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Deep Nitrate Deficit Observed in the Highly Oxygenated East/Japan Sea and Its Possible Cause

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ABSTRACT

We present evidence of denitrification on the continental slopes of the Ulleung Basin (UB) and the Eastern Japan Basin (EJB) near the Tatar Strait (TtS) in the East/Japan Sea (EJS), despite its high water column dissolved oxygen concentrations. Some nutrient concentration data deviate significantly from the fitted regression line of nitrate (N) vs. phosphate (P) in deep waters, indicating a loss of nitrate in the region. The EJS has a lower N/P ratio (ca. 12.4 below 300 dbar) than a traditional Redfield ratio (16). The N/P ratio and oxygen concentration are substantially lower at several locations whose depths are close to the sediment-water interface, near TtS (500 - 1100 dbar) and in UB (1100 - 2200 dbar). The decreased nitrate concentration is smaller than the expected nitrate level (a low N/P ratio of < 12.4), and a secondary nitrite peak near the bottom of these two regions: taken collectively, both indicate the presence of denitrification in the bottom layer. It is speculated that active re-mineralization and denitrification may occur simultaneously along the rich organic matter bottom layer on the slope environment. Denitrification rates are estimated at ~3 - 33 μmol N m^{-2} d^{-1}. Current estimates do not support the previous idea of basin-wide denitrification in EJS, although the N/P ratio is low like in other hypoxic/anoxic seas. A better understanding of the denitrification process is necessary for predicting future changes of nitrogen cycle in the well-oxygenated EJS considering the decadal-scale physical and biogeochemical changes that have occurred.

Key words: Denitrification, N/P ratio, Nitrogen cycle, East/Japan Sea, Ulleung Basin, Tatar Strait

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1. INTRODUCTION

Denitrification is a microbiologically mediated process that reduces nitrate to nitrite and to nitrous oxide and results in the formation of dinitrogen ($NO_3^- \rightarrow NO_2^- \rightarrow N_2O/N_2$) to decompose organic matters in the absence of oxygen. Denitrification occurs under low oxygen conditions in the environment because nitrate is used as an electron acceptor instead of oxygen (Hulth et al. 2005; Brandes et al. 2007; Naqvi et al. 2010). Denitrification removes nitrate from the water deviating the nitrate to phosphate (N/P) ratio to below the traditional Redfield ratio of 16 (Hupe and Karstensen 2000). The East/Japan Sea (EJS) is a marginal sea, with a maximum depth close to 4000 m, adjacent to the western North Pacific Ocean (Chang et al. 2004). The EJS exhibits many open ocean-like features including deep-water formation processes (Talley et al. 2006). Denitrification has not been considered to be a significant process sufficient to affect the nitrogen cycle in the EJS because the sea is well oxygenated throughout the water column (> 190 μmol kg^{-1} at minimum).

The global average N/P ratio of the ocean water column (14.5) lies below the traditional Redfield ratio (16), indicating a potential large-scale nitrogen removal via the denitrification process (Deutsch and Webber 2012). The EJS also shows a low N/P ratio (9.8 to 14.7) compared to the traditional Redfield ratio (Table 1), but its driving mechanism is not yet clearly understood. However, recent studies suggest the possibility of denitrification in the EJS. Deep nitrite readings were observed near the bottom in the deep basins of EJS (Talley et al. 2001; Lee et al. 2007). The basin-wide

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Table 1. Summary of the N/P ratio estimated in the EJS.

N/P ratio			
Ref.	**Whole (W/EJB + UB + YB)**	**UB**	**Season**
Kido and Nishimura (1973)	13.6 (≥ 0m)		summer
Shim et al. (1989)		12.5 (≤ 100 m)	spring
Chung et al. (1989)		13.4 (≤ 150 m)	fall
Yang et al. (1991)		12.1 (≤ 500 m)	fall
		9.8 (≤ 500 m)	winter
Moon et al. (1996)		14.4 (≤ 1000 m)	fall
Chen et al. (1996)	14.7 (300 - 600 m)		summer
	13.0 (≥ 2000 m)		
Yanagi (2002)	11.4 (≥ 0 m)		annual
*** This study**	**12.4 (≥ 300 dbar)**		**summer**

Note:
**1999 observation data.*
W/EJB: Western/Eastern Japan Basin, UB: Ulleung Basin, YB: Yamato Basin.

denitrification rates were estimated at 1.5×10^{10} g N d^{-1} from nitrogen mass balance (Yanagi 2002) and at 0.93×10^{10} g N d^{-1} from organic matter mass balance (Tishchenko et al. 2007). Measured denitrification rates from sediments are 14.1 - 75.3 μmol N m^{-2} d^{-1} at the Dok Island shelf in the Ulleung Basin (Jeong et al. 2009). Cyanobacteria, which are capable of nitrogen fixation in the marine system, cover 10 - 50% of the phytoplankton community in the surface layer of EJS (Kim et al. 2010c). Their presence may reflect a compensation of nitrogen loss from denitrification by the new supply of fixed nitrogen.

Most of these studies mention denitrification in the EJS in passing with no detailed information (Yanagi 2002; Kim et al. 2010c), or sedimentary denitrification (Talley et al. 2001; Lee et al. 2007; Tishchenko et al. 2007; Jeong et al. 2009). In general, sedimentary denitrification occurs if oxygen is depleted in the sediments, even if water column oxygen concentrations near the sediment-water interface are high. Previous estimates of denitrification rates were derived for the entire water column of the EJS (Yanagi 2002; Tishchenko et al. 2007), except for one study of denitrification rates from sediment (Jeong et al. 2009).

Denitrification is generally classified as a water column and benthic denitrification, depending on the source of nitrate. Water column denitrification is driven by the nitrate which is re-mineralized in the water column; and, benthic denitrification is driven by nitrate both from the sediments and the overlying waters. These reactions typically occur under very low oxygen conditions where nitrate becomes the next available electron acceptor for the process. We found deep secondary nitrite peaks in the EJS (Fig. 1), but it is uncertain whether the signals come from bottom water or sediment. We therefore hypothesize that denitrification is occurring within a thick bottom water layer including the sediment surface at certain local areas, such as the Ulleung Basin (UB) and near the Tatar Strait (TtS), instead of the entire EJS. Our questions are, "What evidence supports the denitrification process in the bottom layer?" and "What mechanisms may drive the process?"

The primary goals of this study are to (1) present evidence confirming a denitrification process in the UB and the TtS regions through qualitative and quantitative data analyses, (2) estimate denitrification rates from a nitrate profile analysis using the relationship of the Redfield ratios, and (3) speculate about possible mechanisms which generate this denitrification pattern.

2. DATA

Basin-wide hydrographic observations were made in the summer of 1999 by two expeditions, covering the entire EJS except for the North Korean territorial waters (Fig. 2). The expeditions were conducted via the Circulation Research of East Asian Marginal Seas II (CREAMS II) program as a collaborative research effort among the United States, Russia, and South Korea. More specific cruise information is available in Talley et al. (2004), and the data used for the current analysis were obtained from http://sam.ucsd.edu/onr_data/hydrography.html. Here, we used dissolved oxygen (DO), nitrite, nitrate (N), phosphate (P), and bottom depth for our analysis. Only the data below 300 dbar were analyzed to minimize any influence of seasonal variation. The nutrient data were measured by SIO-ODF (Scripps Institution Oceanography-Oceanographic Data Facility), and the accuracy was within 2% (Talley et al. 2004). The bottom depths at individual stations were obtained from information from the CTD (Conductivity, Temperature, and Depth) casting depth and its height above the bottom (i.e., water-sediment interface). The deep EJS is divided into the Japan Basin (JB), the Ulleung Basin (UB), and the Yamato Basin (YB). We analyzed the Western Japan Basin (WJB) and the Eastern Japan Basin (EJB) separately for the JB with a boundary along 135°E for more convenient presentation (Fig. 2).

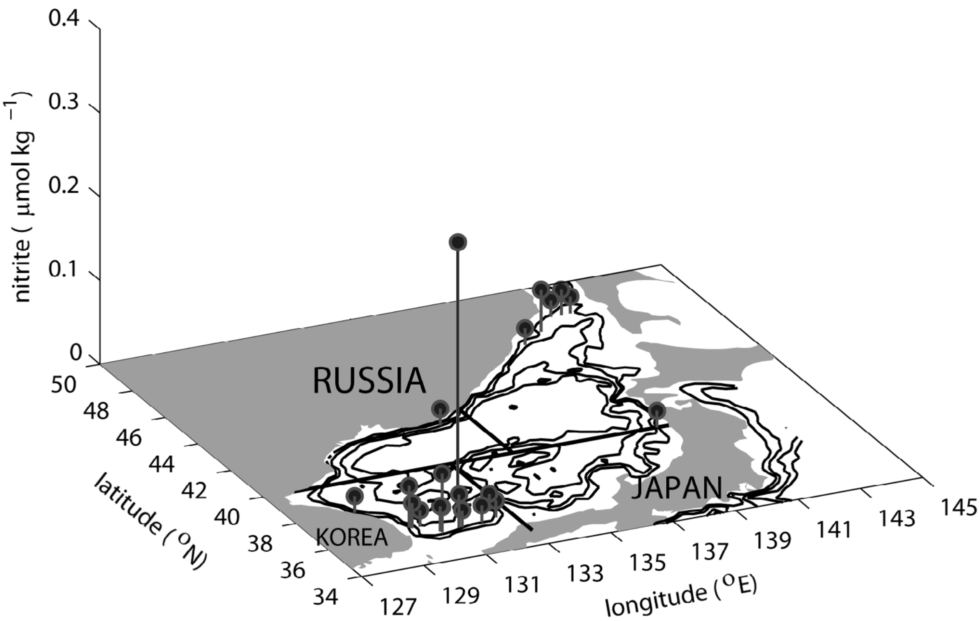

Fig. 1. The distribution of deep nitrite signals (> 0.01 μmol kg^{-1}) found below 300 dbar depths from the CREAMS II observation in the EJS (summer 1999).

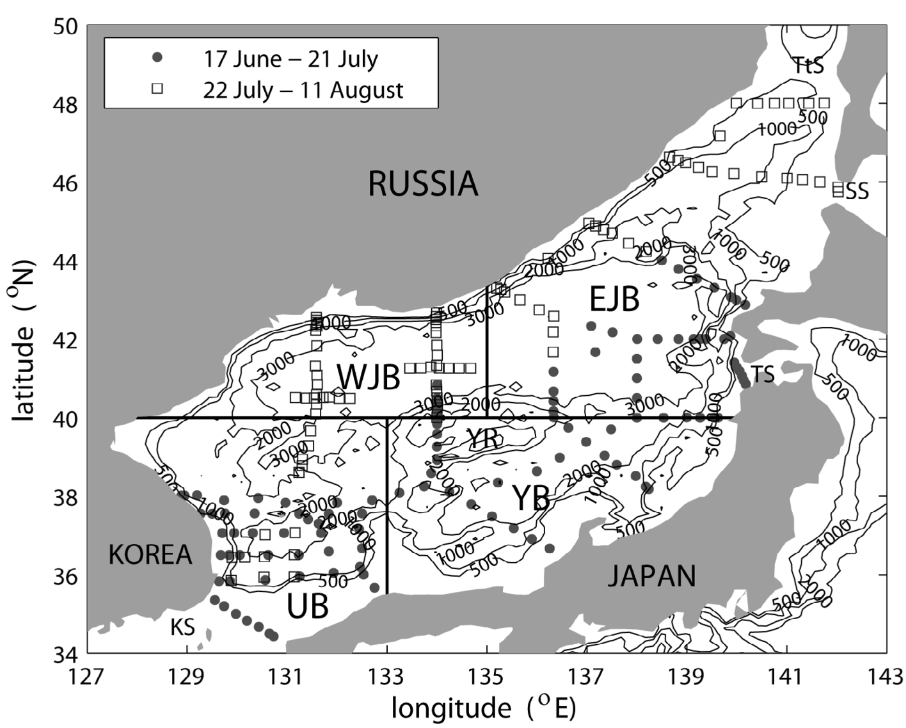

Fig. 2. The hydrographic station map of CREAMS II observation (summer 1999) with topography of the East/Japan Sea (EJS). The EJS has three main basins: JB (Japan basin), YB (Yamato Basin), and UB (Ulleung Basin). It has one rise: YR (Yamato Rise), and four straits: KR (Korea Strait), TS (Tsugaru Strait), ST (Soya Strait), and TtS (Tatar Strait). The JB is divided to the Western Japan Basin (WJB) and the Eastern Japan Basin (EJB) at 135°E for data analysis.

3. RESULTS AND DISCUSSION

3.1 The N/P Ratio of EJS

The N/P ratio of EJS based on the 1999 data was estimated at 12.4 ± 0.1 (Fig. 3a), which is lower than the traditional Redfield ratio of 16. This result may indicate a large-scale denitrification in the sea; however, no direct evidence is available at this time to support that conclusion. Some nutrient data deviate from the fitted regression line at a higher concentration range (Fig. 3b), and this indicates that the nitrate is being depleted by denitrification at certain conditions in the EJS.

The low DO feature is well developed in the EJB near the TtS between the 500 and 1100 dbar depth, and in UB between 1100 and 2200 dbar depth, both near the bottom (Fig. 4a). Nitrite (NO_2^-) is an intermediate nitrogen product

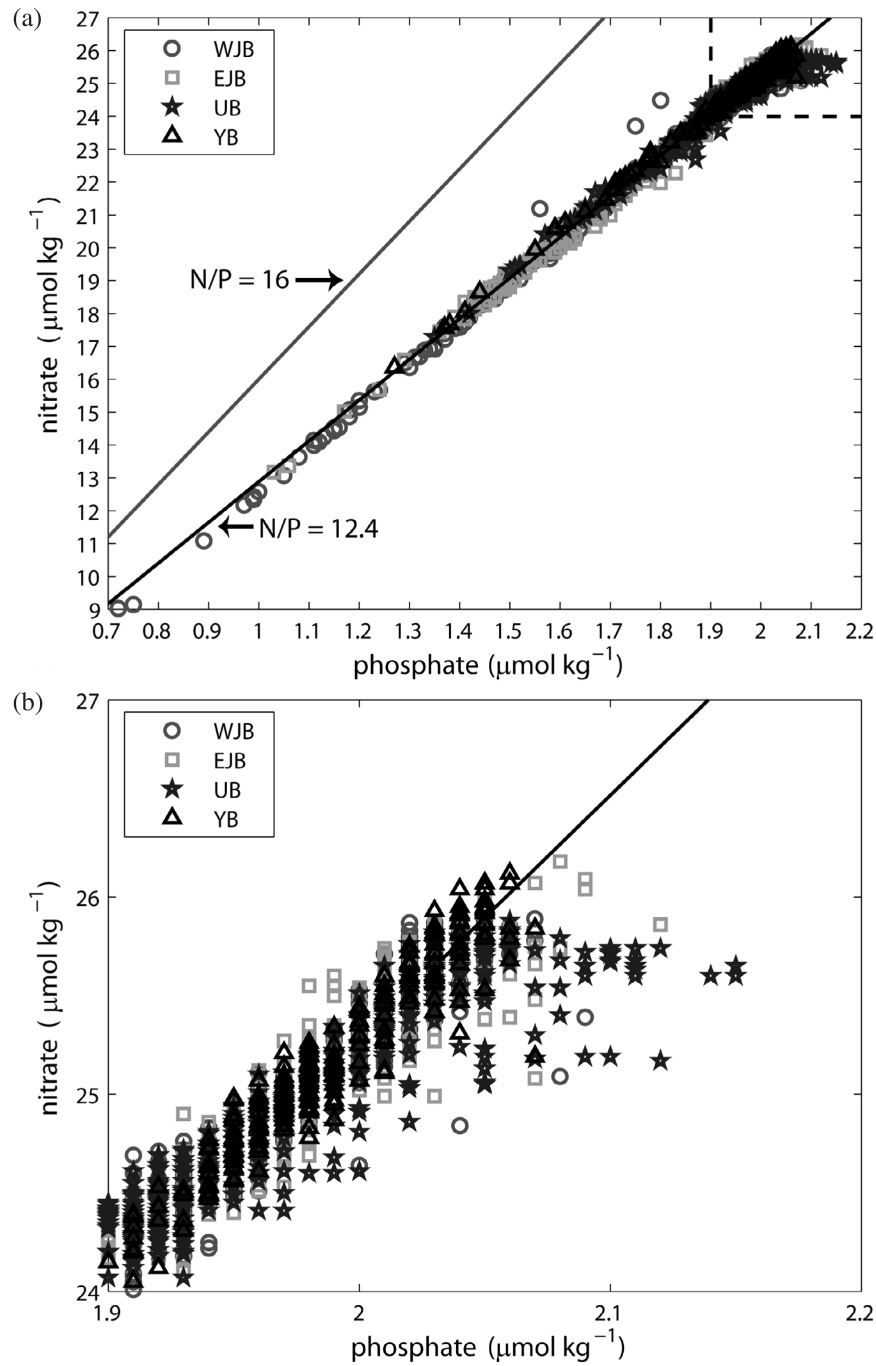

Fig. 3. The N/P ratio of EJS below 300 dbar depths observed during the CREAMS II (summer 1999). (a) The N/P slope estimated by a least square method for the observed data vs. the traditional Redfield ratio line with a slope of 16, and (b) A magnified view of Fig. 3a for the dotted line area for higher nutrient concentration ranges.

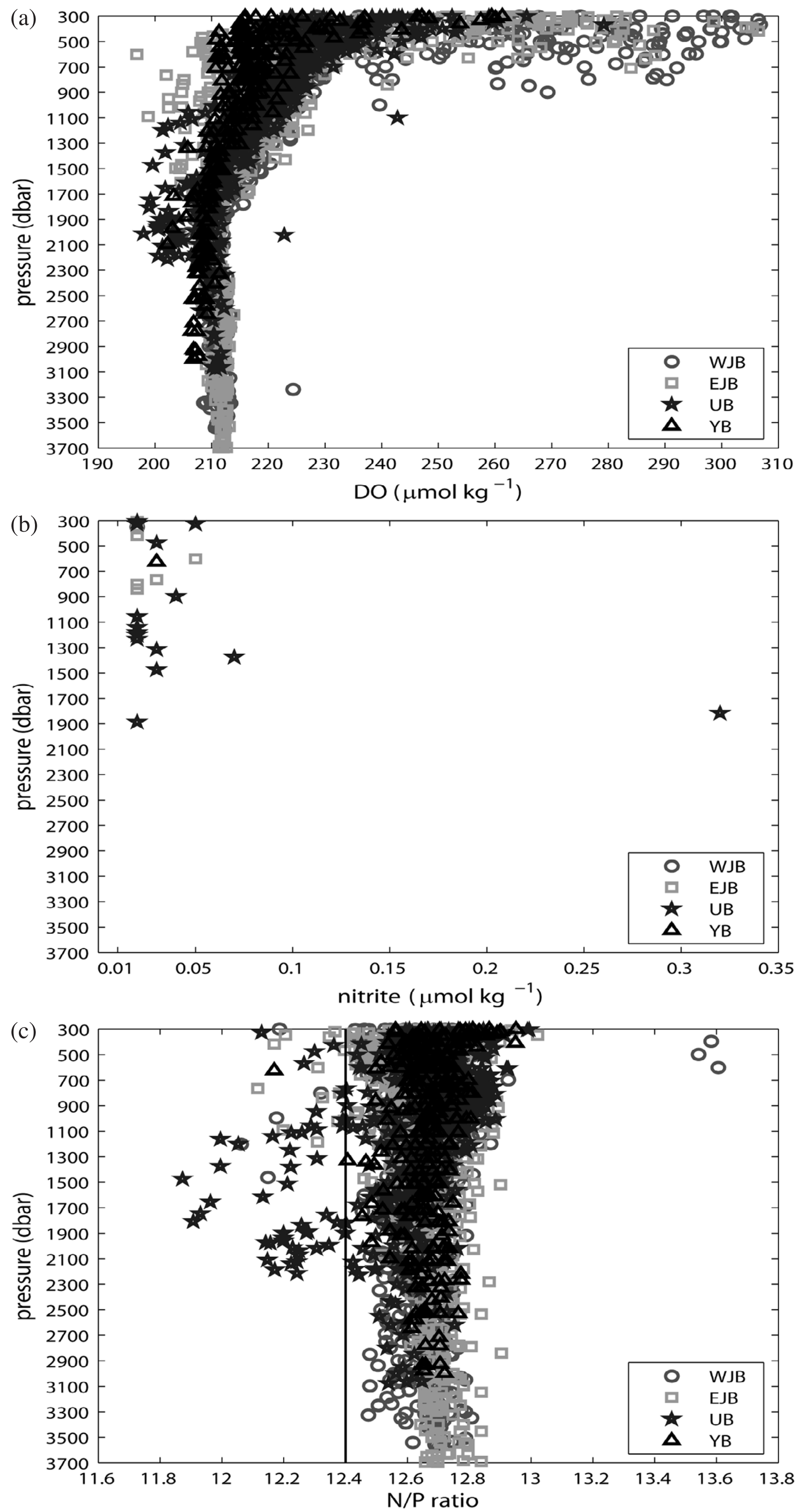

Fig. 4. The vertical distributions of dissolved oxygen, nitrite, and N/P ratio in the EJS observed from the CREAMS II (1999). (a) Dissolved oxygen (μmol kg^{-1}), (b) nitrite (μmol kg^{-1}), and (c) individual N/P ratio. Individual N/P ratio is computed by nitrate concentration, $[NO_3^-]$, divided by phosphate concentration, $[PO_4^{3-}]$, at each data point (i). Different symbols represent individual basins: WJB (circle), EJB (square), UB (star), and YB (triangle). The vertical line in (c) indicates the observed mean N/P ratio (= 12.4).

by nitrification ($NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$), denitrification ($NO_3^- \rightarrow NO_2^- \rightarrow N_2O/N_2$), or dissimilatory nitrate reduction to ammonium (DNRA; $NO_3^- \rightarrow NO_2^- \rightarrow NH_4^+$) and is a useful indicator to distinguish oxidative vs. reductive pathways in the nitrogen cycle (Lomas and Lipschultz 2006). Generally, a primary nitrite peak is produced by nitrification in the shallow euphotic layer, and nitrite below this depth may accumulate by either denitrification or DNRA (Kelso et al. 1997). DNRA occurs primarily in estuarine and coastal sediments in an anaerobic condition (Kaspar 1983; Binnerup et al. 1992; Brandes et al. 2007), and its end product, NH_4^+, is eventually converted to nitrate via nitrification ($NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$). This process, in the long run, conserves nitrogen sources (Burgin and Hamilton 2007); its quantitative significance in deep waters is unknown (Zehr and Kudela 2011). Most of the nitrite concentrations higher than 0.01 μmol kg^{-1} were detected in adjacent areas in the two basins (Fig. 4b). Therefore, nitrite accumulation in the bottom waters of EJS is likely derived from denitrification. A N/P ratio minimum may develop significantly at a low oxygen content layer as a result of nitrate loss (Fig. 4c). Collectively, the features shown in Fig. 4 support the presence of denitrification in the bottom waters of EJS.

3.2 Detailed Analysis of Vertical Property Distribution

The re-mineralization process increases nitrate concentration with depth in the water column as sinking organic matter is decomposed with consumption of DO. Conversely, denitrification decreases nitrate concentration and produces nitrite. We selected two stations (10 and 121) in UB and one station (129) in the EJB near the TtS as representative examples representing the most clear denitrification signals among the stations ($[NO_2^-] > 0.01$ μmol kg^{-1}) (Fig. 1). The vertical profiles of DO, nitrate, phosphate, nitrite, and N/P ratio data at these stations (10, 121, and 129) were analyzed. The profiles at both areas show decreases of DO and nitrate, and an increase of phosphate, lower N/P ratio, and detectable nitrite, simultaneously, suggesting denitrification.

Stations 10 and 121 are located in the mid to lower part of the continental slope of the UB, respectively (Fig. 5a). The DO decreases sharply toward the bottom depth at Stations 10 (1380 dbar) and 121 (1894 dbar) over a few hundred meters of depth (Figs. 5c and e). The phosphate concentration increases toward the bottom, while nitrate concentration decreases slightly near the bottom (Figs. 5d and f). A deep nitrite peak (Figs. 5c and e) and local N/P ratio lower than the basin average (Fig. 5b) are apparent at the bottom layer. Station 129 is located on the upper part of the continental slope in the EJB near the TtS with a relatively shallow bottom depth (609 dbar) (Fig. 5a). The profiles at Station 129 show similar patterns to those of Stations 10 and 121 (Figs. 5b, g, and h).

3.3 Estimation of Denitrification Rates

The N^* (= N - 16P + 2.9 μmol kg^{-1}) method can estimate large-scale denitrification using hydrographic data (Gruber and Sarmiento 1997; Deutsch et al. 2001). If the N^* method is applied in the EJS, the entire water column below 300 dbar shows negative N^* values indicating prevailing denitrification in the EJS. Considering a well-oxygenated water column ($O_2 > 190$ μmol kg^{-1}) of the EJS and evidence addressed in sections 3.1 and 3.2, the N^* method may overestimate denitrification in the EJS. Thus, we adopted an alternative way to estimate the amount of denitrification. The observed nitrate concentrations are a sum of the preformed nitrate and the remineralized nitrate [Eq. (1)]. The preformed nitrate (~11 μmol kg^{-1}) in the cold surface water in the northern EJS is transported into the interior of the EJS along with its deep water formation (Kim et al. 1992). The bottom water layer may have a nitrate sink due to denitrification (Fig. 6). The observed nitrate then can be expressed as:

$$[NO_3]^{z-1}_{obs} = [NO_3]^{z-1}_{pre} + [NO_3]^{z-1}_{remi} \quad (1)$$

and

$$[NO_3]^{z}_{obs} = [NO_3]^{z}_{pre} + [NO_3]^{z}_{remi} - [NO_3]^{z}_{deni} \quad (2)$$

where, the superscripts z-1 and z are the upper and lower boundary depths of denitrification, and the subscripts obs, pre, remi, and deni are for the observed, preformed, remineralized, and denitrified nitrate concentrations, respectively. The depth pairs for z-1 and z for Stations 10, 121, and 129 are 1314 and 1375 dbar, 1784 and 1886 dbar, and 508 and 602 dbar, respectively. If we assume that the preformed nitrate concentrations are the same at the two depths (i.e., $[NO_3]^{z-1}_{pre} = [NO_3]^{z}_{pre}$), the amount of denitrification can be estimated by Eq. (2) - Eq. (1):

$$[NO_3]^{z}_{deni} = (\,[NO_3]^{z-1}_{obs} - [NO_3]^{z}_{obs}\,) + (\,[NO_3]^{z}_{remi} - [NO_3]^{z-1}_{remi}\,) \quad (3)$$

The remineralized nitrate can be substituted by the oxygen consumption or phosphate production as follows:

$$[NO_3]^{z}_{deni} = ([NO_3]^{z-1}_{obs} - [NO_3]^{z}_{obs}) + r_{N/-O2} \times ([AOU]^{z}_{f(PT,S)} - [AOU]^{z-1}_{f(PT,S)}) \quad (4)$$

or

$$[NO_3]^{z}_{deni} = ([NO_3]^{z-1}_{obs} - [NO_3]^{z}_{obs}) + r_{N/P} \times ([PO_4]^{z}_{obs} - [PO_4]^{z-1}_{obs}) \quad (5)$$

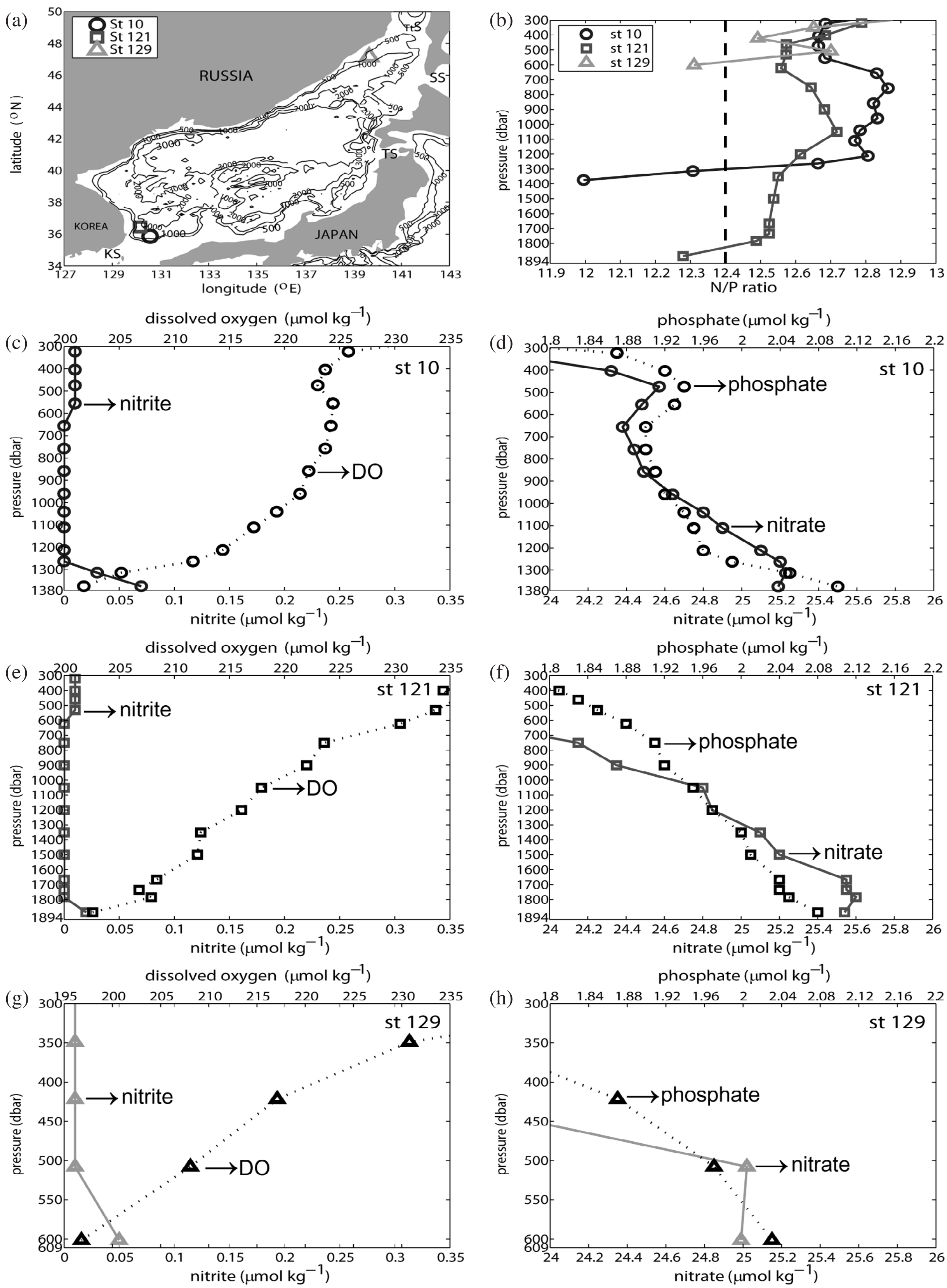

Fig. 5. Vertical profiles of nitrate, phosphate, dissolved oxygen, nitrite, and N/P ratio at two stations (10 and 121) in the UB and one station (129) in the EJB near the TtS. (a) Locations of the three stations in the study area map, (b) vertical profiles of N/P ratio at Stas. 10, 121, and 129 (the dotted line represents the mean N/P ratio of 12.4 of the EJS), (c) - (d) vertical profiles of nitrate (μmol kg^{-1}), phosphate (μmol kg^{-1}), nitrite (μmol kg^{-1}), and dissolved oxygen (μmol kg^{-1}) at Sta. 10, (e) - (f) same property profiles at Sta. 121 as (c) - (d), and (g) - (h) same property profiles at Sta. 129 as (c) - (d).

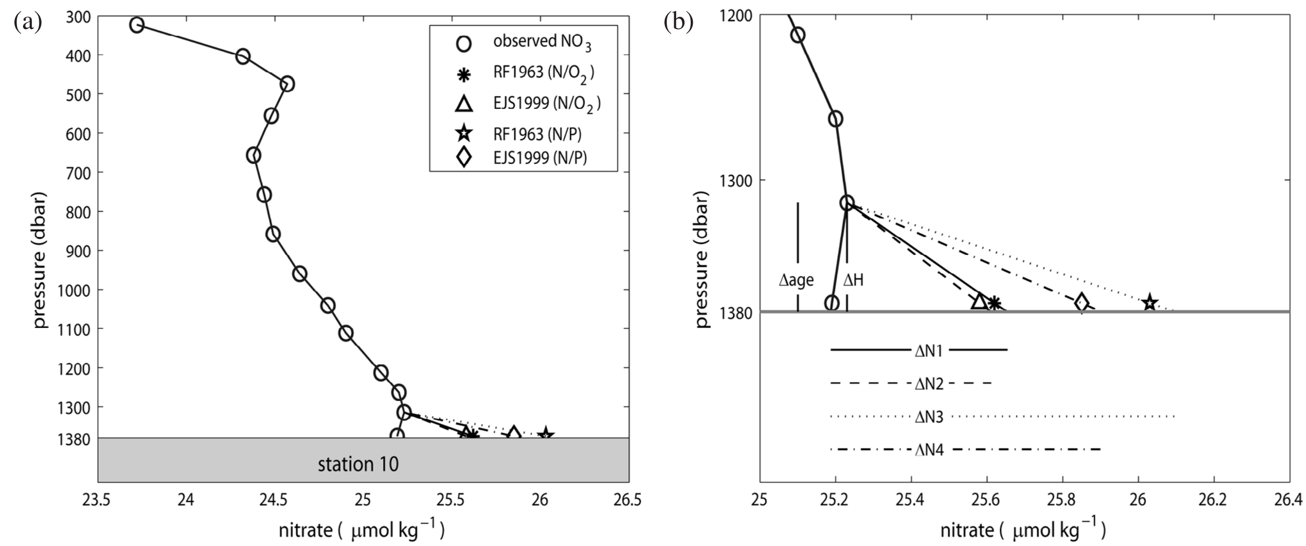

Fig. 6. Vertical profiles of the observed and expected nitrate for the bottom boundary layer at Sta. 10. (a) below 300 dbar, and (b) magnified version of the (a). Circle symbol represents observed nitrate. Asterisk, triangle, star, and diamond symbols represent expected nitrate from $\Delta N/-\Delta O_2 = 16/138$, $\Delta N/-\Delta O_2 = 12.4/118$, $\Delta N/\Delta P = 16/1$, and $\Delta N/\Delta P = 12.4/1$, respectively. ΔN is the different between the expected and observed nitrate concentrations at the sediment surface, ΔH is the height between the upper and lower boundary of the triangular area, and Δage is the estimated relative age difference between the upper and lower boundary of the triangular area. Same approaches were applied to Stas. 121 and 129 to estimate denitrification rates.

where, $[AOU]_{f(PT,\,S)}$ is the apparent oxygen utilization (AOU), which is the difference between the observed DO and the saturated DO calculated as a function of potential temperature (PT) and salinity (S). The surface water oxygen concentration was assumed to be in equilibrium with the atmosphere. Both the observed (12.4/118 and 12.4/1) and traditional (16/138 and 16/1) Redfield ratios for $r_{N/-O2}$ and $r_{N/P}$ were used in the analysis.

The estimated denitrification was ca. 0.4 - 0.9 μmol kg^{-1} at 1375 dbar at Station 10, 0.4 - 0.6 μmol kg^{-1} at 1886 dbar at Station 121, and 0.8 - 1.5 μmol kg^{-1} at 602 dbar at Station 129, respectively (Fig. 6a and Table 2). Station 129 located in the EJS near the TtS showed a slightly higher amount of denitrification.

As shown in Fig. 6b, denitrification rates can be estimated from the triangular area (= 1/2 · ΔN · ΔH), where ΔN is the difference between the observed and expected nitrate concentrations at z, and ΔH is the difference of relative age between the upper (z-1) and lower boundaries (z) of the triangular area. The expected ($= [NO_3]^z_{obs} + [NO_3]^z_{deni}$) and observed nitrate concentrations are extrapolated linearly to the bottom depth (Fig. 6b). The relative age, defined by AOU (μmol kg^{-1}) divided by oxygen utilization rate (OUR; μmol kg^{-1} yr^{-1}), is a way to obtain the information on the time scale of accumulating denitrification readings taken from the bottom layer (Poole and Tomczak 1999; Karstensen et al. 2008; Kim et al. 2010a). It is assumed that the relative age increases with depth and the horizontal advection is small within these two regions. The OUR as a function of depth (z) in the basins can be parameterized as $OUR(z) = 6.592e^{-0.0011\cdot z}$ at UB and $10.680e^{-0.00138\cdot z}$ at EJB (Kim et al. 2010b). When the UB's OUR values (Stations 10 and 121) are transformed into oxygen consumption rates in the bottom layer (i.e., $0.85 - 1.60\,\frac{\mu mol}{kg \cdot yr} \times \rho\left(\frac{kg}{m^3}\right) \times \Delta H(m) = 0.26 - 0.30\,\frac{mmol}{m^2 \cdot d}$), they are compatible with previous values (Kang et al. 2010): 0.24 - 0.30 mmol O_2 m^{-2} d^{-1} with ΔH = 80 - 100 m at the UB. The denitrification rate is then estimated as:

$$deni \cdot rate = \frac{1}{2} \times \Delta N\left(\frac{\mu mol\ N}{kg}\right) \times \rho\left(\frac{kg}{m^3}\right) \times \Delta H(m)/\Delta age(yr) \qquad (6)$$

where, ρ is seawater density. The estimated denitrification rates and the components (i.e., ΔN, ΔH, and Δage) are summarized in Table 2. The estimated denitrification rates near the bottom are approximately 17.5 - 33.2 μmol N m^{-2} d^{-1} at Station 129 on the upper part of the continental slope, 4.2 - 9.1 μmol N m^{-2} d^{-1} at Station 10 on the mid part of the continental slope, and 2.8 - 4.4 μmol N m^{-2} d^{-1} at Station 121 on the lower part of the continental slope (Table 2) which implies that there might be a spatial gradient of denitrification rates along the continental slope. More samples along the continental slope need to be examined in future studies.

Recently, Lee et al. (2010) computed the fraction of carbon input rates, regenerated rates, and burial rates to the primary production (~234 g C m^{-2} yr^{-1}) in the UB sediments as ~4.1% (~9.6 g C m^{-2} yr^{-1}), ~3.0% (~7.0 g C m^{-2} yr^{-1}), and ~1.1% (~2.5 g C m^{-2} yr^{-1}). With a traditional Redfield ratio

Table 2. Estimated denitrification rates in the UB (Stas. 10 and 121) and EJB (Sta. 129) of the EJS. Both the observed (N/O_2 = 12.4/118 and N/P = 12.4/1) and traditional (16/138 and 16/1) Redfield ratios are used for computation of the expected nitrate concentrations.

St. (Basin)	+Obs. NO_3 (μmol kg^{-1})	Exp. NO_3 (μmol kg^{-1})	ΔN (μmol m^{-3})	ΔH (m)	Δage (yr)	Deni. rates (μmol N $m^{-2} \cdot d^{-1}$)	Cont. Slope
129 (EJB)	24.98	26.6 ($R_{N/O_2=16/138}$)	1662	100	7	33.2	Upper
		26.4 ($R_{N/O_2=12.4/118}$)	1465			29.9	
		26.1 ($R_{N/P=16/1}$)	1099			22.4	
		25.8 ($R_{N/P=12.4/1}$)	859			17.5	
10 (UB)	25.18	25.7 ($R_{N/O_2=16/138}$)	483	65	9	4.7	Middle
		25.6 ($R_{N/O_2=12.4/118}$)	438			4.2	
		26.1 ($R_{N/P=16/1}$)	944			9.1	
		25.9 ($R_{N/P=12.4/1}$)	742			7.2	
121 (UB)	25.54	26.3 ($R_{N/O_2=16/138}$)	760	108	26	4.4	Lower
		26.2 ($R_{N/O_2=12.4/118}$)	690			4.0	
		26.1 ($R_{N/P=16/1}$)	606			3.5	
		26.0 ($R_{N/P=12.4/1}$)	485			2.8	

Note:
+Obs. NO_3 is the observed NO_3 linearly extrapolated to the bottom sediment-water interface depth.
ΔN = (Exp. NO_3 - Obs. NO_3) (μmol kg^{-1}) × ρ(kg m^{-3}).
ΔH is the height between the upper and lower boundary of the triangular area shown in Fig. 6.
Δage is the estimated age difference between the upper and lower boundary of the triangular area shown in Fig. 6.

(C/N = 106/16) and organic carbon cycle information provided by Lee et al. (2010), nitrogen input rates, regenerated rates, and burial rates are estimated to be ~1.7, ~1.2, and ~0.5 g N m^{-2} yr^{-1}. Denitrification rates estimated from this study are ~3 - 33 μmol N m^{-2} d^{-1} (= ~0.02 - 0.17 g N m^{-2} yr^{-1}). These estimates (~0.02 - 0.17 g N m^{-2} yr^{-1}) are much lower than the nitrogen burial rates (~0.5 g N m^{-2} yr^{-1}) which implies that at present denitrification is not major mechanism driving low N/P ratio in the EJS.

3.4 Validation of the Estimated Denitrification Rates

The denitrification rates estimated previously (Yanagi 2002; Tishchenko et al. 2007), 1.5×10^{10} and 0.9×10^{10} g N d^{-1}, respectively, are rather large. These values are compared to the estimates of this study through a simple rate transformation. The transformed value for Yanagi (2002), for example, would be:

$$\text{deni} \cdot \text{rate}_{(\text{Yanagi, 2002})} = 1.5 \times 10^{10} \frac{\text{g N}}{\text{d}} \times \frac{1 \text{ mol}}{14 \text{ g}} \Big/ \text{A}$$
$$= 1071.4 \,\mu\text{mol N m}^{-2}\,\text{d}^{-1} \quad (7)$$

where, A (= 1.008×10^{12} m^2) is the surface area of the EJS. The transformed denitrification rates by Tishchenko et al. (2007) would be 661 μmol N m^{-2} d^{-1}. These values are 2 to 3 orders of magnitude larger than the values estimated from this study (~3 - 33 μmol N m^{-2} d^{-1}). The denitrification rates at the hypoxic/anoxic seas, such as the Arabian Sea, the Black Sea, and the northern Gulf of Mexico, where denitrification rates are far greater, are 400 - 3780, 48 - 560, and 504 - 1056 μmol N m^{-2} d^{-1}, respectively (Gardner et al. 1993; McCarthy et al. 2007; Schwartz et al. 2009). The basin-wide estimates by Yanagi (2002) and Tishchenko et al. (2007) are similar to the values from the hypoxic/anoxic seas, even though the EJS is oxygenated throughout the water column. Perhaps, the previous estimates are overestimated since the results (~3 - 33 μmol N m^{-2} d^{-1}) are more comparable to the denitrification rates measured directly from sediments at the shelf of Dok Island in the UB (14.1 - 75.3 μmol N m^{-2} d^{-1}) (Jeong et al. 2009).

3.5 Extended Benthic Denitrification to Bottom Waters vs. 'Aerobic Denitrification'

Our results support the idea that denitrification occurs at certain areas in the UB and EJB near the TtS. However, the high oxygen content of the water column (> 190 μmol kg^{-1}) in the EJS for a conventional denitrification process to occur warrants caution in drawing a simple conclusion. We speculate two potential scenarios: (1) An upward extension of denitrifying bacterial activity in the sediments to the bottom waters at 'micro-reducing environments' caused by high deposition rates of organic matter that might be accompanied with recent trends of warming and decrease in

DO in the bottom layer, and (2) an 'aerobic denitrification,' which utilizes both DO and nitrate in the deep water column of the EJS, although this process has not yet been verified in an ocean system.

The UB is the most productive region in the EJS due to a coupling of coastal upwelling and active eddy feature (Lee and Kim 2003; Hyun et al. 2009). The region near the TtS is also a high primary production area due to the input of the Amur River (Tishchenko et al. 2007). Both regions are famous fishing grounds. These two regions thus would demand high oxygen consumption at the bottom due to high rates of supply and deposition of organic matter (Tishchenko et al. 2007; Lee et al. 2008). Organic carbon flux observed by a sediment trap at 1020 m was ~9 g C m^{-2} yr^{-1} is comparable to that of a Chilean upwelling region where organic carbon accumulation rates were ~3 g C m^{-2} yr^{-1} and is unusually high for deep sediments (Lee et al. 2008). In addition, accumulating sedimentary organic carbon contents reach up to ~4% (Cha et al. 2007; Lee et al. 2010). As inferred from extremely high organic matter inputs to the bottom layer, a 'micro reducing environment' may be formed in the bottom layer (Wolgast et al. 1998), enabling an upward extension of denitrifying bacterial activity from the sediments to the bottom waters above. Recent increases in atmospheric nitrogen deposition flux to the EJS (Kim et al. 2011), warming of the water column (Gamo et al. 2001; Kim et al. 2001, 2004; Min and Kim 2006), oxygen content decreases (Kim and Kim 1996; Chen et al. 1999; Gamo 1999; Kang et al. 2004), and high deposition rates of organic matter (Cha et al. 2007; Tishchenko et al. 2007; Lee et al. 2008, 2010; Hyun et al. 2010) might have created a favorable environment for denitrification in the bottom layer at the two basins in the EJS in recent years.

An 'aerobic denitrification' is a newly found process in which certain bacteria (e.g., *Thiosphaera pantotropha* and *Pseudomonas stutzeri*) are able to use nitrate and DO simultaneously as electron acceptors in their respiration (Robertson and Kuenen 1984a; Robertson et al. 1989, 1995; Su et al. 2001). Both DO and nitrate decrease near the bottom at the current study sites (Fig. 4). Aerobic denitrification can occur in the 90% of DO saturation condition in culture experiments (Robertson and Kuenen 1984b; Su et al. 2001). This gives rise to the implicit possibility wherein aerobic denitrification may occur simultaneously with re-mineralization even in highly oxygenated water. Aerobic denitrification was reported for shallow intertidal waters in the German Wadden Sea (Gao et al. 2010). Sufficient supplies of organic matter and nitrate with high oxygen consumption in the UB and EJB near the TtS might stimulate the aerobic denitrification, using nitrate and DO at the same time.

Although it is difficult to verify our speculations with the current data, this study poses important insights in the modern nitrogen cycle in the EJS. We need to investigate the benthic microbial environments at additional slope and basin sites in the EJS, and model the EJS's denitrification process. A model would help to investigate how bottom water denitrification may contribute to a low water column N/P ratio in the EJS.

4. SUMMARY

Evidence of denitrification was found in the UB and EJB near the TtS based on profile analyses of the N/P ratio, DO, nitrate, nitrite, and phosphate from the 1999 CREAMS II data. A decrease of nitrate concentrations, increase of phosphate concentrations, lower N/P ratio (< 12.4), and deep nitrite peaks in the bottom layer are apparent in these two regions. The denitrification rates were estimated at ~3 - 33 μmol N m^{-2} d^{-1} from the nitrate profile analysis, and were comparable to the denitrification rates measured directly from sediments. Although the detailed mechanism of denitrification in the well-oxygenated EJS is still unclear, we speculate that denitrifying bacterial activity might be active in the bottom waters via 'micro-reducing environments,' or 'aerobic denitrification' may occur in the bottom waters of the EJS. These speculations need to be examined in the future to improve understanding of the EJS's nitrogen cycle.

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