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The role of sediments on the Bering Sea shelf N cycle: Insights from measurements of benthic denitrification and benthic DIN fluxes



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ABSTRACT

Continental shelves are hotspots for sedimentary denitrification, and the loss of N through denitrification can limit primary production in ecosystems. Spatial and seasonal trends in sedimentary denitrification and benthic nutrient fluxes are poorly characterized in the highly productive Bering Sea shelf ecosystem. Through the Bering Sea Ecosystem Study (BEST) program, we measured benthic fluxes of N₂ and dissolved inorganic nitrogen (DIN: NH₄⁺ + NO₂⁻ + NO₃⁻), the extent of coupled sedimentary nitrification/denitrification, and the water column DIN deficit relative to phosphate, as indicated by a modified N* parameter (N**), on the Bering Sea shelf in the spring and summer 2009–2010. We found that sedimentary denitrification is widespread over the shelf, it is fueled mostly through coupled nitrification/denitrification, the net balance of sedimentary DIN flux is near zero over the shelf, and that the water column DIN deficit varies widely according to season and year. In the summer, N** in the surface layer appeared to be strongly affected by non-Redfieldian uptake of inorganic nutrients by phytoplankton in the spring bloom; in the winter, N** was strongly affected by sedimentary denitrification. Our findings indicate that the estimate of total N loss in Bering Sea shelf sediments should be revised upwards by at least 50% to 5.2–6.2 Tg N y⁻¹. In addition, sediments are not a significant source of remineralized N for primary production over the shelf; hence sedimentary denitrification exacerbates N-limitation of the ecosystem.

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1. Introduction

The Bering Sea hosts one of the most productive oceanic ecosystems and provides at least 50% of the U.S. commercial fishery industry (NRC, 1996; Sigler et al., 2010). The vast Bering Sea shelf covers 40% of the Bering Sea surface area, and it is characterized by seasonal sea ice cover that is particularly sensitive to interannual variability in climate (Hunt Jr. et al., 2002; Rho and Whitledge, 2007; Stabeno et al., 2007; Hunt Jr. et al., 2010). Recent studies in the Bering Sea indicate that the area is undergoing rapid change, and climate change effects on nutrient dynamics and the lower trophic levels in the ecosystem are poorly characterized (Grebmeier et al., 2006).

Sedimentary denitrification, that is, the anaerobic microbially mediated conversion of fixed N (nitrogen) to N₂ (gas), is an important sink of bioavailable N in the world ocean. Globally, continental shelves may be the largest sink of fixed N; Seitzinger

et al. (2006) estimated that sedimentary denitrification on continental shelves account for 44% of total global denitrification. As a large sink of fixed N, sedimentary denitrification can negatively influence primary production on many continental shelves (for example, Christensen et al., 1987; Fennel et al., 2006). Previous studies of sedimentary denitrification on the Bering Sea shelf are limited in spatial and temporal distribution, but they have indicated that denitrification is an important N cycle process on the shelf (Haines et al., 1981; Whitledge et al., 1986; Rowe and Phoel, 1992; Henriksen et al., 1993; Tanaka et al., 2004; Granger et al., 2011).

Water column nutrient concentrations on the Bering Sea shelf exhibit clear seasonal patterns and some interannual variability (Whitledge et al., 1986; Rho et al., 2005; Mordy et al., 2012). In the winter, nutrient concentrations are highest on the Bering Sea shelf, and the water column is mixed to the seafloor. In late spring or early summer, following sea ice retreat, the shelf experiences massive phytoplankton blooms, and the timing of these blooms is strongly dependent on the timing of winter sea ice retreat (Hunt et al., 2002; Stabeno et al., 2007). Following the spring bloom, a large part of the shelf (middle shelf, 50–100 m depth) becomes a two-layer system with a wind-mixed nutrient-deplete surface

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layer and a nutrient-replete bottom layer (Mordy et al., 2012). Dissolved inorganic nitrogen (DIN: $\text{NH}_4^+ + \text{NO}_2^- + \text{NO}_3^-$) has been hypothesized to limit late spring and summer productivity on the eastern shelf because of the depletion of DIN in the mixed layer following a bloom event (Whitledge et al., 1988; Rho et al., 2005; Mathis et al., 2010). The concentration of PO_4^{3-} in the bottom layer of spring and summer are similar to the PO_4^{3-} concentration in the winter water column (Mordy et al., 2012). Seasonal variations and distributions of NO_2^- are rarely reported for the Bering Sea shelf, but are usually less than $0.7 \mu\text{M}$ (Granger et al., 2011). Water column NO_3^- is usually highest in the spring (pre-bloom) throughout the water column; in the summer and fall, deep water NO_3^- is usually somewhat depleted as compared with pre-bloom values, but is still at least $5 \mu\text{M}$ (Mordy et al., 2012). On the middle shelf, NH_4^+ concentrations are uncharacteristically high for a well-oxygenated oceanic water column. NH_4^+ concentrations are highest post-bloom (in summer, as compared to the winter) in the bottom layer (“cold pool”), and usually reach $4\text{--}8 \mu\text{M}$, but can be as high as $15 \mu\text{M}$ (Whitledge et al., 1986; Mordy et al., 2008; Granger et al., 2011; Mordy et al., 2012). Efflux of NH_4^+ from sediments following ammonification has been implicated as a cause of these elevated NH_4^+ concentrations (Whitledge et al., 1986; Rowe and Phoel, 1992; Granger et al., 2011). Granger et al. (2011) used a stable isotope approach to estimate that 50–95% of sediment-regenerated NH_4^+ is released into the water column, which could presumably be used to sustain primary production. However, experimentally determined benthic DIN fluxes over the entire Bering Sea shelf are lacking.

The ratio of water column DIN relative to PO_4^{3-} and its associated geochemical tracer N^* [$\text{N}^* = (\text{DIN} - 16 * \text{PO}_4^{3-}) + 2.9$] are commonly used to assess the degree of N deficiency or N excess in a water mass (Gruber and Sarmiento, 1997). Assuming that biomass and remineralization occurs in a N:P ratio = 16 (Redfield stoichiometry; Redfield, 1934, 1958), negative deviations in water column DIN relative to PO_4^{3-} (negative N^*) indicate regions of DIN loss or PO_4^{3-} input, while positive deviations (positive N^*) indicate regions of DIN input or PO_4^{3-} loss (Gruber and Sarmiento, 1997). Consequently, oceanic regions with very high N^* values generally have high inputs of N through N_2 -fixation (such as the North Atlantic), and oceanic regions with very low N^* values are generally regions of intense N loss through sedimentary or water column denitrification (such as the oxygen deficient zones in the Eastern Tropical Pacific; Gruber and Sarmiento, 1997; Codispoti et al., 2001; Deutsch et al., 2007). Several investigators have reported low water column DIN:DIP ratios (relative to Redfield DIN:DIP = 16) at discrete times in the year on the Bering Sea shelf, including April (Granger et al., 2011), August and September (Tanaka et al., 2004), late September (Mordy et al., 2010); only Mordy et al. (2012) has examined seasonal trends (along a 70 m isobath) in nutrient concentrations. To assess seasonal and inter-annual changes in the Bering Sea shelf N deficit, Mordy et al. (2010) established a regional N^* tracer (Codispoti et al., 2001) which accounts for N deficient waters entering the Bering Sea shelf.

Based on limited data sets, sedimentary denitrification has been implicated as the cause of low DIN:DIP ratios on the shelf (Tanaka

et al., 2004). However, the spatial extent, seasonal variability, and magnitude of shelf N loss is poorly constrained. Sedimentary N loss typically occurs through one of two pathways (or a combination of both): direct denitrification and coupled nitrification/denitrification. In direct denitrification, there is flux of NO_3^- into the sediments, and NO_3^- from the overlying water column is the substrate for N loss. In coupled nitrification/denitrification, reduced N-containing organic matter is remineralized to NH_4^+ , nitrified to NO_2^- or NO_3^- , and subsequently denitrified (through either anammox or canonical denitrification; in this paper, we do not differentiate anammox from canonical denitrification). This scenario is characterized by low DIN flux into and out of the sediments co-occurring with N_2 (gas) flux. Coupled nitrification/denitrification may be the dominant pathway of N loss on many continental shelves (Devol and Christensen, 1993; Seitzinger and Giblin, 1996). The pathway of sedimentary N loss on the Bering Sea shelf has not been determined by direct rate measurements over the entire shelf.

In the present study, we measured the role of sediments in remineralization of inorganic N and sedimentary N loss to elucidate sedimentary denitrification pathways and determine the degree to which sediments are a net source or sink of remineralized N to the water column. We also investigated seasonality in water column DIN:DIP ratios to assess the variability of nutrient limitation.

2. Methods

2.1. Study area

The data were collected on a series of 4 cruises from 2009 to 2010 (Table 1) as a part of the interdisciplinary Bering Sea Ecosystem Study (BEST) program. Each cruise sampled the Bering Shelf, from south of St. Lawrence Island to the Aleutian Islands, and from 180°E to 160°W . Hydrographic transects were repeated on each cruise (Fig. 1), except that ice cover prevented sampling on the inner shelf during the spring 2009 and the first 2010 cruise. Station depths ranged from 40 m (inner shelf) to 3500 m (deep, off-shelf).

2.2. Benthic fluxes

2.2.1. Sample collection

Sediment cores were collected with an Ocean Instruments MC 800 multicorer, an eight-tube multi-corer that takes 10-cm diameter cores up to 40-cm in length while preserving the sediment–water interface. Bottom water was also collected at each station using a Niskin bottle attached to the multi-corer.

2.2.2. Whole-core incubation

Whole-core incubations were used to measure benthic dissolved inorganic nitrogen (DIN: $\text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+$) fluxes, aerobic respiration, and denitrification rates. The incubation set-up was the same as that described in Davenport et al. (2012) and modified by Esch et al. (2013). Briefly, 8-cm diameter sub-cores containing about 15 cm of sediment and 10 cm of overlying water were allowed to equilibrate for 24 h at in-situ temperatures (2°C cold van). Then, the overlying water was siphoned off from the core without disturbing the sediment, and it was replaced by niskin-collected bottom water. Cores were sealed with silicone (in 2009) or PVC (in 2010) closures in a manner that avoided trapped air bubbles. Benthic fluxes ($n=2$ or 3) were determined by monitoring nutrient concentration in the overlying water during a period of two to five days after sample collection. The closures contained both an inlet and an outlet. The inlet was connected to a reservoir filled with overlying water from the sample location. When samples were

Table 1
Listing of cruises, dates, and corresponding measurements for this study.

Cruise ID	Ship	Dates	Measurements	Conditions
HLY09-02	R.V. Healy	04/04/09–05/12/09	Sediment: DIN+O ₂ flux water column: nutrients	Ice on inner shelf
Knorr195-10	R.V. Knorr	06/14/09–07/13/09	Sediment: DIN+O ₂ flux water column: nutrients	Largely ice-free
TN249	R.V. Thompson	05/09/10–06/14/10	Sediment: N ₂ flux water column: nutrients	Late advance of sea ice
TN250	R.V. Thompson	06/16/10–07/14/10	Sediment: N ₂ flux water column: nutrients	Largely ice-free

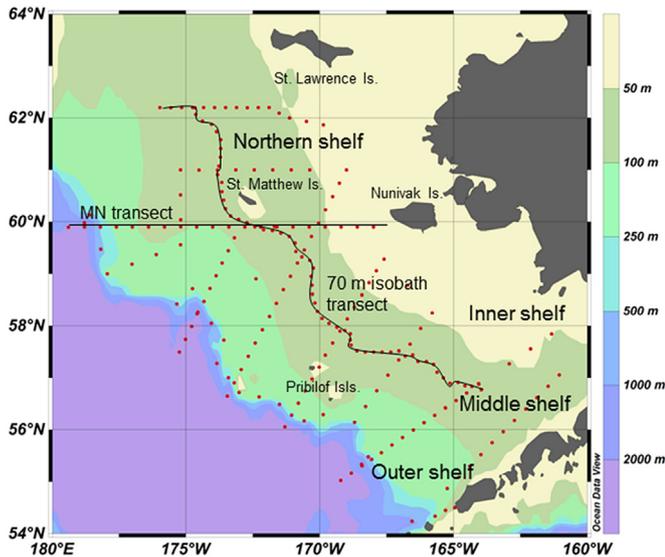


Fig. 1. Typical cruise track for the BEST program. This map is for Knorr 195–10. The MN line and 70 m isobath transects are highlighted.

drawn from the incubation core, the volume removed was replaced with water from the reservoir. All sampling was done without air contamination of the incubation cores.

Oxygen concentration in the overlying water of the incubation cores was measured using a PreSens Microx TX2 fiber optic oxygen meter combined with a flow-through PreSens optode. The optode was calibrated using air-equilibrated seawater and seawater deoxygenated with sodium sulfite. Five mL of overlying water was removed for the measurement. Aerobic respiration was calculated from the change in O_2 concentration during the 2–5 day incubation; we fitted the oxygen concentration for the time series to a 2nd order polynomial. In some instances, only two time points were available; in these cases, we used a two-point slope. This only affected station 35 for HLY0902 and stations 45, 60, and 89 for KN195–10. In a comparison of the 2nd order polynomial fit versus a 2-point linear fit, O_2 respiration calculated with a 2-point linear fit was almost always lower than that of the 2nd order polynomial fit (mean \pm 1 S.D.: 13.8% \pm 9.5%). We calculated the flux according to the formula:

$$J = \left\{ \frac{dc}{dt} \right\}_{t=0} * V * A^{-1} \quad (1)$$

where J is the O_2 flux ($\text{mmol m}^{-2} \text{d}^{-1}$), $\{dc/dt\}_{t=0}$ is the instantaneous change in O_2 concentration at $t=0$ ($\pm 0.4\%$ accuracy at 100% O_2 saturation), V is the volume of the overlying water in the flux core (m^3), and A is the surface area of the core (m^2). Using an error propagation approach, we estimated the maximum uncertainty in the J term to be 1.65%. We corrected the oxygen fluxes to account for the addition of reservoir water to the core incubation. Furthermore, in 2009, the silicone closures had a slow desorption of oxygen, and we corrected the oxygen flux data as previously presented (Davenport et al., 2012; Esch et al., 2013).

To measure DIN concentration, we used a SmartChem autoanalyzer (Westco Scientific) based on methods presented in Gordon et al. (1994). The uncertainty for DIN concentration is 1.1%. DIN fluxes were calculated from the change in nutrient concentration in the overlying water column during the initial part of the core incubation (within the first 2–2.5 days). Changes in nutrient concentration were fitted by linear regression and the flux was calculated according to Eq. (1).

During the 2010 cruises, we used two methods to directly measure sedimentary denitrification rates through dissolved $N_2:Ar$ ratios in the overlying water of the core. First, we measured N_2 , O_2 , and Ar concentrations with a membrane inlet mass spectrometer (MIMS), as described by Chang and Devol (2009) and Kana et al. (1994). The MIMS is a modification to that first described in Kana et al. (1994). Briefly, water from the core outlet was introduced into the vacuum line without alteration using a Rainin peristaltic pump with Viton tubing. Immediately after passing through the silicone capillary membrane inlet and before introduction to the mass spectrometer, the sample passed through a u-tube immersed in liquid N to remove water vapor and CO_2 . The sample was analyzed using a Pfeiffer Vacuum Balzers Prisma 200 quadrupole mass spectrometer. Gas ratios were determined when the signal stabilized after sample introduction to the vacuum line (between 2 and 10 min lapsed until the signal stabilized). We used the average $N_2:Ar$ ratio of 3–5 values recorded within one minute after signal stabilization; the variation among these measurements was always less than 0.1% and usually within 0.05%. The instrument was kept in the same 2 °C cold van for as the core incubations, and temperature was recorded

every hour to ensure that samples and standards were maintained at constant temperature. Salinity standards to calibrate MIMS gas ratios were air-equilibrated and made daily. We did not remove O_2 from the sample prior to introduction to the MIMS, which Eyre et al. (2002) claims can affect the $N_2:Ar$ ratio because of the creation of mass interferences by a combination of oxygen-containing ions. As noted in Chang and Devol (2009) and similar in response to Kana and Weiss (2004), the error in $N_2:Ar$ ratios attributable to O_2 in the sample with this MIMS instrument is 0.06%.

For the MIMS measurements, $N_2:Ar$ ratios were measured over a period of 1–5 days. During the entire whole core incubation, the overlying water column was continuously stirred. The incubation was terminated when the O_2 concentration dropped below 140 μM , which represented approximately 50% of the initial concentration. This ensured that gas ratio measurements were not altered by a change in microbial physiology following a decrease in O_2 concentrations.

Second, we collected and preserved water samples for $N_2:Ar$ ratios and quantification of the absolute N_2 flux from the beginning and end of the dedicated whole core incubations. These samples were collected after the initial equilibration (initial time point) and after 2–3 days of incubation (final time point). Samples of the overlying water were collected without introduction of atmosphere into pre-evacuated and $HgCl_2$ -poisoned 300 ml glass flasks (Emerson et al., 1999; Chang and Devol, 2009). Sample flasks were equipped with gas tight 9 mm-bore Louwers-Hapert single o-ring valves, and were returned to the University of Washington for analysis. Samples were weighed to determine water volume. Following equilibration with the headspace by rotating the flask in a constant temperature water bath for at least 16 h, we removed almost all of the water using a vacuum pump. A known amount of ^{36}Ar spike was added to the headspace gas in order to determine the absolute concentration of N_2 gas in each sample. Then, the headspace gas was pumped through liquid N traps to remove CO_2 and H_2O and cryogenically frozen into a steel finger immersed in liquid He. A Finnigan dual-inlet Delta XL Isotope Ratio Mass Spectrometer (IRMS) was used to measure the dissolved gas ratios (28:40, 29:28, 36:40, 32:40) relative to an in-house gas standard with known gas ratios (Emerson et al., 1999; Hamme and Emerson, 2002). We corrected the gas ratio data (with a series of $N_2:Ar$ gas samples containing different O_2 concentrations) in order to account for the effect of O_2 on the ionization efficiency of the other gases (Emerson et al., 1999; Chang and Devol, 2009). This IRMS procedure to measure gas ratios and absolute N_2 concentration has shown to be precise to 0.1%, which represents 0.5 μM error for a typical N_2 concentration of 500 μM (Emerson et al., 1999).

2.3. Water column nutrients

Samples for nutrient analysis were syringe-filtered using 0.45 μm cellulose acetate membranes, and collected in 30 ml acid-washed, high-density polyethylene bottles after 3 rinses. Samples were analyzed shipboard within 1–12 h of collection. NO_3^- , NO_2^- and NH_4^+ concentrations were determined using a combination of analytical components from Alpkem, Perstorp, and Technicon. We closely followed the WOCE-JGOFS standardization and analysis procedure specified by Gordon et al. (1994), including reagent preparation, calibration of labware, preparation of primary and secondary standards, and corrections for blanks and refractive index. We used the program Ocean Data View (Schlitzer, 2011) to visualize the distribution of water-column nutrients.

2.4. Calculations

The regional N^{**} tracer (Mordy et al., 2010) was used to determine the N deficit that results from the biogeochemical processes occurring solely in the eastern Bering Sea. This estimate of N^{**} in the Bering Sea was determined using data from the outer shelf and slope for reference. The revised offset (5.9) from the original N^* equation published by Gruber and Sarmiento (2.9; 1997) accounts for the fact that water that replenishes the Bering Sea Shelf is already deficient in N. Mordy et al. (2010) defined a Bering Sea N^{**} as

$$N^{**} = \text{DIN} - (\text{PO}_4^{3-} * 15.5) + 5.9, \quad (2)$$

where $\text{DIN} = [\text{NO}_3^-] + [\text{NO}_2^-] + [\text{NH}_4^+]$.

For the 2009 data, we also calculated the sedimentary denitrification rate through a mass balance approach (Devol and Christensen, 1993; Hartnett and Devol, 2003). For this, the denitrification rate (rate of removal of DIN) is the sum of the regenerated NH_4^+ produced by sedimentary aerobic respiration and the DIN flux (where net DIN flux into the sediment is positive and net DIN efflux is negative). Hence, when there was an efflux of DIN from the sediment, denitrification rate is the difference between the NH_4^+ produced by sedimentary aerobic respiration and the net DIN flux out of the sediment. We used a standard Redfield stoichiometry to convert the moles of O_2 respired to moles of regenerated NH_4^+ (106:16; Froelich et al., 1979). Thus, denitrification was calculated according to the following:

$$\text{Denitrification rate} = dO_2/dt(16/106) + \text{flux}(\text{DIN}), \quad (3)$$

where dO_2/dt = oxygen consumption rate and DIN flux is positive into the sediment.

3. Results

3.1. N_2 flux measurements of sedimentary denitrification rates

We measured N_2 flux with both IRMS and MIMS on cruise TN249 on 14 individual cores and compared the results between methods. There was no significant difference between the N_2 flux rates measured with both techniques (Wilcoxon signed-rank test, $p=0.12$, $n=14$) and there was a significant linear regression between both techniques ($R^2=0.68$, $p<0.01$, Fig. 2).

Active sedimentary denitrification was detected at all shelf, slope, and deep stations that were sampled (Fig. 3). The lower range of denitrification rates was similar between the TN249 and TN250 cruise, but during the TN249 cruise there were 2 stations that recorded dramatically higher denitrification rates with the IRMS technique (Fig. 3a; 57.00°N, 170.65°W: 4.06 $\text{mmol N m}^{-2} \text{d}^{-1}$; 59.89°N, 178.89°W: 2.51 $\text{mmol N m}^{-2} \text{d}^{-1}$). For both TN249 and TN250, there were no apparent trends in the distribution of sediment denitrification over the entire Bering Sea shelf (Fig. 3, Table 2). Denitrification rates on the middle shelf (depth 50–100 m) were comparable to those on the outer shelf (depth 100–200 m) for both cruises (Fig. 3). For TN250, denitrification rates were similar in range and distribution for the inner shelf stations (<50 m, $n=3$) compared to the remaining shelf stations (Fig. 3b, $n=13$). Also, we found no apparent differences in the magnitude and distribution of denitrification rates, regardless of technique, north and south of 60°N, the approximate latitude that physically separates the northern and southern shelves (Stabeno et al., 2006).

For both the MIMS and IRMS technique, the denitrification rates were similar in range and mean between the shelf (depth 47–208 m) and slope (depth 381–656 m) stations (Table 2). For cruise TN250, we compared denitrification rates in the deep Bering Sea (depth 1098–2789 m) and shelf (depth 40–149 m) stations. Rates were comparable between deep and shelf stations, although the range for the shelf stations was somewhat greater (Table 2).

3.2. Benthic DIN fluxes and calculated denitrification rates

For the HLY09-02 and Knorr 195-10 cruises, we used a whole-core incubation technique to measure sediment DIN and O_2 flux from shelf stations (depth 31–196 m), and we estimated rates of NH_4^+ regeneration and denitrification using a mass balance approach (Section 2.4). The station sampling date, depth, and location for these analyses can be found in Table 3.

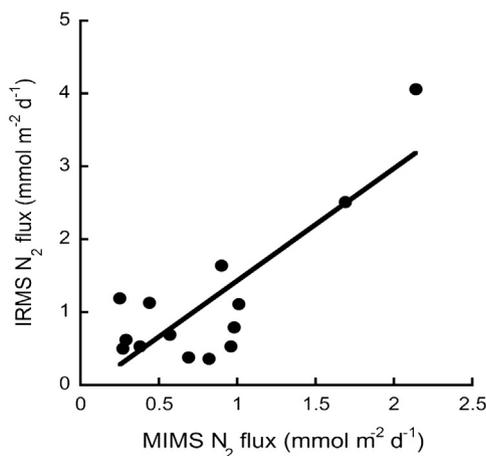


Fig. 2. Correlation (linear regression) of MIMS and IRMS N_2 flux measurements. Each data point represents measurements for both MIMS and IRMS from a single core. $R^2=0.68$, $p<0.01$.

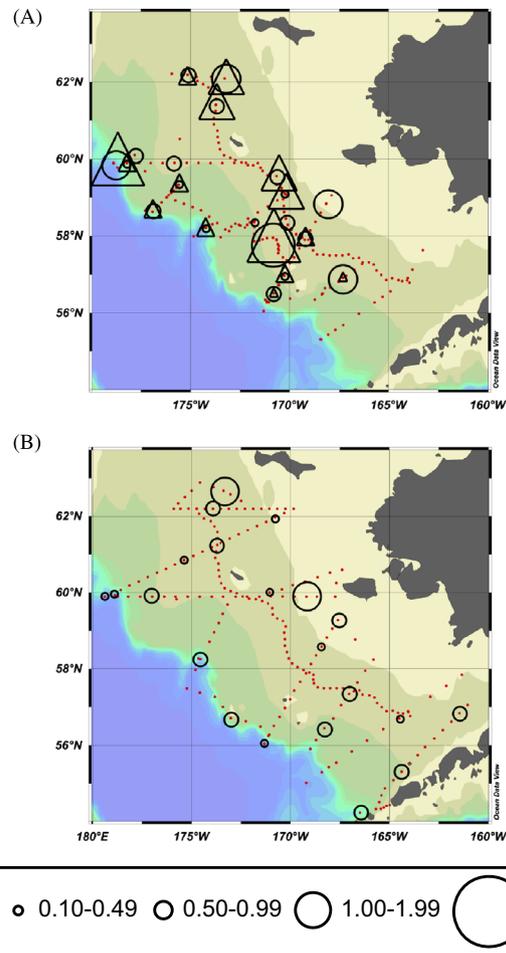


Fig. 3. Denitrification rates on the Bering Sea shelf in 2010. (A) TN249, late spring 2010 (B) TN 250, summer 2010. Rates of N_2 flux ($\text{mmol N m}^{-2} \text{d}^{-1}$) in whole core incubations were measured with isotope ratio mass spectrometry (triangles) and membrane inlet mass spectrometry (circles). Legend indicates the magnitude of the denitrification rate.

For the HLY09-02 cruise (spring 2009), DIN fluxes from cores were variable by station over the entire shelf, but mostly small (range: -0.28 to $0.22 \text{ mmol N m}^{-2} \text{d}^{-1}$; Table 4). NH_4^+ and NO_2^- fluxes were not consistently into or out of the sediments (Table 4). The shelf average flux for both NH_4^+ and NO_2^- was very small and not significantly different than 0 (Table 4). NO_3^- fluxes were out of the sediment for most stations (Table 4), and the shelf-wide sedimentary NO_2^- efflux average was also small ($-0.06 \pm 0.03 \text{ mmol N m}^{-2} \text{d}^{-1}$). The denitrification rate, calculated as the difference between the respiration-generated NH_4^+ flux and measured DIN flux, averaged $0.86 \pm 0.06 \text{ mmol N m}^{-2} \text{d}^{-1}$ (Table 4).

For the Knorr 195-10 cruise (summer 2009), more stations were a sink of DIN from the overlying water column than were a source of DIN to the water column (Table 4). However, similar to the spring measurements, the shelf-wide average for all three DIN fluxes was not significantly different from 0 (Table 4). The denitrification rate was on average higher in the summer than in the spring, although there was more variability among stations (Table 4; average: $1.19 \pm 0.12 \text{ mmol N m}^{-2} \text{d}^{-1}$).

3.3. Water column N deficit

3.3.1. 2009

The spatial distribution of N^{**} values in the water column over the Bering Sea shelf was dramatically different in the 2009 spring mixed water column as compared with the 2009 summer

Table 2
Bering Sea shelf, slope, and deep denitrification rates measured by N₂ flux.

Cruise	Method	Number of stations	N ₂ flux (mmol N m ⁻² d ⁻¹)	
			Range	Mean±1 SD
TN249	IRMS	Slope: 3	0.50–2.52	1.21±0.93
		Shelf: 14	0.34–4.06	1.09±1.13
TN249	MIMS	Slope: 3	0.27–1.69	0.75±0.66
		Shelf: 17	0.25–2.14	0.78±0.49
TN250	MIMS	Deep: 4	0.25–0.80	0.56±0.21
		Shelf: 17	0.23–1.27	0.62±0.30

Table 3
Listing of station sampling date, bottom depth, and location for whole core incubations.

Station	Date (mm/dd/yr)	Depth (m)	Lat. (°N)	Long. (°W)
HLY09–02				
3	04/05/2009	72	58.22	169.12
9	04/07/2009	31	59.96	169.90
17	04/09/2009	104	59.90	174.00
32	04/15/2009	81	62.20	175.14
35	04/16/2009	62	61.96	173.24
39	04/17/2009	53	61.93	171.22
54	04/21/2009	68	58.37	168.72
58	04/22/2009	69	57.45	169.77
65	04/24/2009	111	56.73	170.52
69	04/26/2009	135	59.56	175.20
73	04/27/2009	132	59.59	175.08
83	04/28/2009	95	60.81	174.39
90	04/30/2009	134	59.55	175.15
92	05/01/2009	75	61.57	173.71
93	05/02/2009	58	62.26	172.52
98	05/04/2009	82	62.18	175.15
116	05/06/2009	134	59.56	175.15
Knorr 195–10				
22	06/18/2009	113	56.13	166.13
32	06/20/2009	104	56.75	167.87
45	06/22/2009	70	57.90	169.24
60	06/25/2009	196	57.28	173.84
79	06/29/2009	121	57.16	172.65
89	06/30/2009	66	59.71	170.32
106	07/01/2009	105	59.90	173.99
122	07/05/2009	136	59.56	175.20
130	07/06/2009	65	61.00	171.76
140	07/07/2009	62	62.20	173.11

stratified water column (Fig. 4). Along both the 70 m isobath and MN line transects, spring N^{**} was always negative, and it sometimes approached $-10 \mu\text{mol N}$ (Fig. 4A and C). This sharply contrasts with the N^{**} distribution just one month later when mixed layer N^{**} values were positive over the majority of the shelf. For instance, along the 70 m isobath, positive N^{**} values could be found as deep as 20 m (Fig. 4B). Along the MN line, there were positive N^{**} values down to 75 m (Fig. 4D) and relatively small seasonal changes in deep water N^{**} values (see Mordy et al., 2012). In summer 2009, highly positive N^{**} in surface waters was found consistently offshore of the 70 m isobath and in the southeast (Fig. 6A). Depletion in surface DIP and DIN was evident shelf-wide (Fig. 6B and C).

3.3.2. 2010

Water column N^{**} values and distributions were different in summer 2010 compared to summer 2009. There was no evidence for positive N^{**} values in the mixed layer along the 70 m isobath in either cruise in 2010, except in the extreme southeast corner (Figs. 5 and 6D). Mixed layer N^{**} values for both summer 2010 cruises were similar to the spring 2009 water column and summer

2009 deep waters. During the TN250 cruise on the MN line, positive N^{**} values were recorded in approximately the same location as in summer 2009, but positive N^{**} was detected only to a maximum depth of 35 m (data not shown). On nearly the same calendar days in 2009, N^{**}, DIP, and DIN had a different distribution in 2010 (Fig. 6D–F). As discussed above, positive deviations in surface N^{**} after the seasonal bloom were much less common over the shelf and occurred mainly in two locations (on western MN line and in the southeast corner). DIP and DIN were generally not as highly depleted as in 2009, especially in the inner and middle shelf.

4. Discussion

4.1. Widespread sedimentary denitrification on the Bering Sea shelf

The mean sedimentary denitrification rates were similar for all 3 methods that we used to measure or estimate denitrification rates for this study (Table 5). Our rates are higher than most literature values of Bering Sea shelf denitrification (Table 5), but a direct comparison is complicated by the fact that previous studies used different techniques. Also, without a direct methods comparison, a comparison of rates is complicated by the fact that the Bering Sea is possibly undergoing rapid changes which may affect nitrogen biogeochemical cycling (Grebmeier et al., 2006). Our sedimentary denitrification measurements are higher than those of the deep (>2000 m) Bering Sea (Table 5; Lehmann et al., 2005), and slightly lower than measurements from the more productive Northern Bering Sea/Anadyr waters (Table 5; Lomstein et al., 1989; Henriksen et al., 1993). The average rate for this study is similar to other denitrification rates elsewhere on Arctic shelves: on the Western Arctic shelf, Devol et al. (1997) reported an average sedimentary denitrification rate of $1.3 \text{ mmol N}_2 \text{ m}^{-2} \text{ d}^{-1}$ and Chang and Devol (2009) recorded an average rate of $0.96 \text{ mmol N}_2 \text{ m}^{-2} \text{ d}^{-1}$ in the Chukchi Sea.

Discrete measurements of N₂ flux and mass balance estimates (based on DIN flux and O₂ consumption/NH₄⁺ regeneration) indicate no strong spatial trends in denitrification rates over the shelf. This is in contrast to the conclusions of Granger et al. (2011), the only other paper to date with an extensive survey of nitrogen cycling over the entire shelf. Granger et al. reported a decrease in NO₃⁻ towards inshore and the north and attributed this to increased sedimentary denitrification in these areas.

Because sedimentary denitrification is a heterotrophic process, rates may be expected to be higher post-bloom, when export of organic carbon should be higher than in pre-bloom conditions. In 2009, denitrification rates were determined in both pre-bloom (spring) and post-bloom (summer) conditions, and 3 stations were sampled in both seasons. Two of these stations (59.6°N, 175.2°W, HLY09–02 station 116, Knorr 195–10 station 122; 62.3°N, 172.5°W, HLY09–02 station 93 and Knorr 195–10 station 140) demonstrated higher average denitrification rates in the summer as compared to the spring, although these differences were not significant. The average denitrification rate on the shelf was higher in summer 2009 as compared with spring 2009; again, variability in measured rates preclude a statistical comparison. It is possible that temporal variability correlates with C export, which is predicted to be highly variable as well.

4.2. Benthic DIN fluxes

4.2.1. Exceptionally small DIN fluxes over the shelf

Based on limited direct measurements and modeling studies, previous workers have indicated that Bering Sea shelf sediments are a net source of NH₄⁺ and NO₃⁻ to the water column (Table 5;

Table 4
Measurements of sediment DIN flux, calculated NH_4^+ regeneration, and calculated denitrification rates from whole core incubations in 2009. For each station, measurements are mean and S.D. (parentheses), $n=2$ or 3. For DIN flux measurements, positive values indicate flux into the sediment. Spring/summer shelf averages are accompanied by standard errors.

Station	Sedimentary DIN flux ($\text{mmol N m}^{-2} \text{d}^{-1}$)			NH_4^+ regenerated ($\text{mmol N m}^{-2} \text{d}^{-1}$)	Denitrification rate ($\text{mmol N m}^{-2} \text{d}^{-1}$)
	NH_4^+	NO_2^-	NO_3^-		
HLY09-02					
3	0.16 (0.07)	0.01 (0.003)	-0.25 (0.03)	1.02 (<0.01)	0.94 (0.10)
9	0.06 (0.01)	0.01 (0.002)	-0.08 (0.04)	0.88 (0.12)	0.86 (0.15)
17	0.10 (0.10)	0.00 (0.001)	-0.00 (0.02)	0.55 (0.06)	0.64 (0.16)
32	-0.02 (0.04)	-0.01 (0.004)	0.06 (0.04)	0.61 (0.06)	0.64 (0.14)
35	0.01 (0.02)	0.00 (<0.00)	0.13 (0.05)	1.39 (0.32)	1.54 (0.38)
39	0.02 (0.01)	0.01 (<0.01)	-0.15 (0.06)	1.11 (0.64)	0.99 (0.70)
54	-0.08 (0.08)	-0.01 (<0.01)	0.07 (0.10)	1.19 (0.03)	1.17 (0.04)
58	-0.01 (0.02)	0.01 (0.01)	-0.28 (0.29)	0.90 (0.09)	0.62 (0.23)
65	0.22 (0.39)	0.04 (0.01)	-0.12 (0.10)	0.52 (0.01)	0.66 (0.48)
69	0.01 (0.01)	0.00 (<0.01)	0.14 (0.09)	0.62 (0.20)	0.76 (0.30)
73	0.00 (0.02)	0.00 (<0.01)	-0.08 (0.05)	0.77 (0.13)	0.69 (0.16)
83	0.18 (0.20)	0.00 (0.01)	-0.06 (0.01)	1.01 (0.12)	1.13 (0.06)
90	-0.03 (0.04)	0.01 (0.01)	-0.07 (0.04)	0.67 (0.06)	0.58 (0.01)
92	-0.05 (0.02)	0.00 (<0.01)	-0.16 (0.09)	0.87 (0.03)	0.66 (0.13)
93	0.01 (0.06)	-0.02 (0.02)	0.04 (0.11)	1.02 (0.29)	1.05 (0.09)
98	-0.05 (0.01)	0.03 (0.02)	-0.03 (0.13)	1.16 (0.09)	1.12 (0.01)
116	<0.01 (<0.00)	-0.03 (0.01)	-0.14 (0.10)	0.78 (0.08)	0.61 (0.01)
Spring shelf average (std. error)^a	0.02 (0.02)	0.00 (<0.01)	-0.06 (0.03)	0.88 (0.06)	0.86 (0.06)
Knorr 195-10					
22	0.08 (0.08)	0.01 (0.01)	0.40 (0.089)	1.08 (0.15)	1.56 (0.30)
32	0.01 (0.09)	0.01 (0.003)	0.24 (0.05)	0.90 (0.27)	1.16 (0.29)
45	0.09 (0.06)	0.00 (0.02)	0.27 (0.03)	1.35 (0.30)	1.70 (0.19)
60	-0.02 (0.33)	0.01 (0.01)	-0.06 (0.09)	0.68 (0.12)	0.61 (0.12)
79	0.06 (0.03)	0.00 (<0.01)	0.02 (0.03)	1.20 (0.12)	1.28 (0.16)
89	0.02 (0.01)	0.00 (0.00)	0.06 (0.02)	0.92 (0.04)	1.00 (0.07)
106	-0.10 (0.08)	0.00 (<0.01)	-0.60 (0.19)	1.38 (0.63)	0.67 (0.57)
122	0.10 (0.06)	0.00 (<0.01)	0.01 (0.04)	0.95 (0.27)	1.06 (0.24)
130	-0.14 (0.30)	0.00 (<0.01)	-0.08 (0.05)	1.93 (0.57)	1.71 (0.31)
140	-0.17 (0.04)	-0.01 (<0.01)	0.33 (0.06)	1.14 (0.32)	1.19 (0.26)
Summer shelf average (std. error)^a	0.00 (0.03)	0.00 (<0.01)	0.06 (0.09)	1.22 (0.13)	1.19 (0.12)

^a Seasonal shelf averages and standard errors were determined through linear mixed effect models for DIN Flux and NH_4^+ regeneration. Denitrification averages and standard errors were determined by the means of the station level results and standard errors of the means.

Whitledge et al., 1986; Rowe and Phoel, 1992; Granger et al., 2011). Based on a stable isotope study, Granger et al. (2011) named shelf sediments as the primary source of NH_4^+ to the NH_4^+ -rich (1–15 μM ; Whitledge and Luchin, 1999) cold pool over the middle shelf.

In this study, there was some variability in sedimentary DIN flux between replicates and among stations on the shelf, but shelf-wide, DIN flux was exceptionally low (Table 4). High small-scale variability (between replicate cores) in benthic flux measurements has commonly been reported in northern latitudes, including in the Bering sea (Whitledge et al., 1986; Lomstein et al., 1989; Rowe and Phoel, 1992), in the North Sea (Hall et al., 1996), and in Young Sound, Greenland (Rysgaard et al., 1998). The cause of such variability in parallel measurements is unclear from our data, but spatial variability of benthic invertebrates may be one contributing reason. Indeed, Lomstein et al. (1989) and Henriksen et al. (1993) suggested that DIN fluxes are strongly influenced by infaunal excretion and burrows in the Bering Sea-Anadyr waters and Alaska Coastal Water.

Even with variability among stations, sediment DIN fluxes were small compared to measurements by other workers on the Bering Sea shelf and in the Northern Bering Sea (Table 5). No stations had a NH_4^+ flux out of the sediments as high as that reported by Whitledge et al. (1986) ($-0.26 \text{ mmol N m}^{-2} \text{d}^{-1}$), and only 3 stations had a flux as high as that reported by Rowe and Phoel (1992) ($-0.10 \text{ mmol N m}^{-2} \text{d}^{-1}$). For the 10 stations that demonstrated NH_4^+ flux out of the sediment, the NH_4^+ efflux represented 2–15% of the sediment-regenerated NH_4^+ (remainder remineralized

as N_2 or NO_3^-). The shelf-wide average for NH_4^+ , NO_2^- , and NO_3^- in both seasons was not significantly different than 0 (Table 4, seasonal average ± 1 S.E.). With such low benthic DIN fluxes, remineralization from sediments is an unlikely source of NH_4^+ to the cold pool on the middle shelf in the spring and summer months, the typical months of NH_4^+ accumulation in the cold pool. We propose that a combination of a relatively long residence time (Coachman, 1986), ammonification of spring production (Whitledge et al., 1986), and slow nitrification are the leading contributing factors in the development of high NH_4^+ on the shelf.

4.2.2. Insignificant contribution of sediment-regenerated NH_4^+ to primary production

Since sediment DIN remineralization does not significantly contribute to the DIN inventory of the water column, the benthos cannot be a significant source of regenerated DIN for primary production. If we consider only the 10 out of 27 stations that did demonstrate NH_4^+ flux out of the sediments and propagate the average of the average flux for those 10 stations over the entire shelf, the contribution of sediment remineralization to the water column DIN inventory would represent 0.1–2.1% of N needed to support primary production on the Bering Sea shelf (106 mol C: 16 mol N phytoplankton uptake ratio; primary production 286 Tg C y^{-1} ; Brown et al., 2011). Laursen and Seitzinger (2002) found a similarly low contribution of remineralized DIN to primary production (1%) on the Mid-Atlantic Bight. A direct implication of

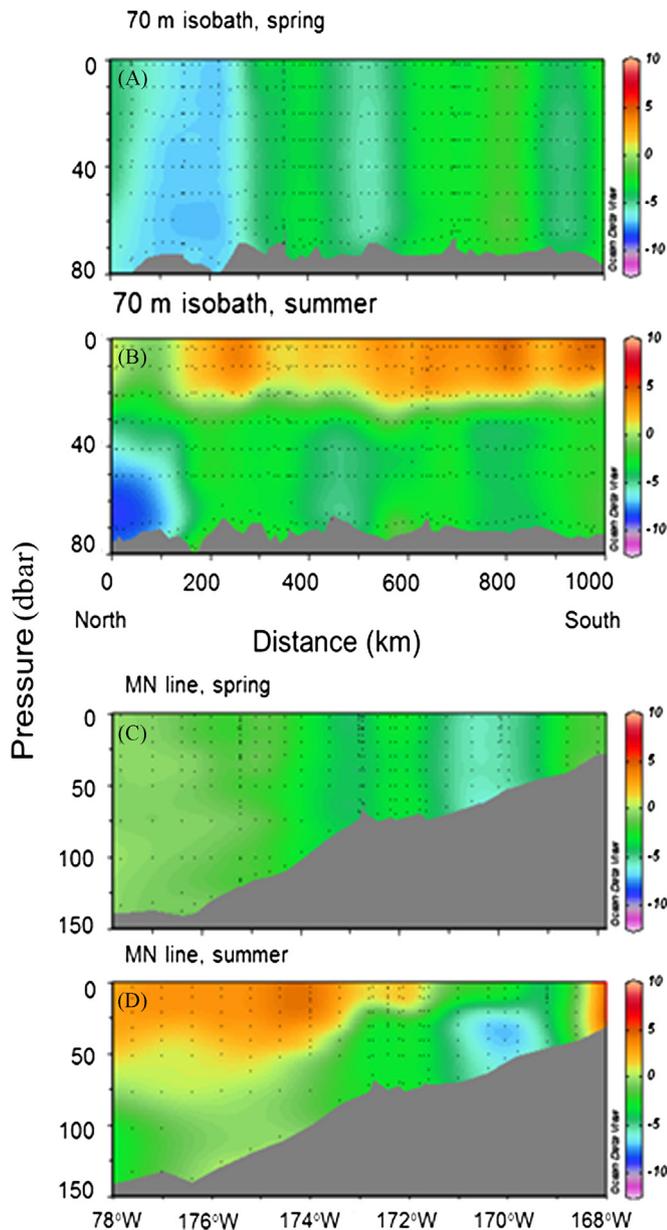


Fig. 4. Spring and summer comparison of water column N^{**} in 2009 along the 70 m isobath (A, B) and MN line (C, D). Scale bar indicates units of $\mu\text{mol kg}^{-1}$.

our benthic flux measurements is that most organic matter-N exported to the sediments is no longer available to primary production and Bering Sea shelf sediments are a stronger sink for water column fixed N than previously measured.

4.2.3. Extensive coupled nitrification/denitrification

Sedimentary N loss on the shelf consumes almost all sedimentary-regenerated N and through the coupled nitrification/denitrification pathway, rather than through direct denitrification (fueled by NO_3^- diffusion into sediments). The observation of very low DIN flux along with the observation of continuous denitrification co-occurring with O_2 consumption, and presumably NH_4^+ regeneration, implies that almost all organic material that is exported to sediments is denitrified or buried. Several studies of other polar continental shelves have demonstrated very low DIN effluxes and suggested that almost all of the sediment-regenerated N leaves sediments as N_2 gas, including studies in Svalbard, Norway (Blackburn et al., 1996; Glud et al., 1998) and in the

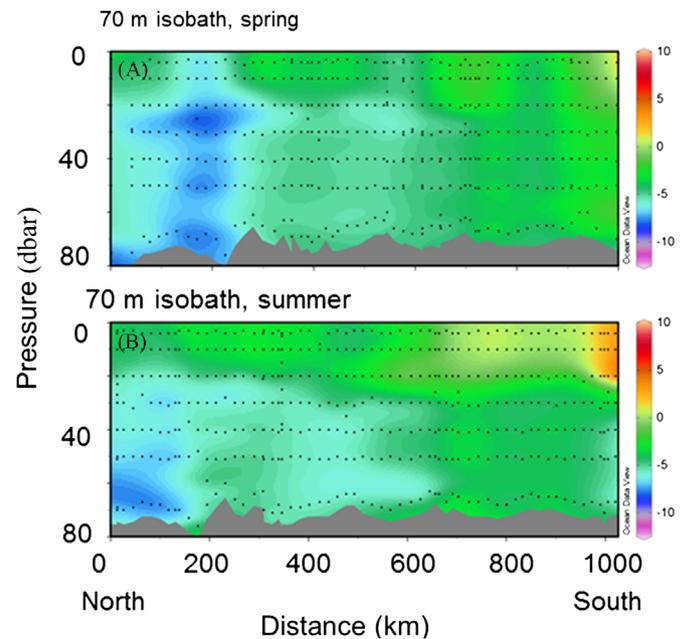


Fig. 5. N^{**} distribution in 2010 along the 70 m isobath during cruise TN249 (A) and TN250 (B). Scale bar indicates units of $\mu\text{mol kg}^{-1}$.

Beaufort and Chukchi Seas (Christensen, 2008). Coupled nitrification/denitrification has been shown to be a significant pathway of N loss on other continental margins, including in the Gulf of Maine (Christensen et al., 1987), eastern North Pacific (Devol and Christensen, 1993; Hartnett and Devol, 2003), North Atlantic and Mid-Atlantic Bight (Seitzinger and Giblin, 1996; Laursen and Seitzinger, 2002) and on the Western Antarctic Peninsula (Hartnett et al., 2008). In contrast, direct denitrification is the dominant N loss pathway in the deep Bering Sea (Lehmann et al., 2007).

Using a mass balance approach for each station, we estimated the importance of coupled nitrification/denitrification versus direct denitrification as pathways of sedimentary N loss. In the spring, only 5 stations demonstrated a net flux of NO_3^- into the sediments, and this flux could account for only 3.3–17.7% of the denitrification rate. More stations (7) in the summer demonstrated net NO_3^- diffusive flux into the sediments, but NO_3^- flux still only represented 1.8–25% of the substrate needed for denitrification at these stations. The remainder of the stations (12 in spring and 3 in summer) exhibited only coupled nitrification/denitrification. Collectively, our results indicate that coupled nitrification/denitrification is the dominant pathway to N loss on the Bering Sea shelf rather than direct denitrification. This agrees with previous studies about Bering Sea shelf sediments (Rowe and Phoel, 1992; Henriksen et al., 1993; Granger et al., 2011), although our study suggests a much higher dependence upon sedimentary coupled nitrification/denitrification than previous studies have predicted.

4.3. Water column N deficit

4.3.1. Interannual variability in N deficit

A comparison of mixed layer nutrients for summer 2009 and summer 2010 reveal different stages of the spring bloom on similar calendar days (Fig. 6). Below the mixed layer, the absolute value of N^{**} in the spring and in the summer are similar throughout the shelf in 2009 and 2010. After the onset of seasonal stratification in 2009 and 2010, surface water N^{**} differed from pre-bloom values both in absolute value and in distribution. The vast depletion of DIP and DIN and change in N^{**} in summer 2009 indicates the end of a spring bloom, the majority of which must

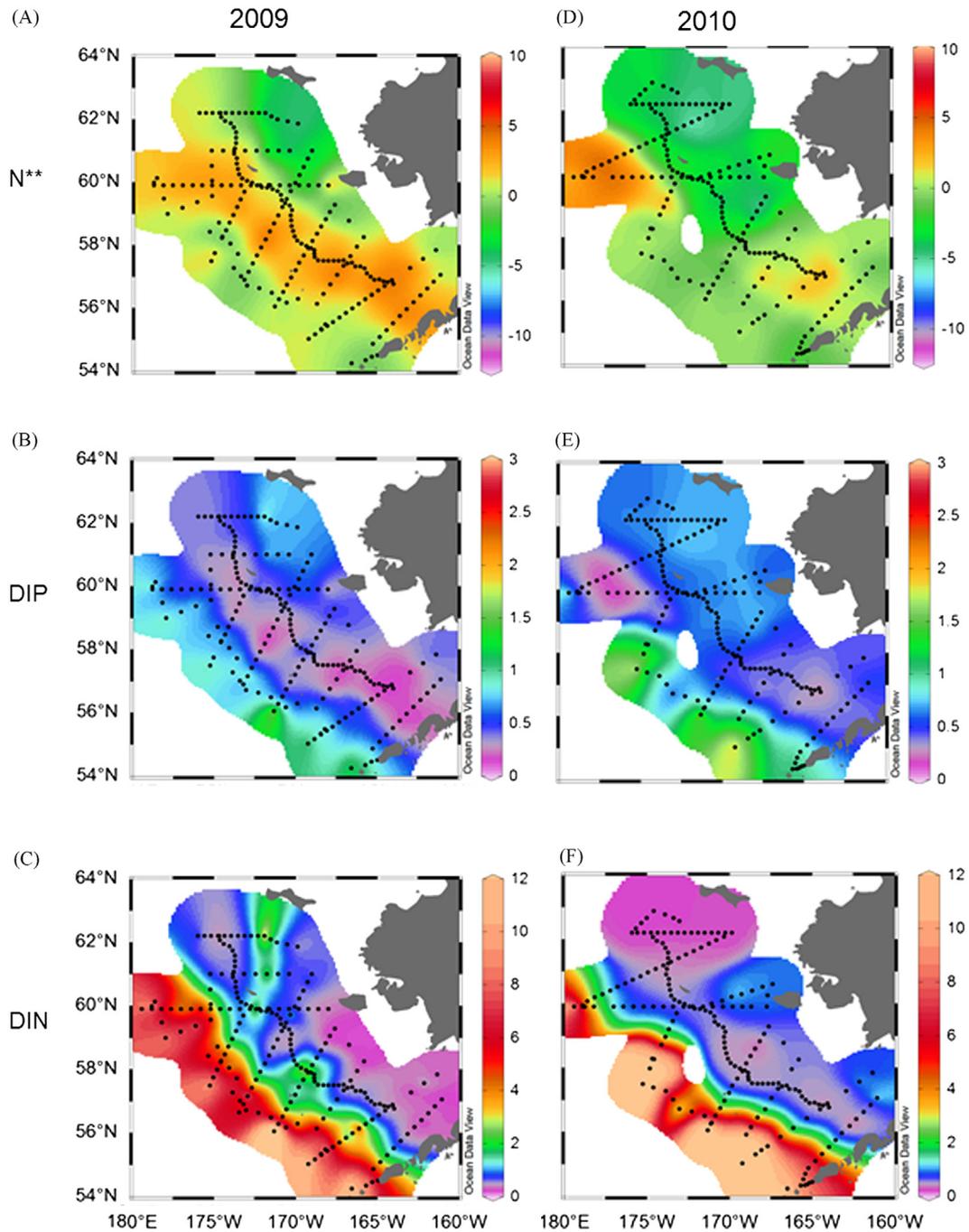


Fig. 6. Surface N^{**} (A, D), phosphate (B, E), and DIN (C, F) on the Bering Sea shelf in summer, 2009 and 2010. Scale bar indicates units of $\mu\text{mol kg}^{-1}$.

have taken place between the 2009 field expeditions (mid-May through mid-June). In contrast to 2009, 2010 was characterized a seasonally late advance of sea ice onto the shelf during May (Napp, 2010). Such a late season advance of ice is expected to bring about a later spring bloom. The depth profile of the 70 m isobath shows a contrast between summer 2009 (Fig. 4B) and summer 2010 (Fig. 5B): after the onset of seasonal stratification in 2010, none of the water column on the 70 m isobath exhibited a positive N^{**} . This contrasts sharply with the same transect a year earlier (Fig. 4B), 2008 (data not shown), and to a lesser extent, 2005 (Mordy et al., 2010), when positive N^{**} deviation over that of the winter N^{**} was found all along the 70 m isobath in the mixed layer. Positive N^{**} deviations did occur in the mixed layer in the southeastern shelf near the Aleutian Islands and on the western section of the MN line (Fig. 6D), but the trend was far from

widespread over the shelf. Stations on the MN line and 70 m isobath were sampled on approximately the same calendar dates (within one day) for the 2009 and 2010 summers, so the variability is not related to differences in sampling dates. Since sedimentary denitrification rates were comparable between 2009 and 2010, we do not suspect interannual differences in N^{**} to result from sedimentary denitrification. These annual differences in mixed layer DIN, DIP, and N^{**} may result from differences in timing of sea ice retreat and may be reflective of ecosystem response to interannual variability in weather conditions (Hunt et al., 2002).

4.3.2. The cause of positive surface N^{**} in 2009

The development of positive surface N^{**} between spring and summer 2009 was quite rapid; there was only one month between

Table 5

A comparison of Bering Sea shelf, northern Bering Sea, and deep Bering Sea benthic N fluxes. A negative DIN flux indicates flux from the sediment to the overlying water column.

Study area (Lat.–Long.)	Number stations	Method	Mean DIN Flux ($\text{mmol N m}^{-2} \text{d}^{-1}$)		Mean denitrification rate ($\text{mmol N m}^{-2} \text{d}^{-1}$)	BS shelf areal N loss (Tg N y^{-1})	Reference
			NH_4^+	NO_3^-			
Bering Sea Shelf							
56°N–57°N 165°W–172°W	3	^{15}N – NO_3^- tracer	ND	ND	0.20	0.50 ^a	Koike and Hattori (1979)
55°N–63°N 163°W–180°E	39	Acetylene blockage of N_2O Reduction	ND	ND	0.36	1.80 ^b	Haines et al. (1981)
56°N–58°N 162°W–170°W	7	Flux of NH_4^+ from box core incubation	–0.26	ND	ND	ND	Whitledge et al. (1986)
55.5°N–58.5°N 162°W–167°W	7	Sediment DIN flux+mass balance	–0.11	–0.38	0.58	3.56	Rowe and Phoel (1992)
55°N–59°N 166°W transect	9	Stoichiometric estimate using water column DIN, DIP	ND	ND	1.10	2.50 ^a	Tanaka et al. (2004)
54°N–63°N 160°W–180°E	15	IRMS, N_2 flux	N/A	N/A	Spring: 1.14	5.2–6.2	This study
	41	MIMS, N_2 flux	N/A	N/A	Spring: 0.62, Summer: 0.76		This study
	27	Sediment DIN flux+mass balance	Spring: 0.02, Summer: <0.01	Spring: –0.06, Summer: 0.06	Spring: 0.86, Summer: 1.19		This study
Northern Bering Sea							
Bering Sea/ Anadyr waters	20	DIN flux from whole core incubation	–0.70	–0.10	1.2	N/A	Lomstein et al. (1989)
Bering Sea/ Anadyr waters	9	DIN flux from whole core incubation	–0.99	0.10	1.35	N/A	Henriksen et al. (1993)
Deep Bering Sea							
Deep (>2000 m)	10	Water column NO_3^- deficit+sediment NO_3^- flux+isotopes	ND	0.05–0.14	0.23	N/A	Lehmann et al. (2005)
Deep (1098– 2789)	4	MIMS, N_2 flux	N/A	N/A	0.56	N/A	This study

ND: no data available; N/A: not applicable.

^a Calculated denitrification for only half of the shelf.

^b Authors indicated gross N loss of 2.2 Tg N y^{-1} and 0.4 Tg N y^{-1} input from N_2 -fixation.

sampling efforts. Although we did not measure sedimentary denitrification in 2009 between those cruises, we did measure active sedimentary denitrification in May and June 2010, and those measurements were similar to 2009. Given the assumption of constant sedimentary denitrification for the month between cruises in 2009 and the observation that the positive increase in N^{**} occurred exclusively in the mixed layer, we do not believe that a decline in denitrification caused the strong positive N^{**} . There are several processes that could be responsible for the positive deviations in N^{**} : (1) riverine runoff, (2) atmospheric N deposition, (3) input of N from N_2 -fixation, and (4) non-Redfieldian uptake of nutrients by phytoplankton.

The shelf waters with the highest increase in N^{**} occur along the middle and outer shelf; without a similar increase on the inner shelf and the large distance between riverine sources and the middle shelf, it is unlikely that riverine runoff is a major cause of positive N^{**} deviations. Also, a comparison of N^{**} and salinity for summer 2009 did not show a trend of increasing N^{**} with decreasing salinity, as would be expected if riverine runoff were a major contributor to positive N^{**} deviations (data not shown). Also, there is not enough atmospheric deposition of nitrogen ($71\text{--}140 \text{ mg N m}^{-2} \text{y}^{-1}$ Duce et al., 2008) to account for the increase in N^{**} during the month between sampling periods. Atmospheric deposition of N could for a maximum of 4% of the change in mixed layer integrated N^{**} from spring to summer.

Water column N_2 -fixation is a common cause of positive N^* in the tropical and subtropical ocean far away from land (Michaels et al., 1996; Gruber and Sarmiento, 1997). Haines et al. (1981)

measured a gross input of N to the Bering Sea shelf from sedimentary N_2 -fixation ($65.2 \text{ } \mu\text{mol N m}^{-2} \text{d}^{-1}$ or 0.4 Tg N y^{-1}), but a lack of N^{**} increase immediately above the sediments argues against sedimentary N_2 -fixation as a cause of positive N^{**} in the surface mixed layer. Also, a recent modeling study suggests that there is a lack of a significant population of diazotrophs in the Bering Sea (Monteiro et al., 2011). Although assays to directly detect diazotrophs (i.e. *nifH* molecular analyses) and N_2 -fixation rate measurements in the water column have not yet been published, N_2 -fixation is likely not a cause of positive N^{**} deviations in the surface waters.

In this study, the relatively quick development of positive N^{**} in the mixed layer co-occurring with the onset of the spring bloom and the rapid depletion of nutrients (especially DIN) in the mixed layer is best explained by non-Redfieldian nutrient uptake and remineralization by phytoplankton, specifically, low phytoplankton biomass N:P. Under rapid growth conditions, phytoplankton have higher cellular P requirements because of the need for P-rich RNA and other cellular reproductive machinery during exponential growth (Klausmeier et al., 2004). Seasonal Arctic and Antarctic diatom blooms have been shown to produce similar non-Redfieldian uptake dynamics, where N:P drawdown ratio was low and the result was an excess of PO_4^{3-} (Rubin et al., 1998; Arrigo et al., 1999; Green and Sambrotto, 2006; Mills and Arrigo, 2010; Deutsch and Weber, 2012). Based on nutrient drawdown ratios between seasons, recent research indicates that Bering Sea phytoplankton along the 70 m isobath drawdown N:P in an average ratio 10.0 ± 2.8 (range: 4.2–17.8; Mordy et al., 2012). This is very close to the diatom biomass N:P

ratio (11:1) that Weber and Deutsch (2010) predicted under peak diatom growth conditions through a Southern Ocean modeling study based on nutrient drawdown.

4.4. Total N loss in the Bering Sea resulting from sedimentary denitrification

We used spring and summer denitrification measurements (from IRMS, MIMS, and sediment DIN mass balance) and a Bering Sea shelf area of 1.2×10^6 km² (Hunt Jr. et al., 2010) to calculate an annual N loss of 5.2–6.2 Tg N y⁻¹. Our results indicate that the previous estimate for Bering Sea shelf total areal N loss should be revised upwards by at least 50%; prior to this study, the highest reported estimate was 3.56 Tg N y⁻¹ (Rowe and Phoel, 1992). Because our sampling effort in the deep basin was limited (4 stations along the margins), we used the annual N loss estimate of 1.27 Tg N y⁻¹ from Lehmann et al. (2005) to calculate total denitrification in the Bering Sea basin. Taken together, N loss for the entire Bering Sea is 6.5–7.5 Tg N y⁻¹. Given an annual primary production of 286 Tg C y⁻¹ for the Bering Sea (Brown et al., 2011) and a phytoplankton uptake ratio of 106 C:16 N, our estimate of sedimentary N loss can account for 15.1–17.4% of total N uptake by phytoplankton. Seitzinger and Giblin (1996) found a similar percentage of N removal by denitrification (13%) on the North Atlantic continental shelves, which was also mostly through coupled nitrification/denitrification. This estimate of sedimentary N loss represents a substantial portion of annual primary production in the Bering Sea.

5. Conclusions

This study is the most extensive field program to date that investigates the two major factors affecting the N deficit on the commercially important Bering Sea shelf, sedimentary denitrification and sedimentary DIN fluxes. In addition, this study is the first to examine seasonal and interannual changes in N deficit in light of the main process affecting its distribution, sedimentary denitrification. The summer positive increase in the Bering shelf-specific geochemical tracer N** most likely indicates that phytoplankton on the shelf drawdown inorganic N and P in a ratio lower than Redfield. Interannual variation in water column N** may reflect differences in the magnitude and fate of the spring bloom, which is related to the timing of sea ice retreat, and not differences in sedimentary denitrification. Sedimentary denitrification is an important sink of water column fixed N, as evidenced by the denitrification rate, the near zero sedimentary DIN flux, and very low N** in the winter. Denitrification is fueled largely through coupled nitrification/denitrification, and not by diffusive NO₃⁻ flux at the sediment–water interface. Based on four separate assays to measure denitrification, we revise upwards the basin-wide estimate of N loss over the shelf to 5.2–6.2 Tg N y⁻¹ and 6.5–7.5 Tg N y⁻¹ for the entire Bering Sea. Given that extensive microbial nitrogen cycling on the shelf sediments causes the benthos to be a negligible source of remineralized N to the water column, sedimentary microbial activity over the entire shelf negatively regulates primary production on the Bering Sea shelf more strongly than previously recognized.

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References

- Arrigo, K., Robinson, D., Worthen, D., Dunbar, R., DiTullio, G., VanWoert, M., Lizotte, M., 1999. Phytoplankton community structure and the drawdown of nutrients and CO₂ in the Southern Ocean. *Science* 283, 365–367.
- Blackburn, T., Hall, P., Hulth, S., Landen, A., 1996. Organic-N loss by efflux and burial associated with a low efflux of inorganic N and with nitrate assimilation in Arctic sediments (Svalbard, Norway). *Mar. Ecol. Prog. Ser.* 141, 283–293.
- Brown, Z., van Dijken, G., Arrigo, K., 2011. A reassessment of primary production and environmental change in the Bering Sea. *J. Geophys. Res. (C Oceans)* 116, C08014.
- Chang, B., Devol, A., 2009. Seasonal and spatial patterns of sedimentary denitrification rates in the Chukchi sea. *Deep Sea Res. (II Top. Stud. Oceanogr.)* 56, 1339–1350.
- Christensen, J., 2008. Sedimentary carbon oxidation and denitrification on the shelf break of the Alaskan Beaufort and Chukchi Seas. *Open Oceanogr. J.* 2, 6–17.
- Christensen, J., Murray, J., Devol, A., Codispoti, L., 1987. Denitrification in continental shelf sediments has major impact on the ocean nitrogen budget. *Glob. Biogeochem. Cy.* 1, 97–116.
- Coachman, L., 1986. Circulation, water masses, and fluxes on the southeastern Bering Sea shelf. *Cont. Shelf Res.* 5, 23–108.
- Codispoti, L., Brandes, J., Christensen, J., Devol, A., Naqvi, S., Paerl, H., Yoshinari, T., 2001. The oceanic fixed nitrogen and nitrous oxide budgets: moving targets as we enter the anthropocene? *Sci. Mar.* 65, 85–105.
- Davenport, E., Shull, D., Devol, A., 2012. Roles of sorption and tube-dwelling benthos in the cycling of phosphorus in Bering Sea sediments. *Deep Sea Res. (II Top. Stud. Oceanogr.)* 65–70, 163–172.
- Deutsch, C., Sarmiento, J., Sigman, D., Gruber, N., Dunne, J., 2007. Spatial coupling of nitrogen inputs and losses in the ocean. *Nature* 445, 163–167.
- Deutsch, C., Weber, T., 2012. Nutrient ratios as a tracer and driver of ocean biogeochemistry. *Annu. Rev. Mar. Sci.* 4, 113–141.
- Devol, A., Christensen, J., 1993. Benthic fluxes and nitrogen cycling in sediments of the continental margin of the eastern North Pacific. *J. Mar. Res.* 51, 345–372.
- Devol, A., Codispoti, L., Christensen, J., 1997. Summer and winter denitrification rates in western Arctic shelf sediments. *Cont. Shelf Res.* 17, 1029–1050.
- Duce, R.A., LaRoche, J., Altieri, K., Arrigo, K.R., Baker, A.R., Capone, D.G., Cornell, S., Dentener, F., Galloway, J., Ganeshram, R.S., Geider, R.J., Jickells, T., Kuypers, M. M., Langlois, R., Liss, P.S., Liu, S.M., Middleburg, J.J., Moore, C.M., Nickovic, S., Oschlies, A., Pedersen, T., Prospero, J., Schlitzer, R., Seitzinger, S., Sorensen, L.L., Uematsu, M., Ulloa, O., Voss, M., Ward, B., Zamora, L., 2008. Impacts of atmospheric anthropogenic nitrogen on the open ocean. *Science* 320, 893–897.
- Emerson, S., Stump, C., Wilbur, D., Quay, P., 1999. Accurate measurement of O₂, N₂, and Ar gases in water and the solubility of N₂. *Glob. Biogeochem. Cy.* 5, 49–69.
- Esch, M., Shull, D., Devol, A., Moran, B., 2013. Regional patterns of iron and manganese reduction rates in the shelf sediments of the southeastern Bering Sea. *Deep Sea Res. (II Top. Stud. Oceanogr.)*, 94, 80–94.
- Eyre, B., Rysgaard, S., Dalsgaard, T., 2002. Comparison of isotope pairing and N₂:Ar methods for measuring sediment denitrification. *Estuaries* 25, 1077–1087.
- Fennel, K., Wilkin, J., Levin, J., Moisan, J., O'Reilly, J., Haidvogel, D., 2006. Nitrogen cycling in the Middle Atlantic Bight: results from a three-dimensional model and implications for the North Atlantic nitrogen budget. *Glob. Biogeochem. Cy.* 20, GB3007.
- Froelich, P., Klinkhammer, G., Bender, M., Luedtke, N., Heath, G., Cullen, D., Dauphin, P., Hammond, D., Hartman, B., Maynard, V., 1979. Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: Suboxic diagenesis. *Geochim. Cosmochim. Acta* 43, 1075–1090.
- Glud, R., Holby, O., Hoffmann, F., Canfield, D., 1998. Benthic mineralization and exchange in Arctic sediments (Svalbard, Norway). *Mar. Ecol. Prog. Ser.* 173, 237–251.
- Gordon, L., Jennings Jr., J., Ross, A., Krest, M., 1994. A Suggested Protocol for Continuous Flow Automated Analysis of Seawater Nutrients (Phosphate, Nitrate, Nitrite and Silicic Acid) in the WOCE Hydrographic Program and the Joint Global Ocean Fluxes Study. WHP Operations and Methods, WOCE Hydrographic Program Office, Methods Manual 91-1, November.

- Granger, J., Prokopenko, M., Sigman, D., Mordy, C., Morse, Z., Morales, L., Sambrotto, R., Plessen, B., 2011. Coupled nitrification-denitrification in sediment of the eastern Bering Sea shelf leads to ^{15}N enrichment of fixed N in shelf waters. *J. Geophys. Res. Oceans* 116, c11006.
- Grebmeier, J., Overland, J., Moore, S., Farley, E., Carmack, E., Cooper, L., Frey, K., Helle, J., McLaughlin, F., McNutt, S., 2006. A major ecosystem shift in the Northern Bering Sea. *Science* 311, 1461–1464.
- Green, S., Sambrotto, R., 2006. Net community production in terms of C, N, P and Si in the Antarctic Circumpolar Current and its influence on regional water mass characteristics. *Deep Sea Res. (I Oceanogr. Res. Pap.)* 53, 111–135.
- Gruber, N., Sarmiento, J., 1997. Global patterns of marine nitrogen fixation and denitrification. *Glob. Biogeochem. Cy.* 11, 235–266.
- Haines, J., Atlas, R., Griffiths, R., Morita, R., 1981. Denitrification and nitrogen fixation in Alaskan continental shelf sediments. *Appl. Environ. Microbiol.* 41, 412–421.
- Hall, P., Hulth, S., Hulthe, G., Landen, A., Tengberg, A., 1996. Benthic nutrient fluxes on a basin-wide scale in the Skagerrak (north-eastern North Sea). *J. Sea Res.* 35, 123–137.
- Hamme, R., Emerson, S., 2002. Mechanisms controlling the global oceanic distribution of the inert gases argon, nitrogen, and neon. *Geophys. Res. Lett.* 29, 2010.10.1029/2002GL015273.
- Hartnett, H., Boehme, S., Thomas, C., McMaster, D., Smith, C., 2008. Benthic oxygen fluxes and denitrification rates from high-resolution porewater profiles from the Western Antarctic Peninsula continental shelf. *Deep Sea Res. (II Top. Stud. Oceanogr.)* 55, 2415–2424.
- Hartnett, H., Devol, A., 2003. Role of a strong oxygen-deficient zone in the preservation and degradation of organic matter: a carbon budget for the continental margins of northwest Mexico and Washington State. *Geochim. Cosmochim. Acta* 67, 247–264.
- Henriksen, K., Blackburn, T., Lomstein, B., McRoy, C., 1993. Rates of nitrification, distribution of nitrifying bacteria and inorganic N fluxes in northern Bering-Chukchi shelf sediments. *Cont. Shelf Res.* 13, 629–651.
- Hunt Jr., G., Allan, B., Angliss, R., Baker, T., Bond, N., Buck, G., Byrd, G., Coyle, K., Devol, A., Eggers, D., Eisner, L., Feely, R., Fitzwater, S., Fritz, L., Gritsai, E., Ladd, C., Lewis, W., Mathis, J., Mordy, C., Mueter, F., Napp, J., Sherr, E., Shull, D., Stabeno, P., Stepanenko, M., Strom, S., Whitledge, T., 2010. Status and trends of the Bering Sea region, 2003–2008. In: McKinnell, S., Dagg, M. (Eds.), *Marine Ecosystems of the North Pacific Ocean, 2003–2008*. PICES Special Publication, pp. 196–267.
- Hunt Jr., G., Stabeno, P., Walters, G., Sinclair, E., Brodeur, R., Napp, J., Bond, N., 2002. Climate change and control of the southeastern Bering Sea pelagic ecosystem. *Deep Sea Res. (II Top. Stud. Oceanogr.)* 49, 5821–5853.
- Kana, T., Darkangelo, C., Hunt, M., Oldham, J., Bennett, G., Cornwell, J., 1994. Membrane inlet mass spectrometer for rapid high-precision determination of N_2 , O_2 , and Ar in environmental water samples. *Anal. Chem. (Wash.)* 66, 4166–4170.
- Kana, T., Weiss, D., 2004. Comment on “Comparison of isotope pairing and N:Ar methods for measuring sediment denitrification” by B.D. Eyre, S. Rysgaard, T. Dalsgaard, P. Bondo Christensen, 2002. *Estuaries* 25, 1077–1087. *Estuaries* 27, 173–176.
- Klausmeier, C., Litchman, E., Daufresne, T., Levin, S., 2004. Optimal nitrogen-to-phosphorus stoichiometry of phytoplankton. *Nature* 429, 171–174.
- Koike, I., Hattori, A., 1979. Estimates of denitrification in sediments of the Bering Sea shelf. *Deep-Sea Res* 26A, 409–415.
- Laursen, A., Seitzinger, S., 2002. The role of denitrification in nitrogen removal and carbon remineralization in Mid-Atlantic Bight sediments. *Cont. Shelf Res.* 22, 1397–1416.
- Lehmann, M., Sigman, D., McCorkle, D., Brunelle, B., Hoffmann, S., Kienast, M., Cane, G., Clement, J., 2005. Origin of the deep Bering Sea nitrate deficit: constraints from the nitrogen and oxygen isotopic composition of water column nitrate and benthic nitrate fluxes. *Glob. Biogeochem. Cy.* 19.
- Lehmann, M., Sigman, D., McCorkle, D., Granger, J., Hoffmann, S., Cane, G., Brunelle, B., 2007. The distribution of nitrate $^{15}\text{N}/^{14}\text{N}$ in marine sediments and the impact of benthic nitrogen loss on the isotopic composition of oceanic nitrate. *Geochim. Cosmochim. Acta* 71, 5384–5404.
- Lomstein, B., Blackburn, T., Henriksen, K., 1989. Aspects of nitrogen and carbon cycling in the northern Bering Shelf sediment. I. The significance of urea turnover in the mineralization of NH_4^+ . *Mar. Ecol. Prog. Ser.* 57, 237–247.
- Mathis, J., Cross, J., Bates, N., Moran, S., Lomas, M., Mordy, C., Stabeno, P., 2010. Seasonal distribution of inorganic carbon and net community production on the Bering Sea shelf. *Biogeosciences* 7, 1769–1787.
- Michaels, A., Olson, D., Sarmiento, J., Ammerman, J., Fanning, K., Jahnke, R., Knap, A., Lipschultz, F., Prospero, J., 1996. Inputs, losses and transformations of nitrogen and phosphorus in the pelagic North Atlantic Ocean. *Biogeochemistry* 35, 181–226.
- Mills, M., Arrigo, K., 2010. Magnitude of oceanic nitrogen fixation influenced by the nutrient uptake ratio of phytoplankton. *Nat. Geosci.* 3, 412–416.
- Monteiro, F., Dutkiewicz, S., Follows, M., 2011. Biogeographical controls on the marine nitrogen fixers. *Glob. Biogeochem. Cy.* 25 (GB2), 003.
- Mordy, C., Cokelet, E., Ladd, C., Menzia, F., Proctor, P., Stabeno, P., Wisegarver, E., 2012. Net community production on the Middle Shelf of the Eastern Bering Sea. *Deep Sea Res. (II Top. Stud. Oceanogr.)* 65–70, 110–125.
- Mordy, C., Eisner, L., Proctor, P., Stabeno, P., Devol, A., Shull, D., Napp, J., Whitledge, T., 2010. Temporary uncoupling of the marine nitrogen cycle: accumulation of nitrite on the Bering Sea shelf. *Mar. Chem.* 121, 157–166.
- Mordy, C., Stabeno, P., Righi, D., Menzia, F., 2008. Origins of the subsurface ammonium maximum in the southeast Bering Sea. *Deep Sea Res. (II Top. Stud. Oceanogr.)* 55, 1738–1744.
- Napp, J., 2010. The Bering Sea: Current Status and Recent Events. vol. 18. PICES Press, Saanich, British Columbia, Canada, pp. 34–36.
- NRC, 1996. *The Bering Sea Ecosystem*. National Academy Press, Washington, D. C.
- Redfield, A., 1934. On the proportions of organic derivative in sea water and their relation to the composition of plankton. In: Daniel, R. (Ed.), *James Johnstone Memorial Volume*. University of Liverpool, pp. 176–192.
- Redfield, A., 1958. The biological control of chemical factors in the environment. *Am. Sci.* 46, 205–221.
- Rho, T., Whitledge, T., 2007. Characteristics of seasonal and spatial variations of primary production over the southeastern Bering Sea shelf. *Cont. Shelf Res.* 27, 2556–2569.
- Rho, T., Whitledge, T., Goering, J., 2005. Interannual variations of nutrients and primary productivity over the southeastern Bering Sea shelf during the spring of 1997, 1998, and 1999. *Oceanology* 45, 376–390.
- Rowe, G., Phoel, W., 1992. Nutrient regeneration and oxygen demand in Bering Sea continental shelf sediments. *Cont. Shelf Res.* 12, 439–449.
- Rubin, S., Takahashi, T., Chipman, D., Goddard, J., 1998. Primary productivity and nutrient utilization ratios in the Pacific sector of the Southern Ocean based on seasonal changes in seawater chemistry. *Deep Sea Res. (I Oceanogr. Res. Pap.)* 45, 1211–1234.
- Rysgaard, S., Thamdrup, B., Risgaard-Petersen, N., Fossing, H., Berg, P., Bondo Christensen, P., Dalsgaard, T., 1998. Seasonal carbon and nutrient mineralization in a high-Arctic coastal marine sediment, Young Sound, Northeast Greenland. *Mar. Ecol. Prog. Ser.* 175, 261–276.
- Schlitzer, R., 2011. *Ocean Data View*.
- Seitzinger, S., Giblin, A., 1996. Estimating denitrification in North Atlantic continental shelf sediments. *Biogeochemistry* 35, 235–260.
- Seitzinger, S., Harrison, J., HBohlike, J., Bouwman, A., Lowrance, R., Peterson, B., Tobias, C., Van Drecht, G., 2006. Denitrification across landscapes and waterscapes: a synthesis. *Ecol. Appl.* 16, 2064–2090.
- Sigler, M., Harvey, H., Ashjian, C., Lomas, M., Napp, J., Stabeno, P., Van Pelt, T., 2010. How does climate change affect the Bering Sea ecosystem? *EOS Trans. Am. Geophys. Union* 91, 457–458.
- Stabeno, P., Bond, N., Salo, S., 2007. On the recent warming of the southeastern Bering Sea shelf. *Deep Sea Res. (II Top. Stud. Oceanogr.)* 54, 2599–2618.
- Stabeno, P., Hunt Jr., G., Napp, J., Schumacher, J., 2006. Physical forcing of ecosystem dynamics on the Bering Sea shelf. In: Robinson, A., Brink, K. (Eds.), *The Global Coastal Ocean: Interdisciplinary Regional Studies and Syntheses, Part B*. Harvard University Press, pp. 1177–1212.
- Tanaka, T., Guo, L., Deal, C., Tanaka, N., Whitledge, T., Murata, A., 2004. N deficiency in a well-oxygenated cold bottom water over the Bering Sea shelf: influence of sedimentary denitrification. *Cont. Shelf Res.* 24, 1271–1283.
- Weber, T., Deutsch, C., 2010. Ocean nutrient ratios governed by plankton biogeography. *Nature* 467, 550–554.
- Whitledge, T., Bidigare, R., Zeeman, S., Sambrotto, R., Rascigno, P., Jensen, P., Brooks, J., Trees, C., Veidt, D., 1988. Biological measurements and chemical features in Soviet and United States regions of the Bering Sea. *Cont. Shelf Res.* 8, 1299–1319.
- Whitledge, T., Luchin, V., 1999. Summary of chemical distributions and dynamics in the Bering Sea. In: Loughlin, T., Ohtani, K. (Eds.), *Dynamics of the Bering Sea*. University of Alaska Sea Grant, Fairbanks, AK, pp. 217–250.
- Whitledge, T., Reeburgh, W., Walsh, J., 1986. Seasonal inorganic nitrogen distributions and dynamics in the southeastern Bering Sea. *Cont. Shelf Res.* 5, 109–132.