

Denitrification in Aquatic Sediments

Review

## MODELLING DENITRIFICATION IN AQUATIC SEDIMENTS

Authors:

Katja Fennel<sup>1,#</sup>, Damian Brady<sup>2</sup>, Dominic DiToro<sup>2</sup>, Robinson W. Fulweiler<sup>3</sup>, Wayne S. Gardner<sup>4</sup>, Anne Giblin<sup>5</sup>, Mark J. McCarthy<sup>4,6</sup>, Alexandra Rao<sup>7</sup>, Sybil Seitzinger<sup>8</sup>, Marie Thouvenot-Korppoo<sup>9</sup>, Craig Tobias<sup>10</sup>

Affiliations:

<sup>1</sup>Dalhousie University, Oceanography, Halifax, NS, Canada

<sup>2</sup>University of Delaware, DE, USA

<sup>3</sup>Louisiana State University, Baton Rouge, LA, USA

<sup>4</sup>The University of Texas at Austin, Marine Science Institute, Port Aransas, TX, USA

<sup>5</sup>Marine Biological Laboratory Ecosystems Center, Woods Hole, MA, USA

<sup>6</sup>Current affiliation: Université du Québec à Montréal, Département sciences biologiques, Montréal, QC, Canada

<sup>7</sup>Woods Hole Oceanographic Institution, Woods Hole, MA, USA

<sup>8</sup>Rutgers University, Institute of Marine and Coastal Sciences, Rutgers/NOAA CMER Program, New Brunswick, NJ, USA

<sup>9</sup>Water Resources Engineering, Helsinki University of Technology, Helsinki, Finland

<sup>10</sup>University of North Carolina Wilmington, Wilmington, NC, USA

# Corresponding author:

Katja Fennel  
Dalhousie University  
Department of Oceanography  
1355 Oxford St  
Halifax, NS, B3H 4J1  
Canada  
Phone: +1 902 494 4526  
Fax: +1 902 494 3877  
Email: [katja.fennel@dal.ca](mailto:katja.fennel@dal.ca)

Keywords: denitrification, diagenetic model, sediment

Abbreviations: dissimilatory nitrate reduction to ammonium (DNRA), oxygen-demand units (ODUs), sediment flux model (SFM), sediment oxygen consumption (SOC)

1 **ABSTRACT**

2 Sediment denitrification is a major pathway of fixed nitrogen loss from aquatic systems.  
3 Due to technical difficulties in measuring this process and its spatial and temporal  
4 variability, estimates of local, regional and global denitrification have to rely on a  
5 combination of measurements and models. Here we review approaches to describing  
6 denitrification in aquatic sediments, ranging from mechanistic diagenetic models to  
7 empirical parameterizations of nitrogen fluxes across the sediment-water interface. We  
8 also present a compilation of denitrification measurements and ancillary data for different  
9 aquatic systems, ranging from freshwater to marine. Based on this data compilation we  
10 reevaluate published parameterizations of denitrification. We recommend that future  
11 models of denitrification use (1) a combination of mechanistic diagenetic models and  
12 measurements where bottom waters are temporally hypoxic or anoxic, and (2) the much  
13 simpler correlations between denitrification and sediment oxygen consumption for oxic  
14 bottom waters. For our data set, inclusion of bottom water oxygen and nitrate  
15 concentrations in a multivariate regression did not improve the statistical fit.

16

17 **INTRODUCTION**

18 Unlike other important macro- and micronutrients, e.g. phosphorus and iron, the reservoir  
19 of bioavailable nitrogen is regulated almost solely by biological activity. Two opposing,  
20 microbially mediated processes, denitrification and nitrogen fixation, regulate the size of  
21 this reservoir. Nitrogen is the major limiting nutrient in marine systems; thus, variations  
22 in its availability have far-reaching consequences. Denitrification is any process by  
23 which combined nitrogen (nitrate, ammonium or organic forms) is reduced to gaseous

1 end products (NO, N<sub>2</sub>O or N<sub>2</sub>) (Devol in press). In the more restrictive, classical  
2 definition, denitrification is a dissimilatory nitrate reduction process during which nitrate  
3 or nitrite (NO<sub>3</sub><sup>-</sup> or NO<sub>2</sub><sup>-</sup>) is reduced anaerobically to any gaseous form of nitrogen by  
4 heterotrophic bacteria (also referred to as canonical denitrification). It is carried out by  
5 ubiquitous, facultatively anaerobic bacteria under suboxic conditions (i.e. at oxygen  
6 concentrations below approximately 2 mg O<sub>2</sub> l<sup>-1</sup> or 63 mmol O<sub>2</sub> m<sup>-3</sup>) and its end product  
7 is N<sub>2</sub> gas. Denitrification in sediments containing ample labile organic matter is often  
8 limited by the availability of nitrate or nitrite. Available fixed nitrogen in sediments is  
9 mostly in the form of ammonium (NH<sub>4</sub><sup>+</sup>, derived from ammonification of organic matter  
10 or dissimilatory nitrate reduction to ammonium under some conditions). Unless there is a  
11 flux of nitrate into the sediment from overlying bottom waters, denitrification in the  
12 sediment depends on local rates of nitrification (the oxidation of ammonium to nitrite or  
13 nitrate by chemoautotrophic bacteria). This combination of processes is commonly  
14 referred to as *coupled nitrification-denitrification*. Denitrification supported by the  
15 physical influx of nitrate is referred to as *direct denitrification*.

16

17 Denitrification is the major pathway of fixed nitrogen loss from aquatic systems. Thus, it  
18 is a critical component of the global nitrogen budget and a balancing mechanism for  
19 removal of anthropogenic nitrogen along the terrestrial-freshwater-marine continuum  
20 (Galloway et al. 2003; Seitzinger et al. 2006). On the global scale, denitrification is an  
21 important feedback mechanism on biogeochemical cycling and in the climate system.  
22 For example, denitrification may have been a major impediment to the initial oxidation of  
23 the planet during the suboxic stage in the Proterozoic (Fennel et al. 2005). Denitrification

1 can produce nitrous oxide ( $N_2O$ , a potent greenhouse gas), which can have important  
2 impacts on climate (Naqvi et al. 2000). In addition, denitrification may contribute to  
3 glacial-interglacial changes in atmospheric  $CO_2$  by decreasing the supply of bioavailable  
4 nitrogen and, thus, biologically fixed carbon during interglacial periods (Altabet et al.  
5 1995; Falkowski 1997).

6  
7 Anaerobic ammonium oxidation (anammox) by nitrite or nitrate has been identified as an  
8 alternative microbial pathway of  $N_2$  production and, from a biogeochemical perspective,  
9 can be considered a denitrifying process (Devol 2008). The possibility of anammox was  
10 originally suggested by Richards et al. (1965) and invoked by various investigators based  
11 on pore water solute profiles (Bender et al. 1989) before the discovery of organisms that  
12 can carry out this process. Anammox was first observed in a wastewater bioreactor  
13 (Mulder et al. 1995). Anammox organisms have been purified from wastewater reactor  
14 biomass and identified in several natural marine systems, such as the suboxic zone of the  
15 Black Sea and the Benguela upwelling system (Kuypers et al. 2003; Kuypers et al. 2005  
16 and references therein), and in Randers Fjord, Denmark (Risgaard-Petersen et al. 2004).  
17 The significance of anammox was demonstrated in a variety of coastal and marine  
18 sediments (Thamdrup & Dalsgaard 2002; Trimmer et al. 2003; Dalsgaard et al. 2003;  
19 Engström et al. 2005). In the following discussions, we adopt the biogeochemical view  
20 of denitrification (inclusive of all processes producing  $N_2$ ) and do not differentiate  
21 between the alternative pathways.

22

1 A first attempt to estimate annual denitrification on a global scale was made recently with  
2 a spatially explicit global analysis of denitrification in all terrestrial, freshwater  
3 (lakes/rivers), estuarine and shelf ecosystems using various models (Seitzinger et al.  
4 2006). A global estimate of denitrification in lakes and reservoirs is presented by  
5 Harrison et al. (this issue). These models are largely based on empirical relationships, for  
6 example, in Harrison et al. (this issue) nitrogen removal is estimated from knowledge of  
7 water depth and residence time in individual lakes and reservoirs. Boyer et al. (2006)  
8 review approaches for modeling denitrification in terrestrial and aquatic ecosystems, and  
9 focused on source-transport models for streams, lakes and rivers. These models aggregate  
10 nitrogen removal processes estimated from empirical functions (typically denitrification  
11 is parameterized as a function of water residence time) but do not explicitly account for  
12 the production and cycling of organic nitrogen.

13

14 Here we describe approaches to estimating denitrification that predict nitrogen fluxes  
15 across the sediment-water interface and can be incorporated into hydrographic ecosystem  
16 models that explicitly describe inorganic and organic nitrogen cycling in the water  
17 column. Hydrographic ecosystem models that focus on estuaries or continental shelves  
18 tend to consider the pathways of sediment nitrogen cycling, (e.g. DiToro & Fitzpatrick  
19 1993; Cerco & Seitzinger 1997; Fennel et al. 2006). Global and basin-scale  
20 biogeochemical models typically ignore sediment denitrification even though this process  
21 has been recognized as an important global nitrogen sink (Christensen 1994) and is  
22 estimated to exceed denitrification in the water column by a factor of 3 (Seitzinger et al.  
23 2006). For example, Meissner et al. (2005) and Moore & Doney (2007) investigate

1 feedbacks between global denitrification and nitrogen fixation in biogeochemical general  
2 circulation models without the inclusion of sediment denitrification.

3

4 Placing denitrification in aquatic sediments in the broader and more complex context of  
5 early diagenesis is helpful. Diagenesis can be considered, “the sum total of processes that  
6 bring about changes in a sediment or sedimentary rock, subsequent to deposition in  
7 water. The processes may be physical, chemical, and/or biological in nature” (Berner  
8 1980, p. 3). Diagenetic processes thus include transport and reaction processes; both can  
9 be the result of biological and physical phenomena (Boudreau 1997).

10

11 Progress in our understanding of diagenetic processes has rested on a close link between  
12 observational approaches and diagenetic modeling, i.e. the idealized mathematical  
13 representation of diagenetic processes (Berner 1980). Boudreau (1997) offers several  
14 reasons for the important role of diagenetic modeling, several of which are relevant to  
15 denitrification. First, many measurements do not provide information about the  
16 interactions of the various processes; they only indicate the net result. With the help of  
17 models one can make quantitative inferences about the relative importance or absence of  
18 individual processes. Second, sampling techniques often disturb the system under  
19 consideration. Many processes are transient and hard to resolve. Denitrification  
20 measurements are particularly time consuming and imprecise, mostly because they either  
21 try to measure a small production rate of  $N_2$  against the high background of atmospheric  
22  $N_2$  or use indirect measurements as a proxy for denitrification. Finally, trusted models  
23 can become tools for prediction. As such, models allow scaling up from local

1 measurements to larger spatial and temporal scales. A strong link between measurement  
2 and modeling is crucial.

3

4 Excellent reviews on diagenetic modeling have been provided by Berner (1980),  
5 Boudreau (1997), DiToro (2001) and Burdige (2006) and will not be replicated here. Our  
6 objectives are (1) to review approaches to diagenetic modeling with a focus on  
7 denitrification, (2) to compile a data set of denitrification measurements and sediment-  
8 water fluxes of oxygen and different nutrient species that encompasses a range of aquatic  
9 sediments, and (3) test the robustness of empirical parameterizations and evaluate one  
10 example of a mechanistically based diagenetic model against the compiled data set.

11

12

### 13 **MODEL APPROACHES**

14 Denitrification depends on and interacts with a range of other processes occurring in  
15 aquatic sediments (e.g. supply of organic matter, diffusive and advective transport of  
16 oxygen and nitrate, nitrification). Our discussion of quantitative descriptions of  
17 denitrification in aquatic sediments is thus best placed in the context of early diagenesis.  
18 We refer to these quantitative descriptions of sediment denitrification as diagenetic  
19 models or biogeochemical sediment models, but recognize that denitrification is just one  
20 of many diagenetic processes. When assessing the importance of sediment denitrification  
21 in nitrogen cycling we are interested primarily in the sediment-water interface fluxes of  
22 nitrogen species; oxidation and reduction of other elements is not discussed here. For  
23 simplicity, we refer to the sum of nitrite ( $\text{NO}_2^-$ ) and nitrate ( $\text{NO}_3^-$ ) as nitrate.

1

2 Many different approaches to modeling early diagenetic processes exist. In terms of  
3 temporal representation, diagenetic models can be *steady state* (concentrations and fluxes  
4 are constant in time) or *dynamic* (the model allows for temporal variations in  
5 concentrations and fluxes). In terms of spatial representation, models often consider  
6 spatial variations only in the vertical dimension. They assume horizontal homogeneity.  
7 In simple cases, the differential equations representing early diagenesis can be *solved*  
8 *analytically* and yield vertically continuous solutions. These are typically steady state  
9 models with simple reaction kinetics. More often the diagenetic equations are not  
10 amenable to analytical solutions. In these cases, the vertical dimension is discretized in  
11 vertical layers and *solved numerically*. In essence the layers represent a vertical  
12 integration over processes and constituents in a vertical slice of sediment. These slices  
13 can be *functional* or *indiscriminate* layers. Functional layers can be defined by the  
14 occurrence of a reaction process or the presence of a dissolved constituent, e.g. an  
15 anaerobic and an aerobic layer. Indiscriminate layers are strictly defined in terms of their  
16 vertical coordinates and assume different functions; for example, they can switch  
17 between aerobic mineralization and denitrification depending on the local oxygen  
18 concentration.

19

20 Alternative approaches that attempt to account for three-dimensional heterogeneities have  
21 been proposed, for example, representing anaerobic microenvironments within individual  
22 particles in an otherwise aerobic environment, or the representation of animal burrows  
23 (Aller 1980, 1988).



1

2 All of these models aim to describe a subset of the occurring diagenetic processes and  
 3 fluxes across the sediment-water interface. Early diagenetic models were developed  
 4 independent of water column biogeochemical models and, to this day, biogeochemical  
 5 models still rarely include diagenetic processes (see the excellent review by Soetaert et al.  
 6 2000). Biogeochemical models that do include some form of diagenesis typically use  
 7 parameterizations (e.g. Fennel et al. 2006), which can be thought of as the most  
 8 simplified quantitative description of early diagenesis.

9

10 The general diagenetic equations for solid constituents,  $S$ , and dissolved constituents in  
 11 the pore water,  $C$ , following Berner (1980) are:

$$12 \quad \frac{\partial(1-\phi)S}{\partial t} = -\frac{\partial}{\partial z}((1-\phi)w_{sed}S) + \frac{\partial}{\partial z}\left((1-\phi)D_B \frac{\partial S}{\partial z}\right) + \sum R(S,C) \quad (1a)$$

$$13 \quad \frac{\partial\phi C}{\partial t} = -\frac{\partial}{\partial z}(\phi w_{pw}C) + \frac{\partial}{\partial z}\left(\phi D \frac{\partial C}{\partial z}\right) + \sum R(S,C) \quad (1b)$$

14 Here  $\phi$  is the porosity (the fraction of sediment volume that is liquid), a dimensionless  
 15 number that varies between 0 and 1. The dissolved constituent  $C$  has units of  $\text{mol m}^{-3}$  of  
 16 pore water only and is multiplied by  $\phi$  to convert to  $\text{mol m}^{-3}$  of sediment (pore water +  
 17 solid).  $C$  represents, for example, the concentrations of oxygen, nitrate or ammonium.  
 18 Likewise, the solid  $S$  has units of  $\text{mol m}^{-3}$  of solid only and is multiplied by  $(1-\phi)$  to  
 19 convert to  $\text{mol m}^{-3}$  of sediment.  $S$  represents, for example, organic carbon or biogenic  
 20 silicate. The time-rate-of-change of solid and dissolved constituents (left hand sides of  
 21 equations 1a and 1b) equals the sum of changes due to vertical advection (first set of  
 22 terms on the right hand side [rhs]), diffusive processes (second set of terms on rhs) and

1 transformations due to biogeochemical reactions (collected in the term  $\sum R(S,C)$ ). The  
2 advection velocities of solids and pore water are  $w_{sed}$  and  $w_{PW}$ , respectively. Bioturbation  
3 of solids (i.e. the “mixing” of sediment by the burrowing action of higher animals) is  
4 often described as a diffusive mixing process with diffusivity  $D_B$ .  $D$  is the pore water  
5 diffusivity.

6

### 7 **Steady-state models**

8 Steady-state models (e.g. Jahnke et al. 1982; Middelburg et al. 1996; Soetaert et al.  
9 1996b; Vanderborght et al. 1977a, b) are an application of the general diagenetic  
10 equations (1a,b), where the left-hand-side is set to equal zero, thus eliminating the time  
11 dependence. Some of these models have been solved analytically, some numerically. An  
12 elegant *analytical solution* to a diagenetic equation of denitrification was derived by  
13 Vanderborght et al. (1977a,b), for fine-grained, organically rich, coastal sediments in the  
14 North Sea. Since the top 3.5 cm of sediment at their site appeared to go through a  
15 continuous cycle of deposition and erosion due to the action of waves and currents, the  
16 authors chose an elevated diffusivity in the well-oxygenated top layer and a diffusivity  
17 more typical of pore water below. By solving the model analytically for silica, fitting  
18 their solution to observed pore water profiles, they obtained an appropriate value for the  
19 diffusivity in the top layer, which was then used in solving the nitrate equation. This  
20 example illustrates two points: (1) processes other than molecular diffusion and  
21 bioturbation can cause vertical mixing of sediment (an accurate parameterization of the  
22 vertical mixing processes is important for making reasonable predictions of  
23 denitrification rates); and (2) the distribution of an independent variable, in this case

1 dissolved silica, can provide a means to determine a reasonable parameterization for  
2 diffusivity. In essence, the silica distribution adds independent information to the  
3 parameterization.

4

5 An example of a steady-state model that is more complex biogeochemically and has to be  
6 solved numerically is that of Middelburg et al. (1996). Their model explicitly resolves  
7 the depth distribution of solid-phase organic carbon and nitrogen, and pore water  
8 concentrations of oxygen, nitrate and ammonium. Reduced manganese, iron and sulfur  
9 are lumped into oxygen-demand units (ODUs). ODU's are oxidized when they come in  
10 contact with oxygen and are transported similarly to the other dissolved substances. This  
11 choice allows one to include the net effect of manganese, iron and sulphur cycles on the  
12 oxygen distribution without having to explicitly model their complex interactions. By  
13 assuming global values for model parameters and applying one porosity profile globally,  
14 Middelburg et al. (1996) arrived at a general parameterization of denitrification and  
15 estimated the global rate of sediment denitrification.

16

### 17 **Layered dynamic models**

18 Dynamic representations of functional layers, e.g. in the Sediment Flux Model (SFM,  
19 DiToro & Fitzpatrick 1993; DiToro 2001), or indiscriminate layers (e.g. in the model of  
20 Soetaert et al. 1996a) are based on the diagenetic equations (1a,b) as well.

21

22 In the SFM (DiToro & Fitzpatrick 1993; DiToro 2001) the sediment is represented by  
23 two functional layers: an aerobic layer directly below the sediment-water interface and an

1 anaerobic layer below. Concentration changes of solid and dissolved constituents are  
2 described by mass balance equations where the change of a constituent within a given  
3 volume is related to the sum of internal sources and sinks of the constituent (i.e. internal  
4 reactions) and its fluxes across the volume boundaries. Essentially, the mass balance  
5 equations are discrete representations of the continuous diagenetic equations. For  
6 example, diffusive processes—which are parameterized by multiplying a diffusivity,  $D$ ,  
7 with the concentration gradient  $\partial c/\partial z$  in the continuous case (see equations 1a,b)—  
8 become mass transfer coefficients in the layered case. The mass transfer rate for oxygen  
9 is parameterized as the ratio of the computed sediment oxygen demand and the dissolved  
10 oxygen concentration in the overlying bottom water and the surface mass transfer rates  
11 for all other dissolved constituents are assumed to be equal to the transfer rate derived for  
12 oxygen (Di Toro 2001).

13

14 The sediment model in Riverstrahler, a model of nutrient cycling in a river system (Billen  
15 et al. 1994; Garnier et al. 1995; Billen & Garnier 1999), is an example for a vertically  
16 integrated (1-layer) diagenetic model. In Riverstrahler, the representation of a river  
17 drainage network is coupled with models of biogeochemical transformations in the  
18 river's water column and underlying sediment (Ruelland et al. 2007). The sediment in  
19 Riverstahler is represented by one layer of deposited and erodable particulate material  
20 assumed to be homogeneously distributed along the vertical dimension and overlying a  
21 layer of consolidated non-erodable sediment. The sediment model is solved in quasi-  
22 steady-state mode, i.e. the sediment model is assumed to reach steady-state during each  
23 sediment model time step. This assumption simplifies the treatment of the diagenetic

1 equations significantly, as most equations can be solved analytically (Thouvenot et al.  
2 2007).

3

#### 4 **Microenvironments**

5 All approaches discussed above assume that processes are local and occur along the  
6 vertical dimension, with rates of diagenetic processes varying only with vertical gradients  
7 in solute concentrations or redox conditions. This assumption has been used traditionally  
8 and may be valid for some sediment types, e.g. muddy sediments and clays. However, it  
9 is not a good assumption for permeable sands, which comprise approximately 70% of  
10 continental shelves worldwide (Emery 1968). Solute exchange in muddy sediments is  
11 driven by molecular diffusion and macrofaunal activity (mixing and pore water  
12 irrigation), but the high permeabilities of sandy deposits permit pore water transport by  
13 advection (Thibodeaux & Boyle 1987; Boudreau 1997). Pore water flows in these  
14 sediments are linked to pressure gradients associated with current-topography  
15 interactions, wave pumping, groundwater discharge, temperature and salinity gradients,  
16 and other factors (Huettel & Webster 2001). Advective flows enhance the supply of  
17 oxidants and fresh organic matter, and the removal of remineralization byproducts (e.g.  
18 CO<sub>2</sub> and reduced electron acceptors) from >10 cm depth in these organically poor  
19 deposits, resulting in intense metabolic activity (Jahnke et al. 2005; Rao et al. 2007).  
20 Some studies have shown microscale spatial heterogeneity in sediment denitrification  
21 rates (Parkin 1987; Gold et al. 1998; Jacinthe et al. 1998).

22

1 Jahnke (1985) published a steady-state model of denitrification in sediment  
2 microenvironments based on Jorgensen (1977), in which reactive microenvironments in  
3 fecal pellets or other organic aggregates are represented as spherical particles of specified  
4 diameter, porosity and reactivity, within which organic matter respiration, and chemical  
5 and biologically mediated redox transformations occur. The distribution, reactivity and  
6 physical characteristics of these reactive particles in sediments are therefore important  
7 unknown parameters, which nonetheless must be specified in the model.

8  
9 Model results were compared to pore water solute profiles measured in fine-grained  
10 deep-sea sediments (Jahnke et al. 1985). This spherical microzone model may be applied  
11 in other modeling frameworks, e.g. in dynamic models, to simulate microzone  
12 denitrification.

13

#### 14 **Parameterizations**

15 Different parameterizations of denitrification have been proposed where denitrification is  
16 a function of one or more environmental factors that can be measured readily or  
17 estimated. Such parameterizations are useful because they can predict denitrification  
18 rates over large spatial and temporal scales, and in the absence of detailed information.  
19 Such parameterizations can also easily be incorporated into regional and large-scale  
20 biogeochemical models. Two examples are (1) a regression between sediment oxygen  
21 consumption and denitrification for estuarine, coastal ocean and continental shelf regions  
22 (Seitzinger & Giblin 1996); and (2) a regression between organic matter sedimentation  
23 flux and denitrification for the open ocean (Middelburg et al 1996). These regressions

1 have been used directly to provide snapshots of shelf-scale and global-scale  
2 denitrification, and as parameterizations in dynamics models (e.g. Fennel et al. 2006).  
3  
4 Middelburg et al. (1996, see also our ‘Steady-state models’ subsection, above) used a  
5 steady-state diagenetic model to derive global rates of denitrification in marine  
6 sediments. They used two different parameterizations, one where sediment  
7 denitrification depends on organic matter sedimentation only, and one where it depends  
8 on organic matter sedimentation, bottom water oxygen, and nitrate concentrations and  
9 water depth. For the purpose of deriving a general parameterization, the authors assumed  
10 global values for rate parameters, limitation and inhibition parameters, and assumed one  
11 porosity profile to be globally applicable. Some parameters were chosen as water-depth  
12 dependent, namely the sediment accumulation rate, the bioturbation rate and the flux of  
13 labile carbon. A sensitivity study revealed that model-predicted denitrification rates  
14 depend most strongly on the sedimentation flux and bottom-water concentrations of  
15 nitrate and oxygen. The authors arrived at their parameterization by multivariate  
16 regression of model-predicted sediment denitrification rates and model inputs  
17 (sedimentation flux, bottom water concentrations, depth). A large number of model  
18 solutions were used in the regression and were derived by randomly varying model  
19 parameters (within specified intervals), bottom-water nitrate and oxygen concentrations,  
20 and organic-matter carbon fluxes.  
21  
22 Organic-matter sedimentation flux is a useful descriptor for the open ocean and (possibly)  
23 deep lakes, but it is of limited use for shallow aquatic systems (e.g. shallow lakes,

1 wetlands, rivers, estuaries and the nearshore coastal ocean), because organic matter  
2 typically settles and is resuspended multiple times before being respired or buried. This  
3 cycle of settling and resuspension is, at best, difficult to measure or quantify. Sediment  
4 oxygen consumption is more easily measured, is closely related to the oxidation of  
5 organic carbon in sediments and, hence, is more useful for shallow systems.

6  
7 A parameterization for coupled nitrification-denitrification for continental shelf  
8 sediments was derived based on measured rates of denitrification and sediment oxygen  
9 consumption from different continental shelf regions by Seitzinger & Giblin (1996). This  
10 parameterization was used to estimate the spatial distribution of denitrification  
11 throughout shelf regions in the North Atlantic basin and suggests that sediment  
12 denitrification is greater than nitrogen inputs from atmospheric deposition and river  
13 sources combined, indicating that onwelling of deep water nitrate is a major nitrogen  
14 source for denitrification on shelves. This parameterization was subsequently used in a  
15 biogeochemical model for the continental shelf area of the North American east coast by  
16 Fennel et al. (2006), who transformed it into a regression between denitrification and  
17 organic matter flux, as this is the relevant quantity predicted by the biogeochemical  
18 model. It was assumed that organic matter is remineralized instantaneously upon  
19 reaching the sediment water interface and that sediment oxygen consumption occurs only  
20 in the oxidation of carbon and the nitrification of ammonium. The same assumptions can  
21 be used to reformulate the parameterization of Middelburg et al. (1996) in terms of  
22 sediment oxygen consumption (SOC). We compare both of these parameterizations with  
23 our data compilation below ('Environmental control on N cycling processes').



1

2 **DATA**

3 **Data compilation**

4 We synthesized a relatively large set of measured denitrification rates with ancillary

5 measurements, including our own unpublished data and data available in the literature.

6 As a minimum requirement for a data point to be considered useful, both denitrification

7 and sediment oxygen consumption rates had to be available coincidentally. Our data set

8 contains 657 data points that meet this minimum requirement. We also compiled

9 approximately 463 data points with coincident measurements of nitrate, ammonium and

10 phosphate fluxes between sediment and bottom water, and bottom water concentrations

11 of oxygen and nitrate. For some of these points, additional information, such as sediment

12 type or primary productivity rates, are available as well.

13

14 Our data originate from different aquatic environments, ranging from freshwater systems

15 (Lake Champlain and Old Woman Creek, Lake Erie) and brackish waters (Chesapeake

16 Bay and Corpus Christi Bay, Gulf of Mexico) to oceanic continental shelves (Arctic,

17 Washington and Middle Atlantic Bight shelves and the East China Sea). Data sources,

18 site descriptions and measurement techniques are listed in Table 1. The data compilation

19 is included as Supplementary Online Material. Denitrification rates were determined by

20 measuring  $N_2:Ar$  ratios with membrane-inlet mass spectrometry (MIMS; Kana et al.

21 1994, 1998), except for the data from Lake Champlain, the University of Rhode Island

22 (URI) mesocosm experiments, Chesapeake Bay and the East China Sea. For data from

23 Lake Champlain, the URI mesocosms and Chesapeake Bay, we calculated denitrification

1 assuming Redfield stoichiometry for organic matter remineralization and a respiratory  
2 coefficient of one (one mol organic carbon remineralized per mol O<sub>2</sub> consumed). We  
3 assume that denitrification accounts for the deficit in dissolved inorganic nitrogen flux  
4 from the sediment with respect to the flux expected based on organic matter  
5 remineralization (using sediment oxygen consumption as reference; see Table 2). For the  
6 data from the East China Sea we calculated denitrification as the difference between the  
7 production rate of ammonium and the sediment efflux of ammonium and nitrate (see  
8 Table 2).

9

### 10 **Mean tendencies**

11 On average, the sediments in our data collection are a net sink of bioavailable nitrogen  
12 with a mean and median denitrification rate of 2.2 mmol N m<sup>-2</sup> d<sup>-1</sup> and 1.5 mmol N m<sup>-2</sup>  
13 d<sup>-1</sup>, respectively, and consumed oxygen at a mean and median rate of 27.0 and 20.1  
14 mmol O<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup>, respectively (Figures 1c, 2a). On average, the flux of nitrate and  
15 phosphate into bottom waters is negligible, with median fluxes of 0.06 mmol NO<sub>3</sub> m<sup>-2</sup> d<sup>-1</sup>  
16 and 0.03 mmol PO<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup> (Figure 1, phosphate flux not shown). Recycled bioavailable  
17 nitrogen is returned to the bottom water as ammonium at mean and median rates of 2.0  
18 and 0.84 mmol N m<sup>-2</sup> d<sup>-1</sup>, respectively (Figure 1b).

19

20 There are 39 data points with net nitrogen fixation in our data set; 15 from Narragansett  
21 Bay sediments, 22 from Corpus Christi Bay and 2 from Old Woman Creek. Biological  
22 nitrogen fixation associated with autotrophic nitrogen fixers, such as cyanobacterial mats  
23 and seagrass beds, occurs in shallow subtropical and tropical sediments, and can be an

1 important nitrogen source (Paerl & Zehr 2000). Nitrogen fixers in Old Woman Creek  
2 and Corpus Christi Bay are probably cyanobacteria (McCarthy et al. 2007, 2008).  
3 However, no cyanobacterial pigments were found in Narraganset Bay sediments, where  
4 high rates (3 to 5 mmol N m<sup>-2</sup> d<sup>-1</sup>) were observed during the summer of 2006 (Fulweiler  
5 et al. 2007). The N<sub>2</sub>:Ar technique only measures the net N<sub>2</sub> flux resulting from both  
6 denitrification and nitrogen fixation, thus masking the individual contributions of both  
7 processes. However, when combined with the isotope-pairing technique (An et al. 2001;  
8 Gardner et al. 2006), individual rates can be estimated simultaneously (with the caveat  
9 that rates may be sensitive to the bottom-water nitrate concentration and thus can be  
10 affected by the addition of isotopically labeled nitrate). Nitrogen fixation and  
11 denitrification occurred simultaneously in estuaries of the northern Gulf of Mexico at  
12 rates an order of magnitude above the observed net N<sub>2</sub> flux (Gardner et al. 2006).  
13  
14 We estimated the nitrification rate as the sum of N<sub>2</sub>, NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> efflux from the  
15 sediment (data points with net N<sub>2</sub> flux into the sediment were excluded from this  
16 calculation). On average (median), 17% of the total sediment oxygen consumption is due  
17 to nitrification of ammonium to nitrite or nitrate.  
18  
19 We assessed the potential contribution of bottom water nitrate to the observed  
20 denitrification flux (i.e. the potential for direct denitrification), assuming that any uptake  
21 of bottom-water nitrate by the sediment would be denitrified. This assumption will  
22 overestimate the importance of direct denitrification where dissimilatory nitrate reduction

1 to ammonium is important. Even so, in most of our data points (75%), the potential  
2 contribution of bottom-water nitrate to the observed denitrification flux was small (<1%).

3  
4 The oxidation of organic carbon in sediments occurs through aerobic mineralization as do  
5 a range of anaerobic processes, including denitrification, and manganese, iron and sulfate  
6 reduction. The rate of carbon oxidation by all processes other than denitrification can be  
7 approximated as the difference between total sediment oxygen consumption and oxygen  
8 consumption during nitrification, assuming a respiratory coefficient of one (one mole of  
9 O<sub>2</sub> is used in the oxidation of one mol of organic carbon; see Giblin et al. 1997, Rysgaard  
10 et al. 1998). We calculated total carbon oxidation as the sum of carbon oxidation by  
11 denitrification, assuming a C:N ratio of 106:84.8, and carbon oxidation by all other  
12 processes based on sediment oxygen consumption (Figure 2b; see Table 2 for detail on  
13 the calculation). The resulting median rate is 19 mmol C m<sup>-2</sup> d<sup>-1</sup> and 11% (median) of  
14 this rate is supported by denitrification (Figure 2c).

15

#### 16 **Environmental control on N cycling processes**

17 A number of studies report relationships between sediment nitrogen cycling processes  
18 and environmental variables/characteristics. For example, a decrease of nitrification (and  
19 subsequent increase of ammonium efflux from the sediment) with decreasing  
20 concentrations of bottom-water oxygen has been observed (Klump & Martens 1987;  
21 Kemp et al. 1990; Caffrey et al. 1993). An increase in the mean ammonium flux from the  
22 sediment with increasing salinity was observed in Texas estuaries and attributed to an  
23 increase in dissimilatory nitrate reduction to ammonium (DNRA) relative to

1 denitrification (Gardner et al. 2006). An increase in total and direct denitrification was  
2 related to increasing concentrations of nitrate in the bottom water (Kana et al. 1998 and  
3 references therein). We used our data compilation, which spans a range of systems and  
4 environmental conditions, to assess whether these relationships are robust across systems.

5  
6 Bottom-water oxygen concentrations in our data set range between 62 and 440 mmol O<sub>2</sub>  
7 m<sup>-3</sup> with a median of 203 mmol O<sub>2</sub> m<sup>-3</sup>. When comparing the median nitrification fluxes  
8 for bottom water oxygen concentrations smaller and larger than 94 mmol O<sub>2</sub> m<sup>-3</sup> (2.2 and  
9 2.3 mmol N m<sup>-2</sup> d<sup>-1</sup>, respectively), only a small and statistically insignificant increase is  
10 seen, probably because we do not have a good representation of low oxygen  
11 environments in our data set.

12  
13 We investigated whether ammonium fluxes increase with increasing salinity in our data  
14 set by comparing total ammonium efflux and the ammonium fraction of the total nitrogen  
15 flux from our two freshwater systems to the flux from Chesapeake Bay, Corpus Christi  
16 Bay and the Middle Atlantic Bight coastal regions (salinities of 0, 15 to 20, 24 to 28 and  
17 30 to 32 PSU, respectively; see Table 1). We found a small, statistically insignificant  
18 decrease in ammonium fluxes with increasing salinity. To account for differences in  
19 sediment type, nutrient loading and organic matter supply to the sediment between these  
20 systems, we also compared the ratio of ammonium efflux to total nitrogen flux and found  
21 an increase with increasing salinities, in agreement with the results from Texas estuaries  
22 (Gardner et al. 2006). However, the differences in median are not statistically significant,

1 hence, no general conclusions about the relationship between ammonium fluxes and  
2 salinity can be drawn.

3

4 We found an increase of total denitrification with increasing bottom water nitrate  
5 concentrations as well as an increase in the ratio of sediment nitrate uptake to total  
6 denitrification (which one can interpret as an increase in the rate of direct denitrification).

7 For bottom water nitrate concentrations below and above  $40 \text{ mmol N m}^{-3}$ , the median  
8 denitrification fluxes are  $1.8$  and  $2.6 \text{ mmol N m}^{-2} \text{ d}^{-1}$ , respectively. The difference is  
9 statistically highly significant ( $p < 0.0001$ ). The median ratios of sediment nitrate uptake  
10 to total denitrification are  $0$  and  $0.83$  for bottom-water nitrate concentrations below and  
11 above  $40 \text{ mmol N m}^{-3}$ , respectively (significant at  $p < 0.001$ ).

12

### 13 **APPLICATION OF DATA TO MODELS**

14 Denitrification in aquatic sediments has long been recognized as an important sink of  
15 fixed nitrogen. Approaches to modeling denitrification are crucial for a meaningful  
16 extrapolation of local estimates of denitrification to larger spatial and temporal scales, as  
17 well as for inclusion of this process in predictive models of aquatic ecosystems. Two  
18 principal approaches for describing the impacts of sediment denitrification on nitrogen  
19 fluxes across the sediment-water interface exist and have been described above ('Model  
20 approaches'): empirical parameterizations and detailed mechanistic descriptions of  
21 diagenetic processes. Integration of these model approaches with measurements is  
22 crucial, but qualitatively different for both approaches. While empirical  
23 parameterizations are inherently data-based, the diagenetic models do not use

1 observations directly. Diagenetic models require specification of a number of model  
2 parameters, the validity of which can typically only be estimated *a posteriori*, by  
3 comparing model predictions with observations.

4

5 Our data compilation allows us to look for relationships between variables that could  
6 potentially be used to improve predictive parameterizations of denitrification, to  
7 reevaluate published parameterizations, and to evaluate the denitrification rates predicted  
8 by diagenetic models. While diagenetic models have typically been applied to specific  
9 sites, the model of Soetaert et al. (1996b) has been generalized to cover the global scale  
10 by means of a meta-analysis (Middelburg et al. 1996). We will use this meta-analysis  
11 below as an example of a diagenetic model. We first discuss a multivariate regression  
12 analysis of our data set and reevaluate the regression between denitrification and  
13 sediment oxygen consumption; we then analyze differences between nitrogen and  
14 phosphate fluxes across the sediment-water interface; finally, we discuss qualitative  
15 differences between parameterizations and diagenetic models by contrasting  
16 denitrification fluxes predicted by a diagenetic model (Middelburg et al. 1996; Soetaert et  
17 al. 1996b) with an empirical relationship derived from our data set.

18

### 19 **Regression analysis**

20 The existence of robust relationships between nitrogen cycling processes and  
21 environmental variables, such as organic matter supply, sediment oxygen consumption,  
22 benthic community structure, sediment type, seasonality or trophic status, and across a  
23 diversity of systems would underpin predictive modeling of denitrification beyond the

1 regional scale of individual studies. We assessed whether previously reported  
 2 relationships, like a decrease of nitrification for low bottom water oxygen concentrations,  
 3 an increase of ammonium efflux with increasing salinity, or an increase in the  
 4 contribution of direct to total denitrification with increasing bottom water nitrate  
 5 concentrations are expressed in our data compilation. The only relationship we found to  
 6 be robust was the increase of direct denitrification with increasing bottom water nitrate  
 7 ('Environmental control on N cycling processes').

8

9 Parameterizations of sediment denitrification have relied on correlations with sediment  
 10 oxygen consumption (SOC), but the inclusion of additional factors like the bottom water  
 11 concentrations of nitrate and oxygen in parameterizations could potentially improve the  
 12 predictive skill of parameterizations. We assessed this possibility for the variables in our  
 13 data compilation by deriving a multiple regression between coupled denitrification ( $J_{N_2}$  in  
 14  $\text{mmol N m}^{-2} \text{d}^{-1}$ ) and the independent variables SOC ( $J_{O_2}$  in  $\text{mmol O}_2 \text{m}^{-2} \text{d}^{-1}$ ), the fluxes  
 15 of phosphate ( $J_{PO_4}$  in  $\text{mmol P m}^{-2} \text{d}^{-1}$ ), nitrate ( $J_{NO_3}$  in  $\text{mmol N m}^{-2} \text{d}^{-1}$ ), ammonium ( $J_{NH_4}$   
 16 in  $\text{mmol N m}^{-2} \text{d}^{-1}$ ) and the bottom water concentrations of nitrate ( $\text{NO}_3$  in  $\text{mmol N m}^{-3}$ )  
 17 and oxygen ( $\text{O}_2$  in  $\text{mmol m}^{-3}$ ) as

$$18 \quad J_{N_2} = -1.7229 - 0.079895 J_{O_2} + 1.9497 J_{PO_4} - 0.4435 J_{NO_3} - 0.14878 J_{NH_4} - 0.0082778$$

$$19 \quad \text{NO}_3 + 0.00687808 \text{O}_2.$$

20 The residuals and standardized partial regression coefficients are shown in Figure 3. The  
 21 standardized partial regression coefficients are all in units of standard deviation and can  
 22 be compared directly to determine the relative effectiveness of the independent variables  
 23 as predictors of the dependent variable,  $J_{N_2}$ . The most effective variables are sediment



1 oxygen consumption and the sediment-water flux of nitrate. In contrast to our  
2 expectation, the bottom-water concentrations of nitrate and oxygen are the least effective  
3 predictors in the overall regression. By iteratively removing the least effective  
4 independent variable (i.e. the variable with the smallest standardized partial regression),  
5 we determined regressions for smaller subsets of the independent variables. It became  
6 apparent that the bottom water concentrations (i.e. variables that are comparatively easy  
7 to measure or estimate) added little predictive power (the  $R$  value decreased  
8 insignificantly, from 0.68 to 0.67).

9  
10 We also derived a linear regression between the coupled nitrification-denitrification flux  
11 and sediment oxygen consumption using all data points in our data set (Figure 4, red line)  
12 and using only data points where no net N fixation occurs (Figure 4, green line). Both  
13 relationships are statistically significant at the 1% level ( $F$  test). The slope of this  
14 relationship (0.09) is comparable to but lower than Seitzinger & Giblin's (1996) slope of  
15 0.12. This discrepancy is not surprising given the larger data set used here. The  
16 relatively low  $R$  value of 0.55 in our regression is likely due to differences in sediment  
17 type and biogeochemical environment across systems. For example, variations in the  
18 relative importance of canonical denitrification and anammox to the total rate of  $N_2$   
19 production would lead to a different stoichiometry and thus different regression  
20 coefficients. The most important difference between anammox and canonical  
21 denitrification is that anammox does not involve oxidation of organic matter. Anammox  
22 is not directly tied to carbon oxidation but depends on the supply of  $NO_3^-$  and  $NO_2^-$  that  
23 is mostly derived from nitrification of ammonium produced in the respiration of organic

1 matter (an indirect link to organic matter oxidation). Hence, the C-to-O-to-N  
2 stoichiometry of N<sub>2</sub> production via the pathway of ammonification → nitrification →  
3 canonical denitrification is different from that of N<sub>2</sub> production via ammonification →  
4 nitrification → anammox. Our data set is not comprehensive enough to assess the  
5 relative importance of both pathways. One would need coincident measurements of  
6 sediment-water fluxes of CO<sub>2</sub>, O<sub>2</sub> and all the nitrogen species.

7

### 8 **Phosphate fluxes**

9 The fate of mineralized phosphate in sediments is qualitatively different than that of  
10 mineralized nitrogen, in that phosphate is bound to iron and manganese minerals under  
11 oxic conditions. It has been suggested that the extent to which phosphate can be bound in  
12 sediments is dramatically different between freshwater and brackish/marine systems, and  
13 that phosphate is essentially a conservative tracer of benthic decomposition in marine  
14 sediments, but is strongly retained in freshwater sediments (Caraco et al. 1990). This  
15 apparent difference was suggested to explain the observed differences in nutrient  
16 limitation between marine and freshwater systems, with nitrogen often limiting in marine  
17 systems and phosphorus more typically limiting in freshwater systems (Caraco et al.  
18 1990).

19

20 We analyzed the N\* ( $N^* = N - 16 \times P$ ) of sediment-water nutrient fluxes to see whether  
21 our data are consistent with the notion that phosphate is a conservative tracer of benthic  
22 decomposition in marine sediments and whether there are systematic differences in the  
23 stoichiometry of the nutrient return flux from sediments between freshwater and marine

1 systems. The  $N^*$  values of total nitrogen ( $N_2 + NO_3^- + NH_4^+$ ) flux versus phosphate flux  
2 are shown in Figure 5 for all our data points and separately for freshwater and marine  
3 systems. In all three cases the mean  $N^*$  is significantly larger than zero which  
4 corresponds to the canonical Redfield ratio of 16 ( $t$ -test,  $p \ll 0.01$ ). Our data thus  
5 indicates that phosphate is retained more strongly than nitrogen in the sediments  
6 represented in our data set (all are overlaid by oxic bottom waters) and hence not a  
7 conservative tracer of benthic remineralization. However, the analysis in Figure 5  
8 includes nitrogen that is returned as biologically unavailable  $N_2$  gas and thus not directly  
9 relevant for assessing nutrient limitation. We repeated the analysis for  $N^*$  calculated  
10 from the bioavailable nitrogen ( $NO_3^- + NH_4^+$ ) flux versus phosphate flux (Figure 6). In  
11 this case the  $N^*$  values are not statistically different from zero ( $t$ -test, 1% significance  
12 level). In other words the stoichiometry of nutrient fluxes from the sediment is  
13 statistically not significantly different from the Redfield ratio of 16. Our data hence  
14 suggest that both processes, phosphate retention in sediments and nitrogen removal  
15 through denitrification, contribute to the N:P stoichiometry of bioavailable nutrients  
16 returned from the sediment. Since our analysis does not suggest consistent differences in  
17 the N:P ratio of returned bioavailable nutrients, sediment nutrient fluxes do not appear to  
18 be a good explanation for the change in nutrient limitation from fresh to salt water, at  
19 least not in our data set which is limited for freshwater systems.

20

### 21 **Diagenetic model versus parameterization**

22 Detailed diagenetic models and simpler empirical parameterizations have different  
23 strengths and limitations. The empirical parameterizations are inherently data-based,

1 have the advantage of being conceptually simple and easy to implement, but they cannot  
2 capture strong non-linearities or system hysteresis, for example the non-linear response to  
3 nutrient reduction observed in the Chesapeake Bay (Kemp et al. 2005). Diagenetic  
4 models are based on a mechanistic understanding of sediment processes, include  
5 nonlinear feedback mechanisms and can include temporal dependencies such as delays or  
6 storage of organic matter. As such they are more flexible and have the potential to  
7 correctly predict system responses to changes in eutrophication status or oxygen supply;  
8 for example, the Sediment Flux Model applied to data from a mesocosm eutrophication  
9 experiment (see our ‘Layered dynamic models’ subsection; DiToro 2001). They can  
10 also be extremely useful tools to further our mechanistic understanding; for example, the  
11 microzone model (see ‘Microenvironments’ subsection) can explain the counterintuitive  
12 observation of rapid denitrification observed in the presence of oxic pore water in  
13 continental shelf sands with very low pore water nitrate concentrations (Rao et al. 2007).  
14 On the other hand, these mechanistic models typically require detailed knowledge about  
15 parameter values, such as reaction kinetics and sediment characteristics. For example,  
16 the microzone denitrification model requires knowledge about the size, reactivity, and  
17 composition of reactive sediment microenvironments. Likewise, layered diagenetic  
18 models require a number of parameters describing reaction kinetics, sediment porosity  
19 and assumptions about organic matter lability.

20

21 Middelburg et al. (1996) applied the diagenetic model of Soetart et al. (1996) to the  
22 global ocean by assuming uniform values for rate, limitation and inhibition parameters,  
23 and a uniform porosity profile. However, their predicted denitrification rates show a

1 markedly different behavior than our data compilation suggests and overestimate the  
2 observations for SOC rates, ranging from 5 to 50 mmol O<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> (Figure 4). Note that  
3 their parameterization relates denitrification to organic matter flux, which we considered  
4 equal to sediment oxygen consumption (assuming steady state and a metabolic quotient  
5 of 1 mol C:1 mol O<sub>2</sub>). Because of the observational and conceptual difficulties with  
6 sedimentation flux in shallow systems, we recommend using SOC instead of  
7 sedimentation flux when deriving parameterizations using denitrification measurements,  
8 although sedimentation flux is typically the relevant quantity predicted by ecosystem  
9 models coupled to hydrodynamic models or General Circulation Models. The poor  
10 agreement between the observed denitrification rates and the rates predicted by the  
11 diagenetic model may indicate that parameters and porosity profiles are not globally  
12 applicable, as had been assumed. This interpretation is consistent with our finding that  
13 bottom-water nitrate and oxygen concentrations were the least effective predictors in our  
14 data set when included in a multivariate regression between denitrification and SOC (they  
15 improved the coefficient of determination only insignificantly), while they were the most  
16 important drivers in determining denitrification in sensitivity studies with the diagenetic  
17 model (Soetaert et al. 1996). Assessing whether this discrepancy is indeed due to  
18 differences like hydrographic setting, sediment type and benthic community across  
19 systems is beyond the scope of this study. In a systematic assessment, one would apply  
20 the diagenetic model to different sites that have detailed observations including pore water  
21 profiles available.

22

23

24 **CONCLUSIONS**

1 There are no conceptual or technical difficulties in applying empirical parameterizations  
2 or diagenetic models to large spatial scales. However, because diagenetic models are  
3 typically tuned to match observations at specific sites there is no guarantee they will  
4 make good predictors across larger spatial scales. The major difficulty thus lies in  
5 evaluating fluxes predicted by diagenetic models against observations. We compared  
6 denitrification rates predicted by a diagenetic model (Middelburg et al. 1996) with  
7 observations in our data compilation after converting the organic carbon sedimentation  
8 flux to sediment oxygen consumption units and found that the diagenetically predicted  
9 fluxes significantly overestimate observed fluxes. Systematic studies will be necessary to  
10 elucidate the underlying reasons; it is likely that regional adaptations of the model for  
11 different environments and sediment types will be necessary. This would require a  
12 spatially explicit characterization of benthic environments/sediment types, along with rate  
13 measurements in all characteristic environments.

14

15 Based on our analysis, we recommend using empirical regressions between SOC and  
16 denitrification for predicting denitrification in oxic bottom waters. We calculated the  
17 linear relationship between sediment denitrification and sediment oxygen consumption  
18 suggested by Seitzinger & Giblin (1996) for the larger data set compiled here and found a  
19 similar regression slope, but a much smaller coefficient of determination (Figure 4). One  
20 reason for the uncertainty in our regression may be variations in the relative importance  
21 of canonical denitrification versus anammox across different systems, since the  
22 underlying stoichiometries are different. Inclusion of bottom water concentrations of

1 nitrate and oxygen in a multivariate regression did not improve the coefficient of  
2 determination significantly.

3

4 For suboxic and anoxic bottom waters (oxygen concentrations below  $63 \text{ mmol O}_2 \text{ m}^{-3}$ )  
5 strong feedbacks on elemental cycling can occur, but these conditions were not  
6 represented in our data set. Perhaps the most relevant feedback in this context is the  
7 inhibition of nitrification and thus denitrification at these low oxygen levels (Childs et al.  
8 2002). A linear parameterization of SOC and denitrification cannot capture this response  
9 and a non-linear multivariate regression based either exclusively on measurements or on  
10 a combination of measurements and model-predicted rates will be necessary for such  
11 cases.

12

13 **Acknowledgements:** Discussions reflected in this paper were initiated in November  
14 2006 at a Modeling Workshop organized by the Research Coordination Network on  
15 Denitrification (<http://www.denitrification.org/>). We thank the organizers and gratefully  
16 acknowledge the constructive criticism from Eric Davidson and two anonymous  
17 reviewers. We thank Jane Tucker for working up the data sets from Massachusetts Bay  
18 and Boston Harbor. Financial support for AEG to work on the manuscript came from  
19 NSF NSF-DEB-0423565. KF, DB and DDT acknowledge support from NOAA CHRP  
20 grant NA07NOS4780191. NOAA publication number 102.

21

1 **Table 1:** Data sources, measurement methods and references.

| <b>Region</b><br>Site Description<br>(# of data points)                             | <b>Salinity</b> | <b>Measurement technique</b>  |
|---|-----------------|---|
| <b>Lake Champlain</b><br>(15)   | 0               | Box core samples were taken; fluxes and overlying water concentrations of NH <sub>4</sub> , NO <sub>3</sub> , PO <sub>4</sub> , O <sub>2</sub> were measured; methods described in Cornwell & Owens (1999); tabulated data from DiToro (2001)                             |
| <b>Old Woman Creek</b><br>hypereutrophic wetland,<br>Lake Erie (72)                 | 0               | Sediment cores were incubated in a continuous-flow system; N <sub>2</sub> :Ar ratios were measured with membrane-inlet mass spectrometry (MIMS); data from McCarthy et al. (2007)   |
| <b>Chesapeake Bay</b><br>eutrophic, seasonally<br>hypoxic estuary (82)              | 15–20           | Box core samples were taken; fluxes and overlying water concentrations of NH <sub>4</sub> , NO <sub>3</sub> , PO <sub>4</sub> , O <sub>2</sub> were measured; methods described in Cowan & Boynton (1996); tabulated data from DiToro (2001)                              |
| <b>Corpus Christi Bay</b><br>estuary on the shoreline of<br>the Gulf of Mexico (55) | 25–29           | Sediment cores were incubated in a continuous-flow system; N <sub>2</sub> :Ar ratios were measured with MIMS; data from McCarthy et al. (2008)  |
| <b>Narragansett Bay</b><br>Mid-Atlantic Bight inner<br>shelf (93)                   | 30–32           | Sediment cores were incubated; N <sub>2</sub> :Ar ratios were measured with MIMS; data from Fulweiler et al. (2007); Fulweiler (2007); Fulweiler & Nixon (in press)   |
| <b>New Jersey Shelf</b><br>coastal ocean in the Mid-<br>Atlantic Bight (20)         | 30–32           | <i>In situ</i> benthic chambers; N <sub>2</sub> :Ar ratios measured with MIMS; data from Laursen & Seitzinger (2002)  |
| <b>Mesocosms</b><br>facility at the Univ. of<br>Rhode Island (139)                  | 30–32           | Fluxes and overlying water concentrations of NH <sub>4</sub> , NO <sub>3</sub> , PO <sub>4</sub> , O <sub>2</sub> were measured in mesocosms; data from the Nutrient Addition Experiment (Oviatt et al. 1986); tabulated data from DiToro (2001)                          |
| <b>Boston Harbor</b><br>Gulf of Maine inner shelf<br>(32)                           | 28–34           | Sediment cores were incubated at <i>in situ</i> temperatures; fluxes of O <sub>2</sub> , PO <sub>4</sub> , NH <sub>4</sub> , NO <sub>3</sub> + NO <sub>2</sub> were measured using standard techniques (Giblin et al. 1997); N <sub>2</sub> :Ar ratios measured with MIMS |
| <b>Massachusetts Bay</b><br>Gulf of Maine inner shelf<br>(48)                       | 32–34           | Same as Boston Harbor   |
| <b>Gulf of Mexico</b><br>Coastal, seasonally hypoxic<br>ocean (36)                  | 32–34           | Sediment cores were incubated in a continuous-flow system; N <sub>2</sub> :Ar ratios were measured with MIMS; data Gardner & McCarthy (unpublished)   |
| <b>Mississippi River Plume</b><br>Gulf of Mexico (4)                                | 32–34           | Benthic chambers; N <sub>2</sub> fluxes estimated stoichiometrically; data from Gardner et al. (1993)   |
| <b>South Atlantic Bight</b><br>(4)  | oceanic         | Sediment oxygen consumption and denitrification calculated from volumetric rates obtained in sediment columns (Rao et al. 2007)   |
| <b>East China Sea</b><br>(21)   | oceanic         | Sediment core incubations; described in Aller et al. (1985)   |
| <b>Different shelf and open<br/>ocean regions</b><br>(41)                           | oceanic         | Data compilation from Middelburg et al. (1997)  |
| <b>Washington Shelf</b><br>continental shelf<br>(17)                                | oceanic         | <i>In situ</i> benthic chambers; N <sub>2</sub> fluxes measured with gas chromatography; data from Devol & Christensen (1993)   |
| <b>Western Arctic Shelf</b><br>Continental shelf<br>(22)                            | oceanic         | <i>In situ</i> benthic chambers; N <sub>2</sub> fluxes measured with gas chromatography; data from Devol et al. (1997)  |

2

3



1 **Table 2:** List of symbols and formulae for derived quantities.  
2

| <b>Symbol</b>  | <b>Description</b>  | <b>Unit</b>  |
|--|---|--|
| $J_{N_2}$  | N <sub>2</sub> flux across sediment-water interface due to sediment denitrification                   | mmol N m <sup>-2</sup> d <sup>-1</sup>   |
| $J_{O_2}$  | O <sub>2</sub> flux across sediment-water interface due to sediment oxygen consumption                | mmol O <sub>2</sub> m <sup>-2</sup> d <sup>-1</sup>                            |
| $J_{NH_4}$   | NH <sub>4</sub> <sup>+</sup> flux across sediment-water interface                                     | mmol N m <sup>-2</sup> d <sup>-1</sup>   |
| $J_{NO_3}$   | NO <sub>3</sub> <sup>-</sup> flux across sediment-water interface                                     | mmol N m <sup>-2</sup> d <sup>-1</sup>   |
| $JP_{NH_4}$  | Production of NH <sub>4</sub> <sup>+</sup> (ammonification rate)                                      | mmol N m <sup>-2</sup> d <sup>-1</sup>   |
| $JP_{NO_3}$  | Production of NO <sub>3</sub> <sup>-</sup> (nitrification rate)                                       | mmol N m <sup>-2</sup> d <sup>-1</sup>   |
| $JP_{CO_2}$  | Production of CO <sub>2</sub> (total carbon oxidation rate)   | mmol C m <sup>-2</sup> d <sup>-1</sup>   |
| $JP_{CO_2;DNF}$  | Production of CO <sub>2</sub> due to denitrification (carbon oxidation attributed to denitrification) | mmol C m <sup>-2</sup> d <sup>-1</sup>   |
| <b>Derived quantities</b>                                |   | <b>Applied to</b>  |
| $J_{N_2} = -J_{O_2}/6.625 - J_{NO_3} - J_{NH_4}$         |   | Data from Chesapeake Bay, University of Rhode Island mesocosms, Lake Champlain |
| $J_{N_2} = JP_{NH_4} - J_{NH_4} - J_{NO_3}$              |   | East China Sea data  |
| $JP_{NO_3} = J_{N_2} + J_{NO_3}$                         |   | All data points with $J_{N_2} > 0$ (i.e. with net denitrification)             |
| $JP_{CO_2} = (106/84.8) J_{N_2} - J_{O_2} - 2 JP_{NO_3}$ |   | All data points with $J_{N_2} > 0$   |
| $JP_{CO_2;DNF} = (106/84.8) J_{N_2}/JP_{CO_2}$           |   | All data points with $J_{N_2} > 0$   |

3  
4

1 **Figure 1:** Histogram, mean (solid line) and median (dashed line) N fluxes in our data set.  
2 Positive values indicate efflux from the sediments. Negative values indicate uptake by  
3 the sediments. Positive and negative outliers are collected in the bins for the largest and  
4 smallest value, respectively.

5 **Figure 2:** Histogram, mean (solid line) and median (dashed line) sediment oxygen  
6 consumption (SOC), total carbon oxidation and the fraction of carbon oxidation carried  
7 out by denitrifiers in our data set. Positive outliers are collected in the bins for the largest  
8 value.

9 **Figure 3:** Residuals (top panel) and standardized partial regression coefficients (bottom  
10 panel) for multiple regression of coupled nitrification-denitrification flux. Independent  
11 variables are sediment oxygen consumption (SOC), sediment-water fluxes of phosphate,  
12 nitrate and ammonium, and bottom water concentrations of nitrate and oxygen (see  
13 'Regression analysis' in 'Results and discussion' for regression coefficients). Regression  
14 coefficients were standardized by multiplying with the ratio of standard deviations of the  
15 independent and dependent variable. Standardized partial regression coefficients can be  
16 compared directly to assess which independent variables are most effective in  
17 determining the denitrification flux.

18 **Figure 4:** Linear regression (red line) of denitrification and sediment oxygen  
19 consumption (SOC) for all of our data points (gray dots) and excluding data points with  
20 net N<sub>2</sub> flux into the sediment, i.e. when net N fixation is occurring (green line, with 50%  
21 confidence limits as dashed lines) in comparison with Seitzinger & Giblin's (1996)  
22 regression (blue line) and Middelburg et al.'s (1996) parameterization (magenta line).

- 1 Note that Middelburg's parameterization relates carbon flux to denitrification flux. We  
2 converted from carbon flux to SOC, assuming a 1 mol C:1 mol O<sub>2</sub> quotient.
- 3 **Figure 5:** Histogram, mean (solid line) and median (dashed line) for N\* of total  
4 remineralized nitrogen (NH<sub>4</sub><sup>+</sup> + NO<sub>3</sub><sup>-</sup> + N<sub>2</sub>) versus phosphate flux (N\*=N-16×P) for all  
5 data points (top), freshwater only (middle) and marine systems only (bottom). The N\* of  
6 zero corresponds to the Redfield ratio and is indicated by the dotted line. Outliers that  
7 fall outside the axis range are collected in the largest and smallest bins.
- 8 **Figure 6:** As in Figure 5, but for bioavailable nitrogen flux (NH<sub>4</sub><sup>+</sup> + NO<sub>3</sub><sup>-</sup>).
- 9

1 **References**

- 2 Aller RC (1980) Quantifying solute distributions in the bioturbated zone of marine  
3 sediments by defining an average microenvironment. *Geochim Cosmochim Acta*  
4 44(12):1955–1965
- 5 Aller RC (1988) Benthic fauna and biogeochemical processes in marine sediments: the  
6 role of burrow structures. In: Blackburn TH, Soerensen J (eds) *Nitrogen Cycling in*  
7 *Coastal Marine Environments*. John Wiley & Sons Ltd;. pp 301–338
- 8 Aller RC, Mackin JE, Ullman WJ, Wang CH, Tsai SM, Jin JC, et al. (1985) Early  
9 chemical diagenesis, sediment-water solute exchange, and storage of reactive organic  
10 matter near the mouth of the Changjiang, East China Sea. *Cont.Shelf Res.*;4(1/2):227-51.
- 11 Altabet MA, Francois R, Murray DW, Prell WL (1995) Climate-related variations in  
12 denitrification in the Arabian Sea from sediment  $^{15}\text{N}/^{14}\text{N}$  ratios. *Nature*  
13 373(6514):506–509
- 14 Bender M, Jahnke R, Weiss R, Martin W, Heggie DT, Orchardo J, et al. (1989) Organic  
15 carbon oxidation and benthic nitrogen and silica dynamics in San Clemente Basin, a  
16 continental borderland site. *Geochim Cosmochim Acta* 53(3):685–697
- 17 Berner RA (1980) *Early diagenesis: A theoretical approach*. Princeton University Press,  
18 Princeton
- 19 Billen G, Garnier J (1999) Nitrogen transfers through the Seine drainage network: a  
20 budget based on the application of the Riverstrahler' model. *Hydrobiologia* 410:139–150
- 21 Billen G, Garnier J, Hanset P (1994) Modelling phytoplankton development in whole  
22 drainage networks: the RIVERSTRAHLER Model applied to the Seine river system.  
23 *Hydrobiologia* 289(1):119–137.
- 24 Boudreau BP (1997) *Diagenetic models and their implementation: Modelling transport*  
25 *and reactions in aquatic sediments*. Springer, Berlin
- 26 Boyer EW, Alexander RB, Parton WJ, Li C, Butterbach-Bahl K, Donner SD, et al. (2006)  
27 Modeling denitrification in terrestrial and aquatic ecosystems at regional scales: current  
28 approaches and needs. *Ecol Appl* 16:2123–2142.
- 29 Burdige DJ (2006) *Geochemistry of Marine Sediments*. Princeton University Press,  
30 Princeton
- 31 Caffrey JM, Sloth NP, Kaspar HF, Blackburn TH (1993) Effect of organic loading on  
32 nitrification and denitrification in a marine microcosm. *FEMS Microbiol Ecol* 12:159–  
33 167
- 34 Caraco N, Cole J, Likens GE (1990) A comparison of phosphorus immobilization in  
35 sediments of freshwater and coastal marine systems. *Biogeochemistry* 9(3):277–290.

- 1 Cerco CF, Seitzinger SP (1997) Measured and modeled effects of benthic algae on  
2 eutrophication in Indian River-Rehoboth Bay, Delaware. *Estuar Coasts* 20(1):231–248.
- 3 Christensen JP (1994) Carbon export from continental shelves, denitrification and  
4 atmospheric carbon dioxide. *Contl Shelf Res* 14(5):547–576.
- 5 Cornwell J, Owens M (1999) Benthic phosphorus cycling in Lake Champlain: Results of  
6 an integrated field sampling/water quality modeling study. Part B: Field studies. Lake  
7 Champlain Basin Program Tech Rep
- 8 Cowan JLW, Boynton WR (1996) Sediment-water oxygen and nutrient exchanges along  
9 the longitudinal axis of Chesapeake Bay: Seasonal patterns, controlling factors and  
10 ecological significance. *Estuaries* 19(3):562–580
- 11 Dalsgaard T, Canfield DE, Petersen J, Thamdrup B, Acuna-Gonzalez J (2003) N<sub>2</sub>  
12 production by the anammox reaction in the anoxic water column of Golfo Dulce, Costa  
13 Rica. *Nature* 422(6932):606–608
- 14 Devol AH (2008) Chapter 6: Denitrification including Anammox. In: Capone D,  
15 Carpenter E, Mullholland M, Bronk D (eds) *Nitrogen in the Marine Environment*.  
16 Elsevier, Amsterdam, pp 263–302
- 17 Devol AH, Christensen JP (1993) Benthic fluxes and nitrogen cycling in sediments of the  
18 continental margin of the eastern North Pacific. *J Mar Res* 51:345–372
- 19 Devol AH, Codispoti LA, Christensen JP (1997) Summer and winter denitrification rates  
20 in western Arctic shelf sediments. *Cont Shelf Res* 17(9):1029–1050.
- 21 DiToro DM (2001) *Sediment flux modeling*. Wiley-Interscience, New York
- 22 DiToro DM, Fitzpatrick JJ (1993) Chesapeake Bay Sediment Flux Model. US EPA  
23 Contract Report, Annapolis
- 24 Emery K (1968) Relict sediments on continental shelves of world. *AAPG Bull*  
25 52(3):445–464.
- 26 Engström P, Dalsgaard T, Hulth S, Aller RC (2005) Anaerobic ammonium oxidation by  
27 nitrite (anammox): Implications for N<sub>2</sub> production in coastal marine sediments. *Geochim*  
28 *Cosmochim Acta* 69(8):2057–2065
- 29 Falkowski PG (1997) Evolution of the nitrogen cycle and its influence on the biological  
30 sequestration of CO<sub>2</sub> in the ocean. *Nature* 387:272–275
- 31 Fennel K, Follows M, Falkowski PG (2005) The co-evolution of the nitrogen, carbon and  
32 oxygen cycles in the Proterozoic Ocean. *Am J Sci* 305:526–545
- 33 Fennel K, Wilkin J, Levin J, Moisan J, O'Reilly J, Haidvogel D (2006) Nitrogen cycling  
34 in the Middle Atlantic Bight: Results from a three-dimensional model and implications

- 1 for the North Atlantic nitrogen budget. *Global Biogeochemical Cycles* 20, GB3007,  
2 doi:10.1029/2005GB002456
- 3 Fulweiler RW (2007) Climate impacts on benthic-pelagic coupling and biogeochemistry  
4 in Narragansett Bay, RI. PhD Dissertation, University of Rhode Island
- 5 Fulweiler RW, Nixon SW (in press) Responses of benthic-pelagic coupling to climate  
6 change in a temperate estuary. *Hydrobiologia*
- 7 Fulweiler R, Nixon S, Buckley B, Granger S (2007) Reversal of the net dinitrogen gas  
8 flux in coastal marine sediments. *Nature* 448:180–182
- 9 Galloway JN, Aber JD, Erisman JW, Seitzinger SP, Howarth RW, Cowling EB, et al.  
10 (2003) The nitrogen cascade. *Bioscience* 53(4):341–356.
- 11 Gardner WS, Briones EE, Kaegi EC, Rowe GT (1993) Ammonium excretion by benthic  
12 invertebrates and sediment-water nitrogen flux in the Gulf of Mexico near the Mississippi  
13 River plume. *Estuaries* 16(4):799–808.
- 14 Gardner WS, McCarthy MJ, An S, Sobolev D, Sell KS, Brock D (2006) Nitrogen fixation  
15 and dissimilatory nitrate reduction to ammonium (DNRA) support nitrogen dynamics in  
16 Texas estuaries. *Limnol Oceanogr* 51(1):558–568
- 17 Garnier J, Billen G, Coste M (1995) Seasonal succession of diatoms and chlorophyceae  
18 in the drainage network of the Seine River: Observations and modeling. *Limnol*  
19 *Oceanogr* 40(4):750–765
- 20 Giblin AE, Hopkinson CS, Tucker J (1997) Benthic metabolism and nutrient cycling in  
21 Boston Harbor, Massachusetts. *Estuaries* 20:346–364
- 22 Gold AJ, Jacinthe PA, Groffman PM, Wright WR, Puffer RH (1998) Patchiness in  
23 groundwater nitrate removal in a riparian forest. *Environ Qual* 27:146–155
- 24 Harrison J, Maranger R, Alexander RB, Cornwell J, Giblin A, Jacinthe PA, et al. (this  
25 issue) The regional and global significance of nitrogen removal in lakes and reservoirs.  
26 *Biogeochemistry*
- 27 Huettel M, Webster IT (2001) Advective flow in permeable sediments. In: Boudreau BP,  
28 Jørgensen BB (eds) *The benthic boundary layer: Transport processes and*  
29 *biogeochemistry*. Oxford University Press, Oxford pp 144–179
- 30 Jacinthe PA, Groffman PM, Gold AJ, Mosier A (1998) Patchiness in microbial nitrogen  
31 transformations in groundwater in a riparian forest. *J Environ Quality* 27:156–164
- 32 Jahnke R (1985) A model of microenvironments in deep-sea sediments: Formation and  
33 effects on pore water profiles. *Limnol Oceanogr* 30(5):956–965

- 1 Jahnke RA, Emerson SR, Murray JW (1982) A model of oxygen reduction,  
2 denitrification, and organic matter mineralization in marine sediments. *Limnol Oceanogr*  
3 27(4):610–623
- 4 Jahnke RA, Richards M, Nelson J, Robertson C, Rao A, Jahnke D (2005) Organic matter  
5 remineralization and pore water exchange rates in permeable South Atlantic Bight  
6 continental shelf sediments. *Contl Shelf Res* 25:1433–1452
- 7 Kana TM, Darkangelo C, Hunt MD, Oldham JB, Bennett GE, Cornwell JC (1994)  
8 Membrane inlet mass spectrometer for rapid high-precision determination of N<sub>2</sub>, O<sub>2</sub>, and  
9 Ar in environmental water samples. *Anal Chem* 66(23):4166–4170
- 10 Kana TM, Sullivan MB, Cornwell JC, Groszkowski KM (1998) Denitrification in  
11 estuarine sediments determined by membrane inlet mass spectrometry. *Limnol Oceanogr*  
12 43(2):334–339
- 13 Kemp WM, Sampou P, Caffrey J, Mayer M, Henriksen K, Boynton WR (1990)  
14 Ammonium recycling versus denitrification in Chesapeake Bay sediments. *Limnol*  
15 *Oceanogr* 35(7):1545–1563
- 16 Kemp WM, Boynton WR, Adolf JE, Boesch DF, Boicourt WC, Brush G, et al. (2005)  
17 Eutrophication of Chesapeake Bay: historical trends and ecological interactions. *Mar*  
18 *Ecol Prog Ser* 303:1–29
- 19 Klump JV, Martens CS (1987) Biogeochemical cycling in an organic-rich coastal marine  
20 basin. 5. Sedimentary nitrogen and phosphorus budgets based upon kinetic models mass  
21 balaces, and the stoichiometry of nutrient regeneration. *Geochim Cosmochim Acta*  
22 51(5):1161–1173
- 23 Kuypers MM, Sliekers AO, Lavik G, Schmid M, Jorgensen BB, Kuenen JG, et al. (2003)  
24 Anaerobic ammonium oxidation by anammox bacteria in the Black Sea. *Nature*  
25 422(6932):608–11
- 26 Kuypers MMM, Lavik G, Woebken D, Schmid M, Fuchs BM, Amann R, et al. (2005)  
27 Massive nitrogen loss from the Benguela upwelling system through anaerobic ammonium  
28 oxidation. *Proc Natl Acad Sci USA* 102(18):6478–6483
- 29 Laursen AE, Seitzinger SP (2002) The role of denitrification in nitrogen removal and  
30 carbon mineralization in Mid-Atlantic Bight sediments. *Contl Shelf Res* 22:1397–1416
- 31 McCarthy MJ, Gardner WS, Lavrentyev PJ, Moats KM, Jochem FJ, Klarer DM (2007)  
32 Effects of hydrological flow regime on sediment-water interface and water column  
33 nitrogen dynamics in a Great Lakes coastal wetland (Old Woman Creek, Lake Erie). *J*  
34 *Great Lakes Res* 33(1):219
- 35 McCarthy M, McNeal K, Morse J, Gardner W (2008) Bottom-water hypoxia effects on  
36 sediment-water interface nitrogen transformations in a seasonally hypoxic, shallow bay  
37 (Corpus Christi Bay, Texas, USA). *Estuar Coasts* DOI 10.1007/s12237-008-9041-z

- 1 Meissner KJ, Galbraith ED, Völker C (2005) Denitrification under glacial and  
2 interglacial conditions: A physical approach. *Paleoceanography* 20(3)
- 3 Middelburg JJ, Soetaert K, Herman PMJ, Heip C (1996) Denitrification in marine  
4 sediments: A model study. *Global Biogeochem Cyc* 10:661–673
- 5 Middelburg JJ, Soetaert K, Herman PMJ (1997) Empirical relationships for use in global  
6 diagenetic models. *Deep-Sea Res I* 44(2):327–344
- 7 Moore JK, Doney SC (2007) Iron availability limits the ocean nitrogen inventory  
8 stabilizing feedbacks between marine denitrification and nitrogen fixation. *Global*  
9 *Biogeochemical Cycles* 21
- 10 Mulder A, van de Graaf AA, Robertson LA, Kuenen JG (1995) Anaerobic ammonium  
11 oxidation discovered in a denitrifying fluidized bed reactor. *FEMS Microbiol Ecol*  
12 16(3):177–183
- 13 Naqvi SW, Jayakumar DA, Narvekar PV, Naik H, Sarma VV, D'Souza W, et al. (2000)  
14 Increased marine production of N<sub>2</sub>O due to intensifying anoxia on the Indian continental  
15 shelf. *Nature* 408(6810):346–349
- 16 Oviatt CA, Keller AA, Sampou PA, Beatty LL (1986) Patterns of productivity during  
17 eutrophication: a mesocosm experiment. *Mar Ecol Prog Ser* 28(1–2):69–80.
- 18 Paerl H, Zehr J. (2000) Marine nitrogen fixation. In: Kirchman DL (ed) *Microbial*  
19 *Ecology of the Oceans*. Wiley-Liss, Wilmington, pp 387–426
- 20 Parkin TB (1987) Soil microsites as a source of denitrification variability. *Soil Sci Soc*  
21 *Am J* 51:1194–1199
- 22 Rao AMF, McCarthy MJ, Gardner WS, Jahnke RA (2007) Respiration and denitrification  
23 in permeable continental shelf deposits on the South Atlantic Bight: Rates of carbon and  
24 nitrogen cycling from sediment column experiments. *Cont Shelf Res* 27(13):1801–1819
- 25 Richards FA, Cline JD, Broenkow WW, Atkinson LP (1965) Some Consequences of the  
26 Decomposition of Organic Matter in Lake Nitinat, an Anoxic Fjord. *Limnol Oceanogr*  
27 10:185–201
- 28 Risgaard-Petersen N, Meyer RL, Schmid M, Jetten MSM, Enrich-Prast A, Rysgaard S, et  
29 al. (2004) Anaerobic ammonium oxidation in an estuarine sediment. *Aquat Microb Ecol*  
30 36(3):293–304
- 31 Ruelland D, Billen G, Brunstein D, Garnier J. SENEQUE: A multi-scaling GIS interface  
32 to the Riverstrahler model of the biogeochemical functioning of river systems. *Sci Total*  
33 *Environ* 375:257–273



- 1 Seitzinger S, Harrison JA, Bohlke JK, Bouwman AF, Lowrance R, Peterson B, et al.  
2 (2006) Denitrification across landscapes and waterscapes: a synthesis. *Ecol Appl*  
3 16(6):2064–2090
- 4 Soetaert K, Herman PMJ, Middelburg JJ (1996a) Dynamic response of deep-sea  
5 sediments to seasonal variations: A model. *Limnol Oceanogr* 41(8):1651–1668
- 6 Soetaert K, Herman PMJ, Middelburg JJ (1996b) A model of early diagenetic processes  
7 from the shelf to abyssal depths. *Geochim Cosmochim Acta* 60(6):1019–1040
- 8 Soetaert K, Middelburg JJ, Herman PMJ, Buis K (2000) On the coupling of benthic and  
9 pelagic biogeochemical models. *Earth-Sci Rev* 51:173–201
- 10 Thamdrup B, Dalsgaard T (2002) Production of N<sub>2</sub> through anaerobic ammonium  
11 oxidation coupled to nitrate reduction in marine sediments. *Appl Environ Microbiol*  
12 68(3):1312–1318
- 13 Thibodeaux LJ, Boyle JD (1987) Bedform-generated convective transport in bottom  
14 sediment. *Nature* 325(6102):341–343
- 15 Thouvenot M, Billen G, Garnier J Modelling nutrient exchange at the sediment-water  
16 interface of river systems. *J Hydrology* 341(1–2):55–78
- 17 Trimmer M, Nicholls JC, Deflandre B (2003) Anaerobic Ammonium Oxidation  
18 Measured in Sediments along the Thames Estuary, United Kingdom. *Appl Environ*  
19 *Microbiol* 69(11):6447–6454
- 20 Trimmer M, Nicholls JC, Morley N, Davies CA, Aldridge J (2005) Biphase behavior of  
21 anammox regulated by nitrite and nitrate in an estuarine sediment. *Appl Environ*  
22 *Microbiol* 71(4):1923–30
- 23 Vanderborght JP, Wollast R, Billen G (1977a) Kinetic models of diagenesis in disturbed  
24 sediments. Part 1. Mass transfer properties and silica diagenesis. *Limnol Oceanogr*  
25 22(5):787–793
- 26 Vanderborght JP, Wollast R, Billen G (1977b) Kinetic models of diagenesis in disturbed  
27 sediments. Part 2. Nitrogen diagenesis. *Limnol Oceanogr* 22(5):794–803











