

Denitrification effects on air-sea CO₂ flux in the coastal ocean: Simulations for the northwest North Atlantic

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Received 26 September 2008; revised 1 November 2008; accepted 20 November 2008; published 27 December 2008.

[1] The contribution of coastal oceans to the global air-sea CO₂ flux is poorly quantified due to insufficient availability of observations and inherent variability of physical, biological and chemical processes. We present simulated air-sea CO₂ fluxes from a high-resolution biogeochemical model for the North American east coast continental shelves, a region characterized by significant sediment denitrification. Decreased availability of fixed nitrogen due to denitrification reduces primary production and incorporation of inorganic carbon into organic matter, which leads to an increase in seawater *p*CO₂, but also increases alkalinity, which leads to an opposing decrease in seawater *p*CO₂. Comparison of simulations with different numerical treatments of denitrification and alkalinity allow us to separate and quantify the contributions of sediment denitrification to air-sea CO₂ flux. The effective alkalinity flux resulting from denitrification is large compared to estimates of anthropogenically driven coastal acidification.

Citation: Fennel, K., J. Wilkin, M. Previdi, and R. Najjar (2008), Denitrification effects on air-sea CO₂ flux in the coastal ocean: Simulations for the northwest North Atlantic, *Geophys. Res. Lett.*, 35, L24608, doi:10.1029/2008GL036147.

1. Introduction

[2] Air-sea fluxes of CO₂ in coastal oceans are much more variable and typically of larger amplitude than fluxes in the open ocean [Thomas *et al.*, 2004; Tsunogai *et al.*, 1999; Cai *et al.*, 2003] and different mechanisms have been proposed to explain this. For example, the large CO₂ uptake in the South China Sea was attributed to a physical mechanism by which winter cooling of shelf water results in an influx of atmospheric CO₂ due to the temperature-driven increase in solubility [Tsunogai *et al.*, 1999]. In contrast the CO₂ uptake in the North Sea was attributed to a biological mechanism whereby the photosynthetic production of organic matter and its subsequent sinking below the seasonal pycnocline drives uptake of atmospheric CO₂ [Thomas *et al.*, 2004]. Cai *et al.* [2003] observed a large efflux of CO₂ in the South Atlantic Bight and attributed this to net heterotrophy fueled by the import organic carbon from intertidal marshes. This diversity of processes and

explanations illustrates the complexity and regional dependence of coastal carbon fluxes. Indeed, a recent analysis of available observations for the North American coastal oceans concluded that “it is unrealistic to reliably estimate an annual flux” [Doney *et al.*, 2004].

[3] Coastal areas are also important sites for sediment denitrification [Devol and Christensen, 1993; Rao *et al.*, 2007; Seitzinger, 1988]. Using a coupled physical-biogeochemical model for the continental shelf of eastern North America we estimated that sediment denitrification removes a significant amount of fixed nitrogen on North Atlantic continental shelves and hypothesized that large sediment denitrification fluxes lead to a decreased capacity for biologically driven uptake of atmospheric CO₂ [Fennel *et al.*, 2006]. Biologically driven CO₂ uptake is due to the incorporation of dissolved inorganic carbon (DIC) into organic matter. The availability of fixed nitrogen, which is typically the limiting nutrient in coastal oceans, sets an upper limit on the amount of DIC that can be incorporated into organic matter. A decrease in nitrogen availability through denitrification decreases the potential for incorporating DIC into organic matter and thus biologically driven uptake of CO₂.

[4] However, the above argument neglects the fact that an alteration of nitrate concentrations affects alkalinity. The partial pressure of CO₂ in seawater (*p*CO₂), which is the relevant carbon variable for air-sea gas exchange, depends on the concentration of DIC, alkalinity, temperature and salinity. An increase in alkalinity will result in a decrease of *p*CO₂ thus driving CO₂ uptake from the atmosphere. Alkalinity is a measure of the charge balance of seawater and increases during nitrate uptake by one alkalinity equivalent per mol nitrate assimilated [Goldman and Brewer, 1980]. As long as all organic nitrogen is returned to the nitrate pool through mineralization of organic matter to ammonium and subsequent nitrification of ammonium to nitrate there is no net effect on alkalinity. However, since denitrification removes nitrate, it also leads to a net increase of alkalinity and a net decrease of *p*CO₂. The denitrification effect on alkalinity is opposite to the organic matter effect described above.

[5] In this paper we assess how changes in nutrient availability and alkalinity due to sediment denitrification affect the air-sea flux of CO₂ in the Mid-Atlantic Bight (MAB; region shallower than 200 m between Cape Cod and Cape Hatteras) using an extended version of our biogeochemical model. The model combines the nitrogen-based biological model described by Fennel *et al.* [2006] with an explicit description of inorganic carbon chemistry and air-sea gas exchange of CO₂. We separate the effects of modified organic matter production and alkalinity by comparing simulations that use a conservative representation of alkalinity, i.e., a simulation where biological sources and

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Table 1. Four Simulations Conducted for This Study

	Without Denitrification	With Denitrification
Conservative alkalinity	Simulation 1	Simulation 2
Non-conservative alkalinity	Simulation 3	Simulation 4

sinks of alkalinity are set to zero, with simulations where the effects of nitrogen transformations on alkalinity are taken into account.

2. Model Description

[6] Our model is 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 eastern North America and the adjacent deep ocean. The biogeochemical component consists of the nitrogen cycle model with parameterized sediment denitrification described by Fennel et al. [2006] and a model of carbonate chemistry following Zeebe and Wolf-Gladrow [2001]. Details of the implementation are given in the auxiliary material.¹

[7] Alkalinity follows salinity to first order [Millero et al., 1998] and is unaffected by air-sea gas exchange of CO₂, but is altered by a number of biogeochemical processes, including calcite formation and dissolution, nitrate uptake and regeneration, and sulfate reduction. Here our goal is to isolate the role of nitrate cycling, particularly denitrification. We used two different options for determining alkalinity: a conservative option where alkalinity is unaffected by biogeochemical processes, and a non-conservative option where changes in alkalinity due to nitrate sources and sinks are included. In the non-conservative case, uptake of one mol of nitrate during primary production increases alkalinity by one mol equivalent and regeneration of nitrate reduces alkalinity accordingly [Goldman and Brewer, 1980]. These two options were run with and without denitrification, leading to a total of four simulations (Table 1). Comparison of Simulations 1 and 2 shows the impact of denitrification on nitrogen cycling and allows us to quantify how air-sea CO₂ fluxes change due to altered production of organic matter without alkalinity effects. Comparison of Simulations 3 and 4 shows the full effect of denitrification on air-sea CO₂ fluxes, including the net increase of alkalinity. Simulation 1 was spun up for six months starting in June 2003 and all four simulations were run for one year starting from the same initial conditions.

3. Results

[8] First, we compare model-predicted values of surface chlorophyll, primary production (PP), and sediment denitrification with estimates from observations. Note that these values are identical for Simulations 2 and 4 because changes in alkalinity do not affect nitrogen cycling in the model.

[9] A comparison of monthly mean surface chlorophyll values from Simulations 2 and 4 with the monthly SeaWiFS

climatology is given in Figure 1. The model captures spatial and temporal chlorophyll variations seen in the SeaWiFS climatology. One notable improvement over our previous simulations [Fennel et al., 2006] is the elevated chlorophyll over Georges Bank, which was not reproduced previously due to the lack of tides. The model underestimates chlorophyll in the Sargasso Sea, especially in winter, but agrees favorably with SeaWiFS chlorophyll on the shelf. Simulated annual PP in Simulations 2 and 4 is equal to 245 gC m⁻² yr⁻¹ in the MAB, which is only slightly lower than observational estimates of 310 gC m⁻² yr⁻¹ for the MAB [O'Reilly et al., 1987] and 290 gC m⁻² yr⁻¹ for the New York Bight [Malone et al., 1983]. The simulated PP in Simulations 1 and 3 (no denitrification) is higher, at 285 gC m⁻² yr⁻¹.

[10] The mean simulated sediment denitrification flux of 0.92 mmol N m⁻² d⁻¹ in the MAB is bracketed by the observational estimates of 0.7 mmol N m⁻² d⁻¹ for the North Atlantic shelves and 1.4 mmol N m⁻² d⁻¹ for the shelf area between Nova Scotia and Cape Hatteras [Seitzinger and Giblin, 1996]. Based on approximately monthly measurements at a site on the inner shelf off New Jersey Laursen and Seitzinger [2002] reported a mean annual flux of 1.7 ± 0.6 mmol N m⁻² d⁻¹ which is similar to mean simulated fluxes in nearshore regions on the MAB shelf (Figure 3a).

[11] We compare surface pCO₂ values for the inner, mid and outer shelf of the MAB (Simulation 4) with available pCO₂ measurements in Figure 2. The model-predicted pCO₂ values are within the range of measured values and agree favorably. The measurements typically fall within one standard deviation of the simulated values, except for the mid shelf, where observations occasionally lie outside the simulated standard deviation. We also calculated the annual air-sea flux of CO₂ for the inner, mid and outer shelf of the MAB and compared those to the observational-based estimates of DeGrandpre et al. [2002] (Table 2). Simulated fluxes for the inner and mid shelf of the MAB agree well with the observational estimate and lie within the margin of error. The simulated flux for the outer MAB shelf is higher. One should note though that the observational estimate for the outer shelf is based on a small number of data points (fewer than the inner and mid-shelf estimates) and that the narrow error margin might be a result of this as well.

[12] As hypothesized, nutrient removal due to sediment denitrification reduces air-sea flux of CO₂. Oceanic CO₂ uptake is higher by 0.17 mol C m⁻² yr⁻¹ in Simulation 1 (without denitrification) than in Simulation 2 (with denitrification), with the most dramatic effect on the mid and outer shelf (Table 2). The decrease in CO₂ uptake from Simulation 1 to Simulation 2 is due to the reduced production of organic matter, which increases pCO₂ thereby decreasing CO₂ uptake. Inclusion of the net increase of alkalinity due to denitrification makes this change smaller. The CO₂ uptake in Simulation 4 is smaller by 0.1 mol C m⁻² yr⁻¹ than in Simulation 3. This difference is due to the combined effect of reduced organic matter production and net increase in alkalinity. We estimated the alkalinity effect on the air-sea CO₂ flux as 0.07 mol C m⁻² yr⁻¹ (Table 2).

4. Discussion and Conclusions

[13] The net increase in alkalinity due to removal of fixed nitrogen by denitrification is significant, with alkalinity

¹Auxiliary materials are available in the HTML. doi:10.1029/2008GL036147.

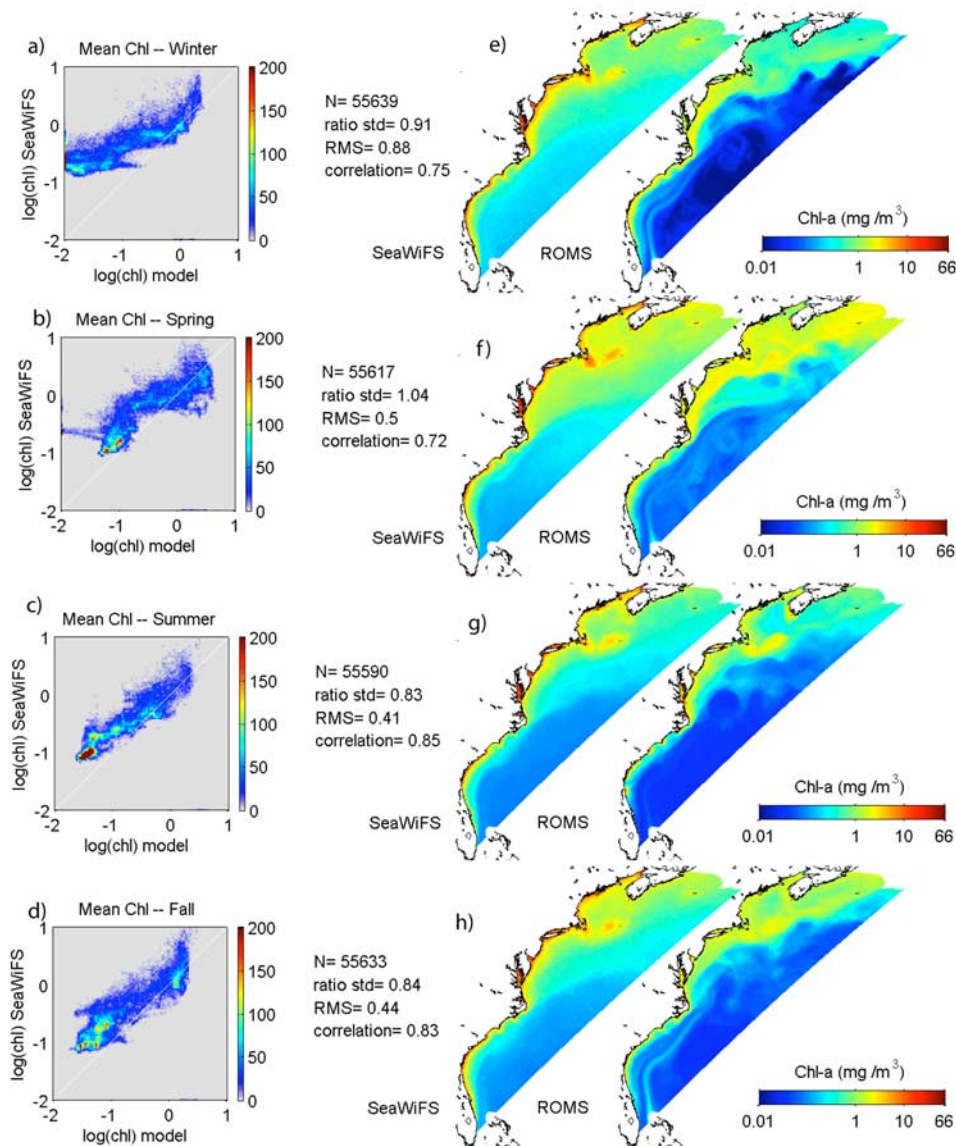


Figure 1. Simulated surface chlorophyll concentration in comparison with monthly mean SeaWiFS chlorophyll. Simulated versus remotely sensed seasonal mean chlorophyll values for each model grid point: (a) winter, (b) spring, (c) summer and (d) fall. The number of data points (N), ratio of standard deviations (ratio std), root-mean-squared error (RMS) and correlation coefficient (R) of the monthly chlorophyll values for each season is given as well. (e–h) Mean surface distributions of (right) simulated and (left; SeaWiFS) remotely sensed chlorophyll.

fluxes of 0.2 to $0.4 \text{ equ m}^{-2} \text{ yr}^{-1}$ on the MAB shelf, on Georges Bank and in near-shore areas of the Gulf of Maine (Figure 3c). Amidst growing concerns about ocean acidification [Fabry *et al.*, 2008; Feely *et al.*, 2004], an alkalinity flux of this magnitude is of interest. Ocean acidification principally results from the anthropogenic increase of DIC, but other processes that decrease alkalinity may contribute to lower-pH (more acidic) seawater as well. Doney *et al.* [2007] recently quantified the biogeochemical impact of atmospheric depositions of reactive sulfur and nitrogen and concluded that the resulting alkalinity flux of -0.01 to $-0.1 \text{ equ m}^{-2} \text{ yr}^{-1}$ to coastal areas downwind of emission centers (including the Northwest North Atlantic) results in pH changes that rival anthropogenic CO₂-driven pH

changes. The denitrification-driven increase in coastal alkalinity, while only partly anthropogenic, is much larger in magnitude and of opposite sign.

[14] Denitrification in continental shelf sediments is globally important in the removal of bio-available nitrogen, with an estimated 250 Tg N yr^{-1} accounting for $\sim 44\%$ of total global denitrification [Seitzinger *et al.*, 2006]. Applying the 1:1 stoichiometry of Goldman and Brewer [1980] this corresponds to an alkalinity flux of 18 Tequ yr^{-1} , a magnitude that is significantly larger than Doney *et al.*'s [2007] estimated alkalinity flux of $-4.22 \text{ Tequ yr}^{-1}$ due to atmospheric deposition. Human activities are altering the nitrogen cycle on a large scale: terrestrial nitrogen inputs have more than doubled compared to pre-industrial levels

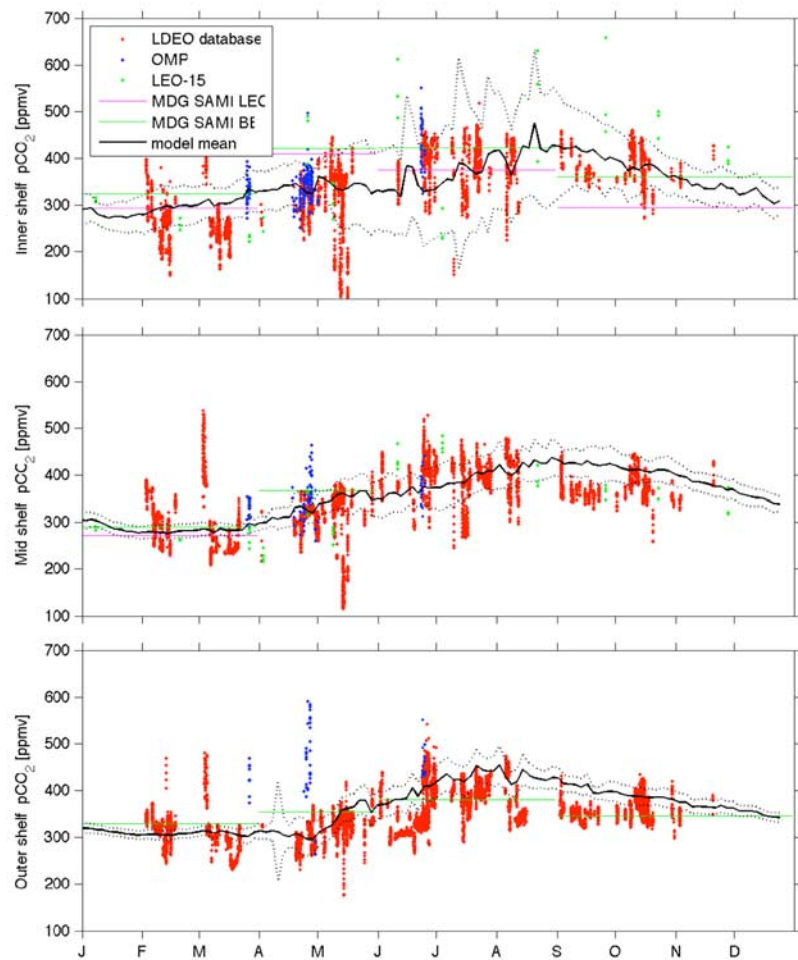


Figure 2. Model-predicted surface $p\text{CO}_2$ values in comparison to available observations for the (top) inner, (middle) mid and (bottom) outer shelf of the MAB. Solid black lines show simulated means and dashed lines indicate the first standard deviation. The red, green and blue dots represent measurements from the LDEO database [Takahashi *et al.*, 2007], time-series measurements at the LEO-15 site on the New Jersey shelf [Boehme *et al.*, 1998] and data from the Ocean Margins Program [Verity *et al.*, 2002], respectively. The solid green and magenta lines indicate mean values from continuous sensors at the LEO and Buzzards Bay sites [DeGrandpre *et al.*, 2002].

and are projected to increase further [Galloway *et al.*, 2004], and sporadic evidence of coastal nitrogen cycling pathways being altered, possibly in response to climate change, exist [Fulweiler *et al.*, 2007]. The contributions of these processes on CO_2 fluxes, alkalinity and pH may be significant.

[15] Carbon fluxes in the coastal oceans are driven by a superposition of distinctly different mechanisms involving

physical, biological and chemical processes. Their magnitude varies strongly in space and time and is likely to be altered in the future as climate change manifests itself, making it difficult to scale up local estimates or predict their future magnitude. A better understanding of the underlying drivers will be crucial for building mechanistic and quantitative understanding of coastal carbon cycling

Table 2. Air-Sea Flux of CO_2 in the Mid-Atlantic Bight^a

	Flux ($\text{mol C m}^{-2} \text{ yr}^{-1}$)		Flux (t C yr^{-1})		Flux Difference ($\text{mol C m}^{-2} \text{ yr}^{-1}$)		
	MDG	Simulation 4	MDG	Simulation 4	Simulation 2 – 1 (Nutrient Effect)	Simulation 4 – 3 (Combined Effect)	Simulation 4 – 3 – 2 + 1 (Alkalinity Effect)
Inner MAB	0.9 ± 0.6	1.02	3.3×10^5	3.8×10^5	–0.10	+0.06	+0.16
Middle MAB	1.6 ± 1.3	1.14	9.0×10^5	6.5×10^5	–0.19	–0.13	+0.06
Outer MAB	0.7 ± 0.1	1.20	3.8×10^5	6.4×10^5	–0.17	–0.14	+0.02
Total MAB	1.10 ± 0.69	1.18	1.6×10^6	1.7×10^6	–0.17	–0.1	+0.07

^aMAB, Mid-Atlantic Bight. Positive numbers indicate flux into the ocean. Observational estimates of DeGrandpre *et al.* [2002] (MDG) are given in comparison to fluxes for Simulation 4. We recalculated MDG’s total CO_2 fluxes using areal sizes of 3.15×10^{10} , 4.80×10^{10} and $4.54 \times 10^{10} \text{ m}^2$ for the inner, mid and outer MAB, respectively. Also given are flux differences due to the nutrient effect, the alkalinity effect and the combined effect due to denitrification.

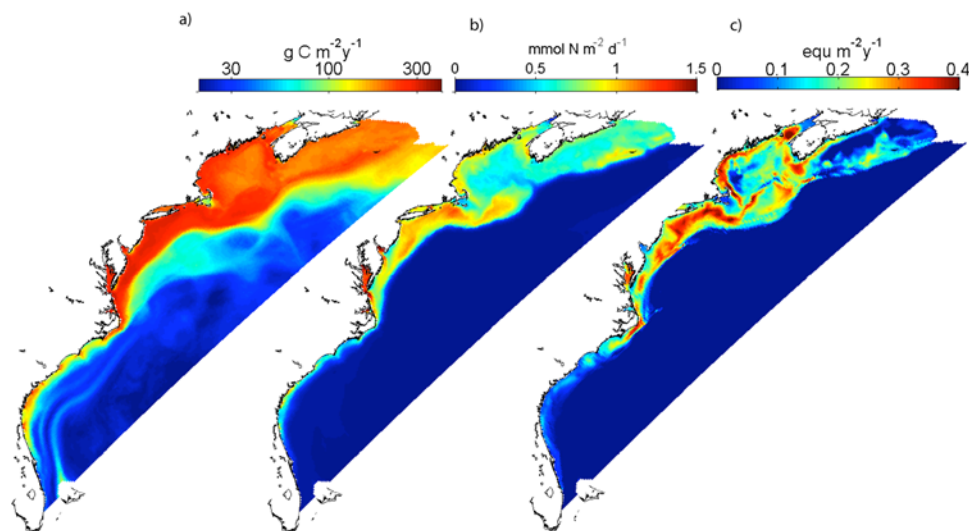


Figure 3. Simulated (a) primary production, (b) sediment denitrification and (c) the annual alkalinity flux due to denitrification. The annual alkalinity flux was calculated as the difference in depth-integrated alkalinity one year after initialization between Simulation 4 (non-conservative alkalinity) and Simulation 2 (conservative alkalinity).

and will have to rely on a combination of observational and modeling approaches.

[16] **Acknowledgments.** We thank Wei-Jun Cai for alerting us to the potential significance of the alkalinity effect at the 2006 Ocean Sciences Meeting and thank Scott Doney and one anonymous reviewer for constructive comments. We gratefully acknowledge support from the PARADIGM project (KF and MP) and the NASA IDS U.S.Ecos project (KF, JW and RN). KF was also supported by NSERC and CFI.

References

- Boehme, S. E., C. L. Sabine, and C. E. Reimers (1998), CO₂ fluxes from a coastal transect: A time-series approach, *Mar. Chem.*, **63**, 49–67.
- Cai, W., Z. A. Wang, and Y. Wang (2003), The role of marsh-dominated heterotrophic continental margins in transport of CO₂ between the atmosphere, the land-sea interface and the ocean, *Geophys. Res. Lett.*, **30**(16), 1849, doi:10.1029/2003GL017633.
- DeGrandpre, M. D., G. J. Olbu, C. M. Beatty, and T. R. Hammar (2002), Air-sea CO₂ fluxes on the US Middle Atlantic Bight, *Deep Sea Res., Part II*, **49**, 4355–4367.
- Devol, A. H., and J. P. Christensen (1993), Benthic fluxes and nitrogen cycling in sediments of the continental margin of the eastern North Pacific, *J. Mar. Res.*, **51**, 345–372.
- Doney, S. C., et al. (2004), Ocean Carbon and Climate Change (OCCC): An Implementation strategy for U. S. Ocean Carbon Research, Univ. Corp. for Atmos. Res., Boulder, Colo.
- Doney, S. C., N. Mahowald, I. Lima, R. A. Feely, F. T. Mackenzie, J. F. Lamarque, and P. J. Rasch (2007), Impact of anthropogenic atmospheric nitrogen and sulfur deposition on ocean acidification and the inorganic carbon system, *Proc. Natl. Acad. Sci. U. S. A.*, **104**, 14,580–14,585.
- Fabry, V. J., B. A. Seibel, R. A. Feely, and J. C. Orr (2008), Impacts of ocean acidification on marine fauna and ecosystem processes, *ICES J. Mar. Sci.*, **65**, 414–432.
- Feely, R. A., C. L. Sabine, K. Lee, W. Berelson, J. Kleypas, V. J. Fabry, and F. J. Millero (2004), Impact of anthropogenic CO₂ on the CaCO₃ system in the oceans, *Science*, **305**, 362–366.
- Fennel, K., J. Wilkin, J. Levin, J. Moisan, J. O'Reilly, and D. Haidvogel (2006), Nitrogen cycling in the Middle Atlantic Bight: Results from a three-dimensional model and implications for the North Atlantic nitrogen budget, *Global Biogeochem. Cycles*, **20**, GB3007, doi:10.1029/2005GB002456.
- Fulweiler, R., S. Nixon, B. Buckley, and S. Granger (2007), Reversal of the net dinitrogen gas flux in coastal marine sediments, *Nature*, **448**, 180–182.
- Galloway, J., F. Dentener, D. Capone, E. Boyer, R. Howarth, S. Seitzinger, G. Asner, C. Cleveland, P. Green, and E. Holland (2004), Nitrogen cycles: Past, present, and future, *Biogeochemistry*, **70**, 153–226.
- Goldman, J. C., and P. G. Brewer (1980), Effect of nitrogen source and growth rate on phytoplankton-mediated changes in alkalinity, *Limnol. Oceanogr.*, **25**, 352–357.
- Haidvogel, D. B., et al. (2008), Ocean forecasting in terrain-following coordinates: Formulation and skill assessment of the Regional Ocean Modeling System, *J. Comput. Phys.*, **227**, 3595–3624.
- Laursen, A. E., and S. P. Seitzinger (2002), The role of denitrification in nitrogen removal and carbon mineralization in Mid-Atlantic Bight sediments, *Cont. Shelf Res.*, **22**, 1397–1416.
- Malone, T. C., T. S. Hopkins, P. G. Falkowski, and T. E. Whitledge (1983), Production and transport of phytoplankton biomass over the continental shelf of the New York Bight, *Cont. Shelf Res.*, **1**, 305–337.
- Millero, F. J., K. Lee, and M. Roche (1998), Distribution of alkalinity in the surface waters of the major oceans, *Mar. Chem.*, **60**, 111–130.
- O'Reilly, J. E., C. Evans-Zetlin, and D. A. Busch (1987), Primary production, in *Georges Bank*, edited by R. H. Backus, pp. 220–233, MIT Press, Cambridge, Mass.
- Rao, A. M. F., M. J. McCarthy, W. S. Gardner, and R. A. Jahnke (2007), Respiration and denitrification in permeable continental shelf deposits on the South Atlantic Bight: Rates of carbon and nitrogen cycling from sediment column experiments, *Cont. Shelf Res.*, **27**, 1801–1819.
- Seitzinger, S., J. A. Harrison, J. K. Bohlke, A. F. Bouwman, R. Lowrance, B. Peterson, C. Tobias, and G. Van Drecht (2006), Denitrification across landscapes and waterscapes: A synthesis, *Ecol. Appl.*, **16**, 2064–2090.
- Seitzinger, S. P. (1988), Denitrification in freshwater and coastal marine ecosystems: Ecological and geochemical importance, *Limnol. Oceanogr.*, **33**, 702–724.
- Seitzinger, S. P., and A. E. Giblin (1996), Estimating denitrification in North Atlantic continental shelf sediments, *Biogeochemistry*, **35**, 235–260.
- Takahashi, T., S. C. Sutherland, and A. Kozyr (2007), Global Ocean Surface Water Partial Pressure of CO₂ Database: Measurements performed during 1968–2006 (version 1.0), http://cdiac.ornl.gov/oceans/ndp_088/ndp088.html, Carbon Dioxide Inf. Anal. Cent., Oak Ridge Natl. Lab., Oak Ridge, Tenn.
- Thomas, H., Y. Bozec, K. Elkalay, and H. J. W. de Baar (2004), Enhanced open ocean storage of CO₂ from shelf sea pumping, *Science*, **304**, 1005–1008.
- Tsunogai, S., S. Watanabe, and T. Sato (1999), Is there a “continental shelf pump” for the absorption of atmospheric CO₂, *Tellus, Ser. B*, **51**, 701–712.
- Verity, P. G., J. E. Bauer, C. N. Flagg, D. J. DeMaster, and D. J. Repeta (2002), The Ocean Margins Program: An interdisciplinary study of carbon sources, transformations, and sinks in a temperate continental margin system, *Deep Sea Res., Part II*, **49**, 4273–4295.
- Zeebe, R., and D. Wolf-Gladrow (2001), *CO₂ in Seawater: Equilibrium, Kinetics, Isotopes*, Elsevier Oceanogr. Ser., vol. 65, Elsevier, Amsterdam.
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