Influence of riverine alkalinity on carbonate species in the Okhotsk Sea


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[1] Comparing data set of carbonate species and other hydrographic chemical properties in 1999, 2000 and 2006 in the Okhotsk Sea, we found that salinity-normalized alkalinity in the subsurface water has shown a rate of increase by 2.6 ± 0.1 μmol kg⁻¹ y⁻¹ while the increase in salinity-normalized dissolved inorganic carbon corrected by AOU was almost half of that in alkalinity. Therefore, pH has increased by 0.013 ± 0.001 pH unit y⁻¹ in the subsurface water (26.5 – 27.3 σθ) which is the origin of the North Pacific intermediate water. This increase in pH could be explained by the increase in alkalinity in the Amur River in the last decade, suggesting a possibility that could mitigate one-fifth of recent ocean acidification in the North Pacific. Citation: Watanabe, Y. W., J. Nishioka, M. Shigemitsu, A. Mimura, and T. Nakatsuka (2009), Influence of riverine alkalinity on carbonate species in the Okhotsk Sea, Geophys. Res. Lett., 36, L15606, doi:10.1029/2009GL038520.

1. Introduction

[2] A recent model calculation predicts that a decrease of pH in the ocean surface water will be caused as the response to the increase of atmospheric CO₂ in the future [e.g., Orr et al., 2005]. Some ocean observations have also shown a decreasing trend of 0.4 ± 0.4 μmol kg⁻¹ y⁻¹ for alkalinity (Alk) and that of 0.0019 ± 0.0003 y⁻¹ for pH during recent decades in the Pacific and the Indian Oceans [Sarma et al., 2002; Feely et al., 2008]. However, these results were estimated based on carbonate species data that have large errors and/or assumptions of no land-ocean interactions with increasing temperature. In the North Atlantic marginal seas and the South China Sea, some investigators also reported the decadal increase of dissolved inorganic carbon (DIC) [e.g., Thomas et al., 2007], suggesting a possibility that pH could decrease in these regions as well as the open ocean. However, the change of pH is still not reported throughout the land-river-ocean system containing the continental marginal seas.

[3] On the other hand, Intergovernmental Panel on Climate Change (IPCC) [2007] reported that global warming has recently been led to changes in the global ocean environment. In the North Pacific, several studies also have reported the same trends as the global one, which has been caused by the weakening of formation/circulation of North Pacific Intermediate Water (NPIW) as a response to the reinforcement of ocean stratification [e.g., Watanabe et al., 2001]. NPIW is centered on 26.8 σθ, which is the only water mass produced in the North Pacific, influencing the climate of the North Pacific. One of the origins is in the Okhotsk Sea. Dense shelf water (DSW) is produced by brine rejection during sea ice formation in the continental shelves and joins rapidly with Okhotsk Sea Intermediate Water (OSIW). OSIW has a ventilation time of several years, and is transported into NPIW [e.g., Ohshima and Martin, 2004]. In addition, snowmelt water and/or monsoon derived rainwater in Siberia bring inflows of high contents of Alk and nutrients into the Okhotsk Sea through the Amur River of which the catchment area is the tenth largest in the world [Andreev and Pavlova, 2009]. This region may have a probability of the recent changes in carbonate species influenced by land-river-ocean interactions as well as recent anthropogenic perturbations. In 2006, we thus revisited the same observation area as examined in 1999 and 2000 in the Okhotsk Sea, and observed the same hydrographic properties to clarify a degree of change of pH with other hydrographic parameters in the Okhotsk Sea.

2. Data and Methods

[4] On the R/V Professor Khromov, we obtained the samples of hydrographic chemical properties from 0 m to 3000 m depth at 34 stations for Alk and DIC, at 51 stations for nutrients (NH₃, NO₂, NO₃, PO₄, Si(OH)₄, DO) during August to early September in 2006, covering a formation area of intermediate water in the Okhotsk Sea (Figure 1). Sampling and measurement methods for each observed property were carried out according to the JGOFs and DOE protocols [Dickson and Goyet, 1994; Knap et al., 1996]. In the Amur River, we observed Alk at 10 stations of even intervals from about 1000 km upriver to the mouth of the river in September 2005 (Figure 1a) and measured them by using the one-point titration method of Ono et al. [1998]. Certified reference materials of Alk and DIC distributed by Prof. A. G. Dickson (Scripps Institution of Oceanography) were used. These were the same procedures as used in the summer of 1999 (July) and 2000 (August). In the same sampling region, data of each property in 2006 were compared to those in 1999 and 2000 by using an isopycnal grid analysis. In the continental shelves of the northern part in summer, a heterogeneous remnant of water mass developed in winter sometimes exists with a minimum of water temperature (θ) above 26.8 σθ [e.g., Wakita et al., 2003]. We thus neglected water mass with θ ≤ −1.5°C and σθ ≤ 26.8 as an anomaly. Additionally, we assumed that water mass below 27.4 σθ has not changed on a decadal time scale, since recent transient tracers as chlorofluorocarbons have been still not found below 27.4 σθ over the Okhotsk Sea throughout 1990s [Yamamoto-Kawai et al., 2004]. By estimating the difference of each property between each cruise based on the deep water data sets below 27.4 σθ in 2000, both Alk and DIC had offsets of 3 ± 1 μmol kg⁻¹. The offset values of NH₃, NO₂, NO₃,
and DO were, respectively, within 0.1 μmol kg⁻¹, 0.02 μmol kg⁻¹, 1 μmol kg⁻¹, 0.1 μmol kg⁻¹, 5 μmol kg⁻¹, and 1 μmol kg⁻¹. While the offsets of nutrients were sufficiently small, it was necessary to make corrections for the offsets of carbonate species in order to clarify these changes. We here made corrections for the offsets of Alk and DIC by subtracting each offset from the raw data.

Using these pairs of Alk and DIC, we calculated the pH_in situ temperature (pH_in situ total hydrogen scale) based on Dickson and Goyet [1994]. Furthermore, in order to estimate the degree of change of the nitrogen cycle that can affect the contents of Alk and pH_in situ, we estimated \( N^* = ([\text{NO}_3^-] + [\text{NO}_2^-] + [\text{NH}_3] - r_{\text{NPP}} \cdot [\text{PO}_4^3-] + 2.9 \) [e.g., Yoshikawa et al., 2006]) as an index of nitrogen fixation-denitrification by using the observed nutrient data. The positive and negative values of \( N^* \) imply the possibilities of nitrogen fixation and denitrification. In the case of focusing on a relative change of \( N^* \) among 1999, 2000 and 2006, we estimated the average rates of change of Alk, pH_in situ, and \( N^* \) in the subsurface water, we can consider the changes in this region on ocean acidification in the North Pacific. In the following sections, we will discuss these changes in this region.

We therefore used \( r_{\text{NPP}} = 16 \). In order to avoid the change of water mass in the isopycnal grid analysis, we also addressed all the data by normalizing them to salinity of 35 using the optimal salinity-normalization scheme with non-zero freshwater end-member [Friis et al., 2003], which were shown with the prefix ‘n’. As a non-zero freshwater end-member, we here assumed to be \( \text{Alk} = 589 \mu\text{mol kg}^{-1}, \text{DIC} = 294 \mu\text{mol kg}^{-1}, \text{AOU} = 0 \mu\text{mol kg}^{-1} \) and \( N^* = 0 \mu\text{mol kg}^{-1} \) based on the climatological riverine data [Andreev and Pavlova, 2009].

3. Results

On the isopycnal horizon of 26.5 \( \sigma_T \) as the remnant of the winter mixed layer, n-Alk decreased from the inner shelf to the offshore (Figure 1a), indicating that the Amur River and the continental shelf significantly affect the spatial distributions of carbonate species in the Okhotsk Sea [e.g., Wakisaka et al., 2003]. Similarly, n-DIC and n-pH_in situ decreased to the offshore while \( n-N^* \) increased (Figures 1b and 1c, n-DIC not shown). Comparing the isopycnal averaged values of all the salinity-normalized hydrographic properties during this period, we found significant changes of Alk, n-pH_in situ and n-N* in the subsurface water (Figure 2 and Table 1; see Figure 1 for the calculation of n-pH_in situ). Although the variations of these properties gradually changed from the inner shelf to the offshore, since the observation area and the sampling points were the same among 1999, 2000 and 2006, we estimated the average rates of change of Alk (Rn-Alk) and n-pH_in situ (Rn-pH_in situ), which increased by 2.6 μmol kg⁻¹ y⁻¹ and 0.013 pH unit y⁻¹, respectively. Rn-pH_in situ was significantly larger than the effect of offset corrections (0.005 ± 0.003 pH unit). On the other hand, the rate of n-N*(Rn-N*) was from −0.8 to −0.5 μmol kg⁻¹ y⁻¹. Furthermore, considering a corrected value of n-DIC from the effect of remineralization of organic carbon (n-DIC* = n-DIC - r_{\text{C/O}_2} \cdot n-AOU, where AOU and r_{\text{C/O}_2} are the apparent oxygen utilization and the stoichiometric ratio of DIC to Oxygen [Anderson and Sarmiento, 1994]), we obtained that the rate of n-DIC* (Rn-DIC*) increased by 1.2 μmol kg⁻¹ y⁻¹ above 27.3 \( \sigma_T \) which was almost half of Rn-Alk (Table 1). Using these pairs of Rn-Alk and Rn-N* on 26.5 \( \sigma_T \) with the atmospheric CO₂ increment during this period, we estimated that Rn-DIC* caused by the increase of atmospheric CO₂ was 0.5 ± 0.1 μmol kg⁻¹ y⁻¹, indicating that the residue of Rn-DIC* was about half of Rn-Alk excluding the influence of Rn-N*. We also found that Alk in the Amur River was almost constant throughout the Amur River, 1867 ± 26 μmol kg⁻¹.

The above trends contained the natural variations and the long-term trends, and it is difficult to distinguish between them due to only three observational data sets in our study. However, it is important to clarify the extent of influences of these changes in this region on ocean acidification in the North Pacific. In the following sections, we will discuss the changes in these properties without a distinction between the natural and the long-term changes.

4. Discussion

4.1. Factors Changing Alk and pH_in situ in the Okhotsk Sea

In order to explain the significant increases of Alk and pH_in situ in the subsurface water, we can consider the following causes: (i) the decrease of δ, (ii) the changes in the
mixing between the Okhotsk Sea and the Pacific and/or the vertical mixing, (iii) the strengthening of CaCO₃ dissolution, (iv) the reinforcement of denitrification, (v) the increase of Ca²⁺ derived from an exterior system of the Okhotsk Sea.

Our study showed an increasing rate of θ of 0.02–0.04°C y⁻¹ above 27.3 σₒ (Table 1), causing the decrease of pH in situ of 0.001 pH unit y⁻¹ far from increasing pH in situ. The value of n-Alk in the North Pacific is lower than that in the Okhotsk Sea (Figure 1a). The recent reinforcement of ocean stratification in the Okhotsk Sea has been already reported [e.g., Osafune and Yasuda, 2006]. In our study, the increasing rates of the saturation states of aragonite and calcite were only 0.03 y⁻¹ and 0.05 y⁻¹, respectively. Rₙ-Alk with Rₙ-DIC being half of Rₙ-Alk were almost found above these saturation state depths. Furthermore, the value of Rₙ-Alk cannot only cause about one-third of the observed increase of n-Alk, although we found Rₙ-Alk from −0.8 to −0.5 μmol kg⁻¹ y⁻¹ (Table 1). Therefore, since the cases of (i)–(iv) can be ignored, the case of (v) could possibly result in most of the increases of Alk and pH in situ in this study.

4.2. Mass Balance of Alk Between the Amur River and the Okhotsk Sea

As an effect derived from an exterior system of the Okhotsk Sea, one of the most probable possibilities is the increase of efflux of Ca²⁺ derived from the change of the outflow characteristics of the Amur River; the increases of riverine discharge and/or the increase of Ca²⁺ content as Alk because Rₙ-Alk with Rₙ-DIC being half of Rₙ-Alk were almost found above the saturation state depths of CaCO₃ in the subsurface. We here tried to estimate the extent of these effects in the Amur River. In order to elucidate the actual net increasing rate of the water column inventory of Alk in the Okhotsk Sea (ΔIₙ-Alk(sea), mol y⁻¹), using the observed data without salinity normalization, we need to consider RₑAlk in addition to Rₙ-Alk as follows:

\[ \Delta I_{\text{n-Alk(sea)}} = A \cdot 10^{-3} \int_{0}^{\text{depth(m)}} \rho_{\text{sea}}(z) \left( R_{\text{Alk}}(z) + R_{\text{N*}}(z) \right) dz \]

where \( A \), \( \rho_{\text{sea}} \), and \( z \) are the sea surface area (m²), the sea water density (kg m⁻³), and the water depth (m), respectively. \( R \) refers to the average rate of increase of one in the parameters of Alk and N* observed during 1999 to 2006 (μmol kg⁻¹ y⁻¹). We estimated \( \Delta I_{\text{n-Alk(sea)}} \) from 0 m to 27.4 σₒ assuming that \( R \) between 0 m and 26.5 σₒ equaled to that on 26.5–26.8 σₒ (Table 1). As the value of \( A \), we addressed the whole area of our observation as the minimum (\( A_{\text{min}} \) 1.6 × 10¹¹ m²) and the area of climatological annual mean ice cover as the maximum (\( A_{\text{max}} \) 4.2 × 10¹¹ m²) [Ohshima et al., 2006]. As a result, we obtained \( \Delta I_{\text{n-Alk(sea)}} \) to be from 1.4 × 10¹¹ to 3.6 × 10¹² mol y⁻¹.

Table 1. Average Increasing Rates of Salinity-Normalized Properties From 1999 to 2006, Rₙ-Alk, Rₙ-N*, RₑAlk in situ and RₑDIC* With Rₒ*.

<table>
<thead>
<tr>
<th>Year</th>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1999</td>
<td>Rₙ-Alk</td>
<td>2.7 (17.8)</td>
</tr>
<tr>
<td></td>
<td>RₑAlk</td>
<td>0.3 (21.2)</td>
</tr>
<tr>
<td>2000</td>
<td>Rₙ-Alk</td>
<td>1.5 (10.2)</td>
</tr>
<tr>
<td></td>
<td>RₑAlk</td>
<td>0.2 (0.9)</td>
</tr>
<tr>
<td>1999</td>
<td>RₑAlk</td>
<td>2.5 (15.1)</td>
</tr>
<tr>
<td></td>
<td>RₑAlk</td>
<td>0.1 (0.9)</td>
</tr>
<tr>
<td>2000</td>
<td>RₑAlk</td>
<td>1.4 (8.2)</td>
</tr>
<tr>
<td></td>
<td>RₑAlk</td>
<td>0.1 (0.9)</td>
</tr>
</tbody>
</table>

*The value in parenthesis is the increased amount of each property during each sampling time interval. The errors showed the standard errors. The average depths of 26.5 σₒ, 26.8 σₒ and 27.3 σₒ throughout the entire period, are 62 ± 15 m, 234 ± 21 m and 750 ± 11 m, respectively.
The Amur River in each five years from 1960 to 2005 with standard errors based on the data of the ROSHYDROMET, Russia. The dash line also shows the linear trend estimated from 1965 to 2000 although it is not significant (p > 0.1).

Considering the change of Alk in the Amur River, it is necessary to estimate the mass balance of Alk in the following three cases to determine the change of $\Delta I_{\text{net-Alk}}$ from 1999 to 2006 in the Okhotsk Sea: (v-a) the content of Alk only changed, (v-b) the river discharge only changed, and (v-c) both the content of Alk and the river discharge changed. Actually, the discharge of the Amur River significantly increased over the past five years, and its average increasing rate was 2.2 $\times$ 10$^{10}$ m$^3$ y$^{-1}$ [The Amur River data provided by ROSHYDROMET, Russia]. Therefore, we tried to examine the cases of (v-b) and (v-c).

In the case of (v-b), we can express $\Delta I_{\text{net-Alk}}$ (river) by the change in discharge of the Amur River ($\Delta D$, m$^3$ y$^{-1}$) as follows:

$$\Delta I_{\text{net-Alk}} = \rho_{\text{river}} \cdot C_{\text{Alk}}(0) \cdot \Delta D \cdot 10^{-3}$$

where $\rho_{\text{river}}$ and $C_{\text{Alk}}(0)$ are the riverine water density (kg m$^{-3}$) and the climatological riverine content of Alk (µmol kg$^{-1}$). We used 589 µmol kg$^{-1}$ for $C_{\text{Alk}}(0)$ based on the average data observed before 1999 [Andreev and Pavlova, 2009]. We obtained $\Delta I_{\text{net-Alk}}$ (river) to be 1.3 $\times$ 10$^{10}$ mol y$^{-1}$ which is only 9% of the minimum value of $\Delta I_{\text{net-Alk}}$ (sea), indicating that the change in the river discharge only makes it not possible to explain the total increase of Alk in the Okhotsk Sea.

In the case of (v-c), we can calculate the changing riverine concentration of Alk ($\Delta C_{\text{Alk}}$) with $\Delta D$ as follows:

$$\Delta I_{\text{net-Alk}} = \rho_{\text{river}} \cdot \left( (C_{\text{Alk}}(0) + D_{\text{Alk}}) \cdot (D(0) + \Delta D) - C_{\text{Alk}}(0) \cdot D(0) \right) \cdot 10^{-3}$$

where $D(0)$ are the climatological riverine discharge (m$^3$ y$^{-1}$), which is 3.5 $\times$ 10$^{11}$ m$^3$ y$^{-1}$ based on the average data observed before 1999 [Andreev and Pavlova, 2009]. Assuming $\Delta I_{\text{net-Alk}}$ (river) being equal to $\Delta I_{\text{net-Alk}}$ (sea), we obtained the ratio of the changing riverine content of Alk to the climatological one ($\Delta C_{\text{Alk}}$) to be from 1.6 to 2.7 times higher than the climatological riverine content of Alk. Actually, the average concentration of Ca$^{2+}$ in the Amur River from 2000 to 2005 changed from 0.16 to 0.26 mmol l$^{-1}$, indicating that Ca$^{2+}$ has increased by 1.6 times (Figure 3). In addition, we observed 1867 ± 26 µmol kg$^{-1}$ of Alk in the Amur River in 2005, which is 3.2 times higher than $C_{\text{Alk}}(0)$. The above results agreed with our estimation, demonstrating that the increase of Alk in the Amur River was the dominant cause for the increase of Alk in the Okhotsk Sea during 1999 and 2006.

Raymond and Cole [2003] reported a decadal increase of alkalinity in the Mississippi River derived from chemical weathering and the subsequent export from the soil to the river, which was linked to the amount and type of land cover. In the region along the Amur River, recent industrialization and development of agriculture in Russia and China has been progressing, and deforestation and loss of wetlands also has been increasing in the past several decades [e.g., An et al., 2007]. IPCC [2007] also reported that this area could be one of the most striking areas in the world with air temperature increasing by more than 0.5°C decade over the last decade. Consequently, the increase of soil dissolution could be progressing. These changes along this river could cause the increase of riverine alkalinity and the subsequent increases of Alk and pH$_{\text{in situ}}$ in the Okhotsk Sea in the last decade.

The effect of increasing Alk and pH$_{\text{in situ}}$ in the Okhotsk Sea would spread over the North Pacific through the subsurface water since the water mass of the Okhotsk Sea is the origin of NPIW that influences the spatiotemporal distributions of physical and chemical properties in the North Pacific [e.g., Watanabe et al., 2001; Sarmiento et al., 2004]. By considering the residence time of NPIW to be 20–30 years [e.g., Watanabe et al., 1994] with the increase of n-Alk in this study (1.4–2.6 µmol kg$^{-1}$ y$^{-1}$) (Table 1), the pH in NPIW may increase by 0.0004 pH unit y$^{-1}$ although a large uncertainty is included, which could mitigate one-fifth of ocean acidification of 0.0019 ± 0.0003 (standard error) pH unit y$^{-1}$ (R$^2$ = 0.27) derived from anthropogenic CO$_2$ uptake by the ocean [Feely et al., 2008]. Our finding indicates that this marginal sea plays a critical role in absorbing the anthropogenic CO$_2$ despite a predicted decrease of pH in the ocean surface waters progressing in the future. Unfortunately, based on our present data, it is difficult to whether the changes of Alk and pH$_{\text{in situ}}$ were caused by only anthropogenic perturbations or not. In order to elucidate whether oceanic pH decreases over the whole ocean, further study on the carbonate system in the marginal seas with large rivers will enable evaluation of the extent of future change in seawater pH.

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References


