

# The role of continental shelves in nitrogen and carbon cycling: Northwestern North Atlantic case study

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**Abstract.** Continental shelves play a key role in the cycling of nitrogen and carbon. Here the physical transport and biogeochemical transformation processes affecting the fluxes into and out of continental shelf systems are reviewed, and their role in the global cycling of both elements is discussed. Uncertainties in the magnitude of organic and inorganic matter exchange between shelves and the open ocean is a major source of uncertainty in observation-based estimates of nitrogen and carbon fluxes. The shelf-open ocean exchange is hard to quantify based on observations alone, but can be inferred from biogeochemical models. Model-based nitrogen and carbon budgets are presented for the Northwestern North Atlantic continental shelf. Results indicate that shelves are an important sink for fixed nitrogen and a source of alkalinity, but are not much more efficient in exporting organic carbon to the deep ocean than the adjacent open ocean for the shelf region considered.

## 1 Introduction

Continental shelves, conventionally defined as ocean areas shallower than 200 m water depth, are the shallow, gently sloping extensions of the continental plates and include marginal seas like the North Sea and the East China Sea. The width of continental shelves varies considerably from a few kilometers at active margins (e.g. at the California and Oregon coasts) to hundreds of kilometers at passive margins (e.g. shelves in the Arctic Ocean).

Continental shelves serve as important link between land and the ocean interior and between the atmosphere and deep ocean (Liu et al., 2000), and play a key role in the global cycling of biologically essential elements such as nitrogen and carbon. Shelves are known to be highly productive

(Longhurst et al., 1995); the majority of the oceanic burial of organic carbon occurs on continental shelves and the adjacent slope (Premuzic et al., 1982; Hedges and Keil, 1995), and shelf sediments are important sites for denitrification (Seitzinger et al., 2006). Many aspects of continental shelf biogeochemistry are discussed in detail in a recent IGBP monograph (Liu et al., 2010).

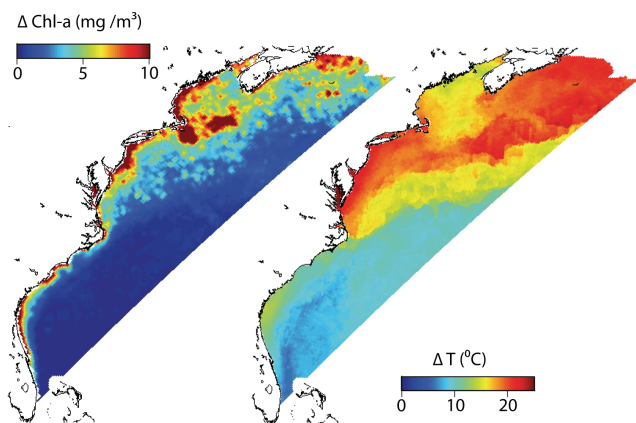
Continental shelf regions may be of disproportionate importance for the oceanic uptake of anthropogenic CO<sub>2</sub>, but regional quantification and global extrapolation of coastal fluxes is highly uncertain due to large spatial and temporal variability and a general undersampling. The amplitude of seasonal changes of surface chlorophyll and surface temperature is higher on shelves compared to the open ocean, as shown, for example, for the Northeastern North American shelves in Fig. 1. The high productivity of shelf systems is in part fueled by the input of nutrients from land, in part by the tight benthic-pelagic coupling that allows nutrients remineralized in shelf sediments to be returned to the euphotic zone on timescales on the order of a year, and in large part by up- and onwelling of nutrients from the open ocean.

Marine biological and biogeochemical responses to climate change and other anthropogenic perturbations will be most relevant to human activities on continental shelves, as fisheries, aquaculture, tourism and resource extraction are concentrated in these regions. Human-induced pressures include coastal eutrophication and development of hypoxia and anoxia, overfishing and acidification.

The objective of this manuscript is to review the role of continental shelves in global nitrogen and carbon cycling by first summarizing insights based on direct observations (Sect. 2), followed by a discussion of model-based inferences about processes that are hard to observe directly or hard to scale up to regional estimates from local observations (Sect. 3). A key uncertainty in observation-based approaches is the magnitude of cross-shelf exchange of material, which can, however, be inferred from biogeochemical models.



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**Fig. 1.** Annual amplitude of surface chlorophyll concentration from the SeaWiFS satellite (left) and of sea surface temperature from AVHRR (right), calculated as maximum monthly mean minus minimum monthly mean, for the Northeastern North Atlantic shelves and adjacent deep ocean. The annual amplitude in chlorophyll is largest in coastal waters of the Middle Atlantic Bight (MAB), on Georges Bank, the Gulf of Maine and the Scotian Shelf. The annual amplitude in sea surface temperature is largest in coastal regions of the MAB and on the Scotian Shelf; tidal mixing in the Bay of Fundy (northern Gulf of Maine) and on Georges Bank lead to comparatively smaller seasonal temperature differences there.

## 2 Role of continental shelves in biogeochemical cycling

### 2.1 Nitrogen cycling

The macro-nutrient nitrogen is the dominant limiting nutrient in the ocean, with the exception of the so-called High Nutrient, Low Chlorophyll (HNLC) regions (the Southern Ocean and the subarctic and equatorial Pacific Ocean), where phytoplankton production is limited by the supply of the micro-nutrient iron (Martin et al., 1994; Boyd et al., 2000). Nitrogen is also the dominant limiting nutrient in estuaries and on continental shelves, where micro-nutrients are available in sufficient supply.

The majority of nitrogen in the ocean and atmosphere is in the form of  $N_2$  gas, which is unavailable to most microorganisms. Most organisms can assimilate only reduced and oxidized forms of inorganic nitrogen, such as nitrate, nitrite and ammonium, which are collectively referred to as reactive, fixed or bio-available nitrogen.  $N_2$  can be utilized only by diazotrophs, i.e. specialized microorganisms containing the enzyme nitrogenase, which allows them to split the stable triple bond in the  $N_2$  molecule and produce bio-available nitrogen. This process is called nitrogen fixation or  $N_2$  fixation. Denitrification, on the other hand, is a process that produces  $N_2$  gas from organic and inorganic bio-available forms and thus represents a sink for bio-available nitrogen. Denitrification occurs in environments with low oxygen concentrations, such as soils, hypoxic and anoxic waters, and sediments.

Inputs of bio-available nitrogen to the coastal ocean have increased dramatically due to an impressive and alarming anthropogenic acceleration of the global nitrogen cycle. Land-based creation of nitrogen is now more than double that of pre-industrial rates. The man-made creation of bio-available nitrogen has increased by an order of magnitude globally from pre-industrial rates of  $\sim 15 \text{ Tg N yr}^{-1}$  in 1860 to  $\sim 156 \text{ Tg N yr}^{-1}$  in 1990 mostly due to fertilizer production, cultivation of leguminous crops, and combustion of fossil fuels (Galloway et al., 2004). While a significant fraction of the anthropogenic nitrogen is denitrified in soils, wetlands, lakes and reservoirs (Seitzinger et al., 2006), river fluxes of bio-available nitrogen have increased from an estimated  $35 \text{ Tg N yr}^{-1}$  in 1860 to  $\sim 59 \text{ Tg N yr}^{-1}$  in 1990 and are projected to reach  $\sim 75 \text{ Tg N yr}^{-1}$  by 2050 (Galloway et al., 2004). Most of this nitrogen reaches coastal waters.

Another vector of anthropogenic nitrogen input to the ocean is atmospheric transport and subsequent deposition of bio-available nitrogen. Global nitrogen deposition to the ocean is estimated to have increased from  $\sim 5.7 \text{ Tg N yr}^{-1}$  in 1860 to  $\sim 54 \text{ Tg N yr}^{-1}$  in 2000 (Duce et al., 2008). For shelf systems, nitrogen inputs from rivers, estuaries and run-off are the largest source of anthropogenic nitrogen, but atmospheric deposition is growing and potentially important as well.

Some shelves already experience dramatic consequences of increased nitrogen inputs. For example, the continental shelf in the Northern Gulf of Mexico receives large inputs of fertilizer-derived nitrogen from the Mississippi river (Donner et al., 2004). This nutrient input leads to excessive production of organic matter (i.e. eutrophication) and, during periods with a stratified water column, the development of a large anoxic region on this shelf, also referred to as a dead zone. The dead zone on the Northern Gulf of Mexico shelf recurs every summer and has grown in size since 1985 (Rabalais et al., 2007) with considerable interannual variability (Bianchi et al. 2010). The occurrence of dead zones is rising globally (Diaz and Rosenberg, 2008), as are other consequences of increased nutrient inputs to shelf regions, such as shifts in community structure and rising occurrence of harmful algal blooms (Glibert et al., 2008).

Continental shelves are thought to play the role of a barrier or filter for river nutrient inputs to the open ocean. An observation-based nitrogen budget for the continental shelves of the North Atlantic Ocean by Seitzinger and Giblin (1996) suggests that sediment denitrification removes significantly more fixed nitrogen than enters from land and atmosphere (sediment burial is a comparatively small sink). The budget summarized available observations of nitrogen fluxes including inputs of fixed nitrogen from rivers, estuaries and atmospheric deposition, and removal of fixed nitrogen due to sediment denitrification and permanent burial. Seitzinger and Giblin (1996) concluded that the continental shelf nitrogen sink must be balanced by significant onwelling of nitrate from the deep ocean, a process that is difficult if not impossible to quantify accurately from observations alone.

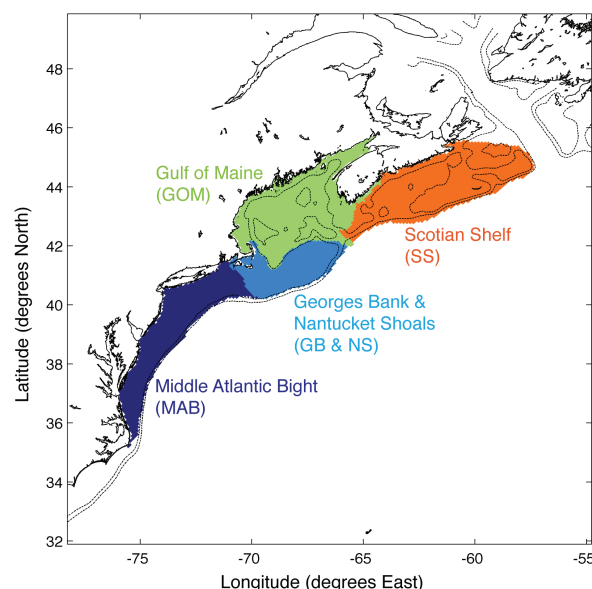
## 2.2 Carbon cycling

The ocean is a large sink for anthropogenic  $\text{CO}_2$  – approximately 50% of  $\text{CO}_2$  emissions from fossil fuel combustion and cement production have been taken up by the ocean (Sabine et al., 2004) – but the ocean's capacity for absorbing  $\text{CO}_2$  is expected to diminish in the future. Accurate quantification and monitoring of the ocean sink is not a trivial task, but it is of economic relevance as the world is moving toward a global market for carbon credits. Especially uncertain and controversial is the contribution of continental shelves to the ocean sink. Several studies over the past two decades suggested that  $\text{CO}_2$  is taken up at higher rates on continental shelves than in the open ocean (e.g., Tsunogai et al., 1999; Thomas et al., 2004), while a large efflux of  $\text{CO}_2$  has been reported for some coastal regions (Cai et al., 2003). Extrapolation of coastal fluxes to the global scale yields estimates of carbon uptake between 0.2 and 1  $\text{Gt C yr}^{-1}$ , which corresponds to 15–70% of the estimated anthropogenic carbon uptake by the ocean, but this is subject to great uncertainty.

The uncertainties about the sign and magnitude of annual fluxes is mirrored in uncertainty about the mechanisms underlying the potentially large uptake of atmospheric  $\text{CO}_2$ . Two distinct mechanisms have been suggested and are collectively referred to as Continental Shelf Pump (CSP).

The first CSP mechanism is physical in nature and thought to operate in mid- and high-latitude systems. In these shelf systems surface water is cooled more strongly than surface water in the adjacent open ocean because it is not subject to deep convection. Convection occurs in the open ocean during winter cooling (surface cooling increases the density of sea water; dense water will sink and mix), keeping surface temperatures at higher levels than on the shelf. Since the solubility of  $\text{CO}_2$  increases with decreasing temperatures, shelf water experiences a larger influx of atmospheric  $\text{CO}_2$ . When the seasonal pycnocline establishes itself during the following spring/summer, the dense and carbon-rich water is capped off, and exchange with the atmosphere is inhibited. If this dense and carbon-rich water is subsequently transported off the shelf due to horizontal advection or isopycnal mixing, the associated carbon will be exported to the deep ocean. Tsunogai et al. (1999) suggested that this mechanism operates in the East China Sea and coined the term Continental Shelf Pump.

Another mechanism for concentrating carbon below the seasonal pycnocline is photosynthetic production of organic matter and subsequent sinking below the seasonal pycnocline. Again, if the carbon-rich water below the pycnocline is moved off the shelf by horizontal transport it could potentially be exported to the deep ocean. The depth to which the carbon is exported would depend on its type: particles will sink, while dissolved organic and inorganic carbon would behave similarly to a passive tracer and not necessarily be exported vertically. Thomas et al. (2004) suggested that the bi-



**Fig. 2.** Geographic shelf regions used for budgets. The dashed lines show the 100 m and 200 m isobaths.

ological CSP mechanism operates in the North Sea, leading to a large uptake of atmospheric carbon there.

It should be stressed that both of the above mechanisms for carbon export critically depend on horizontal transport of carbon-rich water off the shelf. Their existence and quantitative importance is thus hard to verify observationally. The  $p\text{CO}_2$  difference between the surface ocean and atmosphere can be measured relatively easily and can then be used to calculate an instantaneous air-sea flux of  $\text{CO}_2$  based on gas exchange parameterizations (e.g., Wanninkhof 1992) and subject to the assumptions inherent to these parameterizations. However, the air-sea flux of  $\text{CO}_2$  varies seasonally, as well as on shorter times scales (days to weeks) and spatially. A carbon budget based on a net  $\text{CO}_2$  flux inferred from measurements of  $p\text{CO}_2$  and an assumption of steady state is prone to large errors, as  $\text{CO}_2$  uptake in winter and spring can be almost balanced by outgassing in summer and fall. The quantity of interest, the net annual air-sea flux, is a small residual of two opposing fluxes.

It is also relatively easy to measure the concentrations of particulate organic carbon (POC), dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) in seawater and to demonstrate an enrichment of carbon below the seasonal pycnocline (e.g., Fig. 2 in Thomas et al., 2004). However, the existence of a vertical gradient in summer does not imply horizontal export. Even in the absence of horizontal transport of organic matter one would expect waters below the pycnocline to become enriched in carbon during spring and summer. Subsequent vertical mixing of the water column in winter would expose this water again to the atmosphere.  $\text{CO}_2$  uptake during part of the year could thus be perfectly

balanced by outgassing during the rest of the year. If continental shelf systems are sites of significant net uptake of atmospheric CO<sub>2</sub> there must be cross-shelf carbon export.

For the Middle Atlantic Bight (MAB) shelf, several major observational programs sought to quantify the horizontal export of carbon. The Shelf Edge Exchange Processes (SEEP) programs I and II (Walsh et al., 1988; Biscaye et al., 1994) concluded that only a small fraction of particulate carbon (<5%) is exported (Falkowski et al., 1988). This conclusion was reached based on indirect evidence, although a large effort was made during the SEEP programs to quantify cross-shelf fluxes of particulate carbon directly. Results from the subsequent Ocean Margins Program (OMP), which explicitly considered dissolved and suspended forms of organic carbon in the MAB, suggested that export of carbon in these forms could be significant if advective and eddy diffusive transports are large (Verity et al., 2002), but did not quantify these directly.

One aspect that should not be neglected when discussing CSP mechanisms is the generation of alkalinity by anaerobic remineralization processes and its effect on the air-sea flux of CO<sub>2</sub>. An increase in alkalinity leads to a decrease in *p*CO<sub>2</sub>, thus promoting uptake of atmospheric CO<sub>2</sub> by the ocean when high alkalinity water is in direct contact with the atmosphere. The generation of alkalinity is typically associated with the dissolution of calcium carbonate, which mostly occurs below the lysocline in the deep ocean; however, several anaerobic remineralization processes that occur in sediments on continental shelves generate alkalinity as well (Chen, 2002). Principally, alkalinity is generated whenever acids are consumed, for example, during denitrification and during manganese, iron and sulfate reduction. Chen (2002) estimated that between  $16 \text{ and } 31 \times 10^{12} \text{ mol equ yr}^{-1}$  are created globally through these processes on continental shelves, which is significant compared to the production of alkalinity in the open ocean, estimated at  $50 \text{ to } 72 \times 10^{12} \text{ mol equ yr}^{-1}$  globally. It is important to note that only the processes for which the reduced products escape or resist reoxydation lead to a net creation of alkalinity. Most important in this respect is denitrification which produces inert N<sub>2</sub> gas. The generation of alkalinity through sediment remineralization has been observed directly in several systems, for example, in the East China Sea (Chen and Wang, 1999) and in the North Sea (Thomas et al., 2009). Whether the generation of alkalinity on continental shelves enhances uptake of atmospheric CO<sub>2</sub> locally depends on whether the water is in contact with the atmosphere (i.e. vertical mixing versus stratification) and for how long the water resides on the shelf.

### 2.3 Summary

Continental shelves are important to the global cycling of nitrogen, carbon and alkalinity, but observation-based budgets for continental shelf regions are prone to uncertainties, given that cross-shelf exchange of these properties is a crucial com-

ponent that is hard if not impossible to quantify observationally. Models offer the opportunity to quantify the horizontal transport of fixed nitrogen, carbon and alkalinity as discussed in the next section.

## 3 Model-based inferences about shelf biogeochemistry and cross-shelf transport

### 3.1 Model description

Here results from a coupled physical-biogeochemical model are discussed that includes a biological nitrogen cycle model (see Fennel et al., 2006) and a parameterization of the flux and speciation of inorganic carbon (described in Fennel et al., 2008). The nitrogen cycle component is a relatively simple model that includes two species of dissolved inorganic nitrogen (nitrate and ammonium), one functional phytoplankton group, chlorophyll as a separate state variable to allow for photoacclimation, one functional zooplankton group, and two pools of detritus representing large, fast-sinking particles and suspended, small particles. The representation of nitrogen cycling in the water column is similar to other coupled models (e.g., Oschlies 2002; Gruber et al., 2006), but the treatment of sediment remineralization, which is critical for model application to continental shelf regions, is unusual.

The model uses an empirical parameterization of sediment denitrification. Specifically, organic matter that reaches the sediment is remineralized in fixed proportions through aerobic and anaerobic remineralization. The fractions are determined using the linear relationship between sediment denitrification and oxygen consumption that Seitzinger and Giblin (1996; their Fig. 1) calculated for a compilation of published measurements (note that their relationship includes production of N<sub>2</sub> gas through anammox; the term denitrification is used here to denote canonical denitrification *sensu* Devol (2008) and includes all processes that produce N<sub>2</sub> gas). The relationship between sediment denitrification and sediment oxygen consumption published by Seitzinger and Giblin in 1996 was based on 50 data points. A large number of similar measurements have been made since then. Fennel et al. (2009) compiled 648 such measurements across a range of aquatic environments and calculated a new linear regression. Surprisingly the new relationship deviates relatively little from the previously published one; at sediment oxygen consumption rates ranging from 10 to 20 mmol O<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> (typical rates for continental shelf sediments) the denitrification flux predicted by the new relationship is only 10 to 18% smaller than Seitzinger and Giblin's previously published one. However, the coefficient of determination for the recent data compilation is smaller, with an *R* of 0.55, compared to 0.8 for Seitzinger and Giblin (1996).

The biological model is embedded in a high-resolution implementation of the Regional Ocean Modeling System (ROMS, <http://www.myroms.org>) (Haidvogel et al., 2008)

for the continental shelf area of the North American east coast and adjacent deep ocean. The model has a horizontal grid resolution of approximately 10 km, and uses 30 vertical layers in a terrain-following  $s$ -coordinate system. The model's open boundary temperatures, salinities and transports were specified from the data-assimilative Hybrid Coordinate Ocean Model (HyCOM, <http://hycom.org>) of Chassignet et al. (2007) and augmented with barotropic tides from the global analysis of Egbert and Erofeeva (2002). The model was forced with daily air temperature, pressure, humidity and winds from the NCEP reanalysis (Kalnay et al., 1996), using bulk formulae (Fairall et al., 2003).

DIC and alkalinity are included as model tracers (i.e. they are advected and diffused by the physical model), while  $p\text{CO}_2$  is calculated in the surface model layer only. In addition to gas exchange at the air-sea interface, DIC changes locally in the model due to primary production (sink) and respiratory processes (sources) using Redfield stoichiometry. Gas exchange was parameterized using the computed surface ocean  $p\text{CO}_2$ , an atmospheric  $p\text{CO}_2$  of 377 ppm (which is the 2004 mean value observed at the Mauna Loa Observatory), and the gas-transfer velocity of Wanninkhof (1992). DIC and alkalinity are initialized using the  $T$ - and  $S$ -dependent relationships derived by Lee et al. (2000) and Millero et al. (1998), respectively. Riverine alkalinity values were determined using Millero et al.'s (1998) relationship for  $S = 0$ . DIC was assumed to be in equilibrium with atmospheric values of  $\text{CO}_2$  in the river sources. Since the model-predicted air-sea fluxes are very sensitive to the initial concentrations of DIC and alkalinity,  $T$ - and  $S$ -dependent relationships based on more recent data and based on data from the shelf systems under consideration would be more desirable, but aren't available at present.

### 3.2 Nitrogen fluxes and budgets

In addition to calculating the biological sources and sinks of constituents (e.g. nitrate, inorganic carbon, particulate organic matter) through time, the model calculates the advective and diffusive flows of these constituents between grid cells as well as their fluxes across the air-sea and sediment-water interfaces. Budgets for bio-available nitrogen and carbon can be easily derived by integrating these model-predicted fluxes over desired regions and over time.

For total nitrogen, TN ( $\text{mmol N m}^{-3}$ ), a conservation equation can be written for any horizontal grid cell of the model domain as follows:

$$\int_{-H}^0 \frac{\partial \text{TN}}{\partial t} dz = -F_{\text{DNF}} + \int_{-H}^0 \nabla \cdot (\mathbf{u} \text{TN}) dz, \quad (1)$$

where  $t$  and  $z$  represent time (s) and depth (m), respectively,  $H$  is the total water depth (m),  $F_{\text{DNF}}$  is the sediment denitrification flux ( $\text{mmol N m}^{-2} \text{s}^{-1}$ ), and  $\mathbf{u}$  is the 3-dimensional velocity vector. The left-hand-side of Eq. (1) is the so-called

storage term and quantifies the change in TN within the considered volume over time. The term  $-\int_{-H}^0 \nabla \cdot (\mathbf{u} \text{TN}) dz$  represents the horizontal divergence of TN or, in other words, the flux of TN out of the considered volume. A positive horizontal divergence corresponds to horizontal export of matter from the considered volume; a negative divergence corresponds to horizontal import.

The horizontal divergence of TN can be split into contributions from individual nitrogen species, for example, into horizontal divergence of particulate organic nitrogen, PON, and dissolved inorganic nitrogen, DIN. The resulting balance equation is:

$$\int_{-H}^0 \frac{\partial \text{TN}}{\partial t} dz = -F_{\text{DNF}} + \int_{-H}^0 \nabla \cdot (\mathbf{u} \text{DIN}) dz \quad (2)$$

$$+ \int_{-H}^0 \nabla \cdot (\mathbf{u} \text{PON}) dz. \quad (3)$$

For budgeting purposes the geographic regions that were defined based on bathymetric, physical and ecological boundaries in Hofmann et al. (2008; their Fig. 1) are used here (Fig. 2). Each of the terms in Eqs. (2–3) was calculated as model diagnostic and integrated in space over the areas shown in Fig. 2, and in time over calendar years to yield annual nitrogen budgets for these areas (Table 1).

For all shelf regions considered here the horizontal divergence of TN is negative. In other words, there is a net import of nitrogen to these shelf systems. Except for the MAB estuaries the removal of fixed nitrogen through sediment denitrification is either roughly equal to or exceeds the horizontal import of nitrogen. If the nitrogen budget were in steady state over annual time scales, the storage term would be zero and removal of nitrogen through denitrification would be balanced exactly by horizontal import of nitrogen. While none of the regions considered here is in perfect steady state, for the MAB shelf, Georges Bank (GB) and the Scotian Shelf (SS) the storage terms of TN are much smaller than the denitrification flux and the horizontal divergence of TN (with the exception of SS in 2005). Thus, except for the SS in 2005, one can infer that the removal of fixed nitrogen through sediment denitrification is balanced by horizontal import on a timescale of a year.

For the MAB shelf the horizontal divergence term includes import of TN from the estuaries. In order to separate the estuarine inputs from the TN flux across the shelf break and shelf boundaries, the TN input from the estuaries was estimated and subtracted from the horizontal divergence estimates (given in parentheses in Table 1). For the MAB shelf the ratio of horizontal input of nitrogen across the shelf break to sediment denitrification is 26% in 2004 and 62% in 2005. For the SS the ratio is 94% in 2004, and for GB, 67% in 2004 and 91% in 2005. In all these cases a significant fraction of

**Table 1.** Model-based nitrogen budget for the Middle Atlantic Bight (MAB) estuaries, the MAB shelf, Georges Bank (GB) and the Scotian Shelf (SS) for 2004 and 2005. All fluxes are in  $10^{10} \text{ mol N yr}^{-1}$ .

	TN storage	DIN storage	PON storage	denitrification flux	horz divg of TN	horz divg of DIN	horz divg of PON
2004							
MAB estuaries	0.97	0.95	0.017	0.48	−1.45 (1.14)*	−1.55	0.104
MAB shelf	−1.00	−1.03	0.027	2.94	−1.94 (−0.75)**	−2.59	0.64
GB	−0.51	−0.65	0.14	1.55	−1.04	−2.10	1.06
SS	−0.19	−0.23	0.047	2.91	−2.73	−3.37	0.64
2005							
MAB estuaries	0.91	0.89	0.017	0.49	−1.40 (1.19)*	−1.53	0.13
MAB shelf	0.16	0.073	0.085	2.70	−2.86 (−1.67)**	−3.28	0.42
GB	−0.14	−0.31	0.17	1.63	−1.50	−2.65	1.15
SS	−3.52	−3.55	0.031	3.16	0.35	−0.44	0.78

\* Value in parentheses corresponds to divergence without point sources from rivers. In other words, the nitrogen input from rivers ( $2.59 \times 10^{10} \text{ mol N yr}^{-1}$ ) was subtracted.

\*\* Value in parentheses corresponds to nitrogen flux across the shelf break; the nitrogen input from estuaries was subtracted.

sediment denitrification is supported by onwelling of nitrogen from the adjacent open ocean onto the shelf, consistent with the finding of Seitzinger and Giblin (1996).

It is important to note that the horizontal divergence of TN is the sum of the divergence of DIN and the divergence of PON, and that both fluxes have opposite signs. In other words, DIN is imported to the shelf systems, while PON is exported. The ratios between import of DIN and export of PON are 4.0 and 7.8 for the MAB shelf in 2004 and 2005, 5.2 for SS, and 2.0 and 2.1 for GB in 2004 and 2005. This indicates that the tidally mixed GB region is more efficient in exporting PON than the stratified MAB shelf and SS, where more fixed nitrogen is lost due to denitrification.

There is independent observational evidence of the large denitrification sink on the shelf, namely a strong nitrogen deficit with respect to phosphate. An excess or deficit in fixed nitrogen with respect to available phosphate can be quantified by the tracer “excess nitrogen” or  $N^*$ , which is defined as  $\text{NO}_3 - 16 \times \text{PO}_4$ . Photosynthetic production and aerobic remineralization of organic matter do not affect  $N^*$  (assuming they occur in Redfield stoichiometry), however, denitrification decreases  $N^*$  (by removing fixed nitrogen without affecting the availability of phosphate) and  $\text{N}_2$  fixation increases  $N^*$  (by adding bio-available nitrogen). Negative values of  $N^*$  are thus a strong indication of denitrification.

In Fig. 3 nitrate and phosphate data are plotted for a large number of samples from the MAB shelf which were taken over 3 decades. The data were collected on several cruises by the Brookhaven National Laboratories and on cruises during the SEEP programs (Walsh et al., 1988; Biscaye et al., 1994) and the OMP program (Verity et al., 2002). An overwhelming majority of data points have a negative  $N^*$ , which

is remarkable, as  $N^*$  in the open North Atlantic is positive with values between 3 and  $4 \text{ mmol m}^{-3}$  (Sarmiento and Gruber, 2006, p. 194). It is also noteworthy that the minimum  $N^*$  values on the MAB shelf, which are as low as  $-30$  to  $-40 \text{ mmol m}^{-3}$ , are much lower than minimum values found in the oxygen minimum zones off Peru and in the Indian Ocean. The smallest  $N^*$  values in these oxygen minimum zones are  $-9 \text{ mmol m}^{-3}$ .

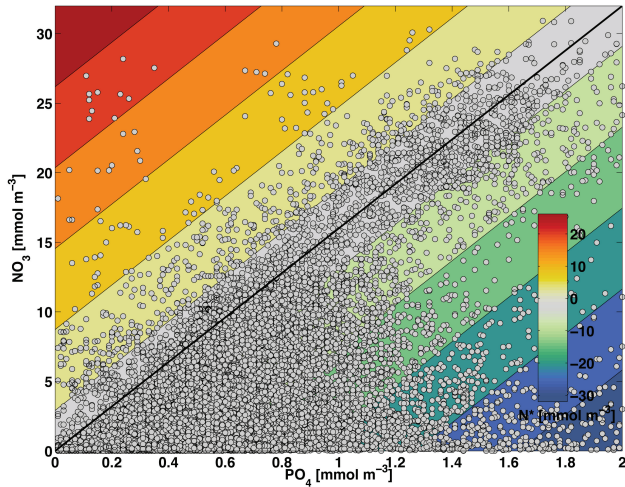
A spatially more explicit distribution of  $N^*$  on the MAB shelf is given for a series of transects (see map in Fig. 4) in Fig. 5. The lowest  $N^*$  values are found on the southernmost section which also illustrates the on-welling of subsurface water from the open North Atlantic onto the shelf, which is characterized by a positive  $N^*$ .

The  $N^*$  distributions serve as qualitative confirmation of the large denitrification sink on the shelf. Since the described model does not include phosphate as separate nutrient the observed  $N^*$  can not be compared with corresponding model-derived fields.

### 3.3 Carbon fluxes and budgets

The removal of fixed nitrogen from the North American continental shelf through sediment denitrification (as discussed in the previous section) has implications for the efficiency of the CSP. On the one hand, denitrification lowers the availability of fixed nitrogen, which in turn reduces the photosynthetic fixation of inorganic carbon into organic matter. Since the biological CSP is principally driven by incorporation of DIC into organic matter, its efficiency should consequently be lower as well. On the other hand, sediment denitrification produces alkalinity, which will promote uptake of atmospheric  $\text{CO}_2$  (as discussed in Sect. 2.2). Predicting the net





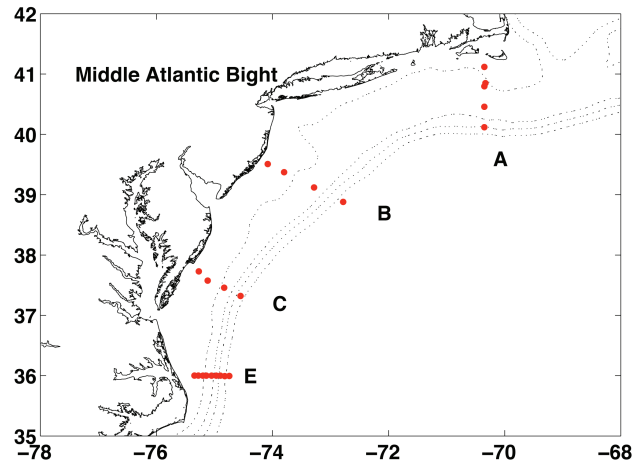
**Fig. 3.** Nitrate plotted over phosphate for 25 790 samples from the MAB shelf. Samples were taken during cruises undertaken by Brookhaven National Laboratories and during the SEEP and OMP programs (see text for details).  $N^*$ , given in color, quantifies the nitrogen excess/deficit with respect to phosphate. The bold line marks  $N^*=0$  and corresponds to the Redfield ratio of 16:1.

effect on the air-sea  $\text{CO}_2$  flux resulting from these two opposing mechanisms based on observations alone is not straightforward, but the effects can be separated with the help the biogeochemical model described above.

The quantitative importance of the two denitrification effects on air-sea gas exchange was quantified by comparing model simulations with and without sediment denitrification and with different treatments of alkalinity (Fennel et al., 2008). The effect of nutrient removal and reduced primary production on the air-sea flux of  $\text{CO}_2$  was a decrease in ocean uptake by 14% and was quantified by calculating the difference in simulated fluxes between two 1-year simulations, both of which had a conservative parameterization of alkalinity (alkalinity behaves essentially like salinity), one without and one with sediment denitrification. Inclusion of the production of alkalinity partly counteracts this decrease. The net effect was quantified by taking the difference between two 1-year simulations that both had a more realistic treatment of alkalinity, i.e. sources and sinks of nitrate were taken into account in its calculation, one with and one without denitrification. The combination of both effects leads to a decrease in ocean uptake of  $\text{CO}_2$  by 8.5%.

The efficiency of the different CSP mechanisms can be quantified in the model as well. As done for fixed nitrogen in Sect. 3.2 (Eq. 1) one can write a conservation equation for total carbon, TC ( $\text{mmol C m}^{-3}$ ), as follows:

$$\int_{-H}^0 \frac{\partial \text{TC}}{\partial t} dz = F_{\text{air-sea}} + \int_{-H}^0 \nabla \cdot (\mathbf{u} \text{TC}) dz. \quad (4)$$



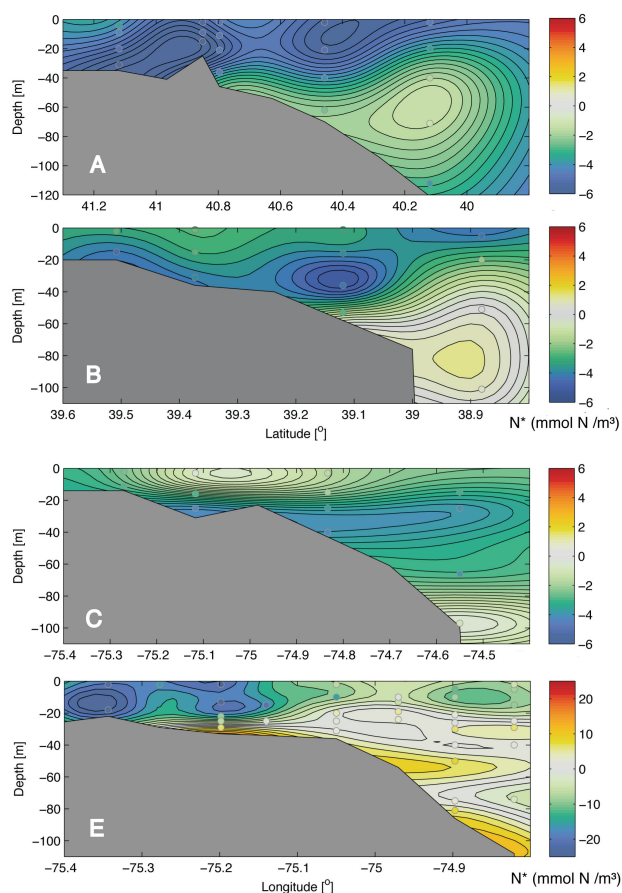
**Fig. 4.** Location of stations on four transects that were sampled during the OMP program.  $N^*$  along these transects are shown in Fig. 5.

Here the left-hand-side term is the storage of TC. It is balanced by the flux of  $\text{CO}_2$  across the air-sea interface into the ocean,  $F_{\text{air-sea}}$  ( $\text{mmol C m}^{-2} \text{s}^{-1}$ ), minus the horizontal divergence of TC, given as  $-\int_{-H}^0 \nabla \cdot (\mathbf{u} \text{TC}) dz$ . The total divergence of TC can be split into its contributions from inorganic carbon (IC) and organic carbon (OC), resulting in

$$\int_{-H}^0 \frac{\partial \text{TC}}{\partial t} dz = F_{\text{air-sea}} + \int_{-H}^0 \nabla \cdot (\mathbf{u} \text{IC}) dz + \int_{-H}^0 \nabla \cdot (\mathbf{u} \text{OC}) dz. \quad (5)$$

Analysis of the individual divergence terms can give insight into the strength of the physical and biological CSP mechanisms. In Fennel and Wilkin (2009) the simulated air-sea fluxes of  $\text{CO}_2$  and the horizontal divergence of OC was integrated spatially for the subregions shown in Fig. 2 for 2004 and 2005. The area-normalized average uptake of atmospheric  $\text{CO}_2$  increases with latitude in the model from  $0.89 \text{ mol C m}^{-2} \text{s}^{-1}$  in the stratified MAB,  $1.67 \text{ mol C m}^{-2} \text{s}^{-1}$  on Georges Bank and in the Gulf of Maine, to  $2.3 \text{ mol C m}^{-2} \text{s}^{-1}$  on the Scotian Shelf. The average horizontal divergence of OC is 3.61, 9.21 and  $4.73 \times 10^{10} \text{ mol C yr}^{-1}$  for the MAB, the region combining Georges Bank and the Gulf of Maine, and the Scotian Shelf, respectively. These results indicate that the relative contribution of the biologically driven CSP is smaller on the Scotian Shelf than in the stratified MAB, and that tidal mixing on Georges Bank significantly increases the strength of the biological CSP, thus enhancing uptake of atmospheric  $\text{CO}_2$  locally. This is in contrast to observations of Thomas et al. (2004), who found persistent outgassing of  $\text{CO}_2$  in the tidally mixed part of the North Sea, possibly due to the local influence of river inputs.

Interannual variability of the air-sea  $\text{CO}_2$  flux in the model is likely significant. Previdi et al. (2009) analyzed two 1-



**Fig. 5.**  $N^*$  along four transects on the MAB shelf (see Fig. 4 for station locations). The contour plots show optimally interpolated fields. The location of data points is shown by the colored circles; the color within circles indicates the observed value.

year simulations that differed only in their atmospheric forcing. Specifically, atmospheric forcing for two years (1985 and 1990) marked by opposite phases of the North Atlantic Oscillation (NAO) was used. The simulated uptake of atmospheric  $\text{CO}_2$  in the MAB and Gulf of Maine was smaller by 25% in 1990 (the high NAO year) compared to 1985. Previdi et al. (2009) used a second-order Taylor series decomposition, a novel analysis technique, to quantify the contribution of processes underlying the forcing-related difference in air-sea  $\text{CO}_2$  flux and showed that the difference in the MAB is mostly explained by differences in wind speed, while changes in sea-surface temperature and new production were more important in the Gulf of Maine. This analysis neglected interannual and longer-term variability that can result from advective modulation of shelf water characteristics, as discussed by Mountain (2003) and Belkin (2004).

Two significant sources of uncertainty in the model simulations described above are (1) the choice of initial and boundary conditions for DIC and alkalinity, which are based on climatological data mostly from the open ocean, and

(2) the lack of dissolved organic carbon (DOC) dynamics. On the continental shelf the DOC pool is significantly larger than the pool of particulate organic carbon (by one to three orders of magnitude; Bauer et al., 2001) and strong gradients in DOC concentration exist between shelf waters and the open ocean (Hopkinson et al., 2002). Exchange of DOC across the shelf break may thus be a significant component of the shelf carbon budget. Adequate representation of DOC dynamics in biogeochemical models critically depends on a mechanistic understanding of DOC sources and transformations.

## 4 Conclusions

Observation-based budgets and biogeochemical model simulations suggest that continental shelves act as a barrier for nitrogen inputs to the ocean from land. This is due to sediment denitrification, which is efficient in removing fixed nitrogen by converting it into the unavailable gaseous form. Shelf sediments are also significant sinks of nitrogen in the ocean's nitrogen budget. Accurate estimation of this nitrogen sink requires reliable estimates of the cross-shelf exchange of inorganic and organic nitrogen forms, which has to rely on a combination of observations and predictive models.

Different mechanisms have been suggested by which continental shelves could contribute significantly to the export of carbon to the deep ocean. In addition to the physical and biological Continental Shelf Pumps, which are analogs to the physical and biological pumps in the open ocean, shelves generate alkalinity through anaerobic remineralization processes in sediments. A major uncertainty in the accurate quantification of the Continental Shelf Pumps is the magnitude of cross-shelf exchange of organic and inorganic carbon. Model simulations for the Northwestern North Atlantic suggest that the increase in area-normalized biological export from shelves compared to the adjacent open ocean is only small.

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