Changes in seawater N:P ratios in the northwestern Pacific Ocean in response to increasing atmospheric N deposition: Results from the East (Japan) Sea

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Abstract

An increase in seawater N:P ratios due to enhanced atmospheric N deposition has recently been reported in the northwestern Pacific Ocean, including the East (Japan) Sea. In the Pacific Ocean, the East Sea is an ideal site to examine this effect since it is fed by the Pacific surface water, which has very low N concentrations relative to P concentrations (N:P < 5), and is located in the downwind area of major N emission sources in China and Korea. In addition, the East Sea is semi-enclosed, without any major river inputs, resulting in a long surface-water residence time (~2 yr for the upper 0–200 m layer). Vertical and horizontal distributions of nutrients determined in the East Sea from 2001 to 2009 showed that the N:P ratios were always lower than 10 in the mixed layer (10–30 m) and constant (N:P = 13 ± 1) in the deep ocean (200–3500 m). A simple mass-balance box model shows that the combined effects of physical (the rapid ventilation of the surface water with a N:P ratio of < 10 into the deep ocean) and biological (remineralization of sinking organic matter) processes result in the low N:P ratios (~13) over the deep water column of the East Sea. This model predicts that N:P ratios in the East Sea will be lower than 14 within the predictable range of atmospheric N input in the next 100 yr, indicating that the N-limited condition in the northwestern Pacific Ocean cannot be shifted to the P-limited condition in the near future.

The global atmospheric N deposition due to anthropogenic activities was found to be approximately threefold greater in the early 1990s (103 Tg N yr−1) compared with that in the 1860s (32 Tg N yr−1). This increase is predicted to continue and reach 195 Tg N yr−1 in 2050 (Galloway et al. 2004). Consequently, the increased inputs of anthropogenic N via the atmosphere have resulted in increased N:P ratios in the lakes of Norway, Sweden, and the United States (Elser et al. 2009) and in a shift from a N-limited to a P-limited condition in large areas of the northwestern Pacific Ocean during the last 30 yr (T. W. Kim et al. 2011). The increased N emissions have led to several environmental effects, such as acidification, reduced total alkalinity, and eutrophication, in the lake and ocean (Vitousek et al. 1997; Doney et al. 2007) and may alter biological production as well as the composition of phytoplankton species (Baron et al. 2000; Fenn et al. 2003).

The East (Japan) Sea is a marginal sea bordered by Russia, Korea, and Japan. The depths of the deepest East Sea basins exceed 3000 m. Water exchange between the East Sea and the North Pacific Ocean occurs through the Korea (Tsushima), Tsugaru, and Soya straits (depth < 130 m). The surface water, which originates from the Kuroshio Current, and a part of the Changjiang River enter the East Sea through the Korea Strait (Lee and Kim 1998). These waters flow out through the Tsugaru and Soya straits to the Pacific Ocean. Tracer studies have shown that the turnover time of the East Sea deep water is on the order of 100 yr (Chen et al. 1999). The East Sea is located downwind of northern China, one of the hotspots of anthropogenic N emission in the world (Mukai et al. 1990; Zhang et al. 2006). In the East Sea, the ratio of dissolved inorganic nitrogen (N) to dissolved inorganic phosphorus (P) below 200 m depth is about 13 (Talley et al. 2004), which is considerably lower than the Redfield ratio (16). The concentrations of N were less than 2.0 μmol L−1 in the mixed layer, with relatively lower N:P ratios (<10), indicating that the East Sea is a strongly N-limited environment (Kim et al. 2010; Kim and Kim 2013). Kim et al. (2010) showed that the N:P ratios decreased exponentially as the concentrations of chlorophyll a increased due to the biological utilization of N and the presence of the excess P in the water column. In association with this N limitation, cyanobacteria contribute 20–65% of the phytoplankton composition in the mixed layer (Kim et al. 2010; Kim and Kim 2013). Recently, an increase in N:P ratios owing to atmospheric N deposition has been reported by T. W. Kim et al. (2011) in the southern part of the East Sea.

In this study, we examine the change in N:P ratios that were obtained from the north–south transect over the period 2001–2009 (Fig. 1). Since the previous report (T. W. Kim et al. 2011) on N:P change in the East Sea is for the southwestern part of the East Sea, our data provide more accurate consequences of atmospheric N deposition in the East Sea. In addition, we established a simple mass-balance model that explains the low N:P ratio over the entire East Sea water column. Based on this box model, we predict a change in the N:P ratio in response to the atmospheric N inputs over the next 100 yr.

Methods

Sampling and analyses—The hydrological and biogeochemical surveys were conducted during three periods: 15 to 27 October 2005 (Sta. 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, and 14) on board the R/V Mikhail Alexeyevich Lavrentiev of the Pacific Oceanological Institute (POI), Russia; 08 to 22 May 2007 (Sta. 1, 2, 4, 6, 8, 10, 11, and 12) on board the R/V Professor Gagarinsky of the POI; and 09 to 18 July
2009 (Sta. 1, 2, 3, 4, and 6) on board the R/V Mikhail Alexeyevich Lavrentyev of the POI (Fig. 1). At most of the stations, the dissolved oxygen (DO), potential temperature, salinity, and pressure were measured using a rosette system with a mounted conductivity–temperature–depth (CTD; Sea-Bird Electronics [SBE] 911+). The DO data were obtained using a CTD-DO sensor, calibrated with the data taken from grab samples analyzed using the Winkler titration method aboard the ship. The temperature sensor used was an SBE-3/F thermometer (resolution: 0.0003 °C). The probes were calibrated at SBE, prior to each cruise. Niskin bottles mounted on the rosette system (with CTD SBE 911+) were used for all vertical water samplings. Seawater samples, each about 100 mL in volume, were filtered on board the ship using Whatman GF/F filters for nutrient analyses. The filtered seawater samples were frozen immediately after filtration and maintained until the analyses began. In the laboratory, the nutrient samples were analyzed by an autoanalyzer (Technicon random access automated chemistry system 2000, Bran+Lubbe, Futura Plus, Alliance). The data for the nutrients obtained by Seoul National University and POI were compared and found to be in good agreement \( r^2 = 0.99 \). The reliability of the inorganic nutrient data was obtained daily by measuring the certified reference material (CRM): MOOS-1 \( (23.7 \pm 0.9 \, \mu \text{mol L}^{-1} \text{ for N and } 1.56 \pm 0.07 \, \mu \text{mol L}^{-1} \text{ for P}) \) from National Research Council. The CRM was measured for each batch of samples. The results were \( 22.8 \pm 0.5 \, \mu \text{mol L}^{-1} \text{ for N and } 1.51 \pm 0.03 \, \mu \text{mol L}^{-1} \) for P \( (n = 12) \), which agreed with the certified value within 5%.

In this study, we define N as the sum of the concentrations of NO\(_3^-\) and NO\(_2^-\), and P as the PO\(_4^{3-}\) concentration. Our nutrient data were compared with those obtained by POI for April 2001 (Sta. 2, 3, 5, 6, 7, 8, 9, and 10), April 2002 (Sta. 5, 6, 8, 10, 11, 12, 13, and 14), and May 2004 (Sta. 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, and 14).

### Results

During the entire monitoring period (2001–2009), the concentrations of N in the surface layer (0–200 m) of the East Sea ranged from 0 \( \mu \text{mol L}^{-1} \) to 22 \( \mu \text{mol L}^{-1} \) (average: \( \mu \text{mol L}^{-1} \))
7.0 ± 6.2 μmol L⁻¹), and those in the deep layer (200–3500 m) of the East Sea ranged from 15 μmol L⁻¹ to 27 μmol L⁻¹ (average: 23 ± 2 μmol L⁻¹; Fig. 2; Table 1). The average concentrations of N in the surface layer were relatively lower in spring (April 2001, April 2002, May 2004, and May 2007) than in fall (October 2005) and summer (July 2009), while those in the deep layer were constant from 2001 to 2009 (Table 1). The concentrations of P in the surface layer of the East Sea ranged from 0.1 μmol L⁻¹ to 1.7 μmol L⁻¹ (average: 0.6 ± 0.5 μmol L⁻¹), and those in the deep layer of the East Sea ranged from 1.1 μmol L⁻¹ to 2.2 μmol L⁻¹ (average: 1.8 ± 0.2 μmol L⁻¹; Fig. 2; Table 1). The average concentrations of P in the entire water column were constant during the last decade (Table 1). The N:P ratios in the surface layer of the East Sea showed large variations ranging from 0 to 16 (average: 8.6 ± 4.6), and those in the deep layer of the East Sea were relatively constant ranging from 11 to 14 (average: 13 ± 1; Fig. 2; Table 1).
Table 1. Average N and P concentrations and N : P ratios in the East (Japan) Sea for the period from 2001 to 2009. Uncertainty is the standard deviation.

<table>
<thead>
<tr>
<th>Year</th>
<th>Surface layer (0–200 m)</th>
<th>Deep layer (200–3500 m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N (µmol L⁻¹)</td>
<td>P (µmol L⁻¹)</td>
</tr>
<tr>
<td>2001</td>
<td>6.4 ± 5.5</td>
<td>0.6 ± 0.4</td>
</tr>
<tr>
<td>2002</td>
<td>5.7 ± 5.7</td>
<td>0.7 ± 0.5</td>
</tr>
<tr>
<td>2004</td>
<td>6.5 ± 6.2</td>
<td>0.5 ± 0.4</td>
</tr>
<tr>
<td>2005</td>
<td>8.6 ± 6.7</td>
<td>0.6 ± 0.5</td>
</tr>
<tr>
<td>2007</td>
<td>6.5 ± 6.0</td>
<td>0.6 ± 0.4</td>
</tr>
<tr>
<td>2009</td>
<td>8.3 ± 6.9</td>
<td>0.7 ± 0.5</td>
</tr>
<tr>
<td>Average</td>
<td>7.0 ± 6.2</td>
<td>0.6 ± 0.5</td>
</tr>
</tbody>
</table>

Discussion

Modeling the mass balance of N and P in the East Sea—Each N and P mass balance in the surface and deep layers of the East Sea can be expressed by the following equations:

\[ I_{\text{surface}} (\gamma) = I_{\text{surface}} (\gamma - 1) + \Delta t \times (F_{\text{air}} + F_{\text{mixing}} - F_{\text{organic export}} + F_{\text{horizontal exchange}}) \]  

\[ I_{\text{deep}} (\gamma) = I_{\text{deep}} (\gamma - 1) + \Delta t \times (F_{\text{organic export}} - F_{\text{mixing}}) \]  

where \( I_{\text{surface}} \) and \( I_{\text{deep}} \) are the inventories (mol) of nutrients in the surface and deep layers, respectively; \( F_{\text{air}} \), \( F_{\text{mixing}} \), \( F_{\text{organic export}} \), and \( F_{\text{horizontal exchange}} \) are the annual flux (mol yr⁻¹) of nutrients by atmospheric deposition, vertical water exchange, the export of organic matter, and net horizontal exchange through the straits, respectively. Here, \( \Delta t \) is the time interval (1 yr) between the year \( \gamma \) of interest and the previous year \( \gamma - 1 \).

In the deep layer, the N and P fluxes through the export of organic matter are calculated to be \( 2.3 \times 10^{11} \) mol N yr⁻¹ and \( 0.14 \times 10^{11} \) mol P yr⁻¹, respectively, based on the utilization of DO in the deep water. In this calculation, DO consumption in the deep water of the East Sea is assumed to be \( 2.4 \pm 0.3 \) mol m⁻² yr⁻¹ measured by Min (1999) using chlorofluorocarbons as a tracer, corresponding to 15 mol C m⁻² yr⁻¹ of carbon export, using the O:C:N:P value of 170:117:16:1 (Anderson and Sarmento 1994). Since this sea is fully closed below the 100 m layer, the horizontal water advection can be neglected in this mass balance. The N and P fluxes from the deep to surface layers through physical mixing are calculated to be \( 3.5 \times 10^{11} \) mol N yr⁻¹ and \( 0.26 \times 10^{11} \) mol P yr⁻¹ by multiplying the vertical water exchange rate of \( 15 \times 10^{12} \) m³ yr⁻¹ through 200 m (Senjyu and Sudo 1996) by the average nutrient concentrations of the deep sea observed from 2001 to 2009 (23 ± 2 µmol L⁻¹ for N and 1.8 ± 0.2 µmol L⁻¹ for P). Since the vertical input terms \( F_{\text{organic export}} \) will be balanced by the vertical output terms \( F_{\text{mixing}} \), under steady state conditions \( I (\gamma) = I (\gamma - 1) \), in the deep layer, the N and P fluxes from the surface to deep layers through physical mixing are calculated to be \( 1.2 \times 10^{11} \) mol N yr⁻¹ and \( 0.12 \times 10^{11} \) mol P yr⁻¹, respectively. Then, if this downward flux through physical mixing is divided by the vertical water exchange rate \( 15 \times 10^{12} \) m³ yr⁻¹, the concentrations of N and P in the sinking surface water are calculated to be \( 7.8 \) µmol L⁻¹ and \( 0.8 \) µmol L⁻¹, respectively. These theoretical concentrations of N and P in the sinking surface water fall into the range of our observed data from 2001 to 2009 in the surface layer (Fig. 2).

Nutrient stoichiometry in the East Sea during the last decade—The N : P ratios decreased steeply from 50 m to the surface (Fig. 3), with no trend of increases during the last decade. The N : P ratios were slightly higher (in the range of 13–16) in the subsurface layer (50–100 m layer), with a notable increase in October 2005. Although this could be a result of anthropogenic N deposition, the anomalies (N : P > 13) correlated well with apparent oxygen utilization (AOU). As the AOU values approached the highest value, the N : P ratio is close to 16 (Fig. 3), indicating that biological regeneration is close to the Redfield ratio. As such, Chen et al. (1996) reported that \( \Delta POC : \Delta AOU \) ratio and average particulate N : P ratio for the phytoplankton population were 0.79 and 16.3, respectively, in the East Sea. Thus, we suggest that such a subsurface increase in N : P ratios is associated with Redfield-like remineralization of sinking organic matter.

In the deep layer, the concentrations of N and P in the East Sea were lower than those in the North Pacific Ocean but higher than those in the North Atlantic Ocean (Fig. 2). The higher nutrient concentrations in the deep East Sea relative to those in the North Atlantic Ocean could be due to higher export production in the East Sea (99 g C m⁻² yr⁻¹; Hahm and Kim 2008) relative to the North Atlantic Ocean (20 g C m⁻² yr⁻¹; Michaels et al. 1994). The N : P ratio (about 13) in the deep East Sea (Fig. 2) is considerably lower than that in the North Pacific and North Atlantic waters.

If the physical export \( (1.2 \times 10^{11} \) mol N yr⁻¹ and \( 0.12 \times 10^{11} \) mol P yr⁻¹) and the biological export \( (2.3 \times 10^{11} \) mol N yr⁻¹ and \( 0.14 \times 10^{11} \) mol P yr⁻¹) are combined, the N : P ratio will become 13.0 at the steady state (Fig. 4). In order to explain such a low N : P ratio, Yanagi (2002) suggested the occurrence of active denitrification in the East Sea. However, the oxygen saturation in the bottom water of the East Sea is about 60% (Talley et al. 2006). Even if we assume the complete denitrification of sinking organic matter below 3000 m (0.18 ± 0.03 mol C m⁻² yr⁻¹; Otosaka et al. 2008), the maximum denitrification rate in bottom sediments would be about \( 0.24 \times 10^{11} \) mol N yr⁻¹,
which is an order of magnitude lower than the N flux due to water ventilation and export production. Thus, denitrification could not be a possible cause of the lower N : P ratios in the East Sea.

**Change in oceanic N : P ratios by increasing atmospheric nitrogen deposition**—Using Eq. 1, we can predict the change in N : P ratios in response to an increase in atmospheric N deposition. All terms, except the net horizontal exchange ($F_{\text{horizontal exchange}}$) and atmospheric input ($F_{\text{air}}$) terms, are obtained from Eq. 2 under steady state conditions (see "Modeling the mass balance of N and P in the East Sea"). The N inventory in the upper 200 m measured in this study is $1.4 \times 10^{12}$ mol. If the N inventory in the upper 200 m is divided by the residence time of the surface water (~ 2 yr), the outflow flux of N through the straits is calculated to be $7.0 \times 10^{11}$ mol N yr$^{-1}$. We assume that this flux is equivalent to the inflow flux of N through the straits under steady state conditions ($F_{\text{horizontal exchange}} = 0$; Fig. 4). Then, the total output fluxes of N through the straits, the export of organic matter, and the vertical water mixing are $1.1 \times 10^{12}$ mol yr$^{-1}$. The residence time of N in the surface layer is calculated to be 1.3 yr by dividing the N inventory by the total output fluxes of N. This residence time agrees very well with that (1.6 yr) obtained by Yanagi (2002). Thus, in the East Sea, about 50% of the N inventory seems to be annually exchanged by the horizontal surface current; 24% of the inventory is annually exported by organic matter and vertical mixing through 200 m; and the rest remains in the surface layer.

The change in the atmospheric depositional fluxes of N ($F_{\text{air}}$) during the last 30 yr is assumed to have changed as shown in Fig. 4. For the next 100 yr, we used two scenarios: the Reference (REF) scenario, which is a sustainable scenario with moderate emission rates, and the Policy Failed Case (PFC) scenario, which is a pessimistic scenario with high emission rates (Ohara et al. 2007). We assume that the flux of atmospheric N to the East Sea is proportional to the anthropogenic N emissions in China (Ohara et al. 2007). The ratio is obtained using the total atmospheric N depositional flux ($79 \times 10^{10}$ mol) for the last three decades reported by T. W. Kim et al. (2011). For the period 2004–2009, we used the average anthropogenic N emissions in China predicted by the REF and PFC scenarios (Ohara et al. 2007) because there is no information on the atmospheric depositional flux of N to the East Sea. Kang et al. (2009) reported that the annual average atmospheric P concentrations over the East Sea have increased by two times in the last decade, which may be in the range of natural variations. However, the atmospheric N fluxes were two orders of magnitude higher than the atmospheric P fluxes to the East Sea during this period. When the variation in P fluxes is considered in our prediction model, the predicted N : P ratios in surface layer for the next 100 yr vary within 2%. Thus, the atmospheric flux of P is neglected in our prediction model.

When these observed and assumed air N input values are plugged into Eq. 1 over the period 1980 to 2009, the N : P ratios in the observed period (2001–2009) become 10.0 and 13.1, respectively, in the surface and deep layers. These results agree very well with our observed data (Fig. 2). The atmospheric N flux from 2010 to 2100 is calculated on the basis of the REF and PFC scenarios of anthropogenic N emissions in China (Ohara et al. 2007). The REF and PFC scenarios project the increase of N emissions to be 203% and 670% in 2100, respectively, relative to the N emissions in 2009. For the next 100 yr, the N : P ratios will increase to 11.3 and 13.6 in the surface and deep layers, respectively, for the REF scenario, while the ratios will increase to 15.5 and 14.7, respectively, for the PFC scenario. Therefore, we
conclude that the N-limited condition of the East Sea cannot be shifted to a P-limited condition under a realistic scenario.

We think that T. W. Kim et al. (2011) reached a wrong conclusion when they found that a large area of the northwestern Pacific Ocean shifts from a N- to P-limited condition, mainly owing to two conceptual problems: slightly enhanced N: P ratios of over 13.1 were observed mostly in the continental shelf waters and the southeastern part of the East Sea, which are influenced significantly by

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**Fig. 4.** Past, present, and future N: P ratios in the East (Japan) Sea. (A) A schematic showing the steady-state fluxes of N and P through water mixing and organic matter settling in the East Sea. (B) Prediction of the change in N: P ratios in response to the change in anthropogenic N inputs during the next century in the East Sea. The solid lines indicate the annual variations in atmospheric N fluxes and N: P ratios in the surface and deep layers during the last 30 yr. The black dotted lines indicate the predicted N: P ratios in the surface and deep layers when applying the Reference (REF) scenario to the next 100 yr; the gray dotted lines indicate those in the surface and deep layers when applying the Policy Failed Case (PFC) scenario to the next 100 yr.
river inputs and discharge of submarine groundwater (Kim et al. 2008; G. Kim et al. 2011) rather than by atmospheric fallouts. Recently, Kim et al. (2013) showed that the waters with high N:P ratios in the continental shelf of this region are mainly from rivers. T. W. Kim et al. (2011) defined excess N (N*, anthropogenic N) to be of a value higher than the N:P ratio of 13.1 and regarded it as a shift to a P-limited condition; although a Redfieldian ratio of 16 should be used, as revealed by our study. This flawed assumption results in artificially high N* values for deep Pacific water. Our N:P ratio data from the central part of the East Sea, which has the largest Asian dust inputs (Jo et al. 2007) and the lowest inputs of river and groundwater, are more reliable for examining the influence of atmospheric inputs. If the Redfield ratio of 16 (as inferred from N:P and AOU plots) is applied for N*, considering our results from the East Sea, the N-limited condition of the northwestern Pacific Ocean will be robust against an increasing trend of atmospheric N inputs to the ocean in the next 100 yr.

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References


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