Marine Chemistry 121 (2010) 157–166

Contents lists available at ScienceDirect

Marine Chemistry

journal homepage: www.elsevier.com/locate/marchem

Temporary uncoupling of the marine nitrogen cycle: Accumulation of nitrite on the Bering Sea shelf

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ARTICLE INFO

Article history:
Received 17 June 2009
Received in revised form 26 January 2010
Accepted 12 April 2010
Available online 18 April 2010

Keywords:
Bering Sea
Nutrient cycle
Nitrite
Nitrogen cycle
Nitrification
Denitrification

ABSTRACT

An unprecedented pool of nitrite (2–5.6 μM) was observed in the well-oxygenated, ammonium-rich bottom waters of Bering Sea middle shelf in fall 2005 on two simultaneous oceanographic cruises. This nitrite pool was located in a transition zone that separated the ice-derived cold pool to the north from warmer waters to the south. The transition zone was influenced by on-shelf flow. The nitrite pool was transitory; it was not apparent 11 days after it was first observed. Several origins of the pool were considered including: truncation of sedimentary denitrification and/or curtailment of anammox (these are dominate pathways in the nitrogen cycle of the Bering Sea), nitrite release from light-limited phytoplankton (light and nutrient conditions were favorable for this mechanism), and truncation of water column nitrification (there was a small decrease of ammonium in the vicinity of the nitrite pool). The occurrence of this pool suggests a temporary uncoupling of the marine nitrogen cycle.

1. Introduction

Nitrite does not usually accumulate in aerobic waters. It is typically a short-lived intermediate in redox pathways of the marine nitrogen cycle. Nitrite concentrations in the open sea are almost always low (<1 μM) with the highest concentrations usually found in the primary nitrite maximum (PNM) at the base of the euphotic zone. The PNM is thought to arise from a suite of mechanisms including excretion of nitrite from light-limited phytoplankton and photoinhibition of nitrite oxidation during nitrification (Lomas and Lipschultz, 2006). Nitrification is the two-step oxidation of ammonium (i.e., ammonium to nitrite, and nitrite to nitrate) with the first step generally rate-limiting, except, for instance, in the presence of photoinhibition.

High levels of nitrite (~1–10 μM) also occur in suboxic and anoxic waters that underlie very productive coastal and oceanic regions; e.g. the Equatorial Pacific, Peruvian Coast and the Arabian Sea. In anoxic layers, denitrification and anaerobic ammonium oxidation (anammox) are the dominate pathways in the nitrogen cycle (Codispoti et al., 2001; Gruber, 2004; Gruber and Sarmiento, 1997). Denitrification is the anaerobic reduction of nitrate to nitrogen gas with nitrite as an intermediate, while anammox is the direct conversion of nitrite and ammonium to nitrogen gas. Hence denitrification is a transitory nitrite source while anammox is a nitrite sink. On continental shelves, sedimentary denitrification and anammox reduce the efflux of reactive nitrogen species from the sediment resulting in a significant loss of nitrogen in overlying waters, and large accumulations of nitrite are observed in thin layers of sediment (Devol, 1991, Rysgaard et al., 2004).

In well-oxygenated waters, such extraordinary levels of nitrite have not been observed. Here we report on two independent observations of unprecedented levels of nitrite in well-oxygenated, ammonium-rich waters in a north–south transition zone on the Bering Sea shelf.

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doi:10.1016/j.marchem.2010.04.004

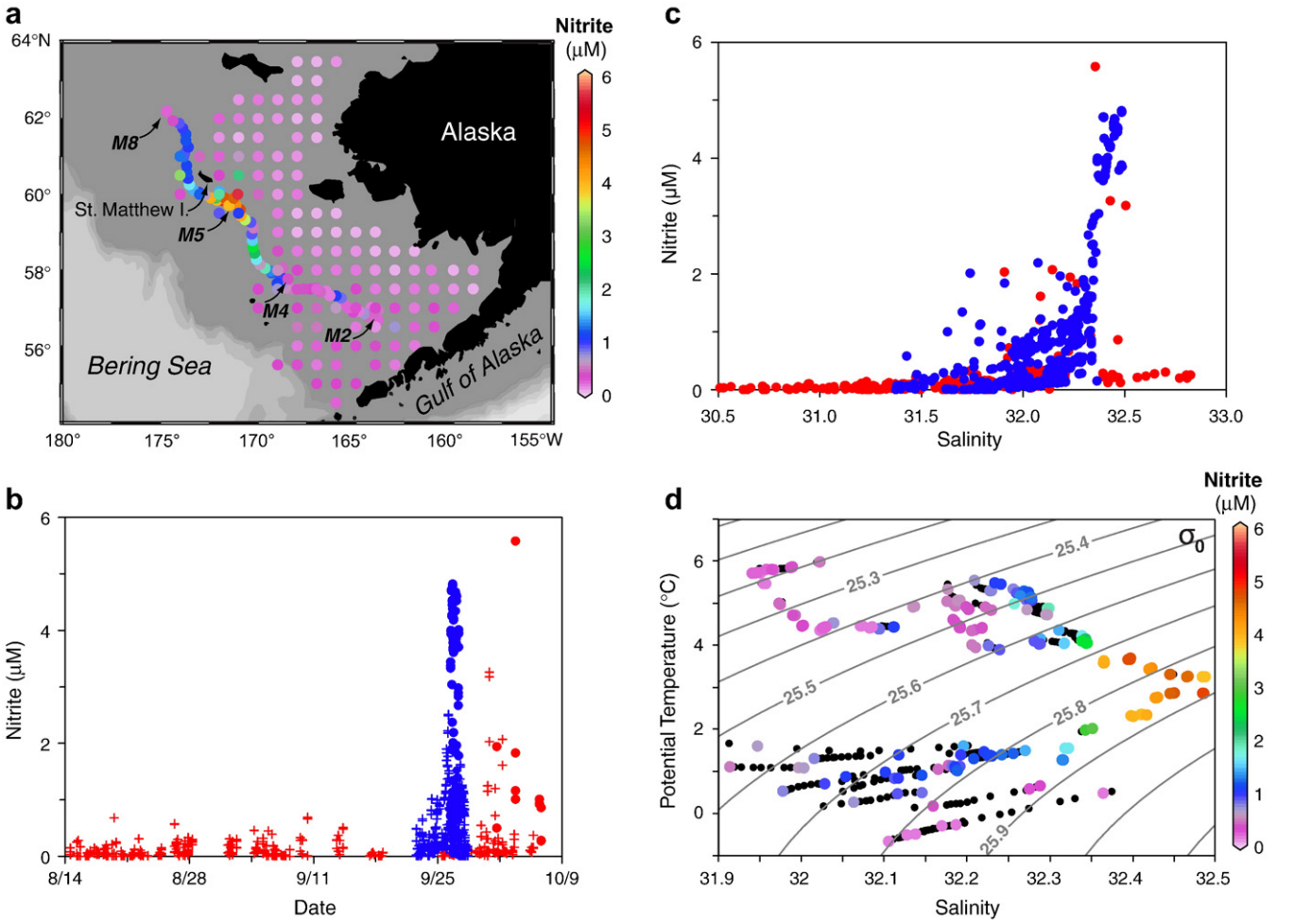

Fig. 1. Characterization of the nitrite maximum. (a) Surface map of station locations with colors indicating the maximum nitrite concentration observed in the water column. Arrows indicate the location of long-term moorings. EcoFOCI stations were tightly spaced along the 70-m isobath with additional stations occupied around several of the long-term moorings while BASIS stations were on a widely spaced grid over the eastern shelf. (b) Nitrite vs. sampling date (crosses) with dots representing stations in the vicinity of the nitrite pool (59.3–60.1°N, 170–172.5°W). Blue symbols represent data from the EcoFOCI cruise and red symbols represent data from the BASIS cruise. (c) Nitrite vs. salinity (21 samples with nitrite <<1μM were fresher than 30.5 and were not shown). Color scheme is identical to (b). (d) T–S plot of bottom water (>50 m) along the 70-m isobath with black dots representing 1 m data and colors denoting nitrite concentrations from samples collected at ~10-m intervals. Water in the transition zone (2.3–3.6 °C) and to the south (>3.6 °C) was sufficiently mixed such that data from each cast often appears as a single point.

2. Methods

Two National Oceanic and Atmospheric Administration (NOAA) cruises collected hydrographic data on the Bering Sea shelf in fall 2005; an Ecosystems and Fisheries-Oceanography Coordinated Investigations cruise (EcoFOCI, September 22–28), and a Bering–Aleutian Salmon International Survey (BASIS, August 14–October 6) (Fig. 1a). Data from the EcoFOCI cruise were collected along the 70-m isobath (~20 km between stations) with nutrient samples collected at 10-m depth intervals from the surface to ~5 m off the bottom. The BASIS grid encompassed the entire eastern shelf, but only three to five depths were sampled, with the deepest bottle 10–20 m off the bottom.

On the EcoFOCI cruise, conductivity–temperature–depth (CTD) measurements were made with a Seabird SBE911[8] plus system with dual sensors for temperature, conductivity, and oxygen, and single sensors for Photosynthetically Active Radiation (285≥2800 nm) and chlorophyll fluorescence. These sensors were calibrated by the manufacturer prior to the cruise. Data were recorded during the downcast, with descent rates of 15 m min^{-1} to a depth of 35 m, and 30 m min^{-1} below that. Salinity calibration samples were collected on most casts and analyzed on a calibrated laboratory salinometer. An oxygen titrator was not available to calibrate the CTD sensor during the cruises; however, the two sensors used were in very good agreement on all casts. We recognize the problem of not having titrated water samples for calibration, but feel that the oxygen values provide patterns of variability that are informative. Dissolved inorganic nutrients (phosphate, silicic acid, nitrate, nitrite and ammonium) were measured at sea on samples collected from Niskin bottles and filtered through 0.45 μm cellulose acetate filters. Measurements were made using automated continuous flow analysis with a segmented flow and colorimetric detection. Standardization and analysis procedures specified by Gordon et al. (1994) were closely followed including calibration of labware, preparation of primary and secondary standards, and corrections for blanks and refractive index. Protocols of Gordon et al. (1994) were used for analysis of phosphate, silicic acid, nitrate and nitrite. Ammonium was measured using an indophenol blue method modified from Mantoura and Woodward (1983).

Chlorophyll samples were filtered through Osmonics glass fiber filters (nominal pore size 0.7 μm), and stored in the dark at −80 °C for several months before extracting in 90% acetone for 24 h.

[8] Reference to trade names does not imply endorsement by NOAA.

Fluorometric determination of chlorophyll concentration (acidification method, Lorenzen, 1966) was made using a Turner Designs TD700 fluorometer calibrated with pure chlorophyll-*a*.

On the BASIS cruise, CTD measurements were conducted primarily with a Seabird SBE9 plus system, but a SBE25 served as a backup and was used for 15 casts. CTD sensors were calibrated by the manufacturer prior to the cruise. Salinity calibration samples were taken daily at one to two sample depths. Discrete samples for dissolved inorganic nutrients were collected from Niskin bottles and stored frozen without filtration. Salinity and nutrient samples were analyzed at a shore-based facility (University of Washington Marine Chemistry Laboratory). Nutrient analysis followed colorimetric protocols set forth by UNESCO (1994) which were comparable to methods used on the EcoFOCI cruise.

In agreement with Dore et al. (1996), we found that freezing generally reduced the precision of nutrient analysis. Nutrient concentrations in frozen samples from the Bering Sea were independent of filtration (slope of filtered vs. unfiltered samples = 1 ± 0.01, $n = 50$, ammonium was not tested). In a direct comparison of EcoFOCI and BASIS methods, replicate frozen samples from the Bering Sea were analyzed with each method and found to be within 0.5 µM nitrate, 0.04 µM nitrite, and 0.7 µM ammonium (SD, $n = 13$).

In addition, we present data from the NOAA biophysical mooring M5 on the eastern shelf (59.9°N, 171.72°W). The mooring was constructed of chain for protection against sea-ice and heavy fishing pressure in the region. Temperature and conductivity were recorded using SBE-37 MicroCAT C-T Recorders at selected depths, and currents were recorded using an upward-looking, bottom-mounted acoustic Doppler current profiler (ADCP). These instruments were calibrated prior to deployment, and the data were processed according to the manufacturer's specifications.

Following the approach of Codispoti et al. (2001), we formed a regional DIN:phosphate relationship comprised of outer shelf and slope data from the eastern Bering Sea, and calculated the DIN residual (N^{**}) as

$$N^{**} = DIN - (PO4 * 15.5) + 5.9. \quad (1)$$

Data for this regional equation were collected during 6 cruises in spring and summer from 2007 to 2009 as part of the Bering Ecosystem

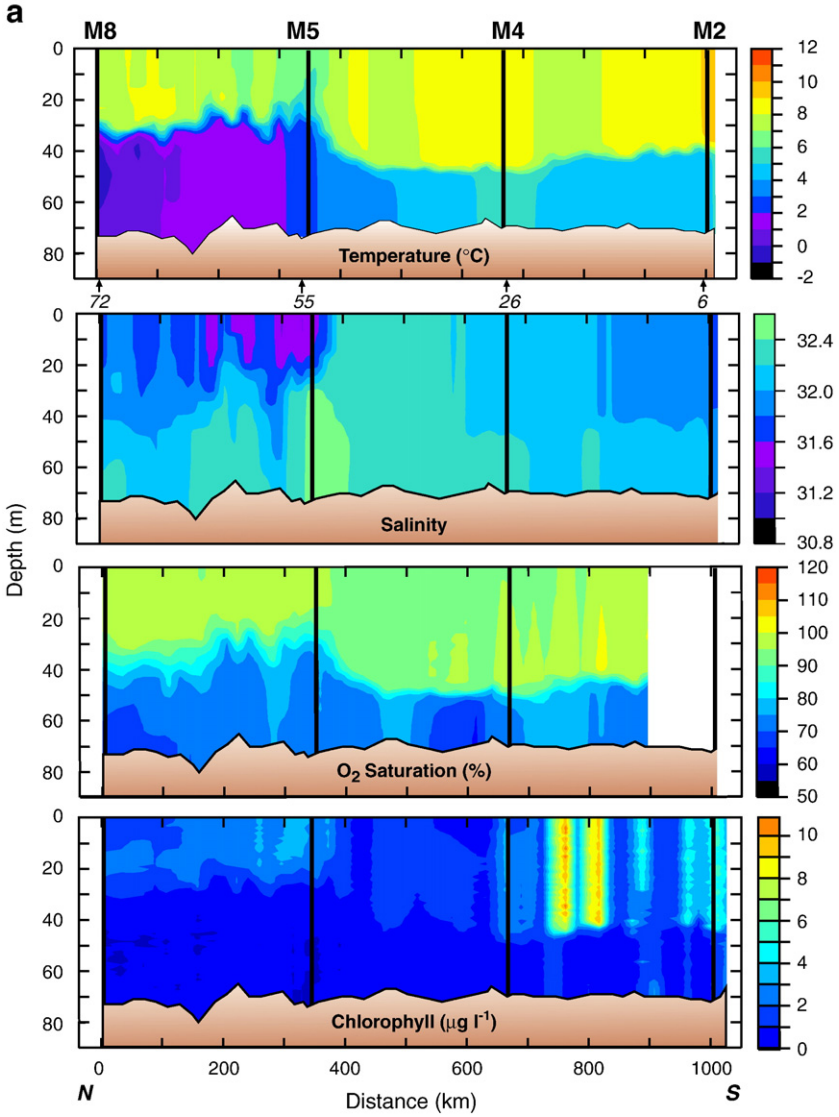

Fig. 2. Sections along the 70-m isobath in September 2005; (a) temperature, salinity, % oxygen saturation, and chlorophyll, (b) nitrate, ammonium, nitrite and N^{**}. The horizontal line on the nitrate plot denotes the 1% light level measured within 5 h of local noon (yellow), or linearly interpolated between daytime casts (magenta). Vertical lines designate mooring locations. Crosses in nitrate and N^{**} denote sample depths for all nutrients.

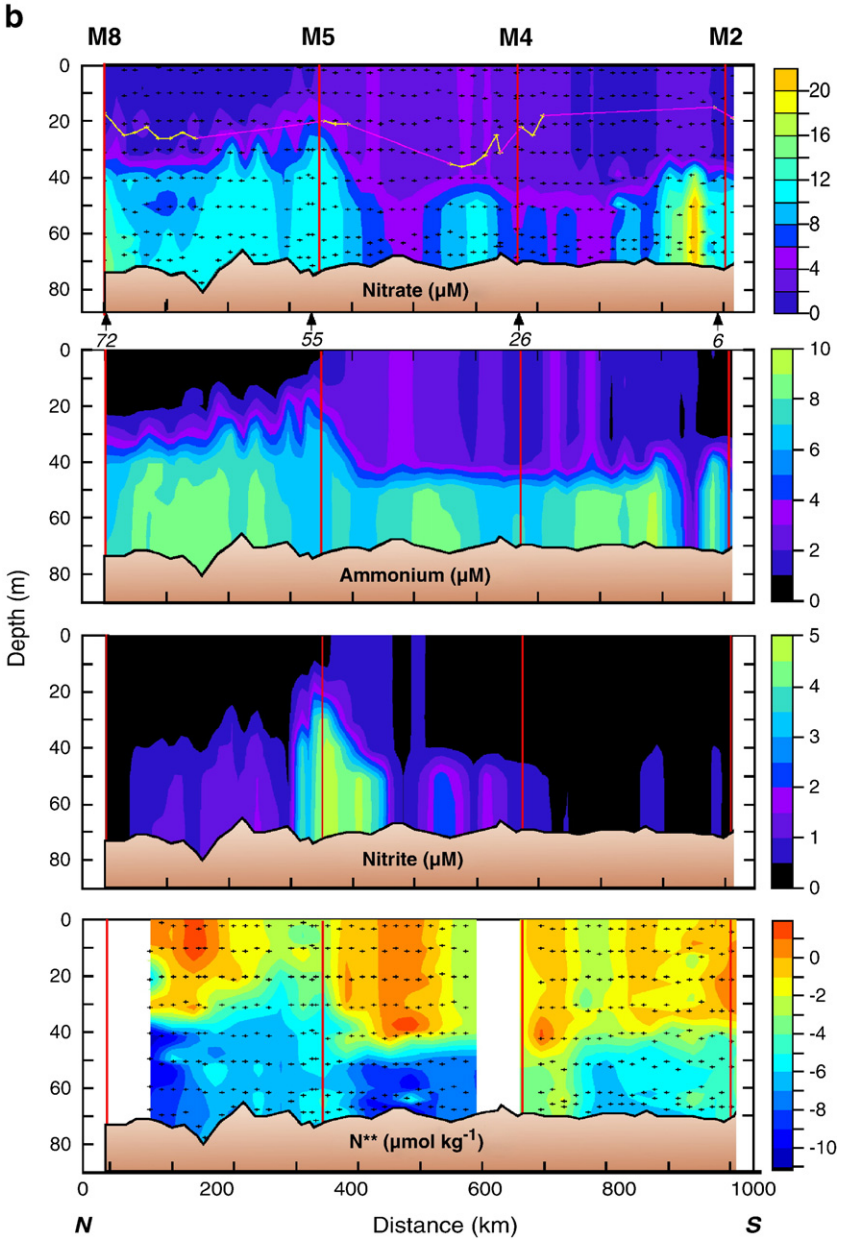

Fig. 2 (*continued*).

Study (BEST, unpublished results, $n = 3023$, 51 points along the x axis had $PO_4 < 0.2$ and were removed, $r^2 = 0.98$).

3. Results

On the middle shelf of the eastern Bering Sea, we observed moderately high nitrite concentrations (~1 μM) north of St. Matthew Island, and observed exceptionally high concentrations (i.e., the "nitrite pool", 2–5.6 μM) to the southeast of the island, and especially near mooring M5 (Fig. 1a). The nitrite pool was observed on two separate NOAA cruises that sampled the region for almost 2 weeks (Fig. 1b): first, EcoFOCI made measurements along the 70-m isobath (September 25–28), followed by BASIS sampling along their more widely spaced grid (September 30–October 6). On October 6, the BASIS cruise reoccupied an area first sampled during the EcoFOCI cruise. Nitrite concentrations had decreased from 4–4.7 μM on September 26 to ~1.0 μM on October 6. Hence, the nitrite pool was present for at least 1 week and maybe longer depending on when it first formed.

Low levels of nitrite (<<1 μM) were observed at all salinities (Fig. 1c). Higher concentrations of nitrite (~1–2 μM) were found in the salinity range of 31.6–32.3, and exceptionally high nitrite concentrations (2–5.6 μM) were found in the relatively narrow salinity range of ~32.3–32.5. In a T–S plot of bottom water (>50 m) along the 70-m isobath (Fig. 1d), the N–S transition zone was unambiguous (2–3.6 °C) and separated the ice-derived "cold pool" (<2 °C) from warmer, more southerly waters that had been ice-free all year. Highest salinities and nitrite concentrations were observed in this transition zone.

Vertical sections along the 70-m isobath helped to determine the breadth of the nitrite maximum and put it into an oceanographic context (Fig. 2). The middle shelf was defined by a strong two-layer system, with more intense stratification over the southern half of the transect (Stabeno et al., submitted). Examining deep water along the entire section, there was a salinity maximum around cast 55 (near

mooring M5), oxygen was >50% saturated everywhere and typically >70% saturated, chlorophyll concentrations were relatively low, nitrate concentrations were ~4–10 µM, and ammonium concentrations were extremely high (~6–9 µM) which is common on the eastern Bering shelf in late summer (Mordy et al., 2008; Whitledge et al., 1986). The nitrite maximum was in the bottom layer located near M5, and coincident with the salinity maximum and a slight drop in ammonium concentration. It was sampled on 13 consecutive CTD casts, and 9 of these casts were along the 70 m line and appear in Fig. 2. The bottom panel in Fig. 2 is a vertical section of N**. N** was mostly negative, indicating the predominance of denitrification on the middle shelf; however, there was not a unique signal concomitant with the nitrite maxima.

Contour maps of bottom water salinity, ammonium and nitrite from the two cruises show that the nitrite pool was associated with a bolus of relatively salty water that likely did not intrude inshore of the 70 m line, and the core of the nitrite pool was coincident with a slight decrease in ammonium (Fig. 3).

Temperatures and salinities of bottom water at mooring M5 have been measured since 2005 (Fig. 4). In deeper water, seasonal temperatures and salinities were generally highest in the fall or winter as the cold pool was advected away and replaced with warmer, saltier water from the south and/or the outer shelf. At the time of the NOAA cruises, temperatures at M5 were 3–4 °C higher than in subsequent years, and salinities were the highest of the time series.

4. Discussion

4.1. Oceanographic setting

The 14-year time series at mooring M2 shows strong multi-year variability with warmest temperatures occurring in 2005 (Stabeno et al., 2010). During the subsequent 3 years, the Bering Sea was colder, with 2008 being one of the coldest years in the time series. Associated with warming and cooling periods are changes in the length and extent of sea-ice coverage (Stabeno et al., 2010), and presumed adaptations by sea life intricately tied to the growth and retreat of seasonal sea-ice. To better understand these changes, EcoFOCI supplemented the M2 mooring with additional moorings along the 70-m isobath (including M5), and, since 2005, accompanied these time series measurements with hydrographic surveys in the spring and fall. In addition, the BASIS shelf-wide survey has been conducted every fall since 2002, with nutrient sampling beginning in 2003.

During EcoFOCI and BASIS cruises in fall 2005, we observed nitrite concentrations as high as 5.6 µM to the southeast of St. Matthew Island in the ammonium-rich bottom layer of the middle shelf. In the 2006 BASIS survey, two additional samples in the upper mixed layer also had elevated (>2 µM) nitrite (not shown): one sample on the slope (55°N, 168°W, 5 m) and one sample on outer shelf (57°N, 171°W, 23 m). These two samples were not associated with other oceanographic features, and will not be discussed. Elevated levels of nitrite were not observed on 13 other expeditions to the eastern Bering Sea between 2006 and 2009.

While nutrient measurements have been made for over 40 years on the Bering Sea shelf, we are unaware of any reports of unusually high (>2 µM) nitrite concentrations. Many of the earlier data sets focused on the southeastern shelf, and were often conducted in spring. Results presented here represent some of the first measurements made in the vicinity of St. Matthew Island during late summer.

In 2005, high levels of nitrite were observed in salty well-oxygenated waters that separated ice-derived cold water (i.e., the cold pool, <2 °C) in the north from warmer water in the south. This transition zone on the middle shelf was set up by the maximum southerly extent of sea-ice, and the maximum ice extent is often

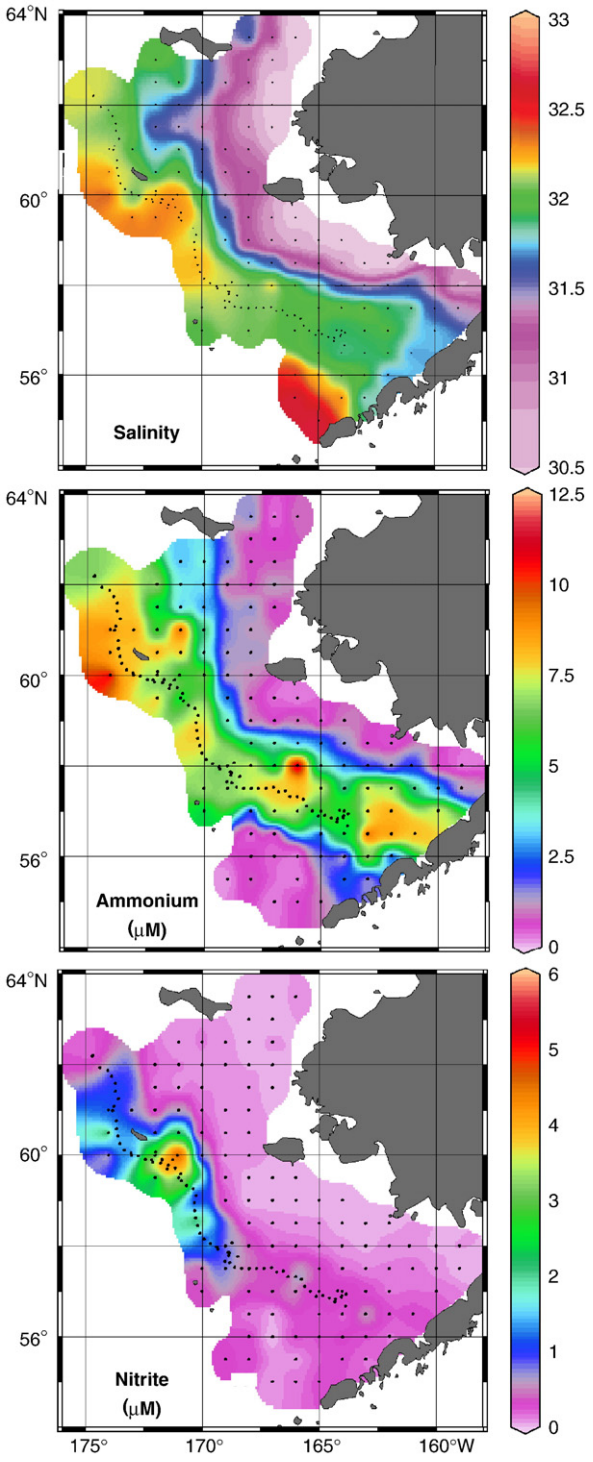

Fig. 3. Surface maps of bottom salinity, ammonium and nitrite. The color scale for salinity has been adjusted to emphasize the salt gradient on the outer shelf.

forced by northerly spring winds that drive the seasonal ice southward (Stabeno et al., 2007). In summer, the location of the transition is modified by local forcing and is generally found just south of St. Matthew Island in the vicinity of M5 (Stabeno et al., 2007).

Salinities in late summer 2005 were the highest of the M5 time series, and were ~0.7 higher than late summer measurements in later years (Fig. 4). Salinity anomalies in the vicinity of M5 were the highest of any year since the BASIS program began in 2002 (S. Danielson, University of Alaska, Fairbanks, pers. comm.). In cold, fresher years

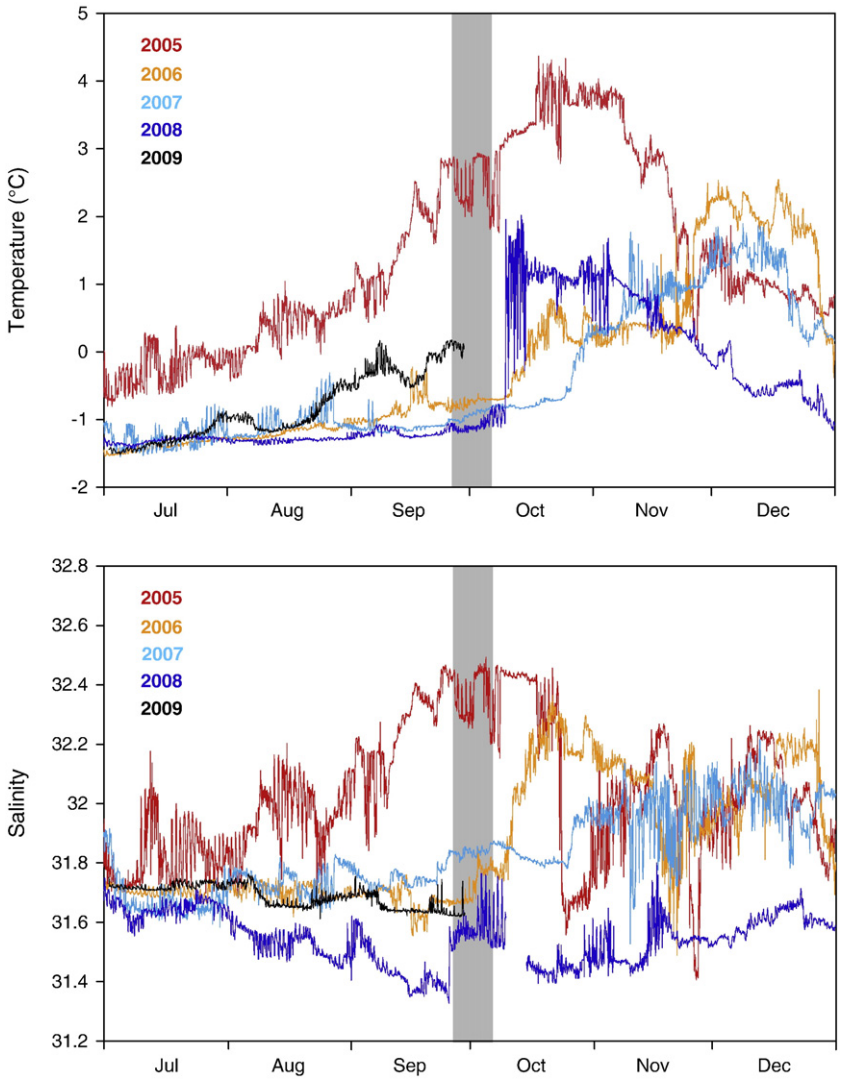

Fig. 4. Time series of temperature and salinity in the bottom layer (52–60 m) at M5 since 2005. The shaded area denotes the period when the nitrite pool was sampled.

with more extensive sea-ice (2006–2009), nitrite concentrations along the 70-m isobath were <1 μM in spring and summer (not shown). Hence, unusually high nitrite was associated with warmer, saltier water.

It was evident that saltier water in the transition zone did not originate on the middle shelf (Fig. 1d). BASIS data with salinities >32.3 were located near the 100-m isobath (80–123 m) southeast of the Pribilof Islands (not including data in the transition zone). We also examined an extensive data set around the Pribilof Islands that was collected in the summer of 2004 (Mordy et al., 2008; Sullivan et al., 2008). Salinities in the range of 32.35–32.5 were found at 75–100 m depth on the outer shelf around the islands. We conclude that on-shelf flow of outer shelf waters is the likely source of high salinity waters in the north–south transition zone.

Direct measurements of on-shelf flow were unavailable at M5 as the moored current meter there failed in 2005. Whereas the mean flow at M5 from other years was westward along the isobath (~1.5 cm s^{-1}), there were occasional events of eastward flow in summer of ~5 cm s^{-1} (Stabeno et al., 2010). Since 1986, satellite-tracked drifters (drogued at 40 m) have been deployed regularly in the Bering Sea to help identify flow patterns (http://www.pmel.noaa.gov/foci/globec/gl_drifters.shtml, January 2010); however, in 2005, there were no drifters in the region. In other years, while many drifter tracks on the outer shelf follow bathymetry (i.e., Fig. 5, 1997 drifter track), on-shelf (northward) flow often originates just west of the Pribilof Islands and extends towards M5 (i.e., Fig. 5, 1990 and 2001 drifter tracks). Because salinities at the M5 mooring steadily increased during summer 2005 (Fig. 4) and waters with salinities of >32.3 were tightly distributed to the south and west of St. Matthew Island (Fig. 3), we hypothesize that during our expeditions an onshore event was occurring, but stalled near the 70 m line much like the drifter tracks in Fig. 5.

4.2. Accumulation of nitrite

Several mechanisms may account for the accumulation of nitrite below the euphotic zone: release from sediments, release from light-limited phytoplankton, and decoupling of nitrification in the water column (Lomas and Lipschultz, 2006).

4.2.1. Uncoupled denitrification, curtailment of anammox

Nitrite is a short-lived intermediate in the nitrification and denitrification pathways of the marine nitrogen cycle, and is the primary electron acceptor during the anaerobic oxidation of ammonium via anammox (Codispoti et al., 2001; Gruber, 2004; Gruber and Sarmiento, 1997). In the Bering Sea, nitrification occurs in the water column and in aerobic sediments, but, due to the well-oxygenated waters, denitrification and anammox are restricted to anaerobic

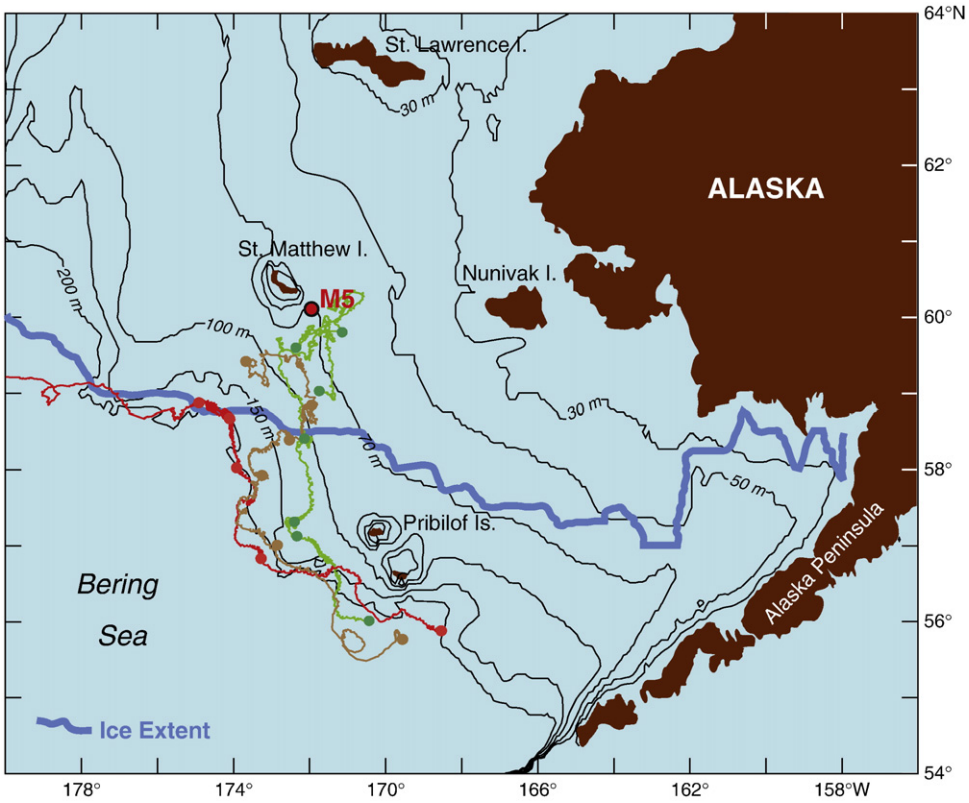

Fig. 5. Map of the southeastern Bering Sea showing mooring locations (red), the maximum ice extent in 2005 (blue), and trajectories of three satellite-tracked drifters drogued at 40 m (1990 in green, 1997 in red, 2001 in yellow). Dark symbols on the drifter tracks denote the first of each month starting in June for the 1997 (red) and 2001 (brown) drifters, and May for the 1990 (green) drifter.

sediments (except for anoxic microzones that may be present around marine snow or in sea-ice, Riemann and Azam, 2002).

When comparing denitrification and anammox activity on arctic shelves, Rysgaard et al. (2004) found that anammox accounted for 1–35% of total N_2 production, making this process an important nitrite sink. Accumulations of nitrite could result if the second step in either the nitrification or denitrification pathways were to become rate-limiting, or if anammox were curtailed. Perhaps such changes were triggered by a ~2 °C warming of overlying waters associated with the onshore flux of warmer outer shelf bottom water in September 2005. If nitrite were derived from the sediments, tidal energy was sufficient to mix away any vertical gradients in the bottom layer.

To ascertain if changes in the nitrite pool were associated with a denitrified/anammox signal in the water column, we examined the distribution of N**. N* is an indicator of denitrification or nitrogen fixation and is simply the nitrate residual from a linear nitrate–phosphate relationship derived from global water column data (Deutsch et al., 2001; Gruber and Sarmiento, 1997). Codispoti et al. (2001) modified this approach to account for the presence of inorganic nitrogen in the form of ammonium or nitrite. Using this modification, we developed a regional estimate of N**. If the observed nitrite pool accumulated at the expense of nitrogen gas (e.g., interruption of denitrification or anammox), then we would expect a less negative N** coincident with the nitrite pool. However, the horizontal variability of N** within the nitrite pool was of similar magnitude as the expected signal (3–5 μM), and we were unable to test the hypothesis using this technique.

Direct measurements of nitrogen loss from sediments in the North Pacific were ~3 mmol m^{-2} day^{-1} (Devol, 1991). Given this rate of sedimentary denitrification, if the process were stopped after the reduction of nitrate to nitrite (no gas production) and the resulting nitrite diffused into the water column, it would take about 44 days to generate the observed nitrite concentrations (the pool averaged 3.8 μM nitrite with a layer thickness of about 35 m). Furthermore, direct flux measurements of sedimentary nitrogen loss in the arctic and Bering Sea were ~2–100 times smaller than in the North Pacific (Chang and Devol, 2009; Devol et al., 1997; Rysgaard et al., 2004). Measurements of the concentration change of nitrite in flux cores collected in this region in July 2008 showed either little change in nitrite or nitrite uptake by sediments (Shull and Devol, unpublished data). Given the above calculation, observations of nitrite release from sediments appear to be too low to account for the observed nitrite pool.

4.2.2. Phytoplankton excretion

Excretion of nitrite by light-limited phytoplankton can be induced by spiking algal cultures with nitrate (reviewed by Collos, 1998). A sudden increase in nitrate disrupts assimilatory pathways by reducing the relative activity of nitrite reductase (Sciandra and Amara, 1994). As a result, nitrite accumulates within the cells and is subsequently released, perhaps due to the toxicity of the nitrite ion (Painter, 1970). In the natural environment, these experiments correspond to localized upwelling events that inject nutrients into the stratified euphotic zone (Collos, 1998).

Lomas and Lipschultz (2006) hypothesized that shoaling of the nitracline relative to the 1% light level would increase light-limited nitrate uptake, and induce nitrite release by phytoplankton. Along the 70-m isobath, nitrate concentrations at the 1% light level were generally <3 μM (Fig. 2). But in the vicinity of the nitrite pool, the nitracline shoaled such that concentrations of nitrate at the 1% light level increased to ~5–6 μM. When examining all EcoFOCI casts within 5 h of local noon (including casts adjacent to the 70 m isobath), extraordinarily high nitrite (>2 μM) in the bottom layer only occurred

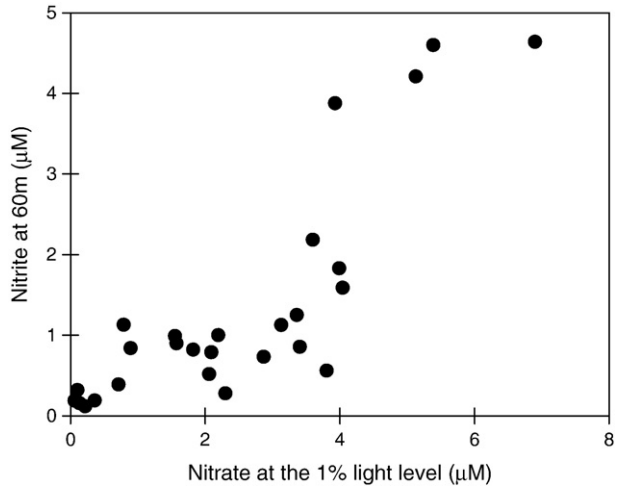

Fig. 6. Nitrite concentrations in the bottom layer (60 m) compared to nitrate concentrations at the 1% light level for EcoFOCI stations that were within 5 h of local noon.

when nitrate at the 1% light level was >3 μM (Fig. 6). There was not a large increase in chlorophyll concentration or % oxygen saturation associated with this feature suggesting that shoaling of the nitracline was recent, and the algal community had yet to fully respond to available nutrients and light. This observation is consistent with the hypothesis that local vertical advection/diffusion events stimulated nitrite excretion at the base of the photic zone, and that nitrite in the bottom layer accumulated at the expense of nitrite oxidation.

A first order test of this hypothesis is to compare rates of nitrite accumulation with rates of nitrate uptake (Table 1). Using the range of integrated nitrite in the deep nitrite pool and a turnover rate for nitrite of 3–7 days (Lipschultz et al., 1996), we estimate a net nitrite accumulation rate of 16–79 mmol m^{-2} day^{-1}.

Comparing this with nitrate uptake rates was complicated because this parameter was not measured in 2005. Rates in Table 1 were calculated by multiplying the range of integrated chlorophyll in the nitrite pool by direct measurements of chlorophyll-specific nitrate uptake across the shelf in spring 1979, 1980 and 1981 (Sambrotto et al., 1986), and by the rate that nitrate was assimilated in the water column during the 2007 spring bloom (Mordy, unpublished data). Direct measurements of chlorophyll-specific nitrate uptake by Sambrotto et al. (1986) were ~20 times smaller than estimates based on the drawdown of nitrate in 2007. Differences in these chlorophyll-specific rates could have arisen from differences in phytoplankton speciation, cellular chlorophyll content, and bloom conditions among other factors.

Further complicating matters was that nitrate uptake rates in Table 1 were based on integrated chlorophyll (these were the units available in Sambrotto et al., 1986). The use of integrated values results in an overestimate of potential nitrite excretion. It is doubtful that assimilated nitrate would be excreted as nitrite in the upper photic zone, or at depths where light-dependent nitrate uptake ceases. Instead, most nitrite excretion is expected at the base of the photic zone. By considering that in the nitrite pool chlorophyll concentrations near the 1% light level (15–25 m) represented 11–26% of integrated chlorophyll (19 ± 5%, $n = 13$), we were able to derive a range of potential excretion rates in Table 1.

Ammonium inhibition of nitrate uptake is a well known phenomena, but is highly variable (Dortch, 1990), and may not occur when cells are light limited (Yin et al., 1998). In the nitrite pool, ammonium concentrations at the 1% light level were ~2–4.5 μM. These concentrations were sufficient to initiate inhibition, and may have provided a preferable nitrogen source to sustain light-limited production.

Given the relatively low phytoplankton biomass concentration in the nitrite pool, our estimated nitrite accumulation rate could only be approached if nitrate uptake was not inhibited by ammonium, if nitrate uptake rates were near maximum, if assimilated nitrate was largely excreted as nitrite, and if nitrite oxidation rates (i.e. nitrite turnover) were very low.

4.2.3. Uncoupled nitrification

In the World Ocean, ammonium concentrations are typically <1 μM. But the Bering Sea is not typical. Ammonium concentrations on the Bering Sea shelf are usually 6–10 μM in summer and fall (Mordy et al., 2008; Saino et al., 1983; Whitledge et al., 1986). In September 2005, bottom water concentrations were in this range (Figs. 2 and 3). There does appear to be a ~1–2 μM decrease in ammonium concentrations concomitant with the nitrite pool (Fig. 2). Such a result would be consistent with uncoupled nitrification. The first step in nitrification is considered rate-limiting; hence, nitrite usually does not accumulate in the ocean. If conditions in the transition zone decoupled these reactions (such that the second step became rate-limiting), this could account for the build-up of nitrite.

An ammonium vs. nitrite plot showed evidence of uncoupled nitrification (Fig. 7). The majority of data had low nitrite concentrations (<0.6 μM) with ammonium varying from zero in surface waters to about 10 μM over the middle shelf. Two trends were also observed, and both trends were comprised of data collected in the vicinity of the nitrite pool. The positive trend was the result of samples that spanned the nutricline, while the majority of samples comprising the negative trend were from the bottom layer. The negative trend had a slope of −0.34 and was significantly different than zero ($n = 170$, $t = -7.47$, $P = 0.0000$). This negative correlation was likely the result of ammonium oxidation into nitrite. Because the slope was much less than 1, this data could only account for approximately 35% of the nitrite pool. Additional nitrite may have been supplied by a secondary source (i.e. phytoplankton excretion), and/or the ammonium pool was being rapidly replenished (i.e. the rate of ammonification was greater than ammonium oxidation). Annual accumulations of ammonium over the middle shelf in summer/fall offer evidence of a seasonal imbalance in rates of ammonification and ammonium oxidation (Whitledge et al., 1986; Mordy et al., 2008).

Table 1
Comparison of estimated nitrite turnover rates with estimated phytoplankton nitrate uptake rates in the nitrite pool (nitrite>3 μM).

	Units	Range of values	
		Minimum	Maximum
Turnover rate in nitrite pool			
Nitrite[a]	mmol m^{-2}	110	238
Turnover time[b]	day^{-1}	7	3
Turnover rate	mmol m^{-2} day^{-1}	16	79
Nitrate uptake in nitrite pool			
Chlorophyll[c]	mg m^{-2}	43	68
Chlorophyll-specific nitrate uptake rate	mmol mg^{-1} day^{-1}	0.022[d]	0.47[e]
Nitrate uptake	mmol m^{-2} day^{-1}	0.9	32
Potential excretion[f]	mmol m^{-2} day^{-1}	0.1	8.3

[a] Mean = 178 ± 40 mmol m^{-2}, $n = 13$.
[b] Lipschultz et al. (1996).
[c] Mean = 57 ± 7 mg m^{-2}, $n = 13$.
[d] Regression slope of nitrate uptake vs. chlorophyll for spring bloom data in 1979–1981 extracted from Figs. 5–7 in Sambrotto et al. (1986), $r^2 = 0.58$, $n = 21$.
[e] The maximum chlorophyll-specific nitrate uptake rate calculated at eight repeat hydrographic stations during bloom conditions in spring, 2007; mean = 0.13 ± 0.16 mmol mg^{-1} day^{-1}. Stations were separated by 14–28 days. Mean nitrate concentration at 20 m was 6 ± 4 μM.
[f] Nitrate uptake multiplied by 11% (minimum) and 26% (maximum) which represents the range of % biomass at 15–25 m in the nitrite pool.

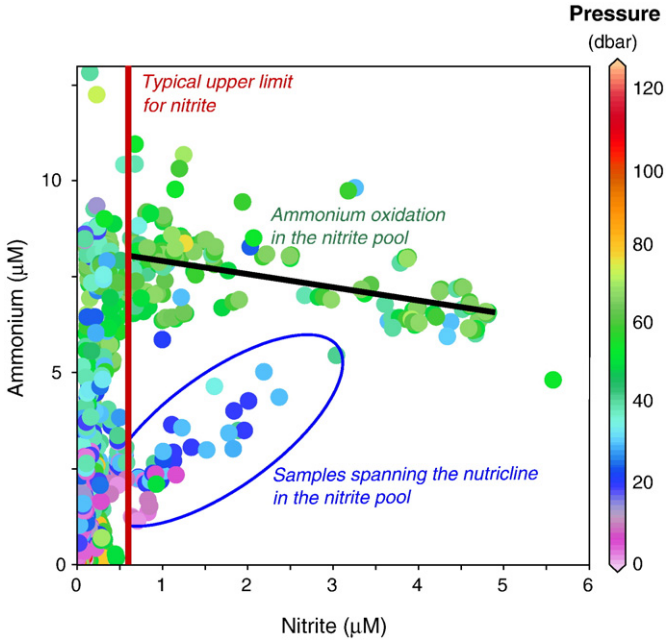

Fig. 7. Concentrations of ammonium vs. nitrite for all data on both NOAA cruises. Colors denote pressure. The black regression line is for data in the upper trend (data with nitrite >0.6 μM and outside the ellipse).

5. Summary

The nitrogen cycle on Bering Sea shelf is complicated as evidenced by denitrified waters and elevated ammonium concentrations in summer. In addition it appears that ephemeral events have large impacts on the concentration of relevant species such as elevated nitrite in the well-oxygenated waters of the Bering Sea in 2005. These observations were unprecedented.

The nitrite pool appeared in a warm year, but was transitory. It was associated with the transition zone on the middle shelf, and occurred in a parcel of well-oxygenated, salty water that was advected from the outer shelf shoreward, but stalled near the 70 m isobath. It was beneath a shoaling nitracline, and was correlated with a small decrease in ammonium. The sedimentary nitrite flux was insufficient to produce such high levels of nitrite. Instead, there was evidence that the nitrite source was ammonium oxidation, although phytoplankton excretion could not wholly be dismissed.

Regardless of the source, nitrite concentrations of this magnitude could only be maintained if the second step in nitrification (oxidation of nitrite) was rate-limiting. We have no data to test the hypothesis that the nitrite pool just simply resulted from a decrease in nitrite oxidation rates. The only conclusion we can draw is that, for reasons yet to be determined, there was a temporary uncoupling of nitrification that resulted in the accumulation of nitrite.

Until BASIS began measuring nutrients in 2003, measurements on the northern shelf in summer were rare. Extraordinary levels of nitrite were not observed on earlier BASIS surveys or on summer EcoFOCI expeditions in 2006–2009 suggesting that nitrite pools are ephemeral. In 2004, Mordy et al. (2008) sampled farther south near the Pribilof Islands, and encountered similar environmental conditions as in 2005 (warm year, high ammonium). Accumulations of nitrite, however, were not observed, even over the outer shelf where the transition zone in 2005 appears to have originated.

This appears to be a serendipitous observation, unique in part because of the transitory nature of the nitrite pool, and infrequent sampling of the region. If the nitrite pool was associated with the northward migration of the transition zone in warm years, then, with climate change, we may see a recurrence of this feature as temperatures similar to those observed in 2005 will become more common (Stabeno and Overland, submitted).

Acknowledgments

We thank the crew and officers of the NOAA ship *Miller Freeman* and the F/V *Sea Storm* for their assistance and effort. We also thank Bill Floering and Bill Parker for overseeing CTD and mooring operations, Eric Wisegarver and Fred Menzia for assisting with the nutrient data, Karen Birchfield, Nancy Kachel, Dave Kachel and Doug Jongeward for assisting with the figures, Kristin Cieciel for assistance in BASIS data collection, CTD processing, and database management, and Colleen Harpold for analysis of chlorophyll samples. We also thank an anonymous reviewer for improving the manuscript. Research was funded by NOAA's North Pacific Climate Regimes and Ecosystem Productivity Program, NOAA's Fisheries and the Environment (FATE) Program, NOAA's Alaska Fisheries Science Center, the North Pacific Research Board (Grants: #517, 602 and 701 to PJS), the Arctic Yukon Kuskokwim Sustainable Salmon Initiative (AYKSSI), and NSF's Office of Polar Programs (Grant ARC0612380 to AHD and DHS). This publication is partially funded by the Joint Institute for the Study of the Atmosphere and Ocean (JISAO) under NOAA Cooperative Agreement No. NA17RJ1232. This research is contribution EcoFOCI-N707 to NOAA's Ecosystems and Fisheries-Oceanography Coordinated Investigations, contribution 3287 to NOAA's Pacific Marine Environmental Laboratory, and contribution 1741 to JISAO.

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