Decadal time evolution of oceanic uptake of anthropogenic carbon in the Okhotsk Sea

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Received 26 November 2012; revised 17 December 2012; accepted 20 December 2012; published 21 January 2013.

[1] Comparing the data sets of chemical transient tracers (trichlorofluoromethane (CFC-11), dichlorodifluoromethane (CFC-12), sulfur hexafluoride (SF6)) among three re-observations from 1993 to 2006 in the Okhotsk Sea, we found the remarkable change in the efficiency of oceanic absorption of anthropogenic carbon (EF) based on the observed change of apparent tracer age. EF above 27.0 σ0 increased by 16% while EF below 27.0 σ0 declined by 27% during the period from 1993 to 2006. Consequently, EF in the entire water column decreased by 14%. We concluded that the recent reinforcement of ocean stratification derived from the ocean warming caused the weakening of water ventilation in this region, indicating that the penetration of atmospheric anthropogenic carbon to the deep ocean interior is becoming difficult. Citation: Watanabe, Y. W., J. Nishioka, and T. Nakatsuka (2013), Decadal time evolution of oceanic uptake of anthropogenic carbon in the Okhotsk Sea, Geophys. Res. Lett., 40, 322–326, doi:10.1002/grl.50113.

1. Introduction

[2] The atmospheric anthropogenic CO2 may be responsible for the observed global warming, strengthening of ocean stratification, decline in phytoplankton productivity, and ocean acidification over several decades [e.g., Watanabe et al., 2001; Chiba et al., 2004; Feely et al., 2004; IPCC, 2007; Sabine et al., 2008]. One possible consequence of warming is a decline in the efficiency of oceanic absorption of anthropogenic carbon with ocean acidification, which might have a positive feedback effect. When considering the present and future balance of anthropogenic carbon in the world, it is necessary to elucidate not only how much anthropogenic carbon the ocean has absorbed and where it is stored, but also how the oceanic uptake of anthropogenic carbon varies with time and how this variability is tied to regional/global scale warming.

[3] 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 σ0, 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 which is the southernmost sea ice region in the Northern Hemisphere, and this sea has already been affected by ocean warming trend [Nakanowatari et al., 2007]. Dense shelf water (DSW) is produced by brine rejection during sea ice formation in the continental shelves of this region 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 alkalinity 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, 2010]. Watanabe et al. [2009] already reported that the recent anthropogenic perturbation of the Amur River possibly led the changes in carbonate species in the Okhotsk Sea. However, it was still unclear how much anthropogenic carbon the Okhotsk Sea temporarily absorbs.

[4] In order to evaluate the oceanic anthropogenic carbon content and its change, the dissolved inorganic carbon (DIC) time series approach would be desirable, but it is difficult for this approach to distinguish the anthropogenic uptake of carbon from the natural uptake without large uncertainties [Sabine et al., 2008]. Therefore, the approaches based on the chemical transient tracer dating technique would be useful such as C* approach [Gruber et al., 1996; Watanabe et al., 2000]. However, these approaches rely on the assumption that a constant air-sea disequilibrium or almost equilibrium. Therefore, in the sea ice formation area where large gas undersaturation possibly exists, it may be difficult to use the tracer dating approach for evaluating the oceanic anthropogenic carbon. To overcome this point, Wakita et al. [2003] proposed the approach based on the temporal differences in DIC and apparent oxygen utilization (AOU) between end-member water masses (ΔDIC-ΔAOU approach) in the sea ice formation region. In the Okhotsk Sea, they estimated the oceanic uptake rate of anthropogenic carbon (ΔCanth) for the intermediate water and that for the surface water to be respectively 1.1 ± 0.9 μmol kg−1 year−1 and 0.7 ± 0.1 μmol kg−1 year−1 as an average value between 1993 and 1999. However, this approach can allow us only to estimate the average value of ΔC(anth) in the whole sea ice formation area but unfortunately not to obtain the spatial distribution of ΔC(anth) in this region. Thus comparing the estimation of oceanic anthropogenic carbon between the ΔDIC-ΔAOU approach and the tracer dating approach, and
consequently confirming the validity of the tracer dating approach for estimating C(anth) in the sea ice formation region, it is possible to elucidate the spatiotemporal distribution of C(anth) in this region by using the tracer dating approach.

We here tried to estimate C(anth) derived from the tracer dating approach [Watanabe et al., 2000; McNeil et al., 2003] in the Okhotsk Sea, and compare this value with ΔC(anth) of the ΔDIC-AAOU approach [Wakita et al., 2003]. Furthermore, we tried to clarify the decadal change of C(anth) and the change in the efficiency of oceanic absorption of anthropogenic carbon (EF) in this region.

2. Data and Methods

On the R/V Professor Khromov, we obtained the samples of hydrographic chemical properties from 0 m to 2000 m at 18 stations for SF6, at 34 stations for total alkalinity (TA) and DIC, and 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 the Okhotsk Sea (Figure 1a). Using 10-liters X-Niskin bottles equipped with a CTD, we drew sea water samples into a 1200 ml glass bottle for SF6, which kept the air-tighten condition. The bottles were stored during the cruise at room temperature and the content of SF6 was measured immediately after the cruise by GC-ECD following the procedure introduced by Watanabe et al. [2003]. The precision of analysis for replicate water samples was usually less than 0.05 fmol kg⁻¹ (fmol = 10⁻¹⁵ mole) for SF6. The North Pacific water below 3000 m depth should be still free of SF6 [Watanabe et al., 2003]. Since the deep water samples of the North Pacific obtained in this sampling method showed average of 0.05 fmol kg⁻¹, we thus made a blank correction by subtracting this value from the measurement values for the Okhotsk Sea. We also used the gravimetric standard gas of SF6 in a 1 µm mesh ground aluminum cylinder with N2 (Nihon Sanso Co. Ltd.) [Watanabe et al., 2003]. The details of the other hydrographic chemical parameters were shown in Watanabe et al. [2009]. In addition, we used the data sets of CFC-11 and CFC-12 in 1993 and 1999 [Wong et al., 1998; Yamamoto-Kawai et al., 2004] with other hydrographic parameters in this region (Figure 1a), which were obtained to clarify the detailed structure of the water masses in this region.

In order to estimate C(anth) in the Okhotsk Sea by using the tracer dating approach, it is necessary to consider the chemical transient tracers’ atmospheric time histories (Figure 1b) and their solubility. In the observation of 1993, CFC-11 data set was available due to the highest oceanic concentration among CFC-11, CFC-12 and SF6. After the middle of 1990s, since the atmospheric concentration of CFC-11 had been declining, CFC-11 data could not be used. Thus, in the observation of 1999, CFC-12 data set was actually available. After 2000s, since it is hard to use CFC-12 due to the decline of its atmospheric concentration, only SF6 could be used to carry out the tracer dating of water mass. The difference in tracer dating among these different chemical transient tracers was less than five years after 1970s [Watanabe et al., 2003]. Therefore, we used the data sets of CFC-11 in 1993, CFC-12 in 1999 and SF6 in 2006 to estimate ΔC(anth) in the Okhotsk Sea.

ΔC(anth) during any period (Δt) after the preindustrial period was estimated according to Watanabe et al. [2000] in the following equation:

\[
\Delta C_{\text{anth}} \left[ \text{µmol kg}^{-1} \text{ year}^{-1} \right] = \left[ C_{eq\left[S, \theta, T_A^0, fCO_2\left(S_0, \theta, T_A^0\right)\right]} - C_{eq\left(S, \theta, T_A^0, fCO_2\left(S_0, \theta, T_A^0\right)\right)} \right] / \Delta t
\]

where \( C_{eq} \) is the oceanic carbon content at the air-sea equilibrium condition, which is expressed as a function of \( S \) (salinity), \( \theta \) (potential temperature), \( T_A^0 \) (preformed total alkalinity) and \( fCO_2 \) (fugacity of atmospheric CO2). \( t \) and \( \tau \) are the sampling date, and the elapsed time since the water mass lost contact with the atmosphere based on the tracer dating approach, respectively. In order to estimate the annual amount of \( \Delta C_{\text{anth}} \), we chose 1 year as \( \Delta t \). In addition, we derived an empirical equation of \( T_A^e \) in the Okhotsk Sea from all the hydrographic data sets of 1993, 1999 and 2006 above 60 m depth as the following multiple regression:

\[
T_A^e\left[ \text{µmol kg}^{-1} \right] = 45.56 S + 1.453 \theta + 0.110 NO + 686.7.
\]

(2)

where \( R^2 \), RMSE and \( n \) are the coefficient of determination, the root mean standard error and the number of samples, respectively. NO is the index for identifying water mass (NO = DO - \( r_{DO, N} N \)) [Broecker, 1974] and \( r_{DO, N} \) is the stoichiometric ratio of DO to the fixed nitrogen. We here used -10.623 as given by Anderson and Sarmiento [1994].
Furthermore, we used the data set of CFC-11 and CFC-12 with more than 0.1 pmol kg\(^{-1}\) (pmol = \(10^{-12}\) mole) and that of SF\(_6\) with more than 0.1 fmol kg\(^{-1}\) as higher concentrations compared to these detection limits, since the mixing effect probably leads to larger uncertainty of \(\Delta C_{\text{(anth)}}\) in the water mass having the tracer content near zero. The difference of tracer dating among CFC-11, CFC-12 and SF\(_6\) led the overall error of \(\Delta C_{\text{(anth)}}\) to be within 0.1 pmol kg\(^{-1}\) year\(^{-1}\).

3. Results and Discussion

3.1. Oceanic Uptake Rate of Anthropogenic Carbon in the Okhotsk Sea

During 1993 and 1999, we found that \(\Delta C_{\text{(anth)}}\) around 26.6 \(\sigma_0\) was 0.9 pmol kg\(^{-1}\) year\(^{-1}\), and \(\Delta C_{\text{(anth)}}\) above 100 m in the northern part of Okhotsk Sea with the sea ice formation was 0.7 pmol kg\(^{-1}\) year\(^{-1}\), respectively, (Figures 2a & 2b), which were almost consistent with the previous values of \(\Delta C_{\text{(anth)}}\) for the intermediate and surface waters that estimated from the DIC-AOU approach [Wakita et al., 2003]. In addition, the water column inventory of \(\Delta C_{\text{(anth)}}\) in this region amounted to about 10 g-C m\(^{-2}\) year\(^{-1}\), which also agreed to the estimation from DIC-AOU [Wakita et al., 2003]. These consistency between the tracer dating approach and the DIC-AOU approach suggested the air-sea disequilibrium to be small and almost equilibrium in this region, indicating that it is possible to use the tracer dating approach to estimate the spatial distribution of \(\Delta C_{\text{(anth)}}\) at least in the Okhotsk Sea.

![Figure 2](http://odv.aw.de). Figure 2. Oceanic uptake rate of anthropogenic carbon (\(\Delta C_{\text{anth}}\), pmol kg\(^{-1}\) year\(^{-1}\)) in the Okhotsk Sea. (a) 1993; (b) 1999; (c) 2006. Color and line contours are \(\Delta C_{\text{anth}}\) and the water depth (m), respectively. We used the Ocean Data View to draw these figures [http://odv.aw.de].

3.2. Change in the Efficiency of Oceanic Absorption of Anthropogenic Carbon in the Okhotsk Sea

Even if \(E\)F decline, it is possible that \(\Delta C_{\text{(anth)}}\) increases due to the increase of atmospheric \(CO_2\) with time. For estimating the change of \(E\)F, it is necessary to exclude the influence of the increasing atmospheric \(CO_2\) on \(\Delta C_{\text{(anth)}}\). We here carried out the following procedures. Assuming \(\tau\) in 1993 to be constant with time and giving the atmospheric \(CO_2\) concentrations in 1999 and 2006, we estimated the expected distribution of the oceanic uptake rate of anthropogenic \(CO_2\) (\(\Delta C_{\text{(anth)}}\) \(\text{exp}\)) and that in 2006. Dividing the actual \(\Delta C_{\text{(anth)}}\) by \(\Delta C_{\text{(anth)}}\) \(\text{exp}\), we estimated the changes of \(E\)F in 1999 and 2006 compared to \(E\)F in 1993 (Figure 3). The change in \(E\)F of more than 1 means an increase of the efficiency of oceanic absorption of...
anthropogenic carbon compared to 1993. On the contrary, the change in EF of less than 1 does a decline of the efficiency of oceanic absorption.

[12] EF above 27.0 $\sigma_\theta$ corresponding to the center of NPIW gradually increased with time from 1993 to 2006 while EF below 27.0 $\sigma_\theta$ decreased. In 2006, EF above 27.0 $\sigma_\theta$ increased by 1.4, and EF below 27.0 $\sigma_\theta$ declined by 0.6, suggesting that EF in the shallower layer was reinforced in the past thirteen years. One of the most suitable possibility to cause the increase of EF in the shallower layer is that the decline of water mass production derived from recent ocean warming in this region [Nakanowatari et al., 2007] may cause the weakening of penetration of DSW into the deeper ocean interior, and EF in the shallower layer consequently increased with the decline of EF in the deeper layer. As similar to the change of ventilation system in this region, in the Japan Sea, the slowdown of the bottom-water formation with an enhancement of intermediate water formation has been reported [Gamo, 2011; Park et al., 2008].

[13] Even if EF increased in the shallower layer, it is necessary to consider how EF changed in the entire water column of the Okhotsk Sea. We here estimated the time evolutions of EF in the shallower layer (26.4 $\sigma_\theta$ - 27.0 $\sigma_\theta$), the deeper layer (27.0 $\sigma_\theta$ - 27.6 $\sigma_\theta$) and the entire water column of the Okhotsk Sea with considering the thickness of water mass (Figure 4). During the period from 1993 to 2006, EF in the shallower layer increased by 16 % while EF in the deeper layer decreased by 27 %. Consequently, EF in the entire water column decreased by 14 %, indicating that EF in the entire Okhotsk Sea continued to weaken in an annual rate of about 1% from 1993.

[14] Our assumption for evaluating the change of EF was only that $t$ in 1993 was constant with time. Thus the changes of other hydrographic parameters may contribute to the change of EF. In Eqn. (1) for estimating $\Delta T(A_{\text{arb}})$ we found the decadal increase of $T(A)$ in the shallower layer, which was almost equivalent to the actual increase of EF above 27.0 $\sigma_\theta$. Watanabe et al. [2009] reported the recent increase of TA by 1.4 mmol year$^{-1}$ above 27.0 $\sigma_\theta$ in the Okhotsk Sea, which was derived from the increase of TA in the Amur River of which the catchment area is the tenth largest in the world. The increase of TA can explain 92% of the increase of EF above 27.0 $\sigma_\theta$ indicating that the increase of TA with the weakening of DSW penetration caused the increase of EF in the shallower layer of this region. On the other hand, the decline of EF below 27.0 $\sigma_\theta$ can not be explained by the other hydrographic changes except the weakening of water ventilation in the Okhotsk Sea. Therefore, we concluded that the decline of water mass production derived from recent ocean warming in this region caused the weakening of penetration of DSW and the decline of EF in the deeper layer by 27 % while the increase of TA in the shallower layer mitigated the decline of EF, which led to the entire decrease of EF by 14 % in the Okhotsk Sea in the period from 1993 to 2006.

[15] In the North Pacific subpolar region where is located downstream from the Okhotsk Sea, EF has already decreased by 10 % from 1980s to 1990s [Watanabe et al., 2001]. In the Japan Sea as a marginal sea with the overturning circulation system that is similar to the Okhotsk Sea, no penetration of anthropogenic carbon into the deeper ocean interior was found in the past decade due to considerable slowing of water ventilation although EF did not be estimated quantitatively [Park et al., 2008]. The slowdown of overturning circulation system in the other marginal seas and/or the downstream regions would enable anthropogenic carbon to penetrate only into shallower layers, which consequently may prevent the accumulation of anthropogenic carbon into the deeper ocean interior. In order to elucidate whether EF declines over the whole ocean, further study on the ocean carbonate cycle in other overturning circulation systems will allow us to evaluate the extent of future change in oceanic absorption of anthropogenic carbon.

[16] Acknowledgments. We would like to express our gratitude to A. Scherbinin, S. Yarosh (FERHR, Russia), Y. Volkov (HYDORMET, Russia) and M. Wakatsuchi (Hokkaido Univ.). We also extend our profound thanks to anonymous reviewers for their fruitful comments.

References


