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**Sediment  
denitrification and O<sub>2</sub>  
dynamics**

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# Role of sediment denitrification in water column oxygen dynamics: comparison of the North American east and west coasts

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## Abstract

The occurrence of hypoxic conditions in the coastal ocean has been increasing in the last decade. Low oxygen concentrations, either natural or anthropogenically driven, can severely affect coastal marine ecosystems. A deeper understanding of the oxygen cycle is required in order to improve numerical models and to predict the timing and severity of hypoxia. In this study we investigate the effect of sediment denitrification on oxygen concentrations in bottom waters over the continental shelf. We used a coupled physical-biological model based on the Regional Ocean Modelling System (ROMS) to compare summer simulations with and without denitrification within the sediments for two North American shelves: the Middle Atlantic Bight (MAB) and the Vancouver Island Shelf (VIS). These regions belong to Western and Eastern Boundary Current Systems, respectively, and are characterized by different physical and biological dynamics. Both models assume coupled nitrification-denitrification within the sediments. Denitrification represents a loss of bioavailable nitrogen through the production of dinitrogen gas, with the potential to affect biogeochemical cycles. In our MAB model, denitrification within the sediments efficiently decreases the total pool of available nutrients, since recycled nitrogen supports most of the primary production in that region. The diminished primary production and consequent decrease of organic matter flux to the seafloor leads to less sediment oxygen consumption and higher oxygen concentrations in bottom waters. However, on the VIS changes in regenerated nitrogen barely affect primary production due to the efficient supply of new nutrients through wind-driven upwelling during summer and the nutrient-rich coastal current. We recommend that modelling experiments focusing on oxygen dynamics (as well as oxygen budget calculations) should include this process in coastal regions where regenerated primary production dominates productivity.

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## 1 Introduction

Anaerobic remineralization processes become important where oxygen concentrations are low in the water column, and in the sediment layer, below the oxygenated upper few millimetres (Jørgensen, 1982). Nitrate ( $\text{NO}_3^-$ ) is the first electron acceptor used in place of oxygen in the decomposition of organic matter because its energy yield is the highest after oxygen (Sørensen et al., 1979; Middelburg and Levin, 2009). The remineralization of organic matter using  $\text{NO}_3^-$  is known as “denitrification”. In contrast to aerobic remineralization, end products of denitrification are dinitrogen gas or nitrous oxide and not readily available to most primary producers (Seitzinger, 1988). Thus, this anaerobic process represents a loss of bioavailable nitrogen from the ecosystem and affects water column processes such as primary production and nitrification, with repercussions for the carbon and oxygen cycles. For instance, recent studies in the Middle Atlantic Bight (MAB) and North Sea suggest that the presence of denitrification within the sediments plays an important role in the uptake of atmospheric carbon dioxide ( $\text{CO}_2$ ) by the coastal ocean (Fennel et al., 2008; Thomas et al., 2009). A high-resolution model of the MAB shows that the loss of bioavailable nitrogen by sediment denitrification decreases primary production, leading to a smaller influx of atmospheric  $\text{CO}_2$  into the ocean than in simulations where denitrification is ignored (Fennel et al., 2008). Observations in the North Sea suggest that anaerobic degradation of organic matter in the sediments (e.g., denitrification, sulphate reduction) represents the largest source of total alkalinity in shallow areas, which provides a stronger control on pH and surface partial pressure of  $\text{CO}_2$  than dissolved inorganic carbon (Thomas et al., 2009).

Many studies have focused on the effect of low oxygen concentrations (i.e., hypoxic conditions) on denitrification within the sediments (e.g., Kemp et al., 1990; Middelburg and Levin, 2009). We look instead at the effect of sediment denitrification on oxygen concentrations in bottom waters over the shelf. The water column processes affected by sediment denitrification have the potential to alter oxygen concentrations in several different ways. Firstly, a decrease in primary production due to less available nitrogen

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leads to a smaller flux of organic matter reaching the sediments. Consequently, there is a decrease in remineralization and oxygen consumption by the sediments, contributing to higher oxygen concentrations in bottom waters (“Process 1”). Secondly, the decreased sediment remineralization also diminishes the source of ammonium ( $\text{NH}_4^+$ ) to the water column. Therefore, nitrification (the aerobic oxidation of  $\text{NH}_4^+$  to  $\text{NO}_3^-$ ) decreases in the water column, resulting in less oxygen consumption and a potential to increase oxygen concentrations (“Process 2”). Lastly, we need to consider the source of  $\text{NO}_3^-$  for the denitrifying bacteria in the sediments.  $\text{NO}_3^-$  can be provided by the above water column (“direct denitrification”) or by nitrification within the sediments (“coupled nitrification-denitrification”). Where the latter dominates, oxygen is taken from the water column to fuel nitrification in the sediments. Hence, coupled nitrification-denitrification leads to an increased oxygen consumption from the sediments, which can contribute to a decrease in oxygen concentrations (“Process 3”). In contrast, direct denitrification represents an extra sink of fixed nitrogen for the water column, with the potential to further decrease primary production (“Process 1”). These pathways connecting sediment denitrification and oxygen concentrations in the water column have not been explored in detail. Given the crucial role of oxygen in marine ecosystems and the interest in understanding and predicting coastal hypoxia, we need to identify all the mechanisms that control oxygen concentrations. An improved constraint of key local processes (such as sediment denitrification) will allow for the development of better models for coastal hypoxia, as pointed by Peña et al. (2010).

Here we investigate the role of denitrification within the sediments as a driver of oxygen concentrations in bottom waters over the shelf. Two similar coupled biological-physical models, applied to the Eastern and Western Coastal Boundary Systems of North America, are used to evaluate the role of different environmental settings in the connection between oxygen and sediment denitrification. The two shelves studied are the broad MAB and the narrower Vancouver Island shelf (VIS). Located in the central section of the United States east coast, the MAB extends from Cape Hatteras in the south to Nantucket Shoals in the north (right-hand inset in Fig. 1). A large-scale,

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coastal current system originating in the Labrador Sea brings cool and relatively fresh waters onto the Scotian Shelf (Chapman and Beardsley, 1989). In the Gulf of Maine, these waters mix with the warmer, more saline Slope Water, forming the Shelf Water that predominates in the MAB (Smith, 1983; Ramp et al., 1985). Shelf Water remains separated from Slope Water offshore by the shelf-break front, and only limited intrusions of offshore waters occur, such as entrainment of warm Gulf Stream rings and smaller eddies and mixing with Slope Water (e.g., Bisagni, 1983; Garvine et al., 1988; Walsh et al., 1988). Input of “new” nutrients from offshore waters is limited, leading to a predominant role of “regenerated” nutrients (i.e., inorganic nitrogen generated by oxidation of organic matter on shelf waters and sediments). Observations suggest that 50–80% of total phytoplankton growth in summer is supported by regenerated production (i.e.,  $\text{NH}_4^+$  assimilation) in the upper mixed layer of the MAB (Harrison et al., 1983).

The VIS represents the northern end of the California Current System (CCS) on the Canadian west coast (left-hand inset in Fig. 1). Northwesterly winds drive upwelling during summer while downwelling-favourable winds prevail in winter (Strub et al., 1987a,b). Shelf waves forced by winds further south in the CCS also drive upwelling on the VIS (Freeland and Denman, 1982). The Vancouver Island Coastal Current (VICC) flows northward near the coast, bringing nutrient-rich and relatively fresh waters from the Juan de Fuca Strait to the shelf (Thomson et al., 1989). Summer observations indicate the episodic presence over the continental shelf of upwelled waters from the California Undercurrent as well as the influence of VICC waters on the VIS (Mackas et al., 1987). These two water sources supply nutrients to the shelf, fuelling new production (i.e.,  $\text{NO}_3^-$  assimilation) and the growth of large diatom cells (Ianson et al., 2003; Harris et al., 2009).

We compare simulations from the biological models described in Fennel et al. (2006, 2008) and Bianucci et al. (2011) for the MAB and VIS, respectively, with particular focus on the effect of sediment denitrification on bottom water oxygen. Our comparison shows that denitrification within the sediments affects bottom oxygen concentrations

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in the MAB, but not on the VIS. These results derive from different nutrient dynamics in the two regions, namely the predominance of regenerated versus new nutrients in the MAB. Where regenerated nutrients support most of phytoplankton growth, the loss of bioavailable nitrogen through sediment denitrification significantly affects oxygen concentrations in bottom waters. However, in a region like the VIS where nutrients are supplied from external sources (e.g., upwelling from offshore, transport from the VICC), oxygen concentrations are not significantly affected by anaerobic sediment processes. These results imply that consideration of sediment denitrification in studies of coastal hypoxia (e.g., in modelling experiments or budget analyses) is important, especially in regions where recycled nutrients fuel most of the primary production.

## 2 Model experiments and analysis

The selected study areas represent coastal systems with different physical and biological dynamics. Both regions were modelled with the Regional Ocean Modelling System (ROMS, <http://myroms.org>, Haidvogel et al., 2008). The 3-D model for the MAB was developed and described by Fennel et al. (2006). For the VIS, a quasi-2-D model was used to represent a vertical section of a transect perpendicular to isobaths (Bianucci et al., 2011). In addition to the different dimensions (2-D vs. 3-D), the models differ slightly in their biological components. While both models use the same nutrient, phytoplankton, zooplankton, and large detritus structure, the MAB model has a pool of small detritus while the VIS model includes dissolved organic matter (DOM) instead. The latter does not sink and has longer remineralization time scales than the small detritus pool in the MAB model. Despite this difference, the models have similar ecosystem dynamics and each model reproduces the biogeochemical characteristics of its region. Three different sediment parameterizations were implemented in the VIS model; here, we choose the same parameterization as in the MAB model (instantaneous remineralization of particulate organic matter reaching the seafloor). Both models consider coupled nitrification-denitrification and assume the following stoichiometry

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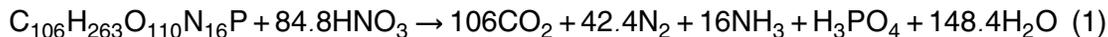
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for denitrification and nitrification:



For further details on the models, their equations, and their evaluation, refer to Fennel et al. (2006, 2008), Bianucci (2010), and Bianucci et al. (2011). These models offer an opportunity to perform an inter-shelf comparison.

To evaluate the effect of sediment denitrification on bottom oxygen concentrations, we compared simulations in each region with and without this process. The change in bottom oxygen due to the presence of denitrification within the sediments was calculated as the relative difference in the bottom layer oxygen fields between experiments:

$$\Delta\text{O}_2 = 100 \% \times \left( \text{O}_2^{\text{DNF}} - \text{O}_2^{\text{NoDNF}} \right) / \text{O}_2^{\text{NoDNF}}, \quad (3)$$

where the superscripts DNF and NoDNF indicate simulations with and without sediment denitrification, respectively. In the case of primary production, we analyzed the absolute difference between experiments, since productivity offshore tends to be considerably lower than over the shelf, such that even small changes in production lead to large relative changes. Therefore,  $\Delta\text{PP} = \text{PP}^{\text{DNF}} - \text{PP}^{\text{NoDNF}}$ , where PP is the vertically integrated total primary production. Modelled total primary production represents the combination of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  assimilation.

Oxygen budgets for the bottom 10 m of the water column were used to analyse the processes that drive  $\Delta\text{O}_2$  over the shelf. For any given process (e.g., advection, remineralization in the sediments, etc.), the corresponding term of the budget was obtained by integrating the process over time and over the bottom 10 m. These estimates were averaged horizontally over shelf regions shallower than 200 m. The sum of all budget terms gives a spatial average of the total change in oxygen concentrations in the bottom 10 m for the period of study, in units of  $\text{mmol-O}_2 \text{ m}^{-2}$ . The VIS model was run only from 16 July to 29 September to capture the upwelling season, so we used the same time window of 75 days to analyse results from the MAB.

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### 3 Results

Simulations with and without sediment denitrification (DNF and NoDNF experiments, respectively) allow us to evaluate the effect of this anaerobic process on near-bottom oxygen concentrations over both shelves. The mean  $\Delta O_2$  in the bottom layer of the models (average of 75 days) shows larger changes in the MAB than on the VIS (Fig. 2). On the VIS, the mean  $\Delta O_2$  only varies as a function of distance from the shelf break, due to the 2-D ( $xz$ -plane) model domain (Fig. 2a, blue curve). Changes on the VIS are negligible, within  $\pm 0.2\%$ . In the MAB, mean  $\Delta O_2$  was positive mostly everywhere (Fig. 2b), meaning that sediment denitrification resulted in an increase in near-bottom oxygen. To compare with the VIS changes, we selected two representative transects in the northern and southern MAB, near Long Island and Chesapeake Bay, respectively (black and red lines in Fig. 2b).  $\Delta O_2$  over the shelf in the northern transect is  $\sim 10\%$ , while values in the southern transect exceed  $45\%$  (Fig. 2a, black and red curves). In the southern MAB, oxygen concentrations increased up to  $182 \text{ mmol m}^{-3}$  due to the presence of denitrification in the sediments. There, the NoDNF simulation reached hypoxic conditions ( $O_2 < 60 \text{ mmol m}^{-3}$ ) in areas shallower than 15 m.

The loss of bioavailable nitrogen due to denitrification within the sediments decreased total primary production significantly in the MAB (Fig. 3). While total production on the VIS barely changed between DNF and NoDNF experiments ( $-0.01 \text{ g C m}^{-2} \text{ d}^{-1} < \Delta \text{PP} < 0$ , Fig. 3a, blue curve), mean  $\Delta \text{PP}$  over the MAB is  $-0.15 \text{ g C m}^{-2} \text{ d}^{-1}$  with minima of  $-1 \text{ g C m}^{-2} \text{ d}^{-1}$  near Cape Hatteras (Fig. 3b). The representative MAB transects show larger  $\Delta \text{PP}$  than the VIS both offshore and inshore of the shelf break (Fig. 3a). As waters leave the shelf at Cape Hatteras, flowing along the northern edge of the Gulf Stream (Ford et al., 1952), they transport shelf nutrients offshore. In the DNF simulation, the concentration of bioavailable nitrogen transported offshore was lower than in the NoDNF experiment, leading to the observed decrease of primary production offshore of the shelf break. New primary production represents  $\sim 50\%$  of the total primary production on the VIS compared with  $\sim 25\%$  in the MAB.

Oxygen concentrations in bottom waters can change due to both physical and biological processes (Fig. 4). Vertical mixing tends to increase oxygen in the bottom, since upper layers usually have higher oxygen concentrations. However, advection can either increase or decrease oxygen over the shelf, depending on the direction of the currents and the horizontal oxygen gradients. All biological processes in the bottom layers of the water column (sediment and water column remineralization and nitrification) consume oxygen. In the MAB, bottom oxygen increases during the 75 days of analysis in both simulations (positive “Net Budget” columns in Fig. 4), mainly due to the effect of vertical mixing. In contrast, both VIS experiments lost oxygen through onshore advection of low-oxygen waters and biological consumption. Furthermore, the relative importance of the different biological processes varied between study areas. On the VIS, sediment remineralization dominated the biological consumption of oxygen. However, sediment and water column remineralization were similar in the MAB in the NoDNF experiment, while water column remineralization was the largest oxygen sink in the DNF simulation.

The comparison of the oxygen budgets between the DNF and NoDNF experiments shows which processes led to the different magnitudes of mean  $\Delta O_2$  (Fig. 4). On the VIS, oxygen consumption by the sediments increased slightly in the DNF simulation with respect to the NoDNF experiment (Fig. 4a, grey and black bars, respectively), corresponding to “Process 3” mentioned in Sect. 1 (extra oxygen consumption from coupled nitrification-denitrification). Moreover, oxygen consumption by nitrification decreased in the DNF case due to less available  $NH_4^+$  in the water column (“Process 2” from Sect. 1). As these changes are small and balance each other, variations in oxygen are negligible on this shelf (Fig. 2a, blue curve). However, in the MAB oxygen consumption by the sediments decreased sharply when denitrification was enabled (Fig. 4b, grey bars), following “Process 1” (less sediment mass to be remineralized due to diminished primary production). This effect resulted in the higher oxygen concentrations and positive  $\Delta O_2$  in the bottom layers of the MAB model (Fig. 2b). Changes in the remaining biological processes (water column remineralization, nitrification) in the DNF simulation contributed to a lesser extent to the decrease in oxygen consumption.

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Physical processes (advection, vertical mixing) re-adjusted themselves to the new oxygen gradients in the DNF simulation, compensating only partially for the smaller sinks of oxygen.

#### 4 Conclusions

5 The role of denitrification within the sediments has been examined previously with respect to air-sea CO<sub>2</sub> fluxes and carbon storage in the coastal ocean (Fennel et al., 2008; Thomas et al., 2009). Here, we investigated the effect of this anaerobic process on the oxygen concentrations of bottom waters and found different behaviour in our two study regions. The loss of bioavailable nitrogen through sediment denitrification significantly decreased total primary production in the MAB, such that less organic matter reached the seafloor in the DNF simulation compared with the NoDNF experiment. Therefore, the DNF simulation shows a decrease in sediment remineralization and consequent decrease of sediment oxygen consumption. This diminished consumption leads to higher oxygen concentrations in the bottom layer and positive  $\Delta O_2$  (Fig. 2b).  
10 However, sediment denitrification barely affects total primary production on the VIS. The small changes in sediment remineralization and nitrification balance each other and result in bottom  $\Delta O_2 \sim 0$  (Fig. 2a, blue line).

These results suggest that the effect of sediment denitrification on bottom oxygen concentrations depends on the effect of this anaerobic process on total primary production. If regenerated or recycled nutrients support most of the primary production, an alteration of the amount of bioavailable nitrogen produced by the sediments can affect total primary production over the shelf. In contrast, if nutrients from external sources (e.g., upwelled from the deep ocean) largely sustain phytoplankton growth, then a loss of recycled nitrogen from denitrification in the sediments does not strongly affect total  
15 primary production.

Waters in the MAB have spent a long time over the continental shelf off Northeastern North America, since the coastal current system starts in the Labrador Sea (Chapman

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and Beardsley, 1989). The strong signal of sediment denitrification found in these waters provides evidence of the long residence time and the importance of nutrient regeneration on the shelf (Fennel, 2010). Observations indicate that recycled nutrients support high productivity in the MAB (Falkowski et al., 1988). In our model results,  $\text{NH}_4^+$  assimilation represented  $\sim 75\%$  of total production, which agrees with previous observational studies (50–80%, Harrison et al., 1983). Furthermore,  $\text{NO}_3^-$  assimilation in this region cannot be thought of as “new” production supported from external sources of  $\text{NO}_3^-$ . The long residence over the shelf allows for nitrification to transform regenerated  $\text{NH}_4^+$  into  $\text{NO}_3^-$ . Moreover, as mentioned in Sect. 1, the input of  $\text{NO}_3^-$  from offshore waters in the MAB is limited. However, on the VIS external sources of nutrients significantly contribute to primary production, such as the nutrient-rich VICC and wind-driven summer upwelling (e.g., Whitney et al., 2005; Hickey and Banas, 2008).

Intercomparison studies are fundamental to understanding the heterogeneous global coastal ocean. Ideally, the comparison of modelling experiments for different coastal regions would be done with physical models that follow the same set up and have identical biological models. These conditions are extremely hard to meet, since regional models are usually developed to study questions specific to a particular geographical location. The models used in this study are based on the same circulation model (ROMS), although in different physical configurations (quasi-2-D vs. 3-D). Their biological components differ only slightly in the modelling of two detritus pools (MAB) vs. a large detritus and a dissolved organic matter pool (VIS). Both models adequately reproduce the main physical (e.g., temperature, salinity) and biological (e.g., chlorophyll,  $\text{NO}_3^-$ ) characteristics of the two regions (see Fennel et al., 2006, 2008; Bianucci et al., 2011), allowing us to carry out this intercomparison. Our conclusions about the role of regenerated vs. new nutrients in each region are consistent with previous studies (e.g., Harrison et al., 1983; Falkowski et al., 1988; Ianson et al., 2003; Hickey and Banas, 2008).

The biological models used here assumed coupled nitrification-denitrification in the sediments (i.e., nitrification of  $\text{NH}_4^+$  provides all the  $\text{NO}_3^-$  for denitrification), so the

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sediments do not exchange  $\text{NO}_3^-$  with the water column (Fennel et al., 2006; Bianucci et al., 2011). This assumption affects the results, since direct denitrification would create an additional sink of bioavailable nitrogen and may further alter the oxygen cycle. We are confident that this assumption is adequate for the MAB, where estimations from a long-term ecosystem observatory site (LEO-15) showed that coupled nitrification-denitrification supported 91–100 % of total denitrification (Laursen and Seitzinger, 2002). No estimations of sediment denitrification are available for the VIS area. On the Washington shelf, just south of the study region, coupled nitrification-denitrification represents about 60 % of total denitrification (Devol, 1991), suggesting that direct denitrification may be significant on the VIS. However, given the external sources of new nutrients on the VIS, direct denitrification is not likely to affect primary production and oxygen concentrations significantly.

A relevant characteristic shared by our two study regions is that both are normoxic shelves, i.e. oxygen concentrations tend to be above the hypoxic threshold. Non-zero bottom water oxygen concentrations are required for coupled nitrification-denitrification to occur in the sediments (e.g., Kemp et al., 1990), since nitrification is an aerobic process. Moreover, the parameterization used in our models relies on the observed correlation between denitrification and sediment oxygen consumption (Seitzinger and Giblin, 1996; Fennel et al., 2006; Bianucci et al., 2011), and is recommended only for oxic environments (Fennel et al., 2009). For instance, this parameterization does not consider that hypoxic bottom waters decrease coupled nitrification-denitrification rates in the sediments (Kemp et al., 1990, 2009). Furthermore, hypoxic conditions can affect nutrient cycling within the sediments in indirect ways, e.g. by reducing benthic macrofauna bio-irrigation and bioturbation (Kemp et al., 2009; Middelburg and Levin, 2009).

The motivation for this work was to improve the understanding of the cycling of oxygen by assessing the role of denitrification within the sediments. Our results indicate that sediment denitrification can impact the oxygen concentrations on shelf regions where recycled nutrients support most of phytoplankton growth. In these regions,

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sediment denitrification should be considered as a factor influencing oxygen dynamics, since its effects are large enough to help maintain concentrations above the hypoxic threshold.

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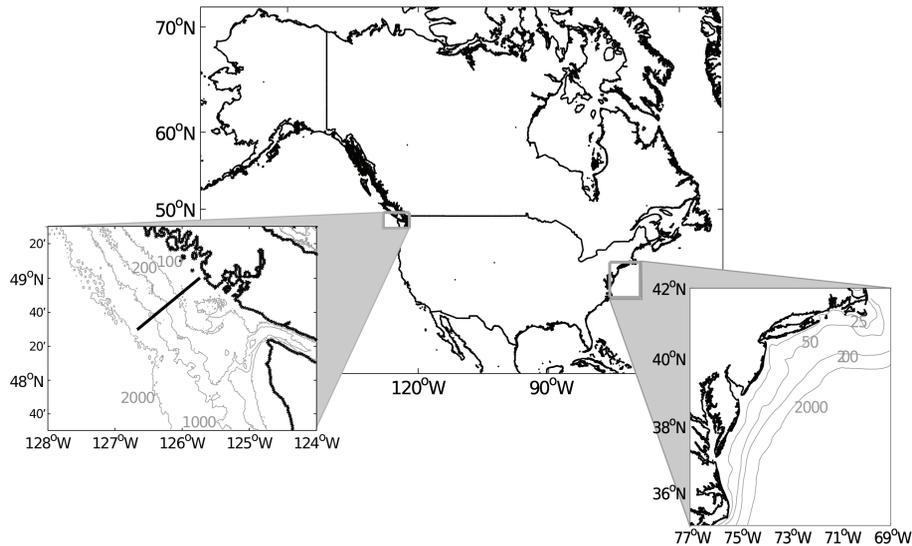
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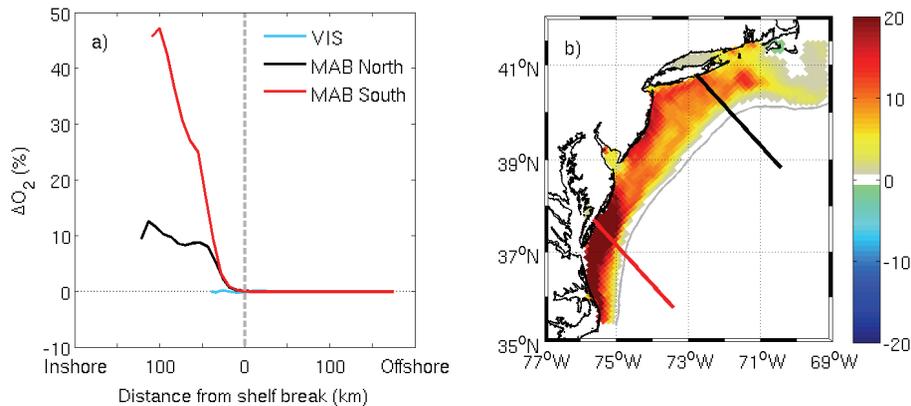
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**Fig. 1.** Map of North America showing the Middle Atlantic Bight (MAB) in the east (right inset) and the Vancouver Island Shelf (VIS) in the west (left inset). The location of the transect represented by the VIS model is shown by the black line in the left inset, which also shows the 100, 200, 1000, and 2000 m isobaths off the VIS. The inset on the right shows the 25, 50, 200, and 2000 m isobaths from the MAB model bathymetry.

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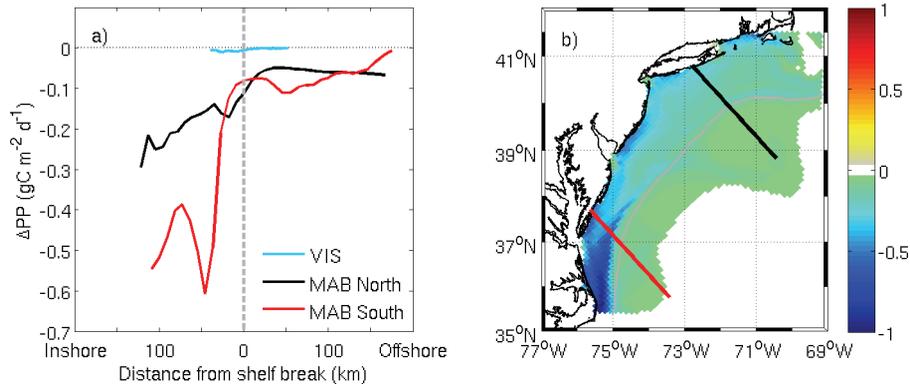
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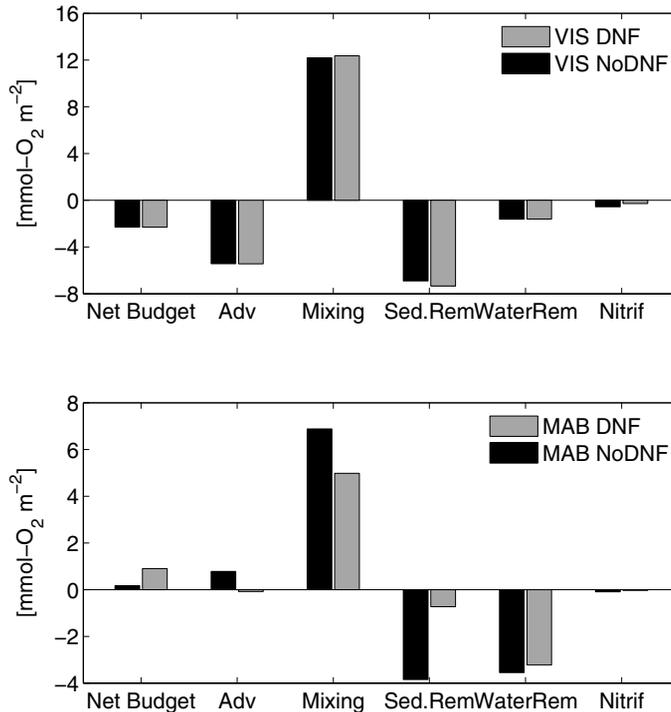
**Fig. 2.** Change (in %) of oxygen concentrations in the near-bottom layer of the two models ( $\Delta O_2$ ). **(a)**  $\Delta O_2$  as a function of distance from the shelf break in the VIS quasi-2-D model and in two transects from the MAB model. **(b)** Map of  $\Delta O_2$  for MAB domain, showing the two transects used in **(a)**. The dashed vertical line in **(a)** indicates the position of the shelf break (200 m isobath), shown as a grey contour in **(b)**.

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**Fig. 3.** Change (in  $\text{gC m}^{-2} \text{d}^{-1}$ ) of vertically integrated primary production ( $\Delta PP$ ). **(a)**  $\Delta PP$  as a function of distance from the shelf break in the VIS quasi-2-D model and in two transects from the MAB model. **(b)** Map of  $\Delta PP$  for MAB domain, showing the two transects used in **(a)**. The dashed vertical line in **(a)** indicates the position of the shelf break (200 m isobath), shown as a grey contour in **(b)**.



**Fig. 4.** Contributions to the O<sub>2</sub> budget for the bottom 10 m of the water column of the modelled shelves (depth ≤ 200 m): (top) VIS and (bottom) MAB. Experiments with and without denitrification in the sediments are shown as grey and black bars, respectively. The bottom axis reads: net budget (sum all of budget terms), advection (horizontal plus vertical), vertical mixing, sediment remineralization, remineralization of organic matter in the water column and nitrification in the water column. Positive fluxes are into the near-bottom layer.