

## The significance of water column nitrification in the southeastern Bering Sea

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**Abstract** Nitrate is considered the nutrient that limits new primary production in the southeastern Bering Sea shelf. Nitrate regenerated through biological nitrification has the potential to significantly support primary production as well. Here we use measurements of the specific rate of water column nitrification in a 1-D ecosystem model to quantify the resupply of nitrate from nitrification in the middle shelf of the southeastern Bering Sea. Model sensitivity studies reveal nitrification rate is an important control on the dominant phytoplankton functional type, and the amount of nitrate in summer bottom waters and in the winter water column. Evaluation of nitrification using the model supports the hypothesis that increases in late-summer nitrate concentrations observed in the southeastern Bering Sea bottom waters are due to nitrification. Model results for nitrate replenishment exceed previously estimated rates of 20-30% based on observations. The results of this study indicate that nitrification, potentially the source of up to ~38% of the springtime water column nitrate, could support ~24% of the annual primary production.

**Key words** Arctic, Southeast Bering Sea, water column nitrification.

### 1 Introduction

In the southeastern Bering Sea, like other productive high latitude seas, most of the primary production is fuelled by nitrate. Much of this nitrate is thought to be new nitrate originating from Pacific waters that flow through several Aleutian passes and deep basin waters that upwell onto the shelf. Another source that has received little attention until recently is the biological regeneration of nitrate from ammonium, or nitrification. A recent synthesis of open ocean measurements indicates that nitrification is a very important factor in the euphotic nitrogen cycle<sup>[1]</sup>. In this paper, we investigate the role of nitrification in supplying the nitrate needed for the primary production that sustains the world class fisheries of the Bering Sea and potentially the arctic food web beyond the Bering Sea.

Observations suggest significant nitrification in bottom waters on the southeastern Bering Sea shelf. Starting at the time of spring bloom, ammonium regenerated from sinking organic nitrogen accumulates in the middle shelf bottom waters until concentrations markedly decrease in September-October<sup>[2]</sup>. The coincidental increase of nitrate in these bottom wa-

ters has been hypothesized to be the result of in situ nitrification. Processes and Resources of the Bering Sea Shelf (PROBES) studies of benthic release show evidence of ammonium consumed as nitrate is released<sup>[3]</sup>. However, the net nitrate flux from mid-shelf sediments was found to play a minor role in seasonal replenishment of nitrate over the shelf. Tanaka *et al.* (2004)<sup>[4]</sup> have suggested that the slightly lighter isotopic composition of nitrate observed in the bottom water of the middle shelf might be due to new nitrate input by nitrification. With the onset of winter mixing, nitrate regenerated in summer bottom waters mixes upwards to the surface.

Measurements of nitrification rates at Skan Bay, Alaska, show that nitrification occurs throughout the water column<sup>[5]</sup>. In central North Pacific waters, Wada and Hattori (1971)<sup>[6]</sup> observed that light does not inhibit nitrification. This observation has since been corroborated by the synthesis of worldwide measurements that show no clear increase in specific nitrification rates with depth<sup>[1]</sup>. Worldwide values are noted to vary substantially, with rates spanning four orders of magnitude. The median is  $0.195 \text{ d}^{-1}$ . In this synthesis of observations, no significant relationship with either time of year or latitude was found, but the low number of observations could be obscuring any relationship that may exist. The measurements of Hattori *et al.* (1978)<sup>[5]</sup> and Wada and Hattori (1971)<sup>[6]</sup>, are the most representative of the Bering Sea, being the closest to the location.

This ecosystem modeling study was undertaken to examine the role of water column nitrification in the Bering Sea. In particular, what is the resupply of nitrate from nitrification? And, how much of the annual primary production is supported by regenerated nitrate? Given the uncertainties and sparse observations, we conducted a sensitivity study to evaluate a range of nitrification rates and the consequences of parameter selection.

## 2 Methods

A vertically resolved 1-dimensional (1-D) ecosystem model incorporating nitrification was employed to examine this process on the middle shelf of the Bering Sea. The model was applied at the NOAA/PMEL M2 mooring site (Figure 1, water depth = 74 m) where a time series of biophysical measurements has been generated for over the last decade. Small mean flow at the M2 site supports the assumption that it is reasonable to use a 1-D vertical model in this region<sup>[7,8]</sup>. The model was run for years 1997<sup>[9]</sup> and 2003. These two years are representative of different sea ice conditions on the shelf. In year 1997, sea ice was present at M2 from mid-March until April 10. In 2003 annual sea ice did not extend this far south. For 2003, a time series of nitrate concentrations at the M2 mooring site from May through December was available for model validation<sup>[10]</sup>.

The 1-D coupled ice-ocean ecosystem model of Jin *et al.* (2007)<sup>[9]</sup> has ten compartments: three microalgae (pelagic diatoms, flagellates and ice algae), three zooplankton (copepods, large zooplankton, and microzooplankton), three nutrients (nitrate + nitrite, ammonium, and dissolved silicon) and detritus. The seawater ecosystem component is based on the Physical Ecosystem Model (PhEcoM)<sup>[8,11]</sup> adapted from Eslinger *et al.* (2001)<sup>[12]</sup>, and the ice algae ecosystem model of Jin *et al.* (2006b)<sup>[13]</sup>. A physical model including a 2.5-level turbulence model is coupled to the biological model described above. The model is forced by tides, wind, shortwave radiation, and surface heat and salt

flux, and restored to available observed daily sea surface temperature and salinity. Initial temperature and salinity conditions, and nitrate concentration ( $12 \mu\text{M}$ ) were taken from the M2 mooring data.

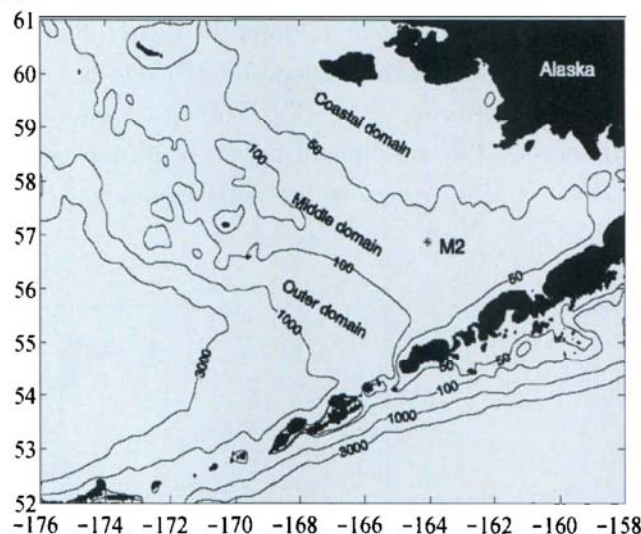


Fig. 1 Topography of southeastern Bering Sea. The NOAA-PMEL biophysical mooring site M2 is marked with an asterisk in the middle domain<sup>[8]</sup>.

Nitrification is modeled simply as the ‘decay’ of ammonium to ‘regenerated’ nitrate at a constant specific rate — the simplest assumption, given the current uncertainties related to the process. The nitrogen cycle processes of denitrification and nitrogen fixation, and horizontal transport of nitrate are not included in the model. A specific nitrification rate of  $0.015 \text{ d}^{-1}$  was chosen as the model standard value based on estimated *in situ* nitrite production rates from the North Pacific Ocean<sup>[6]</sup> and a study using spike abundance of the  $^{15}\text{N}$  isotope tracked from ammonium to the nitrite and/or nitrate pools in the Aleutian Islands of Alaska<sup>[5]</sup>. Oxidation of ammonium was measured by tracking the abundance of labeled ammonium added at a concentration of ten  $\mu\text{g-atoms N/l}$ . The rates measured from the tracer technique were similar to the rates estimated from 4-day concentration changes of nitrate, nitrite and ammonium within experimental bottles, and from 18 day *in situ* changes of these nutrients in the water column of Skan Bay, Unalaska Island, Alaska. We define the specific nitrification rate,  $\lambda_{\text{nitrif}}$ , as the ammonium oxidation rate divided by the corresponding ammonium concentration. The standard value of  $0.015 \text{ d}^{-1}$  for  $\lambda_{\text{nitrif}}$  is at the lower end of the range of observed rates worldwide. The model was run for years 2003 and 1997 using this standard  $\lambda_{\text{nitrif}}$ . In addition to running the model with no nitrification for year 2003, two more  $\lambda_{\text{nitrif}}$ ’s of  $0.03$  and  $0.06 \text{ d}^{-1}$  were tested. To evaluate the sensitivity of the model results to these three  $\lambda_{\text{nitrif}}$ ’s (i. e.  $0$ ,  $0.03$  and  $0.06 \text{ d}^{-1}$ ), we compared simulated (1) annual net primary production (NPP), (2) diatom NPP, (3) flagellate NPP, (4) year-end integrated water column nitrate and (5) year-end nitrate concentration at 11–15 m depth to observations and model results using the standard  $\lambda_{\text{nitrif}}$ .

### 3 Results and Discussion

Model results shown in Figure 2a illustrate the very repeatable spring drawdown of nitrate during the phytoplankton bloom in May followed by nearly depleted values in the summer. These yearly events are recorded in a composite of mooring and water bottle samples from 11–15 m depth at the M2 mooring site (1997–2005) (Figure 2b from Staben *et al.* 2006<sup>[10]</sup>). The record shows a fall enrichment period of nitrate concentrations starting around early-October, which is also evident in the 2003 model run (Figure 2a).

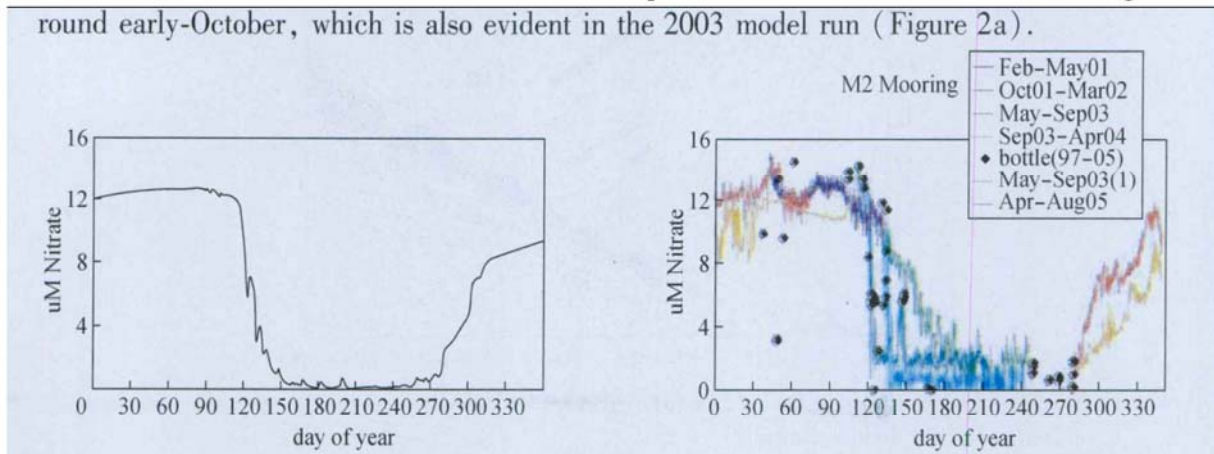


Fig. 2 Time series of (a) simulated nitrate concentrations (this study) and (b) nitrate measurements (Staben *et al.* 2006)<sup>[10]</sup> at depth 11–15 m at the M2 site. The black diamonds are data from shipboard measurements.

The standard  $\lambda_{\text{nitrif}}$  of  $0.015 \text{ d}^{-1}$  produces the closest match of the model results to the observational data. Figure 3 shows the comparison of mooring fluorometer data with simulated total phytoplankton at 12 m depth for year 2003. The comparison of mooring fluorometer data with simulated total phytoplankton at 12 m depth for year 1997 is an even better match (see Figure 4a in Jin *et al.* 2006b<sup>[13]</sup>). No nitrification and higher rates of nitrification ( $0.03$  and  $0.06 \text{ d}^{-1}$ ) result in lower and higher concentrations of nitrate at 11–15 m depth (Table 1; 4.2, 11.4, and 12.3, respectively), compared to  $10 \mu\text{M}$  observed in 2003 (Figure 2b; day 0 value for year 2004) and  $9.6 \mu\text{M}$  using the standard  $\lambda_{\text{nitrif}}$  of  $0.015 \text{ d}^{-1}$ .

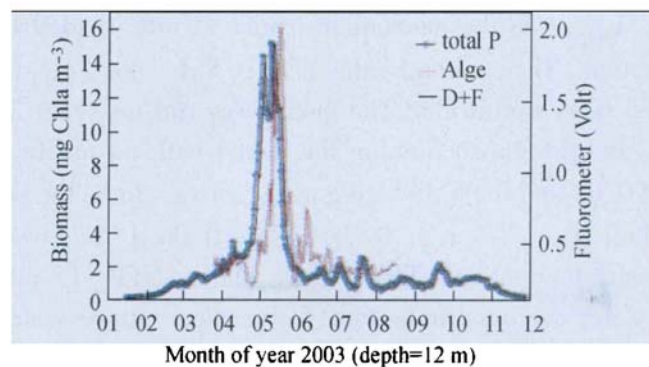


Fig. 3 Time series of fluorometer observations and simulated total phytoplankton biomass at depth of 12 m.

Specific nitrification rate also appears to affect the proportion of phytoplankton net pri-



mary production (NPP) among different phytoplankton types (Table 1), but not total NPP. Higher  $\lambda_{\text{nitrif}}$ 's favor diatom production in the model. This predilection is likely due to input of ammonium from the senescing spring bloom and rapid conversion of ammonium to nitrate. Complete turnover in the ammonium pool in less than 24 h may be possible, even in surface waters<sup>[1]</sup>. Regeneration of nitrate in the model occurs early in surface waters when diatoms are the dominant bloomers. Grazing on the diatoms then routes the N through secondary producers and sinking detritus making fewer nutrients available in the euphotic zone for flagellate production.

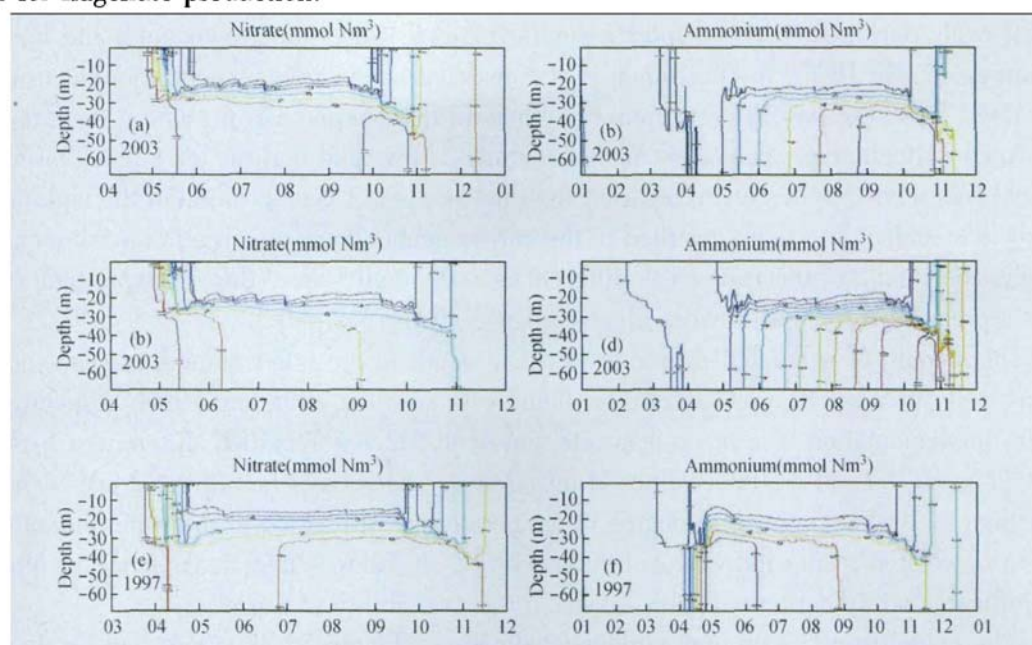


Fig. 4 Depth-time contour plots of simulated nitrate for year (a) 2003 with nitrification, (c) 2003 without nitrification, and (e) 1997 with nitrification, and ammonium for year (b) 2003 with nitrification, (d) 2003 without nitrification, and (f) 1997 with nitrification.

Table 1. The influence of selected parameter values on simulated total net primary production (NPP  $\text{g C m}^{-2} \text{ y}^{-1}$ ), diatom NPP, flagellate NPP, year-end integrated water column nitrate, and year-end nitrate concentration at 11–15 m depth. The observed year-end nitrate concentration at 11–15 m depth was  $10 \mu\text{M}$  (day 0 for year 2004 in Figure 2b).

Nitrification Rate ( $\text{d}^{-1}$ )	Year	Net Primary Production (NPP)	Diatom NPP	Flagellate NPP	Year-end nitrate ( $\text{mmol N m}^{-2}$ )	Year-end nitrate at 11–15 m depth ( $\mu\text{M}$ )
No nitrification	2003	90.4	19.8	70.6	294	4.2
0.015 (standard)	2003	90.6	28.1	62.4	665	9.6
0.03	2003	90.2	40.8	49.3	785	11.4
0.06	2003	91.2	51.0	40.1	860	12.3
0.015 (standard)	1997	83.7	1.9	35.6	615	8.7

Even though modeled total NPP is not impacted by the selection of  $\lambda_{\text{nitrif}}$ , the amount of nitrate remaining in the simulated water column at the end of the year is. A factor of two increase in the rate results in a 15% increase in mid-winter column integrated nitrate (Table 1). No nitrification halves the amount of nitrate left, while using a rate of  $0.06 \text{ d}^{-1}$  results in a 23% increase in nitrate in the water column come January 1, 2004. Higher mid-winter nitrate is reflected in the higher concentrations of nitrate below the mixed layer. Ni-

trate below the summer mixed layer will only impact the total NPP if mixed upwards into the euphotic zone, by e. g. storm, wind or convective mixing. This implies that a change in climate towards more storms may result in higher NPP. On the other hand, if warming trends resulting in stronger ocean stratification continue these occurrences may be lessened.

Ammonium concentrations begin to increase in bottom waters following the onset of sinking phytoplankton and detritus. As summer progresses, nitrate concentrations increase as the ammonium concentrations decrease in late-summer (Figures 4a and 4b). This pattern is not seen in the absence of nitrification (Figures 4c and 4d). Contour plots for the annual cycle during PROBES display a similar pattern of declining ammonium and increasing nitrate<sup>[2]</sup>. In 1997, the maximum in the modeled ammonium concentration occurred in mid-May. This year was different from the others in that sea ice was present at the site from Mid-April through May. An earlier modeling study<sup>[9]</sup> revealed that the phytoplankton bloom in 1997 was seeded by ice algae released from the sea ice. Decomposition of the sinking sea ice algae to ammonium likely resulted in the earlier ammonium concentration maximum. Although, the timing of the maxima is different in individual years, the recurring pattern for these representative years provides clear evidence of nitrification.

The amount of simulated nitrate at 11-15 m depth in the water column at year-end varies as well, 9.5 vs. 8.7  $\mu\text{M}$  nitrate on January 1, for year 2004 and 1997, respectively. Recent implementation of a moored nitrate sensor at M2 has recorded differences between years (Figure 2b). Mid-winter values of nitrate were observed to be at least 2  $\mu\text{M}$  higher in 2004 than in 2003. Timing and degree of temperature stratification of the water column appear to be related to the individual differences<sup>[10]</sup>. It follows then that change in climate that influence stratification will play a role in the availability of nitrate.

The model results with and without nitrification (Figure 5) illustrate that by the end

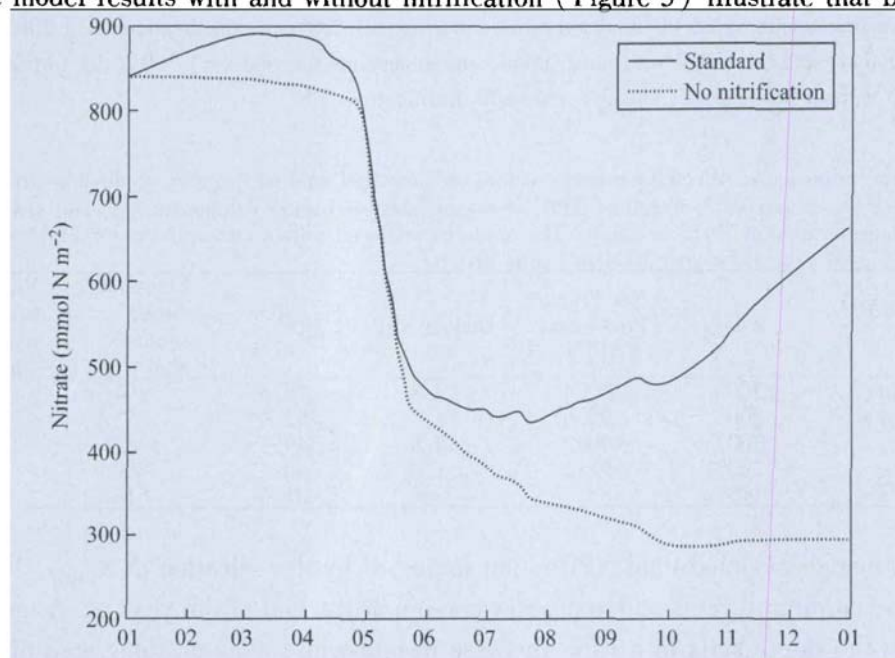


Fig. 5 Model time series comparing water column nitrate content for model runs with nitrification (solid line) and without nitrification (dashed line) for year 2003.

of the year, well over half of the nitrate in the water column is regenerated nitrate; an amount equal to  $\sim 38\%$  of the initialized nitrate content when the model run started on January 1, 2003. This amount is somewhat higher than the estimated 20-30% nitrate input through nitrification<sup>[3]</sup> based on PROBES time series data. To estimate how much the amount of regenerated nitrate would contribute to annual primary production, we initialized the model run for 2003 with 38% less nitrate (i. e.  $7.5 \mu\text{M}$  instead of  $12 \mu\text{M}$ ). The result was 24% less primary production over the year-long model simulation period.

## 4 Conclusions

Knowledge of nutrient sources, including nitrification, is needed to understand the impact of a changing climate on the nitrate supply on which arctic marine life critically depends. Nitrification is a difficult process to quantify<sup>[1]</sup>. More measurements of nitrification rates are needed, especially in Arctic waters where virtually none exist.

When measurements are limited, using a model is an especially good way to gain insights and help focus scientific efforts on critical questions. One question raised by this modeling study is, how does nitrification rate impact the dominant phytoplankton type? We found that different  $\lambda_{\text{nitrif}}$ 's do not significantly impact total primary production (i. e. simulated NPP), but rather the contribution to primary production from specific phytoplankton types supported by the available N shifts. It therefore follows that any change in environmental or ecological factors that impact the two different groups of bacteria that convert ammonium to nitrite and nitrite to nitrate in seawater has the potential to influence the dominant phytoplankton functional type. The results of this modeling study also suggest that at even the relatively low nitrification rates observed in the vicinity of the Bering Sea and in sub-arctic Pacific waters, nitrification is an important source of the nitrate available for primary production.

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