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N deficiency in a well-oxygenated cold bottom water over the Bering Sea shelf: influence of sedimentary denitrification

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Abstract

Anomalously low ratios of dissolved inorganic nitrogen (DIN) to dissolved inorganic phosphorus (DIP) were found in a well-oxygenated cold bottom water over the southeastern Bering Sea shelf during late summer. Our study shows that the anomalously low DIN/DIP ratios are caused by sedimentary denitrification. The estimated sedimentary denitrification rates, ranging from 0.7 to 1.5 mmol/m²/day, are similar to values previously reported for continental shelf regions. An annual rate of sedimentary denitrification in the Bering Sea shelf can be, at a low limit, in the order of 2.5 Tg N/yr. This corresponds to roughly one-third of the annual net supply of the nitrate to the Bering Sea shelf and, at least, 2.5% of annual global denitrification rate in oceanic sediments, implying that the sedimentary denitrification in the Bering Sea shelf could be a significant sink of nitrogen in both regional and global scales.

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1. Introduction

Availability of nutrients, such as nitrate and phosphate in surface waters generally control primary production in the ocean, resulting in a downward flux of organic carbon, which, with respiration, causes consumption of oxygen in bottom waters and sediments. Intensive oxygen

consumption in the water column and sediment by decomposition of organic matter leads to anoxia and consequently to denitrification, which can reduce nitrate to N₂ (e.g. Hattori, 1983). The amount of fixed nitrogen (NH₃, NO₂, NO₃) in the ocean is largely regulated by the balance between biological processes of nitrogen fixation and denitrification, while the amount of phosphorus (PO₄) is mainly determined by both river runoff from the land and burial in sediments (Gruber and Sarmiento, 1997). Thus, those processes could contribute to the change of the N/P ratios both in

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global and regional scales. The Bering Sea ecosystem is characterized by a seasonal variation in primary production, which is related to increases in incident radiation and sea ice melt. It maintains one of the world's most abundant biological resources. Since much organic matter is not exported from the Bering Sea shelf to the open ocean, it accumulates on the shelf and may be utilized by the benthic ecosystem (Walsh and McRoy, 1986). Therefore, the Bering Sea shelf must play important roles in nutrient dynamics as well as material cycling.

Low N/P ratios in the water column over the continental shelf of the southeast Bering Sea have been observed repeatedly. Because there is no oxygen depletion in the water column of this region even in summer season, the low N/P ratios are thought to be formed by three possible scenarios, namely, (1) denitrification in sediment of the continental shelf, (2) supply of nitrate affected by denitrification from the deep water oxygen minimum in the North Pacific, and (3) addition of extra phosphate from particulate sources in the water column or sediments. Although there are several studies focused on the nitrogen transformation in the Bering Sea shelf such as denitrification and decomposition (Koike and Hattori, 1979; Lomstein et al., 1989; Rowe and Phoel, 1992; Devol et al., 1997), nutrient dynamics associated with change in the N/P ratio is still poorly understood.

In this study, we identify the most plausible cause for the low ratios of dissolved inorganic nitrogen (DIN: NH_3 , NO_2 , NO_3) to dissolved

inorganic phosphorus (DIP: PO_4) in the water column over the continental shelf of the southeast Bering Sea, with an estimation of DIN deficit relative to DIP, and the implications in the context of the global oceanic nitrogen budget are also discussed.

2. Sampling and analytical methods

Oceanographic observations and sample collections were made during cruises of the research vessel *Mirai* (September 2000 and August 2001). The study area was covered by a transect in the southeast Bering Sea between 55°N and 59°N along 166°W . The sampling locations were basically the same for both cruises except for a station at 59°N , 166°W in 2000 (Fig. 1). Seawater samples were collected using Niskin bottles mounted on a CTD-rosette. Nutrients, including nitrate, nitrite, ammonium and phosphate were immediately measured with an AutoAnalyzer (TRACSS) on the board using standard methods of Grasshoff et al. (1983) with some modifications. The detection limits for the nitrate and phosphate analyses was estimated to be twice the precision of each nutrient method which was approximately $0.2\ \mu\text{M}$ nitrate and $0.05\ \mu\text{M}$ phosphate. Dissolved oxygen (DO) was determined by the Winkler method (Winkler, 1888; Carpenter, 1965). The seawater samples for oxygen isotopic composition of water were stored in 50 ml glass bottles. The isotope analysis was performed using the Thermoquest CO_2 gas–water isotopic equilibrium device with

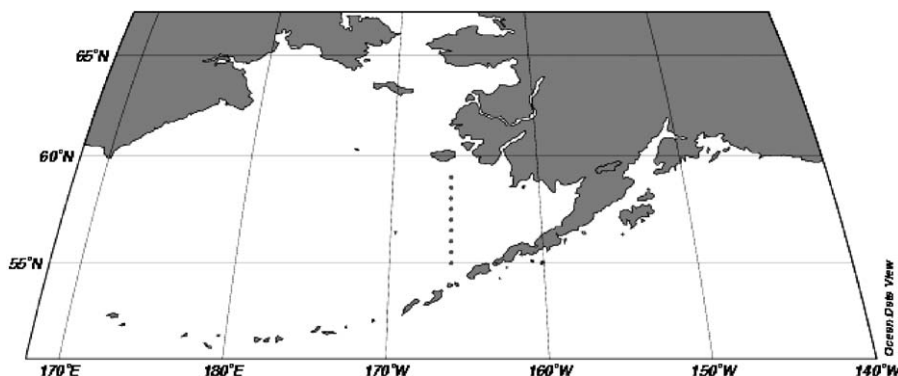


Fig. 1. Map showing sample locations along a transect in the southeast Bering Sea.

the Finnegan Mat 252 Mass Spectrometer. The oxygen isotope ratio ($\delta^{18}\text{O}$), relative to the VSMOW standard water, was reported with the conventional delta notation (‰). For nitrogen isotopic analysis of nitrate, the filtrate ($<0.7\ \mu\text{m}$, 2.5–3 l) was transferred to a glass bottle and preserved with HCl (Liu and Kaplan, 1989). A modified procedure for the determination of natural isotope abundance of nitrate-nitrogen was used and was described in Tanaka and Saino (2002). The nitrogen isotope ratios ($\delta^{15}\text{N}$) were measured with the Finnegan Mat Delta Plus Mass Spectrometer and expressed in the conventional delta notation (‰) relative to that of atmospheric nitrogen.

3. Results and discussions

3.1. Chemical and hydrological characters on the Bering Sea shelf

Temperature and salinity in summer for the Bering Sea shelf are shown in Figs. 2(a), (b), 3(a) and (b). The shelf waters could be separated into three domains, where inner, middle and outer shelf areas are associated with water depth as well as the characteristics of temperature and salinity distributions (Coachman, 1986; Stabeno et al., 2001). The inner domain water column (water depth $<50\ \text{m}$) is well mixed as a result of both tidal and wind mixing. In the middle domain (water depth 50–100 m), a two layered water column is developed during summer, since surface water is heated and wind mixing is not sufficient to stir the whole water column in the presence of positive buoyancy flux. The bottom layer is also very well mixed through the turbulent effects of tidal oscillations (Coachman, 1986; Kachel et al., 2002). The outer domain (water depth 100–200 m) is comprised of a surface wind mixed layer and a bottom tidal mixed layer separated by an intermediate layer. It is generally considered that the shelf waters receive an annual excess of precipitation over evaporation, freshwater runoff from Kuskokwim and Kvichak rivers, and sea ice melting (Kinder and Coachman, 1978). Therefore, along the cross shelf transect in the southeastern Bering Sea, salinity

decreased from 33 psu to ~ 31 psu toward the inner domain (Figs. 2(b) and 3(b)). Another striking feature was that a cold water mass is often observed on the bottom of the entire middle domain (Figs. 2(a) and 3(a)) which has been defined by the 2°C isotherm. Compilation of 25 years of sea ice data has indicated that there are rather large interannual variations of the cold pool with a mean extent of $\sim 200\ \text{km}$ but having a maximum extent of $\sim 1300\ \text{km}$ (Wyllie-Echeverria and Wooster, 1998). The timing of the seasonal ice cover is often quite variable from year to year (Stabeno et al., 2002).

A previous study reported that significant mean flow (1–10 cm/s) exists over the outer shelf, generally directed toward the northwest, but with a cross-shelf or cross-isobath component. Flow of a similar magnitude (1–6 cm/s) to the outer shelf occurs in the coastal region, paralleling to the 50 m isobath (north-westward). Mean flow in the middle shelf is insignificant because a superposition of variable current direction lead to very weak ($\sim 1\ \text{cm/s}$), statistically insignificant, vector-mean flows (Schumacher and Kinder, 1983). Direct current hydrographic measurements indicate that advection by the mean flow is so small that it does not affect the hydrographic structure significantly in this domain during ice-free season (Schumacher et al., 1979). Indeed, little temporal variations in salinity at southeast Bering Sea shelf both at the end of winter and fall were observed (Coachman, 1986). In addition, the salinities in waters at both outer shelf and inner shelf seem to be constants (33.2 psu at outer shelf: ~ 32 psu at inner shelf) (Coachman, 1986) but more recent data have found salinity values as low as 30.8 psu (Kachel et al., 2002). Therefore, it is assumed that salinity in the cold water mass on the middle domain in summer is determined by a result of mixing of two components from outer shelf and inner shelf during winter, and remained through the spring and summer time. Indeed, when values of seawater $\delta^{18}\text{O}$ are plotted against salinity, a highly correlated relationship between the oxygen isotopic composition of water and salinity is found (Fig. 4). Certainly, the relationship observed in summer shows that the spatial distribution of salinity is regulated by the mixing

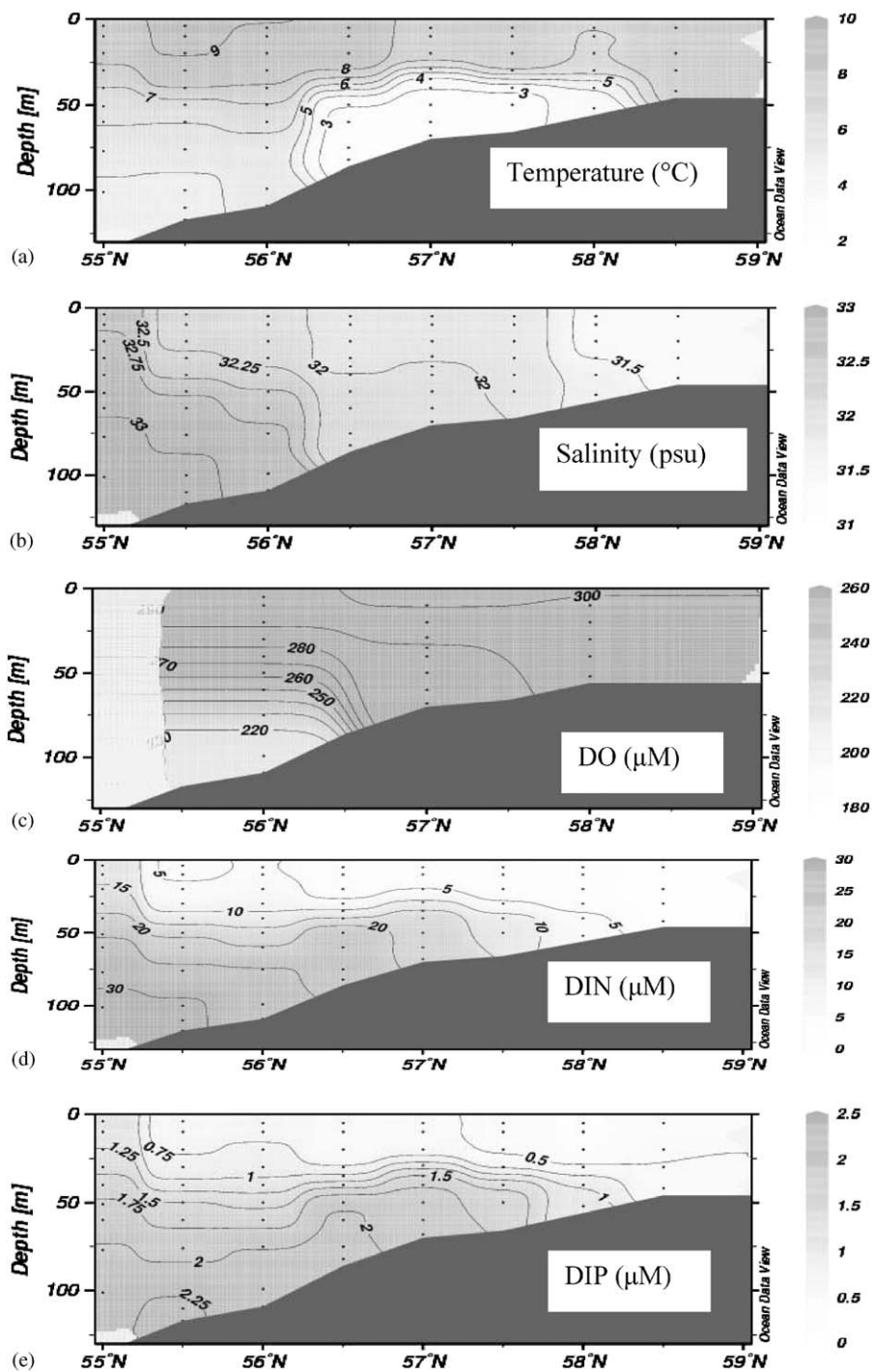


Fig. 2. Transect sections of (a) temperature, (b) salinity, (c) dissolved oxygen, (d) DIN, and (e) DIP in the southeastern Bering Sea during September 1–4, 2000.

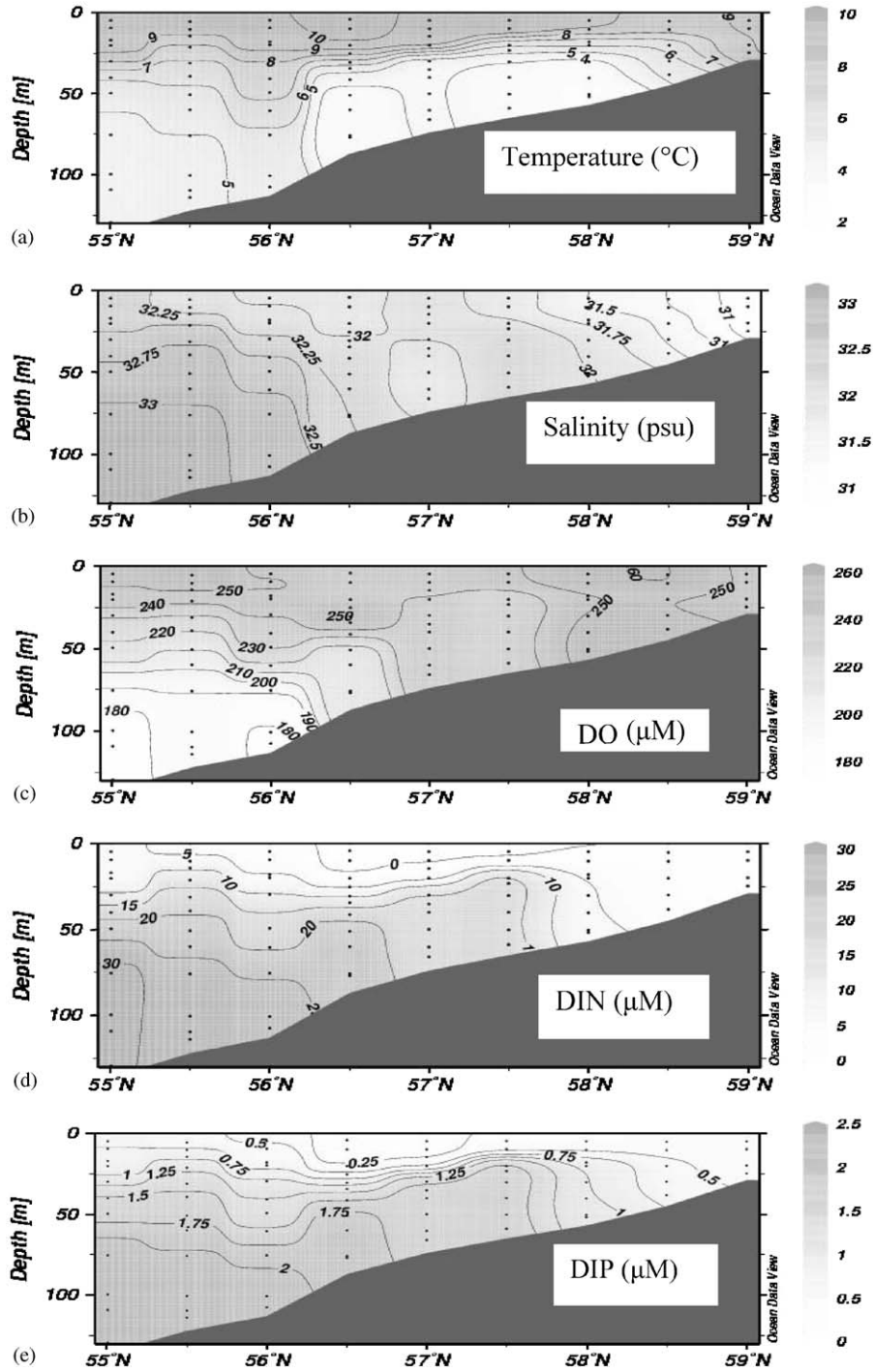


Fig. 3. Transect sections of (a) temperature, (b) salinity, (c) dissolved oxygen, (d) DIN, and (e) DIP in the southeastern Bering Sea during August 28–30, 2001.

of the waters from both the outer shelf and inner shelf.

Distributions of DO, DIN and DIP are presented in Figs. 2(c), (e), 3(c) and (e). The concentrations of DIN and DIP along the transect generally showed a decrease in concentrations towards the inner domain (Figs. 2(d), (e), 3(d) and (e)), and these trends are similar to the salinity distribution below the mixed layer ($< \sim 30$ m). It is known that freshwater from Alaska riverine waters and sea ice has an oligotrophic condition (Guo et al., 2004; Tanaka et al., unpublished data), a cross-shelf mixing of nutrient-rich shelf break water could be the primary mechanism of nutrient supply to the entire shelf, especially in the winter (Coachman and Walsh, 1981). On the other hand, since nutrients are utilized by phytoplankton in the euphotic zone during spring and summer, their concentrations, when determined at the end of summer, were very low in the upper mixed layer. Such a low concentration of nutrients in summer represented the minimum values after spring bloom (Whitledge et al., 1986). The DIP concentration, in general, followed the trend of DIN concentration. DIN in the surface water was depleted, whereas the DIP remained in an appreciable amount. Therefore, it appears that DIN was an important limiting factor for phytoplankton growth in the study area. A vertical section of DO

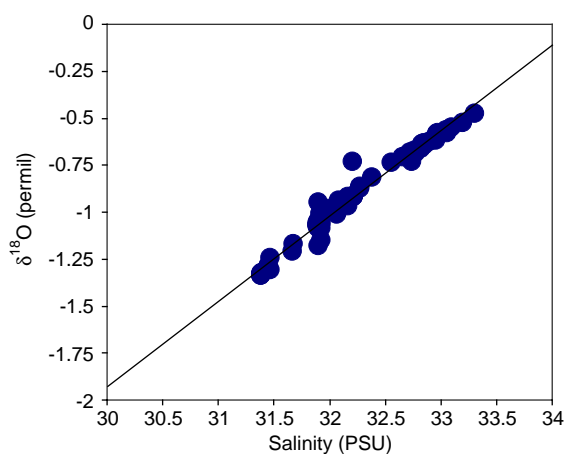


Fig. 4. Relationship between oxygen isotopic composition of water and salinity in the southeastern Bering Sea during September 1–4, 2000. The determination coefficient of the regression line is $r^2 = 0.97$.

is presented in Fig. 2(c). DO concentrations generally show a gradual decrease with increasing depth, even in the inner shelf. The minimum DO concentration on the cross shelf section was $\sim 180 \mu\text{M}$ in the bottom of the outer domain (Fig. 2(c)).

The vertical distributions of nitrogen isotopic composition of nitrate are shown in Fig. 5. These were measured at 55°N , 56°N , and 57°N along the 166°W transect line. Their values seemed to increase slightly from bottom to surface layer, except for the station at 57°N , 166°W where the nitrogen isotopic values increased with increasing nitrate concentration. The variations of nitrogen isotopic composition of nitrate below the mixed layer depth (~ 30 m) ranged narrowly from 3.9‰ to 5.2‰. The values are within typical ranges observed in the deeper layer of the world ocean.

3.2. Relationship between DIN and DIP concentration in different water masses

According to the relationship between DIN and DIP concentrations, the study area can be characterized as three different hydrological and nutrient regimes (Fig. 6). The first regime is associated with mixed layer waters (~ 30 m) over the shelf. Despite DIN concentrations being almost depleted in this region, DIP still remained

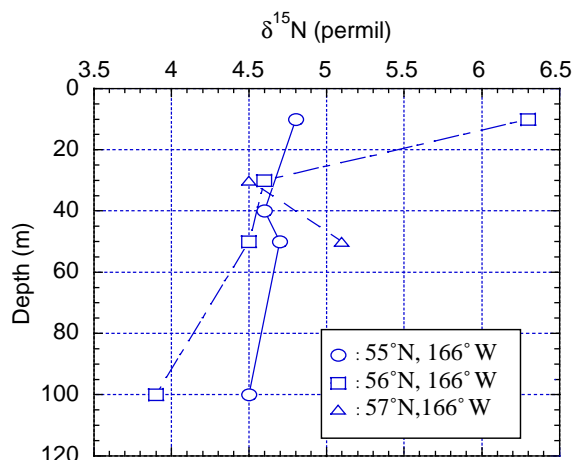


Fig. 5. Vertical profile for nitrogen isotopic composition of dissolved nitrate observed at 55.0°N (\circ), 56.0°N (\square) and 57.0°N (\triangle) along 166.0°W in August 28–30, 2001.

at a relatively higher concentration, varying from 0.2 to 0.8 μM . As the ratio of DIN to DIP utilized by plankton ($\text{N/P}=16$) is higher than that of nutrients supplied from the deeper layer to the surface layer (e.g. Wu et al., 2000), the depletion of DIN in the surface mixed layer could be faster than that of DIP. It is therefore considered that primary production in the study area was regulated by the amount of DIN in the surface layer.

The second regime is characterized by lines of slope $\text{N}=16.2 \times \text{P}$ in 2000, and $\text{N}=15.7 \times \text{P}$ in 2001. In terms of the DIN and DIP relationship, this regime is similar to the first group (Fig. 6) and the concentration of DIN and DIP varied from 13.4 to 30.8 and 1.2 to 2.3 μM , respectively. Such high concentrations of DIN and DIP should be largely supplied from the North Pacific (Whitledge et al., 1986; Hansell et al., 1993). Indeed, the large determination coefficients of these slopes could

imply that the relationships between DIN and DIP are formed simply by physical mixing of subsurface and deeper waters.

The third regime is featured with a slightly lower ratio of DIN to DIP compared to the second group. These features of nutrient distributions were only observed in the cold water ($\leq 4^\circ\text{C}$) mass, which resided over the middle shelf (Fig. 2a). The cold water mass was known to be formed during winter and remained hydrologically isolated at the bottom of the middle shelf through summertime (Coachman, 1986). Therefore, the ratio of DIN to DIP observed in the cold water mass during summer could be altered by a biological process, such as denitrification, after the water mass was isolated on the bottom in spring. Recent observations indicate that relatively high salinity, nitrate and phosphate concentrations were present and were reasonably persistent during the summers of 1998–2000. Those small-scaled features (50–100 km width) were probably related to eddies but the exact mechanism is unknown (Stabeno et al., 2002).

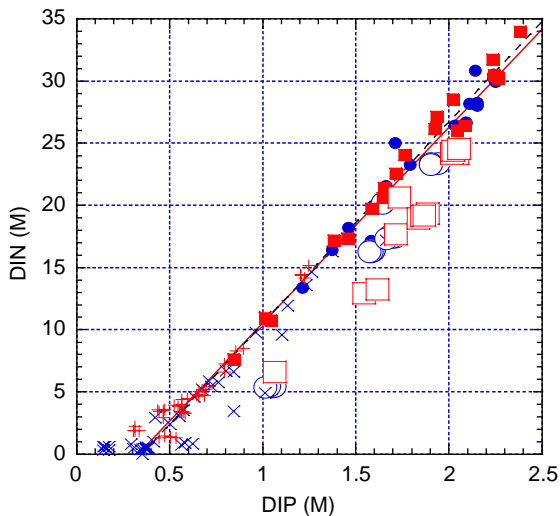


Fig. 6. Relationship between DIN and DIP. Open square (2000) and circle (2001) represent samples taken from cold water observed at the middle shelf. Solid square (2000) and circle (2001) denotes samples taken from outer shelf below mixed layer depth. Plus (2000) and cross (2001) show sample collected from upper mixed layer. Dotted and solid regression lines were obtained from nutrients data at outer shelf below the mixed layer depth in both 2000 and 2001. The relationships of DIN versus DIP are characterized by lines of slope $[\text{DIN}] = 16.22 \times [\text{DIP}] - 5.70$ in 2000 and $[\text{DIN}] = 15.74 \times [\text{DIP}] - 5.15$ in 2001, respectively, and their determination coefficients of the regression lines are $r^2 = 0.98$ in 2000 and $r^2 = 0.95$ in 2001, respectively.

3.3. DIN and DIP regeneration in the cold water mass

In order to understand the relationship between DIN (or DIP) and salinity without the effect of nutrient utilization by phytoplankton in the surface mixed layer, we plotted DIN and DIP concentrations against salinity below the upper mixed layer of the outer and middle shelves, and observed different patterns of relationship between DIN and DIP with salinity both inside and outside of the cold water mass (Figs. 7(a) and (b)). Note that the inner shelf has a well-mixed water column where nutrients were almost consumed by phytoplankton at the end of summer, although the shelf was reported to have some nutrients in the end of winter (Hansell et al., 1993). The relationships of DIN versus salinity are characterized by lines of slope $[\text{DIN}] = 24.80 \times [\text{Salinity}] - 791.12$ in 2000 and $[\text{DIN}] = 25.86 \times [\text{Salinity}] - 827.03$ in 2001, respectively, and their determination coefficients of the regression lines are $r^2 = 0.91$ in 2000 and $r^2 = 0.91$ in 2001, respectively (Figs. 7(a) and (b)). The relationships of DIP versus salinity are

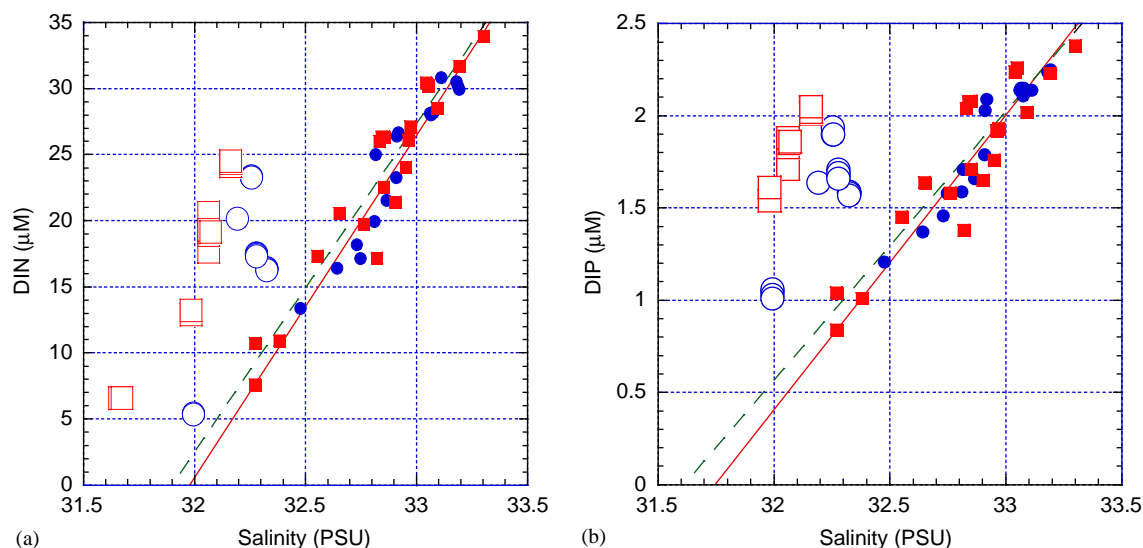


Fig. 7. (a) DIN versus salinity and (b) DIP versus salinity. Plotted data include samples collected from waters below mixed layer depth in the cold water mass (\square , 2000; \circ , 2001) and outer shelves (\blacksquare , 2000; \bullet , 2001). Dotted and solid regression lines were from samples collected below the mixed layer depth from outer shelves both in 2000 and 2001, respectively.

featured by lines of slope $[\text{DIP}] = 1.46 \times [\text{Salinity}] - 46.02$ in 2000 and $[\text{DIP}] = 1.59 \times [\text{Salinity}] - 50.68$ in 2001, respectively, and their determination coefficients of regression lines are $r^2 = 0.90$ in 2000 and $r^2 = 0.84$ in 2001, respectively (Figs. 7(a) and (b)). Interestingly, Hansell et al. (1993) also reported that the magnitude of the cross-shelf mixing in the southeastern Bering Sea during winter appears to be remarkably constant from year to year, resulting in a highly correlated and predictable end of winter relationship between nitrate concentration and salinity. They confirmed that the nitrate–salinity relationship from the southeastern Bering Sea shelf at the end of winter demonstrated the result of cross-shelf mixing through winter. On the other hand, the slope value of the relationship between DIN (or DIP) and salinity within the cold water mass was relatively high compared to that observed at the outer shelf, implying that new DIN and DIP were added to the cold water mass from winter to summer due to remineralization of organic matter in the cold water mass. The relationship between DIN and DIP observed within the summer cold water mass could be explained by the addition of DIN and DIP to the cold water mass. We could estimate amount of apparent DIN and DIP input

from the expression:

$$\begin{aligned} &\text{Amount of apparent DIN or DIP input} (\text{mmol N/m}^2) \\ &= \{ \{ [\text{DIN or DIP}]_{\text{cold water mass}} \\ &\quad - (A \times [S]_{\text{cold water mass}} - B) \} \\ &\quad \times (\text{depth of cold water mass}) \}, \end{aligned} \quad (1)$$

where $[\text{DIN or DIP}]_{\text{cold water mass}}$ is the DIN (or DIP) concentration (mmol N/m^3), $[S]_{\text{cold water mass}}$ is salinity in the cold water mass, A and B represents the slope and y -intercept of the regression line of DIN (or DIP) versus salinity, respectively (Figs. 7(a) and (b)), and the “depth of cold water mass” shows the height of the water column (m). Assuming that water column stratification started from May, when the water column typically begin to be stratified, we could calculate apparent DIN and DIP input rates by dividing Eq. (1) by 120 days (May–August). The estimated DIN and DIP input rates are 1.2–6.7 $\text{mmol N/m}^2/\text{day}$ and 0.1–0.5 $\text{mmol P/m}^2/\text{day}$, respectively (Table 1). These are averaged values from May to late summer. However, it must be stressed that the values could be in error since any exchange for nitrogen and phosphate at the bottom water–sediment interface is not considered in the estimation. The estimated values (1.2–6.7 $\text{mmol N/m}^2/\text{day}$)

Table 1
Properties of temperature, salinity, concentrations of DIN, and DIP in the cold water mass observed at middle shelf, rates of N and P input into water column and their N/P ratio, and rate of N loss from sediment

Cruise	Location (Lat., Long.)	Depth range (m)	Temperature (°C)	Salinity (psu)	DIN (μM)	DIP (μM)	N input rate ($\text{mmol}/\text{m}^2/\text{day}$)	P input rate ($\text{mmol}/\text{m}^2/\text{day}$)	N/P	Rate of N loss ($\text{mmol}/\text{m}^2/\text{day}$)
MR00k06	56.5°N, 166°W	40–86	2.90±0.31	32.14±0.45	23.51±1.64	1.97±0.13	6.7	0.4	16.5	—
MR00k06	57.0°N, 166°W	35–76	2.66±0.06	32.06±0.00	18.83±0.68	1.83±0.07	4.3	0.3	14.3	1.5
MR00k06	57.5°N, 166°W	40–66	2.67±0.03	31.98±0.00	13.03±0.20	1.58±0.05	2.4	0.2	12.1	1.5
MR00k06	58.0°N, 166°W	40–56	3.53±0.08	31.67±0.00	6.55±0.03	1.06±0.00	1.6	0.1	14.6	0.7
MR01k04	56.5°N, 166°W	41–87	3.66±0.15	32.24±0.03	22.70±1.42	1.86±0.12	6.1	0.5	12.5	0.5
MR01k04	57.0°N, 166°W	30–74	4.05±0.00	32.32±0.00	16.32±0.07	1.58±0.01	2.8	0.3	8.7	1.2
MR01k04	57.5°N, 166°W	30–65	3.63±0.01	32.28±0.00	17.45±0.08	1.68±0.02	2.8	0.3	9.4	1.1
MR01k04	58.0°N, 166°W	30–57	2.96±0.01	31.99±0.00	5.40±0.03	1.04±0.02	1.2	0.2	6.0	1.3

are higher than the values previously measured for the nitrogen regeneration rate from sediments in early summer southeast Bering Sea (Rowe and Phoel, 1992; 0.1–1.4 $\text{mmol N}/\text{m}^2/\text{day}$), which may imply that the regenerated nutrients from both the water mass and the sediments might contribute to the increase in the DIN and DIP in the cold water mass.

3.4. DIN deficiency and its controlling factors

Ratios of the apparent DIN to DIP input into the cold water mass ranged from 6 to 16.5 (Table 1), significantly lower than the N/P ratio (~ 16) of the suspended organic matter produced mainly from phytoplankton and zooplankton. This indicates that, in addition to remineralization, there exist other process(es) controlling the anomalously low N/P ratios in the cold water mass.

The magnitude of DIP released from surface sediments is determined by the redox condition in the sediment. The preferential release of phosphate from anoxic coastal marine sediments (Ingall and Jahnke, 1994) could potentially lead to a decrease in the ratio of DIN to DIP in the overlying seawater. However, when overlying water is oxic, like the case in the study area, the phosphate flux from the surface sediment to the overlying water tends to be suppressed (Klump and Martens, 1981; Boyton and Kemp, 1985; Sundby et al., 1986; Koop et al., 1990), resulting in nutrients with a higher N/P ratio released from the coastal sediments. Although previous studies on simultaneous flux measurements of DIN and DIP from oxygenated marine coastal sediments are very limited, the mean ratios of DIN and DIP regenerated in oxygenic marine sediments in off-shore waters is ~ 14 (Martens et al., 1978), close to the ratio of total nitrogen to organic phosphorus reported for sediments (~ 12) in the high latitude environment (Ruttenburg and Goni, 1997). This implies that preferential release of DIP to that of DIN from oxic sediments cannot be a significant process in lowering the N/P ratio in the oxygenated surface sediment.

The second probable cause for the anomalously low ratios of DIN to DIP in the cold water mass includes a process of the DIN loss in the cold

water. The possible process is that the DIN, mainly nitrate and nitrite, would be partially influenced by denitrification and subsequently reduced to N_2 . The apparent input ratios of DIN to DIP in the water column could be lower, as a result of denitrification processes. However, it is unlikely that denitrification takes place in the water column in our study area, since the DO level is still substantial, which prevents denitrification (Figs. 2(c) and 3(c)). However, the denitrification process is also known to occur in an anoxic layer beneath an oxic layer of the sediment. Indeed, sedimentary denitrification in the bottom sediments of the study area has been confirmed by the results of incubation with ^{15}N tracer (Koike and Hattori, 1979). Since the cold water mass could be regarded as an in situ benthic chamber on the sediments, the N/P ratio in the cold water can be strongly influenced by sedimentary biological processes. The denitrification consumes DIN in pore water in the anoxic sediment layer underneath the surface oxic layer of the sediment, resulting in a strong concentration gradient of DIN including pore water in the oxic layer of the sediment. The concentration gradient then drives flux of DIN from bottom water to the sediment by diffusion. Assuming that, under the steady state, thickness of the oxic layer (DO penetration depths) in the sediment is 1 cm (Brandes and Brandes and Devol, 1995), and the diffusion coefficient of nitrate in pore waters is $\sim 1 \times 10^{-5} \text{ cm}^2/\text{s}$ (Boudreau and Guinasso, 1982), the nitrate in the overlying water could penetrate into the oxic layer of the sediment in 28 h. It is therefore suggested that concentrations of DIN in the bottom waters of the southeastern Bering Sea would be reduced by sedimentary denitrification, leading to a decrease in the N/P ratio in the cold water mass.

The nitrogen isotopic composition of nitrate sampled below the surface mixed layer depth shows fairly constant values ranging from 3.9‰ to 5.2‰, regardless of different ratios of DIN and DIP in the bottom water of our study area. These nitrogen isotopic values are quite similar to or slightly lower than those of deeper waters reported for other parts of oceans (Wu et al., 1997, for the Eastern North Pacific; Sigman et al., 1999, for the Antarctic Ocean; Tanaka et al., unpublished for the Western North

Pacific). Although we do not find a specific relationship between concentration and isotopic composition of nitrate in the water column below the mixed layer depth, the slightly lighter isotopic composition of nitrate observed in the bottom layer might be due to new nitrate input by nitrification. Since we did not observe a DO concentration lower than $1 \mu\text{M}$ in the water column where denitrification could take place, it is less likely that the denitrification can markedly occur in the oxygenated water column. As mentioned before, an anaerobic condition could also be found in the interior of the particulate organic matters such as detritus, fecal pellets and marine snow even in the oxic water. In such anaerobic microsites, the denitrifiers are able to reduce nitrate (Aldredge and Cohen, 1987). Intensification of the occurrence of the anaerobic microsites might be one of the possibilities leading to the low N/P ratios in the cold water mass. It is known that the nitrogen isotopic fractionation factor during the denitrification process in the water column is large ($\epsilon = 25\text{--}27\%$; Brandes et al., 1998; Altabet et al., 1999; Voss et al., 2001). Since no significant enrichment of nitrogen isotopic composition of nitrate has been observed, it should be concluded that denitrification must be insignificant in the water column. Sedimentary denitrification has been reported not to alter the nitrogen isotopic composition of nitrate in the overlying water on the shelf (Brandes and Devol, 1997).

By assuming that the ratios of DIN to DIP in the cold water mass of the middle domain started to change from May, after the cold water mass was formed, an average rate of denitrification in the bottom waters of the middle shelf at each station could be estimated from the difference in the relationship between middle (cold water) and outer domain, which is not affected by sedimentary denitrification:

$$\begin{aligned} & \text{Amount of apparent N loss (mmol N/m}^2\text{)} \\ &= \{ \{ [\text{DIN}]_{\text{cold water mass}} \\ & \quad - (C \times [\text{DIP}]_{\text{cold water mass}} - D) \} \\ & \quad \times (\text{depth of cold water mass}) \}, \end{aligned} \quad (2)$$

where $[\text{DIN}]_{\text{cold water mass}}$ is the DIN concentration (mmol N/m^3) in the cold water mass, $[\text{DIP}]_{\text{cold water mass}}$ is the DIP concentration in the

cold water mass, the C and D represent slope and y -intercept of the regression line of DIN versus DIP, respectively (Fig. 6), and the “depth of cold water mass” means the height of the water column (m). Assuming that water column stratification started in May, as we obtained the apparent DIN (or DIP) input rate in the previous section, we could evaluate rate of the apparent N loss. The estimated denitrification rates, ranging from 0.7 to 1.5 mmol/m²/day (Table 1), are similar to values of previous studies for the Bering Sea and Chukchi Sea (0.49–2.88 mmol/m²/day; Devol et al., 1997), even though the denitrification rates estimated by previous studies were made by different methods (e.g. N₂ flux measurement and stoichiometric estimate). Previous methods for estimating denitrification rate, such as on board incubation and/or in situ benthic chamber experiments, depend largely on the sampling location and their sedimentary conditions (e.g. sand, silt and so on). In contrast, our estimate of the sedimentary denitrification rate is an average of the much wider area and should be more representative in terms of regional denitrification rate, compared to those derived from very limited sampling sites.

3.5. Implications

There is still a controversial issue on whether or not the nitrogen budget is balanced in present oceans (e.g., McElroy, 1983; Codispoti, 1995; Gruber and Sarmiento, 1997). Therefore, it is crucial to evaluate rates for nitrogen losses and sinks in the ocean.

However, estimates of the rates for nitrogen losses and sinks still have large very uncertainties. One of the reasons is due to the uncertainties in loss rates by sedimentary denitrification (12–100 Tg N/yr; Liu and Kaplan, 1984; Codispoti and Christensen, 1985; Devol, 1991; Christensen, 1994; Middelburg et al., 1996). In the Bering Sea shelf, the sedimentary denitrification is believed to occur in, at least, half of the shelf (Koike and Hattori, 1979), where the sediments consist of fine sand or silt (Sharma, 1974). It is also reported there is no difference in rate of sedimentary denitrification between summer and winter on the shelf of the Chukchi Sea, north of the Bering

Sea shelf (Devol et al., 1997). Since half of the Bering Sea shelf area is 4.5×10^5 km² an average annual rate of denitrification in the Bering Sea shelf could be computed to be 2.5 Tg N/yr from our daily mean estimate of N loss rate (1.1 mmol/m²/day). This value corresponds to roughly one third of the annual net supply of the nitrate onto the Bering Sea shelf estimated as the difference between physical supply and biological utilization of nitrate (Hattori and Wada, 1974). Our results clearly show that sedimentary denitrification in the Bering Sea shelf is significant in terms of the nitrogen budget in this region. With respect to the sedimentary denitrification, the annual loss of DIN in this area is equal to 2.5% of the annual DIN loss in the oceanic shelf sediments (100 Tg N/yr; Middelburg et al., 1996) as a lower limit, while the Bering Sea shelf represents ~3% of the total area of world continental shelves. The Arctic Shelf region, including the Bering Sea shelf occupies ~25% of global continental shelves. If the sedimentary denitrification rate in the Bering Sea shelf is typical for the high latitude regions, considering the magnitude of oceanic sedimentary denitrification (12–100 Tg N/yr; Liu and Kaplan, 1984; Codispoti and Christensen, 1985; Devol, 1991; Christensen, 1994; Middelburg et al., 1996), the shelves in the high latitude region could lose DIN by ~20 Tg N/yr through the denitrification and it, indeed, would play an important role in regulating the nitrogen budget in the present oceans.

4. Conclusions

Anomalously low ratios of DIN to DIP were found over the continental shelf of the southeastern Bering Sea during late summer. It was mainly observed in a cold-water mass, which resided in the bottom of the middle shelf. The N/P ratio change was largely caused by denitrification in the anoxic layer of sediments. At the low limit, the average rate of sedimentary denitrification is estimated to be 1.1 mmol/m²/day. Based on the daily rate of the sedimentary denitrification, the annual denitrification rate in the Bering Sea shelf is calculated to be 2.5 Tg N/yr, corresponding

to 2.5% of annual global denitrification rate in oceanic sediments.

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