Oceanic Suess effect of $\delta^{13}C$ in subpolar region: The North Pacific

Takayuki Tanaka, Yutaka W. Watanabe, Shuichi Watanabe,¹ and Shinichiro Noriki
Graduate School of Environmental Earth Science, Hokkaido University, Sapporo, Hokkaido, Japan

Nobuo Tsurushima
National Institute for Environmental Studies, Tsukuba, Ibaraki, Japan

Yukihiro Nojiri
National Institute for Environmental Studies, Tsukuba, Ibaraki, Japan

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[1] We propose a simple approach for estimating the recent oceanic Suess effect of $\delta^{13}C$ in the subpolar region of the North Pacific, an area which experiences a large seasonal variability of carbonate species, due to the biological activity and vertical water mixing. This approach is based simply on time-series data of $\delta^{13}C$ from July 1997 to July 2001 and an equation of the Fourier sine expansion. Applying our approach to the fixed sampling location in the western North Pacific, station ‘KNOT’, we estimated values of $-0.012\%_o - 0.016\%_o$ for the Suess effect of $\delta^{13}C$ with an amplitude of $1.3\%_o$ and $1.0 \mu$mol-C kg$^{-1}$ with an increase rate of dissolved inorganic carbon with an amplitude of $134 \mu$mol-C kg$^{-1}$ in surface water. The Suess effect of $\delta^{13}C$ in this region was a similar value to that estimated in the Southern Ocean producing the deep water, while it was half as much as values estimated in the subtropical regions which experience a small seasonal variability. The ratio of Suess effect to the increase rate of dissolved inorganic carbon was $-0.012\%_o$ (1 mol km$^{-1}$)$^{-1}$, which was different from the global mean values calculated by recent modeling study. Therefore, we conclude that the Suess effect of $\delta^{13}C$ in the polar and subpolar regions is generally smaller than found in other regions, suggesting that it is necessary to reevaluate the uptake rate of anthropogenic carbon which has been based on the assumption that the ratio is uniform over the entire ocean.


1. Introduction

[2] The anthropogenic CO$_2$ released to atmosphere, such as from the burning of fossil fuels and deforestation, is depleted in the heavier carbon stable isotope because of the preferential uptake of $^{12}C$ during photosynthetic utilization of CO$_2$ by plants. Anthropogenic CO$_2$ has therefore decreased the $\delta^{13}C$ of atmospheric CO$_2$ [Friedli et al., 1986]. This decrease also affects the oceanic $\delta^{13}C$ of dissolved inorganic carbon (DIC) through the gas exchange between the atmosphere and ocean and is recognized as the oceanic Suess effect of $\delta^{13}C$ [Böhm et al., 1996]. Hereafter we refer to S-$\delta^{13}C$ as the Suess effect of $\delta^{13}C$.

[3] The accumulation rate of oceanic anthropogenic carbon has recently been estimated by using the oceanic S-$\delta^{13}C$ [Quay et al., 1992; Tans et al., 1993; Bacastow et al., 1996; Heimann and Maier-Reimer, 1996; Keir et al., 1998; Gruber and Keeling, 2001; Quay et al., 2003]. The method used in most cases was to compare the $\delta^{13}C$ of DIC between cruises with sufficient time intervals to allow resolution of the relatively small long-term $\delta^{13}C$ decrease. In this way, it has hardly been considered that the $\delta^{13}C$ in the ocean has seasonal variability, when S-$\delta^{13}C$ is estimated. On the other hand, the lack of sufficient high quality historical $\delta^{13}C$ data has caused difficulty in obtaining exact estimation of S-$\delta^{13}C$. To overcome the problems, long time-series observations have been carried out since late 1980s in the subtropical region as Bermuda (BATS; 31°50’N, 64°10’W) and Hawaii (HOT; 22°45’N, 158°00’W). Long-time series observations including measurement of carbon specise, however, have only been carried out at these two subtropical stations over the world oceans.

[4] Heimann and Maier-Reimer [1996] concluded that the oceanic penetration depth of $^{12}C$ and $^{13}C$ derived from anthropogenic CO$_2$ should be the same, because the anthropogenic time histories of $^{12}C$ and $^{13}C$ have been similar after preindustrial era. Using a three-dimensional model, they estimated the ratio of S-$\delta^{13}C$ to the increase rate of DIC ($\Delta l$) as $^{12}C$ (dynamic constraint ratio, D) to be a constant value of $0.016\%_o$ (1 mol km$^{-1}$)$^{-1}$ in the world ocean. However, the equilibration time of $\delta^{13}C$ and DIC between atmosphere and ocean surface differ by one order of magnitude. Consequently, it is possible that the difference in the residence time of surface water mass causes the spatial variability of D. In fact, McNeil et al. [2001] reported that in the Southern Ocean, D ranged from $-0.015\%_o$ to $-0.007\%_o$ (1 mol km$^{-1}$)$^{-1}$, which is smaller than the value by Heimann and Maier-Reimer [1996]. McNeil et al. [2001], however, compared only the snap shot data sets with a decadal time scale such as the GEOSECS data set in the 1970s and the WOCE data set in the 1990s without considering any seasonal variability. Therefore, whether this
lower ratio actually occurs in the short residence time of subpolar and polar waters remains contentious.

[5] We here propose a simple approach for estimating the recent oceanic S-δ13C in the subpolar region using the high quality time-series data set of δ13C from July 1997 to July 2001 and an equation of the Fourier sine expansion. We applied the approach to a new time-series station KNOT in the western North Pacific subpolar region, and tried to clarify whether the value for D is uniform over the world ocean or not, and whether a lower D occurs in the polar and subpolar regions.

2. Sampling and Methods

[6] Time-series observations have been carried out from July 1997 to July 2001 at the station, ‘KNOT’, mainly by three research vessels: T/S Hokusei Maru, R/V Bousei Maru and R/V Mirai. Station KNOT is located at 44°N, 155°E in the southwestern part of the North Pacific subpolar region. Seawater samples for 13C analysis were collected in 100 ml glass bottles, immediately poisoned with saturated solution of HgCl2 after sampling, and stored under refrigeration in the dark. In the laboratory, the CO2 gas samples for δ13C were extracted from the sea water by using the modified method of Kroopnick [1974], and were measured using a mass spectrometer (Finnigan MAT, Delta S). The unit is expressed as the per mil deviation of the 13C to 12C isotopic ratio relative to PDB standard material. The precision of δ13C measured for replicated analysis (n = 9) was less than ±0.02‰. We also found the variability of δ13C among the different cruises to be 0.02‰-0.13‰. Comparing the values of DIC below 3000 m water depth in six cruises. To confirm the consistency of data during the observational period, we compared the values of δ13C between 1999 and 2003 for the duplicated water samples collected in 1999, which showed that the variability was within ±0.02‰-0.13‰ (n = 5).

[7] The content of DIC was determined by the method described in the handbook of DOE [1994] with a newly developed automatic DIC titration system [Tsurushima et al., 2002]. We corrected the content of DIC by using the certified reference materials provided by A. Dickson, Scripps Institute of Oceanography, and consequently we estimated 0.1% as the variation of DIC. While we also developed automatic DIC titration system [Bousie et al., 1994] and consequently we estimated 0.1% as the variation of DIC. We also found the variability of DIC among the different cruises to be 0.2% mol-C kg⁻¹. Comparing the values of DIC below 3000 m water depth in each cruises, we have used all our data without any correction of bias in δ13C and DIC in this study.

[8] Because station KNOT is located just north of the subarctic front [Kono, 1997], high salinity-water mass derived from the subarctic region sometimes penetrates into the area of station KNOT. High-salinity waters (>33.2) were observed four times in surface water at KNOT (on 26 June in 1998, 10 May in 1999, 5 June in 1999 and 22 July in 1999) [Tsurushima et al., 2002], and we did not use this data set during the periods.

3. Results and Discussion

3.1. The Seasonal Change of δ13C at Station KNOT

[9] For the δ13C obtained in surface water at station KNOT, we found that a maximum occurs in July and a minimum in February, and the amplitude between February and July approximates 1.2‰-1.3‰. The difference of δ13C in the high latitude based on the time-series data was first observed amplitude, which agreed with the shot snap data in a previous study [Quay et al., 2003].

[10] Based on the model calculation for the oceanic condition at station KNOT [Fujii et al., 2002], the water mixed-layer generally reaches a maximum in March and the nutrient concentrations in surface water reach minima in the early October. The δ13C in surface water may become a minimum in March due to the supply of lower δ13C from deep water to surface and a maximum in October due to the high biological activity. It is possible that the amplitude of δ13C in the surface water is underestimated due to the lack of data in March and early October.

[11] Thus, we used the following simple equation to evaluate the actual amplitude of δ13C based on our data, assuming on the annual oceanic seasonal cycle of carbon to be constant over time with the gas exchange of CO2 at air-sea interface, the biological activity in summer and the vertical mixing in winter. We here tried to apply an equation of the Fourier sine expansion to the changes of δ13C and DIC, and separated the observed changes of δ13C and DIC into a linear trend component and an oscillation component. That is

\[ x = a \cdot y + b + c \cdot \sin(2\pi(y - d)/e) \]

where x refers which of δ13C or DIC, ‘y’ is the calendar year and ‘a’, ‘b’, ‘c’, ‘d’ and ‘e’ are constants. The change of gas exchange due to the recent atmospheric CO2 increase will cause a linear trend, while the changes due to biological activity and water mixing will lead to a sinusoidal trend.

[12] We applied a least squares sine fit to the time-series data of δ13C and DIC at station KNOT in which the amplitude, phase and slope are allowed to vary in order to minimize the residuals. We estimated the amplitude to be 1.3‰-1.4‰ for δ13C and 134 μmol-C kg⁻¹ for DIC with the periodicity of 1.0 yr (Figure 1). The amplitude of DIC agreed with the previous time-series data [Wong et al., 2002]. This amplitude of δ13C from observational time-series data is the first observational based estimation at high latitude.

[13] At BATS as the fixed observational point in the North Atlantic subtropical region, the amplitudes were approximately 0.20-0.30‰ for δ13C [Bacastow et al., 1991; Gruber et al., 1999] and 35 μmol-C kg⁻¹ for DIC [Bates et al., 1996]. At HOT as in the North Pacific subtropical region, the amplitudes were 0.16‰-0.30‰ for δ13C [Gruber et al., 1999] and 15 μmol-C kg⁻¹ for DIC [Winn et al., 1994]. Both amplitudes of δ13C and DIC at KNOT in the North Pacific subpolar region are 5 to 10 times larger than the other two data sets for BATS and HOT, suggesting that the higher productivity in the subpolar region could cause larger amplitudes of δ13C and DIC.

3.2. Oceanic Suess Effect of δ13C at Station KNOT

[14] Estimating the large seasonal change of δ13C and DIC, we also simultaneously can evaluate S-δ13C as the linear trend component. We found that S-δ13C to be -0.012 ± 0.010‰ for 13C yr⁻¹ with the annual periodicity (Figure 1a, Table 1), which is the first estimation in the subpolar region by using a time-series data set.
consistent with the meridional trend of S-$\delta^{13}$C from comparison with two snapshot observational data sets between the 1970s and the 1990s in the Pacific shown by Quay et al. [2003].

[16] The extent of S-$\delta^{13}$C primary depends on the residence time of water mass at the surface. If the surface waters have a long residence time enough to equilibrate $\delta^{13}$C between the air and sea, the Suess effect can be larger and vice versa [Sonnerup et al., 1999; McNeil et al., 2001]. In the subtropical region with a long residence time due to the high stability of surface water compared to the subpolar region, both S-$\delta^{13}$C of BATS and HOT equal values calculated on the basis of the equilibration with the atmospheric $\delta^{13}$C [Quay et al., 2003]. On the other hand, S-$\delta^{13}$C was small at KNOT, because KNOT is located in the subpolar zone with the deep water upwelling and is an area where intermediate water is produced.

3.3. Dynamic Constraint Ratio in Subpolar Region

[17] Moreover, to estimate D, we also found that $\Delta I = 1.0 \pm 0.9$ $\mu$mol-C kg$^{-1}$ yr$^{-1}$ as the linear trend (Figure 1b, Table 1), which closely approximated the expected value under the equilibration between air and sea at KNOT [Wakita et al., 2002]. Decadal change in dissolved inorganic carbon at Station KNOT ($44^\circ$N, $15^\circ$E) in subarctic western North Pacific, submitted to the Journal of Oceanography, 2003]. In the subpolar region, $\Delta I$ was reported to be 1.32 $\mu$mol-C kg$^{-1}$ yr$^{-1}$ at BATS in the North Atlantic [Bates et al., 2002] and 1.0 $\mu$mol-C kg$^{-1}$ yr$^{-1}$ at HOT in the North Pacific [Winn et al., 1998] (Table 1).

[18] Using the decreasing $\delta^{13}$C and the increasing DIC in the subpolar and subtropical region (Stations KNOT, HOT and BATS), we found that D to be $-0.012\%$ ($\mu$mol kg$^{-1}$)$^{-1}$ $[-0.012\%\cdot\delta^{13}$C yr$^{-1}/1.0$ $\mu$mol-C kg$^{-1}$ yr$^{-1}$] at KNOT in the subpolar region, $-0.018\%$ ($\mu$mol kg$^{-1}$)$^{-1}$ at BATS and $-0.025\%$ ($\mu$mol kg$^{-1}$)$^{-1}$ at HOT in subtropical region (Table 1). The recent model calculation results of Heimann and Maier-Reimer [1996] demonstrated that the averaged D over the global ocean was $-0.016\%$ ($\mu$mol kg$^{-1}$)$^{-1}$. We thus suggest that D in the subpolar region is lower than in the subtropical region and is not a constant value over the entire ocean, and that the spatial variation in D could yield under- and/or over-estimations of the oceanic anthropogenic carbon uptake if the constant value of D was used to estimate the oceanic anthropogenic carbon uptake. Our study indicates

Table 1. Comparison of the Estimations for the Suess Effect of $\delta^{13}$C (S-$\delta^{13}$C), the Increase Rate of DIC ($\Delta I$) and the Dynamic Constraint Ratio (D)

<table>
<thead>
<tr>
<th>&lt;Observational time-series data&gt;</th>
<th>Suss effect (S-$\delta^{13}$C) ($%$ of $\delta^{13}$C yr$^{-1}$)</th>
<th>Increase rate of DIC ($\Delta I$) ($\mu$mol kg$^{-1}$ C yr$^{-1}$)</th>
<th>Dynamic constraint ratio (D) ($%$ ($\mu$mol kg$^{-1}$)$^{-1}$)</th>
<th>Remarks</th>
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</thead>
<tbody>
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<tr>
<td>subpolar</td>
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<tr>
<td>North Pacific (44°N, 155°E)</td>
<td>KNOT</td>
<td>$-0.012$</td>
<td>$1.0$</td>
<td>$-0.012$</td>
</tr>
<tr>
<td>North Atlantic (31°56’N, 64°10’W)</td>
<td>BATS</td>
<td>$-0.025$</td>
<td>$1.3$</td>
<td>$-0.018$</td>
</tr>
<tr>
<td>North Pacific (22°45’N, 158°00’W)</td>
<td>HOT</td>
<td>$-0.025$</td>
<td>$1.0$</td>
<td>$-0.025$</td>
</tr>
<tr>
<td>Global ocean</td>
<td></td>
<td>$-0.016$</td>
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</tbody>
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Figure 1. Time-series data of $\delta^{13}$C and DIC in surface water (0–10 m) at station KNOT in the western North Pacific from 1997 to 2001. The open circles and solid triangle represent the subpolar water mass and the high-salinity water mass (>33.2) derived from the subtropical water mass. The fitting curve equations applied to the $\delta^{13}$C and DIC data set in the subpolar water mass were as follow; (a) $\delta^{13}$C = $-0.012 y + 26 + 0.65 \sin (2\pi (y - 1983)/1.0)$ (R = 0.97, SE = 0.02%$\cdot\delta^{13}$C, p < 0.1). (b) DIC = 1.0 $y + 29 + 67 \sin (2\pi (y - 1960)/1.0)$ (R = 0.96, SE = 2.5 $\mu$mol-C kg$^{-1}$, p < 0.1). The solid and dash lines show the linear trend and fitted curve, respectively.

[15] The S-$\delta^{13}$C in the subtropical region are reported to be $-0.025 \pm 0.002\%$ $\delta^{13}$C yr$^{-1}$ at BATS in the North Atlantic [Bacastow et al., 1996; Gruber et al., 1999], and $-0.025 \pm 0.002\%$ $\delta^{13}$C yr$^{-1}$ at HOT in the North Pacific [Gruber et al., 1999] (Table 1). The S-$\delta^{13}$C at KNOT was only half as much as those at two time-series stations in the subtropical region. This subtropical/subarctic difference is
that it is necessary to reevaluate the oceanic uptake of anthropogenic carbon because the assumption of D being uniform over the ocean is suggested not to be valid for the subpolar region.

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References


