygen consumption for the combined continental shelf data (slope = 0.116) is similar to, although slightly lower than, that found for the combined data from seven estuarine and freshwater ecosystems (slope = 0.142; Seitzinger 1990). The latter relationship was developed from direct N_2 flux measurements in conjunction with simultaneous SOD measurements. Those denitrification rates included both coupled nitrification/denitrification and direct denitrification of nitrate from the overlying water. The inclusion of both sources of nitrate for denitrification in the estuarine and freshwater relationship may be responsible for the higher slope relative to our continental shelf relationship which just considers coupled nitrification/denitrification.

We did not use denitrification rates that were estimated from acetylene block measurements. In addition to blocking N_2O reduction to N_2 , acetylene also blocks nitrification (Hynes & Knowles 1978, 1984; Bremner & Blackmer 1979). The acetylene block method has been shown to markedly underestimate denitrification rates in estuarine and freshwater sediments, particularly when nitrification and denitrification are closely coupled (Kemp et al. 1990; Seitzinger et al. 1993). In this paper we are attempting to estimate denitrification coupled to nitrification.

Oxygen uptake vs. primary production

In order to apply the relationship developed above between denitrification and sediment oxygen consumption (eq. 1) to a wide range of geographical locations, we investigated the relationship between primary production and sediment oxygen consumption. The assumption was that because the source of organic matter decomposed in the sediments, resulting in oxygen consumption, largely originates from phytoplankton production, the large scale spatial distribution of sediment oxygen consumption should reflect the large scale spatial distribution of primary production.

Data were compiled for sixteen continental shelf regions in which both primary production and sediment oxygen consumption rates were available

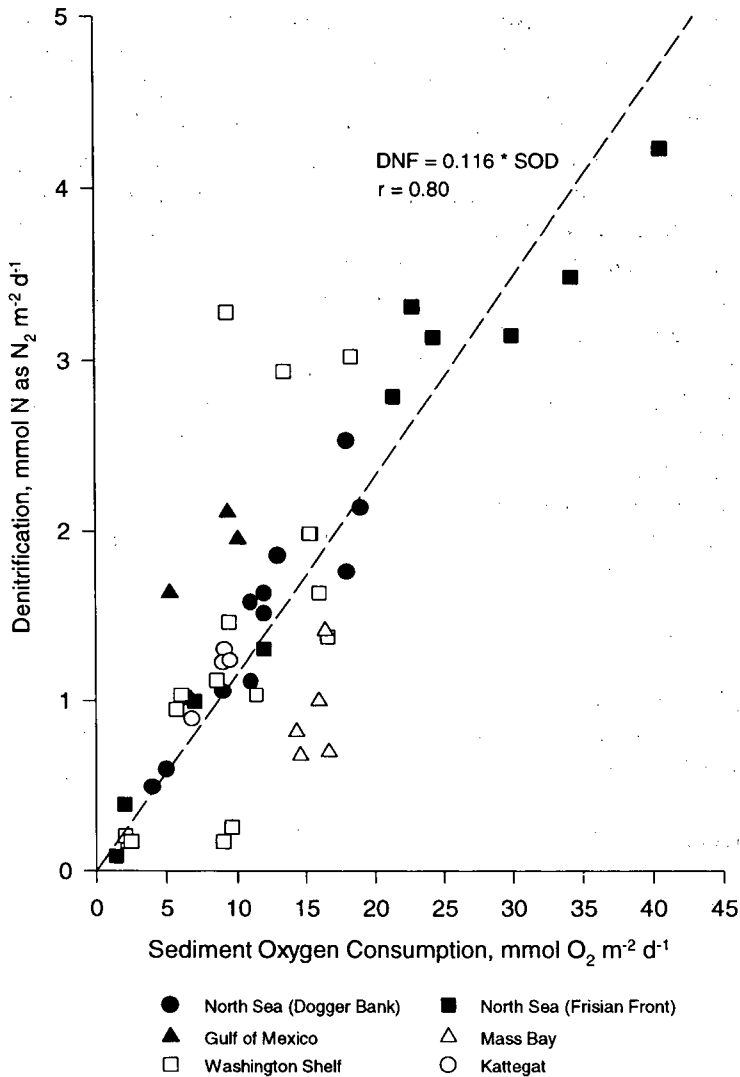


Figure 1. Relationship between denitrification rates coupled to sediment nitrification and sediment oxygen consumption rates in various continental shelf regions. Dashed line indicates regression line. Washington shelf (Devol & Christensen 1993, adjusted for N_2 production due to nitrate from overlying water) and Massachusetts Bay (Kelly & Nowicki 1993; Giblin et al. 1994) data are from direct N_2 flux measurements; North Sea (Raaphorst et al. 1990, 1992), Gulf of Mexico (Gardner et al. 1993), and Kattegat region of the Baltic (Enoksson et al. 1990) data are from stoichiometric calculations (see text for details). Data from Flint & Kamykowski (1984) are not shown, although they follow the same general pattern; oxygen uptake and denitrification rates were very high relative to the data shown which resulted in compression of the graphed data.

(Figure 2). In most cases the two processes were not measured concurrently; whenever possible we used data for similar time frames (e.g., summer or annual) (Figure 2). The data include sites from depths ranging from 14–200 meters. For five regions, (Gulf of Maine, Georges Bank, and Scotian, Newfoundland and Labrador shelves), the authors used data from a variety of stations to determine the relationship between O_2 uptake and temperature; this temperature response then was used to calculate an annual average O_2 uptake to compare to annual primary production data (Grant et al. 1991). In that study, measurements in both sandy and muddy sediments were made and an average O_2 uptake for these shelf regions was calculated based on the amount of each sediment type in the region (Grant et al. 1991). Data from the other twelve studies represent the average of a number of measurements at specific locations and were not corrected for sediment type on a regional basis. However, the measurements come from a variety of sediment types ranging from coarse sands to fine muds. Over half of the data sets are annual averages; the rest generally are concentrated during the summer season.

Based on the above data, a linear relationship was found between sediment oxygen consumption and phytoplankton production (Figure 2):

$$\text{SOD} = 0.164 * \text{PhytoProd} \quad (2)$$

where SOD is in $\text{mmol } O_2 \text{ m}^{-2} \text{ d}^{-1}$ and PhytoProd equals phytoplankton production as $\text{mmol C m}^{-2} \text{ d}^{-1}$ (regression line fit through origin). Although the regression is significant (at 0.001 level), the scatter in the data is fairly large and the number of areas is small. Nixon (1983) examined a number of estuaries and calculated that 23.8% of the primary production and allochthonous carbon inputs were mineralized in the sediments. The correlation coefficient of the regression of the data collected by Nixon (1981) was much higher than we obtained from the regression of the shelf data. One important source of variation in our data set may be the portion of carbon produced in various shelf areas that is advected off the shelf and not mineralized *in situ* (Lee et al. 1991; Walsh 1983; Christensen 1989).

This relationship (eq. 2) suggests that approximately 16% of the carbon produced in surface waters is mineralized on the bottom, assuming a respiratory coefficient (organic carbon: O_2 by moles) of 1. This is consistent, if somewhat conservative, relative to other shelf studies where more complete carbon budgets have been constructed or where carbon delivery to the bottom has been measured using sediment traps. For example, about 25% of the shelf primary production is used by the benthos off southern New England (Rowe et al. 1988) and off the Amazon (Aller et al. 1991). In the Canadian Arctic, 31–53% of the primary production in the overlying water reached the bottom at 33 m, based on sediment trap data (Atkinson & Wacasey 1987).

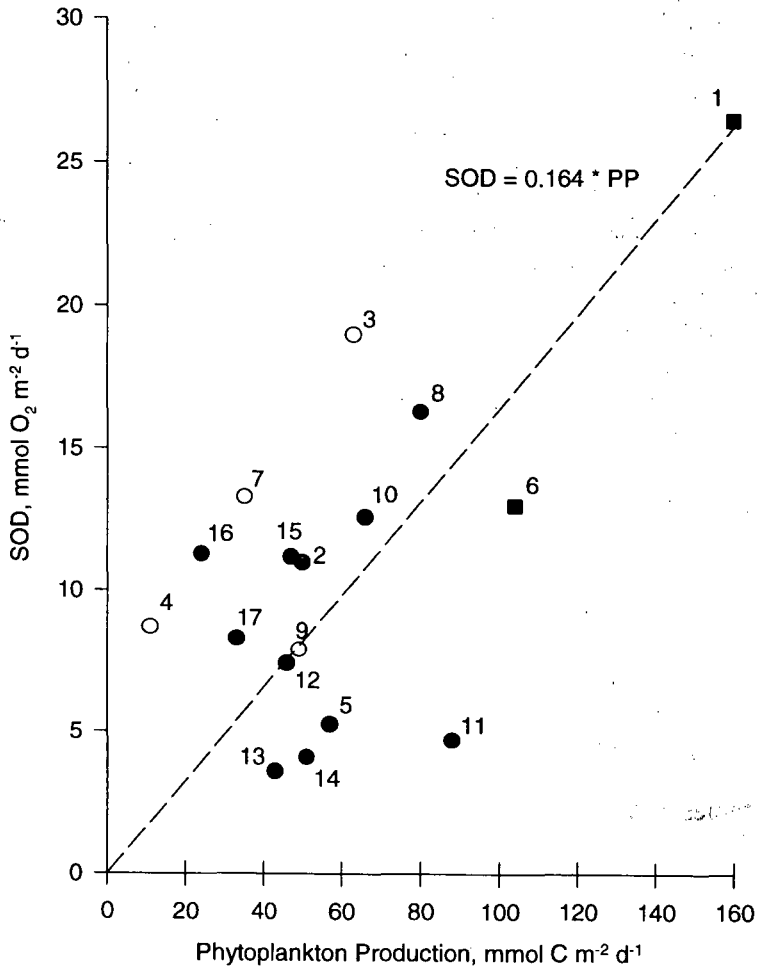


Figure 2. Relationship between sediment oxygen consumption rates (SOD) and phytoplankton production rates in a variety of continental shelf regions. Dashed line indicates regression line. Data sources: 1) South Atlantic Bight (Hanson et al. 1981; Yoder et al. 1985), 2) New York Bight Apex (Rowe et al. 1988), 3) Bering shelf (Grebmeier & McRoy 1989), 4) Alaska Coastal (Grebmeier & McRoy 1989), 5) North Sea, Dogger Bank (deWilde et al. 1984), 6) North Sea, Dogger Bank (Raaphorst et al. 1990), 7) Belt Sea and Kattegat (Jorgensen & Revsbech 1989), 8) Massachusetts Bay, 30–33 m (Giblin et al. 1994; Kelly & Nowicki 1993), 9) Gulf of Mexico (Gardner et al. 1993; Sklar & Turner 1981; Flint & Rabalais 1981), 10) Gulf of Maine, 11) Georges Bank, 12) Scotian Shelf, 13) Newfoundland Shelf, and 14) Labrador Shelf (10–14 from Grant et al. 1991), 15) North Sea, 25–31 m and 16) North Sea, 32–81 m (Upton et al. 1993), 17) Kattegat (Enoksson et al. 1990; Rydberg et al. 1990). summer data ■; annual data ●; other ○.

This is similar to sediment trap data from the North Sea where 20–35% of the primary production reached the bottom at 100 m (Davies & Payne 1984) and in the Baltic where at 40 m, 25% of the production reached the bottom (Forsskahl et al. 1982). Vertical carbon fluxes below the photic zone in the Mississippi River plume and inner Gulf of Mexico shelf region (Redalje et al. 1992) are on the order of 20% to 30% of the primary production values reported (see below). The somewhat lower percent of organic carbon mineralization in sediments found in our relationship (16%) relative to the above studies may be due to a number of factors. For example, reduced end products of anaerobic metabolism (e.g. sulfides) may be stored in the sediments, and/or some of the organic matter deposited to the sediment surface may be decomposed in the water column following resuspension.

In this data set the variation in the percentage of the primary production that reaches the bottom cannot be explained by depth. Even when data within regions are compared there is no strong correlation between depth and primary production mineralized on the bottom. For example, in the North Sea, sites at 31–81 m had a greater percentage of the primary production reaching the bottom than sites at 25–31 m (Upton et al. 1993) (Figure 2). At sites off Eastern Canada, sediment type rather than depth explained most of the variation in oxygen uptake (Grant et al. 1991).

Our finding that depth is not a major factor controlling the percentage of primary production which reaches the bottom may seem surprising because several other studies have shown a strong correlation of oxygen uptake with water depth (Devol & Christensen 1993; Christensen 1989; Rowe et al. 1988; Martin et al. 1987) or depth to the mixed layer (Hargrave 1973). However, those studies included data from stations extending to depths far greater than 200 m. When only the data from 200 m and less are examined, the correlation becomes much weaker or disappears. Our findings are similar to those of Nixon (1981) who found no relationship between sediment oxygen uptake and carbon inputs to the bottom in coastal sediments with water depths from 3 m to 70 m. Based on the information presented above, we did not use depth as a variable in our calculations.

Extrapolation to the North Atlantic Shelf

The relationship between sediment oxygen consumption and denitrification (eq. 1) was combined with the relationship between sediment oxygen consumption and phytoplankton production (eq. 2) to arrive at a model of denitrification as a function of phytoplankton production:

$$\text{DNF}_c = 0.019 * \text{PhytoProd} \quad (3)$$

where DNF_c equals denitrification coupled to sediment nitrification ($\text{mmol N as N}_2 \text{ m}^{-2} \text{ d}^{-1}$) and PhytoProd equals phytoplankton production ($\text{mmol C m}^{-2} \text{ d}^{-1}$) in the overlying water. This relationship suggests that approximately 13% of the N incorporated into phytoplankton in shelf waters is eventually denitrified in the sediments via coupled nitrification/denitrification, assuming a C:N ratio of 6.625:1 for phytoplankton.

Phytoplankton production rates for each region within the North Atlantic Basin were compiled and used to calculate regional denitrification rates (eq.3) (Table 1). The primary production data were taken from a wide variety of sources (see footnotes, Table 1). In a few cases, such as for the Mid-Atlantic Bight and part of the North Sea, the estimates are based upon data with good spatial and temporal coverage. However, for most regions we had to extrapolate from short term studies made in a restricted area. For areas where only limited data sets were available, we used lower estimates so that our calculated rates of denitrification would also be conservative.

The total amount of N removed by coupled nitrification/denitrification in each region was calculated from the estimated denitrification rate per unit area for that region (eq. 3) and the area of the continental shelf in that region (Pilson & Seitzinger, this vol.). The continental shelf boundary was chosen operationally as the 200 m bathymetric contour.

Results and discussion

Denitrification (coupled nitrification/denitrification) rates per unit area predicted by the model are highest for the continental shelf region between Cape Hatteras and the southern extent of Florida ($2.34 \text{ mmol N as N}_2 \text{ m}^{-2} \text{ d}^{-1}$) and lowest for Hudson Bay, the Baffin Island region, and Greenland (0.11 to $0.15 \text{ mmol N as N}_2 \text{ m}^{-2} \text{ d}^{-1}$) (Table 1; Figure 3a). Within latitudinal belts, average denitrification rates were lowest ($0.45 \text{ mmol N as N}_2 \text{ m}^{-2} \text{ d}^{-1}$) in the high latitudes ($>45^\circ \text{ N}$), intermediate ($0.71 \text{ mmol N as N}_2 \text{ m}^{-2} \text{ d}^{-1}$) in the tropics ($0-20^\circ \text{ N}$), and highest ($1.3 \text{ mmol N as N}_2 \text{ m}^{-2} \text{ d}^{-1}$) in the mid-latitudes ($20^\circ \text{ N}-45^\circ \text{ N}$) (Table 1). The area weighted average denitrification rate for continental shelf sediments in the North Atlantic Basin is $0.69 \text{ mmol N as N}_2 \text{ m}^{-2} \text{ d}^{-1}$.

Although denitrification rates per unit area are lowest in the high latitudes, due to the large area of continental shelf in the high latitudes ($3,252,268 \text{ km}^2$; Pilson and Seitzinger, this vol.), the total N removal by denitrification ($53 \times 10^{10} \text{ mol N y}^{-1}$) is similar to that in the mid-latitudes ($60 \times 10^{10} \text{ mol N y}^{-1}$) (Table 1; Figure 4). The Gulf of St. Lawrence/Grand Banks area and the North Sea are responsible for seventy-five percent of the denitrification in the high latitude region (Figure 3b). N removal by denitrification in the western

Table 1. Estimated N removal by sediment denitrification coupled to nitrification in various continental shelf regions. See text for explanation of calculations.

Region	Area ¹ km ²	Prim. prod. ² mmol C m ⁻² d ⁻¹	Denitrification mmol N as N ₂ m ⁻² d ⁻¹	Denitrification for region mol N y ⁻¹
<i>>45° N latitude</i>				
Greenland	159,897	8	0.15	0.89 × 10 ¹⁰
Iceland	107,272	18	0.34	1.34 × 10 ¹⁰
Hudson Bay	780,178	6	0.11	3.25 × 10 ¹⁰
Baffin Is. region	348,350	6	0.11	1.45 × 10 ¹⁰
Labrador	147,955	51	0.97	5.23 × 10 ¹⁰
G. St. Law. & Gr. Bank	518,998	43	0.82	1.55 × 10 ¹¹
North Sea	1,095,734	32	0.61	2.43 × 10 ¹¹
Norway Shelf	93,884	23	0.44	1.50 × 10 ¹⁰
Total	3,252,268			5.35 × 10 ¹¹
Average			0.45	
<i>20° N–45° N</i>				
N Scotia/Hatteras	361,042	71	1.35	1.78 × 10 ¹¹
Hatteras/S. Florida	137,364	123	2.34	1.17 × 10 ¹¹
Gulf of Mexico	573,565	49	0.93	1.95 × 10 ¹¹
African self	144,476	83	1.58	8.32 × 10 ¹⁰
Spain and Portugal	51,435	80	1.52	2.85 × 10 ¹⁰
Total	1,267,882			6.02 × 10 ¹¹
Average			1.30	
<i>0–20° N</i>				
Central and S. America	279,799	49	0.93	9.51 × 10 ¹⁰
Amazon Shelf	389,562	31	0.59	8.37 × 10 ¹⁰
Caribbean Islands	194,956	20	0.38	2.70 × 10 ¹⁰
African Shelf	273,848	46	0.87	8.74 × 10 ¹⁰
Total	1,138,165			2.93 × 10 ¹¹
Average			0.71	
Overall totals	5.66 × 10 ⁶			143 × 10 ¹⁰
Average			0.69	

¹ Continental shelf areas from Pilson and Seitzinger (this vol.) calculated from the NOAA ETOPOS data base.

² *Greenland, Iceland, Hudson Bay and Canadian Arctic* – For Hudson's Bay and most other Arctic shelf regions off Canada, including the area around Baffin Island, we used a primary production value of 27 gC m⁻² y⁻¹ (Harrison et al. 1982). We used a value of 80 gC m⁻² y⁻¹ for the western and southern tip of Greenland (Atkinson & Wacasey 1987; Steemann-Nielsen

Table 1. Continued.

& Hansen 1960) for an average of $35 \text{ gC m}^{-2} \text{ y}^{-1}$ for the entire Greenland shelf. We used $80 \text{ gC m}^{-2} \text{ y}^{-1}$ for the Iceland shelf by extrapolating Steemann-Nielson & Hansen's (1960) data to a 120 day growing season.

Labrador Shelf – We used the estimate of Grant et al. (1991) who calculated a yearly average production of $225 \text{ gC m}^{-2} \text{ y}^{-1}$ based upon July and Sept production data at three sites.

Newfoundland Shelf including Grand Banks – We used Grant et al.'s (1991) value of $190 \text{ gC m}^{-2} \text{ y}^{-1}$. Grant et al. (1991) used published ^{14}C production data and assumed a 10 month growing season. Their estimate compares well with that of Prasad & Haedrich's (1994) who used satellite detectable Chl a and a model to estimate production as $193 \text{ gC m}^{-2} \text{ y}^{-1}$.

North Sea and surrounding areas – We used the primary production of Joint & Pomroy (1993) for the southern and central North Sea. Their estimates for the southern areas are roughly consistent with estimates that Reid et al. (1990) made from a compilation of the literature, but Reid et al.'s (1990) estimated values for primary production in the central North Sea ($250 \text{ gC m}^{-2} \text{ y}^{-1}$) are nearly twice that measured by Joint and Pomroy. We used Joint and Pomroy's lower estimate which was less heavily biased toward the more productive coastal areas. For the northern North Sea we used a value of $150 \text{ gC m}^{-2} \text{ y}^{-1}$ which is the low end of the range given in Reid et al. (1990). We used a value of $102 \text{ gC m}^{-2} \text{ y}^{-1}$ for the primary production of the Celtic Sea (Joint et al. 1986) and $144 \text{ gC m}^{-2} \text{ y}^{-1}$ for the Kattegat. The area weighted average for the entire North Sea region was $140 \text{ gC m}^{-2} \text{ y}^{-1}$.

Norway – Harrison et al. (1982) cite a study where rates of $1.12 \text{ gC m}^{-2} \text{ d}^{-1}$ were measured. Assuming 120 day growing season this would yield a production of $134 \text{ gC m}^{-2} \text{ y}^{-1}$. Off shore in the Norwegian Sea, Bodungen et al. (1990) has measured somewhat lower values of about $90 \text{ gC m}^{-2} \text{ y}^{-1}$. For our calculations we assumed a value of $100 \text{ gC m}^{-2} \text{ y}^{-1}$.

Northwestern Atlantic Shelf: Gulf of Maine to Cape Hatteras – We used a value of $310 \text{ gC m}^{-2} \text{ y}^{-1}$ from the data of O'Reilly and Bush (1984) for shelf primary production between Nova Scotia and Cape Hatteras. Their primary production data was based upon the results of 23 surveys (628 stations occupied) made along the Northwestern Atlantic shelf between 1977–1980.

South Atlantic Bight – Cape Hatteras to the tip of Florida – The complicated hydrographic controls on productivity in the South Atlantic Bight make it difficult to determine the primary production of the entire region from the limited data available (Lee et al. 1991; Yoder et al. 1985). We have used a value of $630 \text{ gC m}^{-2} \text{ y}^{-1}$ for the production of the inner shelf areas. This value is equal to the lower value found by Verity et al. (1993) for two stations off Skidaway Island but somewhat higher than the production of $550 \text{ gC m}^{-2} \text{ y}^{-1}$ found by Thomas (1966) to the south. We used a value of $360 \text{ gC m}^{-2} \text{ y}^{-1}$ for production on the outer shelf (Yoder 1985). We assumed that the outer shelf is approximately a third the area of the entire shelf (Lee et al. 1991).

Gulf of Mexico – We used an average rate of $290 \text{ gC m}^{-2} \text{ y}^{-1}$ for the Northern Gulf of Mexico which is what has been found on the shelf offshore of Barataria Bay (Skalar & Turner 1981). Flint and Rabalais (1981) report a primary production value of $177 \text{ gC m}^{-2} \text{ y}^{-1}$ for the shelf off of Texas. We used this value for the southwestern Gulf. Primary production off Western Florida is lower than that found in the Northern Gulf (Walsh 1983). In the absence of good data for this region we also used a primary production rate of $177 \text{ gC m}^{-2} \text{ y}^{-1}$. When adjusted for area this gives an average of $215 \text{ gC m}^{-2} \text{ y}^{-1}$ for the entire Gulf of Mexico.

African Shelf 20° N to 35° N From 20° N to the Straits of Gibraltar at 35° N, we used an average annual value of $365 \text{ gC m}^{-2} \text{ y}^{-1}$. Most of the studies in this region suggest that the primary productivity averages over $1 \text{ gC m}^{-2} \text{ d}^{-1}$ over the annual cycle (Gabric et al. 1993; Huntsman & Barber 1977 and references therein; Berguis et al. 1993).

Table 1. Continued.

Spain and Portugal – We used a value of $350 \text{ gC m}^{-2} \text{ y}^{-1}$ for the entire region. Average daily production values for the Bay of Biscay and Galician coast off of Spain are on the order of $1 \text{ gC m}^{-2} \text{ d}^{-1}$ (Fernandez et al. 1993; Varela 1992).

Central and South America – Older data suggest that on average the production over much of this area is about the same as the southwestern Gulf of Mexico with higher rates off Venezuela (Koblentz-Mishke et al. 1970 as redrawn in Berger 1989). The absolute values given for primary productivity given in Koblentz-Mishke et al. (1970) appear very low (less than $60 \text{ gC m}^{-2} \text{ y}^{-1}$) throughout the entire region. However, the relative distribution of production is consistent with satellite maps of chlorophyll a and more recent production data. Based upon the distribution of production in Koblentz-Mishke et al. (1970) we assigned the same value of $215 \text{ gC m}^{-2} \text{ y}^{-1}$ to the Central and South American shelves as to the southwestern Gulf of Mexico.

Amazon Shelf – DeMaster et al. (1991) measured ^{14}C primary production from $0\text{--}4^\circ \text{ N}$ off the Amazon River out to the 100 m contour during falling and high river discharge periods (August and May, respectively). Their average productivity for the entire region was $2.5 \text{ gC m}^{-2} \text{ d}^{-1}$ which would extrapolate to $900 \text{ gC m}^{-2} \text{ y}^{-1}$. This rate is not typical of the production further offshore where nutrient concentrations are low (Ryther et al. 1967). We used an average of $450 \text{ gC m}^{-2} \text{ y}^{-1}$ for the Amazon shelf region between $0\text{--}4^\circ \text{ N}$. For the Amazon shelf north of 4° N ($4^\circ \text{ N}\text{--}12^\circ \text{ N}$) we assigned a value of $87 \text{ gC m}^{-2} \text{ y}^{-1}$ based on the broad scale distribution of production and nutrients in Koblentz-Mishke et al. (1970) and Ryther et al. (1967). The area weighted average for the entire Amazon Shelf region between 0 and 12° N was $135 \text{ gC m}^{-2} \text{ y}^{-1}$.

Caribbean Islands – Very few studies have been carried out in the shelf regions of Caribbean Islands. Hopcroft et al. (1990) reported that the phytoplankton productivity in shelf waters off Kingstown, Jamaica were $240 \text{ gC m}^{-2} \text{ y}^{-1}$ but this region appears to be influenced by nutrient inputs from Kingston. Offshore, values of less than $100 \text{ gC m}^{-2} \text{ y}^{-1}$ are more typical of this area (Beers et al. 1968). We used a value of $88 \text{ gC m}^{-2} \text{ y}^{-1}$ for this region.

Africa Shelf 0 to 20° N – Between $0\text{--}20^\circ \text{ N}$ we used a value of $200 \text{ gC m}^{-2} \text{ y}^{-1}$ based upon the spring and summer rates measured offshore by Mahnken (1969) (which extrapolated over the year average $200\text{--}300 \text{ gC m}^{-2} \text{ y}^{-1}$) and Longhurst's (1983) lower numbers ($100\text{--}160 \text{ gC m}^{-2} \text{ y}^{-1}$) from an annual primary productivity model of the inshore region at 8° N .

North Atlantic ($96 \times 10^{10} \text{ mol N y}^{-1}$) is two times greater than in the eastern North Atlantic ($47 \times 10^{10} \text{ mol N y}^{-1}$) (Figure 4). This is primarily due to differences in the area of continental shelf in the two regions, as the average denitrification rate per unit area is similar in the western and eastern North Atlantic (0.67 and $0.73 \text{ mmol N as N}_2 \text{ m}^{-2} \text{ d}^{-1}$, respectively) (Table 1).

We are attempting to predict average denitrification rates for relatively large regions of the continental shelf. Rates of denitrification for any particular area within a region may be higher or lower than the predicted rates, due to smaller scale variability in such factors as sediment type or locally high primary production rates in upwelling regions. Still, it is instructive to compare the rates of denitrification estimated from our model to rates of denitrification measured or predicted by other methods within various regions. The only direct measurements of denitrification for North Atlantic shelf sediments are in Massachusetts Bay. Model predicted rates of 1.35 mmol

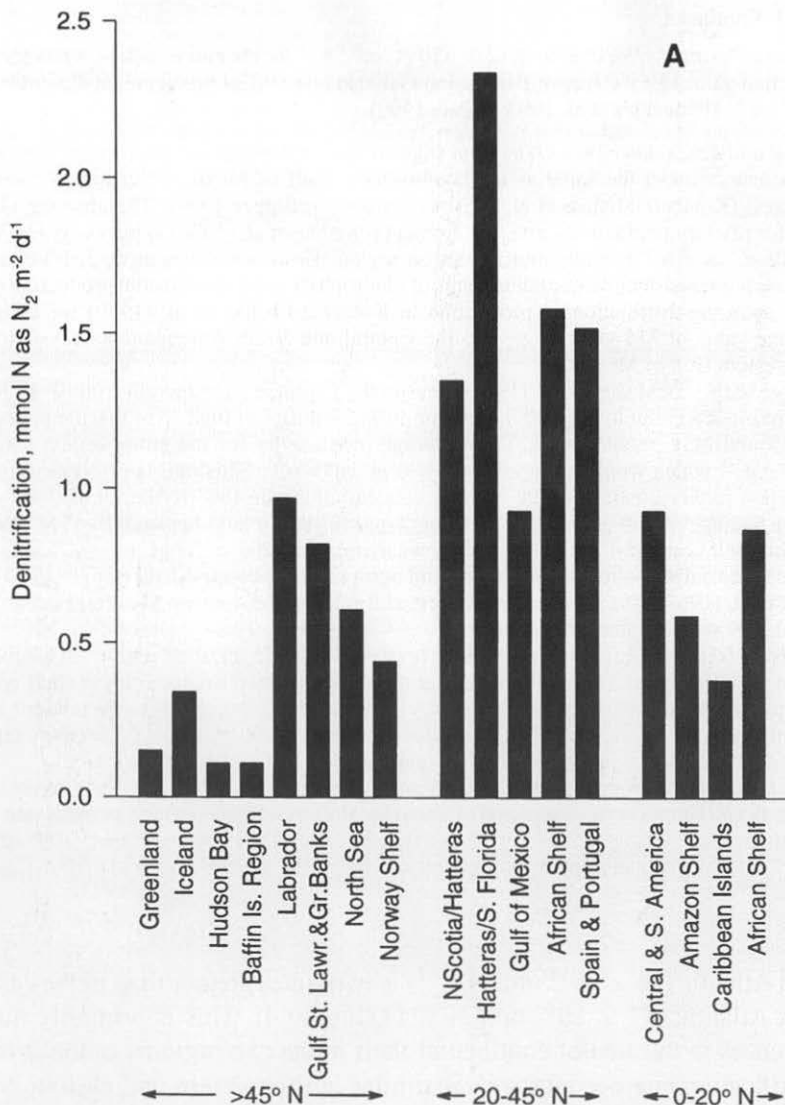


Figure 3. Model predicted rates of denitrification coupled to sediment nitrification for various continental shelf regions in the North Atlantic Basin: a) denitrification rates per unit area (mmol N as N₂ m⁻² d⁻¹), and b) N removal by region (mol N × 10¹⁰ y⁻¹; e.g. Nova Scotia/Hatteras = 17.8 × 10¹⁰ mol N y⁻¹).

N as N₂ m⁻² d⁻¹ (Nova Scotia to Cape Hatteras region) (Table 1) are within the range of the directly measured rates of ≤0.24 to 2.56 mmol N as N₂ m⁻² d⁻¹ in Massachusetts Bay (Giblin et al. 1994). Denitrification rates in the Gulf of Mexico estimated from our model calculations were 0.93 mmol

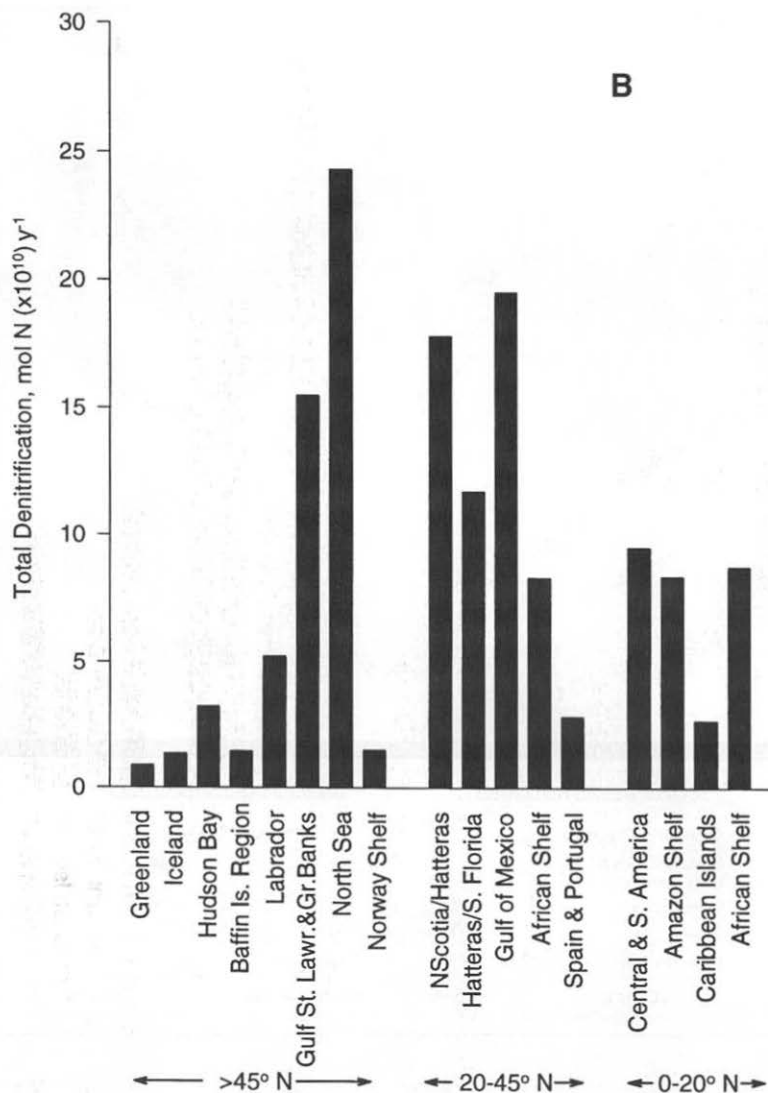
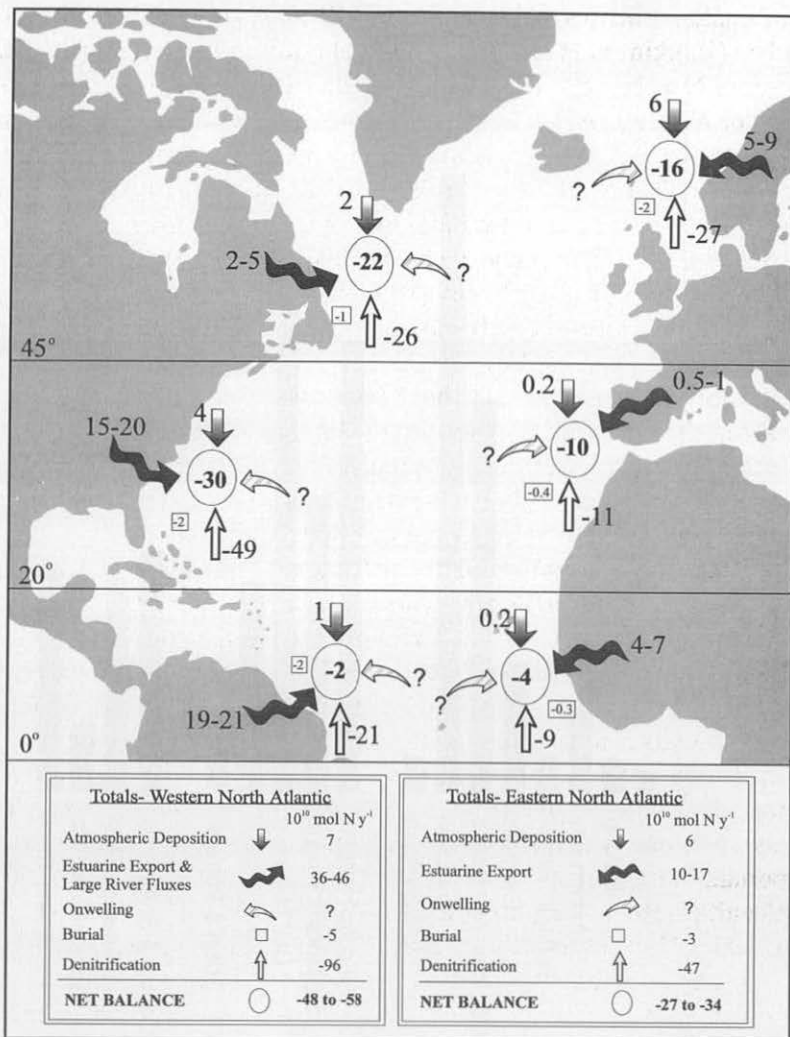


Figure 3. Continued.

N as $\text{N}_2 \text{ m}^{-2} \text{ d}^{-1}$, which is within the range of rates reported by Gardner et al. (1993) for the northern Gulf of Mexico (0.5 to 1.68 $\text{mmol N as N}_2 \text{ m}^{-2} \text{ d}^{-1}$) based on stoichiometric calculations. In the South Atlantic Bight (located within our Cape Hatteras to S. Florida region), denitrification rates in excess of 3.2 $\text{mmol N as N}_2 \text{ m}^{-2} \text{ d}^{-1}$ were calculated for a hard bottom community based on the deficit of the measured benthic DIN effluxes relative



to the phosphate effluxes and assuming a Redfield stoichiometry of 16:1 (N:P by moles) (Hopkinson et al. 1991); those rates are similar to our predictions (2.34 mmol N as N_2 $m^{-2} d^{-1}$). Model-predicted rates for the North Sea are 0.61 mmol N as N_2 $m^{-2} d^{-1}$ which is consistent with denitrification rates reported for that region based on models of pore water nutrient profiles (0.34 to 2.74 mmol N as N_2 $m^{-2} d^{-1}$, Billen (1978); 0.06 to 0.54 mmol N as N_2 $m^{-2} d^{-1}$, Raaphorst et al. (1990)). However, rates of denitrification for the North Sea estimated from acetylene block measurements (0.0012 to 0.2 mmol N as N_2 $m^{-2} d^{-1}$, Law & Owens (1990); 0–0.3 mmol N as N_2 $m^{-2} d^{-1}$, Lohse et al. 1993) are considerably lower than our model calculated rates. One explanation is that our model estimates coupled nitrification/denitrification, while the acetylene block method has been found to markedly underestimate coupled nitrification/denitrification in some aquatic sediments (Seitzinger et al. 1993). In summary, our model estimates of denitrification for continental shelf regions appear conservative based on comparisons of model estimates for specific regions relative to rates reported in the literature.

We calculate that a total of 143×10^{10} mol N y^{-1} is removed via coupled nitrification/denitrification on the North Atlantic continental shelf (Table 1). Our model is expected to underestimate total sediment denitrification because it does not include direct denitrification of nitrate from the overlying water. The stoichiometric approach that we used to calculate denitrification rates only provides an estimate of denitrification coupled to sediment nitrification. Nitrate diffusing, or transported by macrofauna irrigation, into the sediments is another source for denitrification and was not included. There are some shelf sites where nitrate uptake from the overlying water is relatively unimportant in supporting denitrification when compared to coupled nitrification/denitrification (Raaphorst et al. 1990; Hopkinson et al. 1991; Kelly & Nowicki 1993; Giblin et al. 1994). However, in Washington shelf and Gulf of Maine sediments, denitrification of nitrate from the overlying water was estimated to be similar to, or greater than, denitrification coupled to

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Figure 4. Known sources and sinks of N for continental shelf regions in the western and eastern North Atlantic Basin by latitudinal zone. The input of N to the continental shelf from estuarine export plus fluxes from rivers that discharge directly on the shelf was calculated from Nixon et al. (this vol.). Atmospheric deposition of $NO_y + NH_x$ (wet plus dry deposition) was calculated from Nixon et al.'s (this vol.) summary of Prospero et al. (this vol.). Burial of N in shelf sediments exclusive of major river deltas was calculated based on the primary production data in Table 1 and Nixon et al.'s (this vol.) assumption that 0.25% to 1.25% of the primary production with a C/N (molar) ratio of 10 is buried. The balance of the indicated sources and sinks is indicated within the closed circles; the mid-point of the range in estuarine export/large river fluxes for a region was used for that calculation. The contribution of N from onwelling of nutrient rich slope water is not known, but is hypothesized to account for the additional N input needed to balance the N budget.

sediment nitrification (Christensen et al. 1987a; Devol 1991; Devol & Christensen 1993). Similarly, over an annual cycle in the Aarhus Bight, nitrate from the overlying water and nitrification within the sediment were equally important in supporting denitrification but the relative importance of each changed seasonally (Jensen et al. 1990). Sediments took up nitrate in about half of the benthic flux measurements made off Cap Blanc, Africa (Rowe et al. 1977) and in the New York Bight (Florek & Rowe 1983). The rates of nitrate disappearance in these studies could support direct denitrification rates of 0.1 to 1.6 mmol N as N_2 $m^{-2} d^{-1}$. This range is comparable to the range of coupled nitrification/denitrification rates predicted by our model (Table 1), and suggests that N removal by direct denitrification may be of a similar magnitude to coupled nitrification/denitrification. While coupled nitrification/denitrification appears to be related to organic matter deposition, the magnitude of direct denitrification is likely to vary spatially as a function of bottom water nitrate concentration. Clearly, a complete analysis of the contribution of the continental shelf to the nitrogen budget should include denitrification of nitrate from both direct and coupled sources. One approach that could be taken to estimate direct denitrification of nitrate from the overlying water is to model nitrate input into sediments due to diffusion and to transport by macrofauna based on bottom water nitrate and macrofaunal distributions in shelf regions. However, such an analysis awaits future efforts.

Sources of nitrogen to the continental shelf region to support the estimated denitrification include nitrogen transport by rivers, atmospheric deposition and onwelling of deeper slope water. The rate of coupled nitrification/denitrification that we estimate for North Atlantic shelf regions (143×10^{10} mol N y^{-1}) is approximately one and a half times as great as the total nitrogen transport by rivers in the North Atlantic Basin (94×10^{10} mol N y^{-1} ; Howarth et al., this vol.). Given that a significant amount of N is removed by denitrification within estuaries before being exported to the shelf (Seitzinger 1988), the actual input of river N to continental shelf areas is considerably less. Nixon et al. (this vol.) estimated that of the 94×10^{10} mol N y^{-1} transported by rivers in the North Atlantic Basin, only 46 to 63×10^{10} mol N y^{-1} are transported to the shelf, with the remainder removed within estuaries by denitrification, burial or fish harvesting (Table 2). Thus, inputs of N to the shelf from river transport can account for only a third to less than half of the N required to support the estimated denitrification on the shelf. Additional sources of N to the shelf from atmospheric deposition (Nixon et al., this vol. based on Prospero et al., this vol.) or biological N_2 -fixation (Nixon et al., this vol.) are considerably smaller than needed to balance the shelf N budget (Table 2). Total known inputs amount to 59 to 76×10^{10} moles N y^{-1} , which accounts for only fifty percent or less of the N needed to supply the

Table 2. Known sources and sinks of nitrogen for the North Atlantic continental shelf (see text).

	10 ¹⁰ moles N y ⁻¹
Known inputs	
Estuarine export + large river fluxes ¹	46–63
Biological N ₂ -fixation ³	0.2
Atmospheric deposition ²	13
Total	59–76
Known sinks	
Denitrification (coupled nitrification/denitrification)	143
Burial in shelf sediments ³	2–9
Fish landings ³	3–4
Export from shelf	?
Total	148–156
Net balance (onwelling?)	–72 to –97

¹ Estuarine export plus fluxes from large rivers that discharge directly on the shelf from Nixon et al. (this vol.)

² Atmospheric deposition of NO_y + NH_x (wet plus dry deposition) from Nixon et al.'s (this vol.) summary of Prospero et al. (this vol.)

³ Nixon et al. (this vol.)

estimated denitrification (143×10^{10} mol N y⁻¹). A comparison of known inputs and known sinks (including denitrification, burial in shelf sediments, and fish landings) suggests that at least 72 to 97×10^{10} mol N y⁻¹ would be needed from other sources to balance the shelf N budget (Table 2). This is a minimum estimate as direct denitrification of nitrate from the overlying water is not included in the denitrification removal term.

A view of the known sources and sinks of N in the western and eastern North Atlantic and by latitudinal zone provides an additional perspective (Figure 4). Overall, in the western North Atlantic known inputs can account for only approximately half of N required to supply the estimated denitrification; in the eastern North Atlantic known inputs are only about a third to half of the N required for denitrification. (The burial term is a small number in all regions, amounting to a N sink less than ten percent of that removed by denitrification.) A more detailed comparison can be made by latitudinal zone. In some regions the known N inputs are close to sufficient to supply the estimated N removal by denitrification. For example, in the tropical regions (0 to 20° N) of both the western and eastern North Atlantic, inputs of N from estuarine export, fluxes from large rivers directly onto the shelf, and atmo-

spheric deposition are approximately equal to the loss through denitrification and burial (Figure 4). In other regions, the known N inputs can account for only approximately half of the estimated N removal by denitrification; this is the case in the mid-latitudes (20° to 45° N) of the western North Atlantic and the high latitudes ($>45^{\circ}$ N) of the eastern North Atlantic. In the high latitudes of the western North Atlantic and mid-latitudes of the eastern North Atlantic, the known inputs are very out of balance with the N removal terms. In those regions, known inputs can account for only about 10% of the N needed to supply the estimated removal by denitrification.

Onwelling of nitrate rich slope water onto continental shelves is known to be a major source of nitrogen in various shelf regions. Unfortunately, slope transport of nitrogen onto the shelf has not been adequately quantified for the North Atlantic Basin as a whole. However, in the two regions for which we have data, it appears that slope transport is of the correct magnitude to balance the shelf N budget. A minimum estimate of slope water nitrate transport to the South Atlantic Bight (our Cape Hatteras to S. Florida region) from Lee et al. (1991) (9.3×10^{10} mol N y^{-1}) combined with N export from estuaries (0.6 to 1.2×10^{10} mol N y^{-1} ; Nixon et al., this vol.) is similar to our estimated N removal by denitrification (11.7×10^{10} mol N y^{-1} ; Table 1). In the Mid-Atlantic Bight (our Nova Scotia to Cape Hatteras region), Csanady (1990) estimated that 11.4×10^{10} mol N y^{-1} are transported by slope water onto the shelf along a 900-km stretch, which when combined with N export from estuaries in this region (1.3 to 2.6×10^{10} mol N y^{-1} ; Nixon et al., this vol.), is within approximately 30% of our estimated N removal by denitrification (17.8×10^{10} mol N y^{-1} ; Table 1). The above studies suggest that onwelling of slope water is of the magnitude needed to balance the shelf N budgets in the two regions where data are available. However, further studies of N transported by slope water onto various shelf regions throughout the North Atlantic Basin are required to determine if this holds true for other regions.

The magnitude of all nitrogen sources to the total North Atlantic is uncertain. It is presently not known if there are sufficient sources of new nitrogen entering the North Atlantic gyres to support the onwelling of N to continental shelf areas needed to support the denitrification rates calculated here. However, recent estimates of nitrate creation in the upper 1000 m of the Sargasso Sea (3.7 to 6.4×10^{12} moles NO_3^- y^{-1}) by Michaels et al. (this vol.) could potentially supply the required denitrification in the shelf regions. Michaels et al. (this vol.) have postulated N_2 -fixation as a likely source for the created nitrate, or dissolved organic N mineralization.

The North Atlantic shelf makes up only 20% of the total continental shelf area in the ocean. If the coupled nitrification/denitrification rates we calculate for the North Atlantic can be extrapolated to the globe, the continental shelf

sediments are an important oceanic sink of nitrogen removing more than 7.2×10^{12} mol N y^{-1} ($100 \text{ Tg N } y^{-1}$). This is a minimum estimate of sediment denitrification since it only includes coupled nitrification/denitrification and does not include direct denitrification of nitrate from the overlying water. The current estimate is two times higher than that made by Christensen et al. (1987a) (3.6×10^{12} mol N y^{-1}) for continental shelves, whose estimate in turn was considerably higher than the earlier estimates of between 0.4×10^{12} to 1.8×10^{12} mol N y^{-1} (Hattori 1983; Liu & Kaplan 1984). Although this global loss is large (7.2×10^{12} mol N y^{-1}), it appears that it could easily be supported by the onwelling of nitrate from the deep sea to the global shelves (40×10^{12} mol N y^{-1}) as estimated by Walsh (1991).

The analyses presented here reinforce and flesh out the idea of Christensen et al. (1989), that denitrification in shelf sediments is removing a significant amount of N inputs to continental shelf regions. Furthermore, denitrification in Atlantic continental shelf regions appears to be an important sink for N in the Atlantic Basin as a whole (Michaels et al., this vol.). This large N sink in continental shelf regions likely contributes to N limitation in those regions. The areal rates of denitrification that we calculate are consistent with recent measurements and do not appear to be extremely high. However, the number of areas where measurements have been made is small and has been biased towards temperate regions. Clearly more measurements of denitrification in a variety of regions and sediment types are needed.

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