Improved Method for Calculating Anthropogenic CO₂ in the Upper Layer of the North Pacific Subtropical Gyre along 175°E

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Seawater samples were collected in the North Pacific along 175°E during a cruise of the Northwest Pacific Carbon Cycle Study (NOPACCS) program in 1994. Many properties related to the carbonate system were analyzed. By using well-known ratios to correct for chemical changes in seawater, the CO₂ concentration at a given depth was back calculated to its initial concentration at the time when the water left the surface in winter. We estimated sea-surface CO₂ and titration alkalinity (TA) in present-day winter, from which we evaluated the degree of air-sea CO₂ disequilibrium in winter. Using a correction factor for air-sea CO₂ disequilibrium in winter, we reconstructed sea-surface CO₂ in pre-industrial times. The difference between the back-calculated initial CO₂ and sea-surface CO₂ in pre-industrial times should correspond to anthropogenic CO₂ input. Although the mixing of different water masses may cause systematic error in the calculation, we found that the nonlinear effect induced by the mixing of different water masses was negligible in the upper layer of the North Pacific subtropical gyre along 175°E. The results of our improved method of assessing the distribution of anthropogenic CO₂ in that region show marked differences from those obtained using the previous back-calculation method.

1. Introduction

Carbon dioxide (CO₂) is the greenhouse gas that contributes most to global warming. The CO₂ concentration in the atmosphere has been increasing over the past two centuries due to anthropogenic CO₂ emission (Neftel et al., 1985; Friedli et al., 1986; Keeling et al., 1989). The observed increase in CO₂ concentration in the atmosphere represents only about half the anthropogenic CO₂ emissions. This implies that the other half is currently moving into the surface of the earth. The major sinks are oceans and terrestrial ecosystems. The oceans take up CO₂ by air-sea gas exchange at the surface. The flux of CO₂ depends on the difference between the CO₂ partial pressures in the atmosphere and the ocean. When the atmospheric CO₂ concentration increases, the oceanic uptake of carbon dioxide increases correspondingly. The terrestrial biosphere absorbs CO₂, but it is very difficult to make a quantitative evaluation of the uptake of anthropogenic CO₂ by the terrestrial biosphere. To predict the future level of atmospheric CO₂, a quantitative understanding of the carbon cycle is quite important. Many researchers have attempted to estimate the oceanic uptake of anthropogenic CO₂ (Tans et al., 1990; Enting and Mansbridge, 1991; Quay et al., 1992; Robertson and Watson, 1992; Sarmiento and Sundquist, 1992; Sarmiento et al., 1992; Tsunogai et al., 1993; Watanabe et al., 1996). The difficulty in estimating the uptake of anthropogenic CO₂ is due to its insignificance, compared with the natural abundance of carbon in the oceans. Further, most carbon in seawater exists as dissolved inorganic carbon (TCO₂), which undergoes chemical changes in seawater and thus makes it difficult to evaluate the net increase in TCO₂ resulting from anthropogenic CO₂ input.

The back-calculation method is one of the strategies used to separate anthropogenic CO₂ signals from observed TCO₂ data having a large natural variation (Brewer, 1978; Chen and Miller, 1979; Chen and Pytkowicz, 1979; Chen, 1982, 1993). By correcting for the change in CO₂...
due to both remineralization of organic matter and dissolution of CaCO₃, one can back calculate observed TCO₂ to its initial concentration at the time when the water lost contact with the atmosphere (TCO₂₀). Consequently the increase in TCO₂ due to anthropogenic CO₂ input can be determined as the difference between back-calculated initial TCO₂ (TCO₂₀) and that estimated for the pre-industrial times (TCO₂₀_preind). We introduce the computational details of the method in the following sections. One of the major problems with this method is the mixing of different water types. The mixing of waters with poorly known initial concentrations can cause large uncertainty in the results given by the method (Shiller, 1981). If we can determine the appropriate initial concentrations and the mixing ratio of each end-member, the error induced by mixing can be excluded.

Choice of the appropriate TCO₂₀_preind is an important subject. Gruber et al. (1996) suggested an improved method that was not affected by this problem. However, the spatial coverage of their estimation was insufficient and the oceanic uptake of anthropogenic CO₂ remains unknown, for example, in the North Pacific. Because the water mass structure of the North Pacific is quite complicated, careful consideration is necessary in using the back-calculation method for this region.

Observational data obtained during the Northwest Pacific Carbon Cycle Study Program (NOPACCS) showed that a large part of the water between 42°N and 16°N above a depth of 300 m is considered to be generated from simple mixing of end-members originating in the surface of this region. We therefore focused on this region and attempted to apply the back-calculation method in this study. We chose an area of water in which were preserved the initial concentrations at the time when the water left the surface in the winter just before the observations. Using the data from this area of water, we determined initial TA (TA₀) and TCO₂₀, and then evaluated the degree of air-sea CO₂ disequilibrium at the sea surface in winter. Using the correction for air-sea CO₂ disequilibrium, we reconstructed TCO₂₀_preind with thermodynamic equations. In this area of water, because we could determine the initial concentrations of those end-members, we were able to provide reliable estimates of oceanic CO₂ increase by the back-calculation method as improved in this study.

2. Source of Data

The data we used in this study were collected during cruise NH94-1 (April to May 1994) aboard the R/V Hakurei-maru. The observation cruises were conducted as part of the NOPACCS program. The sampling locations are shown in Fig. 1. NOPACCS has been operating in the North Pacific along 175°E since 1990. During the NOPACCS NH94-1 cruise, samples were collected to a depth of around 300 m at most stations. Samples from deeper than 300 m were collected at a limited number of

Fig. 1. Sampling locations in the Pacific Ocean along 175°E.
Fig. 2. Profiles of (a) potential temperature, (b) salinity and (c) $\sigma_\theta$. 

Anthropogenic CO$_2$ Calculation
stations. We therefore focused on the region above about 300 m in the following discussions. Profiles of potential temperature, salinity and potential density (σθ) are shown in Fig. 2.

3. Measurements

Seawater samples for the analysis of dissolved O₂, TA, and TCO₂ were collected at all the stations with 12-L Niskin bottles (General Oceanics, Florida). Dissolved O₂ was determined on board the ship using the Winkler titration procedure with an automated titrator. The precision of dissolved O₂ measurements was usually 0.2 µmol·kg⁻¹. TA was measured using an automated potentiometric titration system with an open titration cell. The analytical precision of TA was estimated to be 0.3% c.v. and the accuracy was uncertain. Samples for TCO₂ measurements were collected in 100-mL glass bottles and placed in a refrigerator until measured to minimize biological activity. About 30 min before measurement, the sample bottles were placed in a water bath to bring the sample temperature to analytical conditions. TCO₂ was determined on board the ship using a modified gas chromatographic method (GC) (Weiss and Craig, 1973; Gamo and Horibe, 1980). Most of the samples were measured on the day of sampling. The precision of TCO₂ analysis was estimated to be approximately 0.2% c.v. for replicate seawater samples. The TCO₂ was calibrated against Na₂CO₃ solutions of four concentrations prepared gravimetrically. Measurement of TCO₂ in certified reference material (CRM) distributed by Dr. A. G. Dickson of the Scripps Institute of Oceanography was conducted during a NOPACCCS cruise in April to May 1995, using the same analytical method as in this study. According to the results, TCO₂ determined by our GC system was about 9 µmol·kg⁻¹ lower than that certified for the reference material. Although the TA and TCO₂ data probably contain some bias, the bias would provide an insignificant effect in the anthropogenic CO₂ signal calculated by the method that we use in the following section. In this study we have therefore not applied any correction to the TA and TCO₂.

4. Method

4.1 Conceptual aspects of the previous back-calculation method

Back calculation is one of the strategies used to determine the increase in TCO₂ from observational data. The concept of the back-calculation method is summarized as follows (Chen, 1982):

\[
\text{excess} \text{TCO}_2 = \text{TCO}_2^0 - \text{TCO}_2^0 \text{preind} = \text{TCO}_2 - \Delta \text{TCO}_2,\text{carb} - \Delta \text{TCO}_2,\text{org} - \text{TCO}_2^0 \text{preind} = \text{TCO}_2 - 0.5(\text{TA} - \text{TA}^0) - \text{R} \cdot \text{AOU} - \text{TCO}_2^0 \text{preind} \ (1)
\]

where excessTCO₂ is a measure of increase in TCO₂ due to anthropogenic CO₂ input; superscript 0 represents the initial concentration at the time when the water lost contact with atmosphere; TCO₂, TA and O₂ represent observed concentrations; TCO₂^0 preind is the initial TCO₂ for the water formed in the pre-industrial times; ∆TCO₂,carb is the TCO₂ change derived from production and dissolution of CaCO₃; ∆TCO₂,org is the TCO₂ change derived from net production and remineralization of organic matter; AOU is apparent oxygen utilization, defined as the difference between the measured value of O₂ and the saturation value of O₂; and R is the appropriate stoichiometric ratio for carbon remineralization to oxygen utilization. Since TCO₂^0 preind cannot be determined directly from observational data, TCO₂^0 preind was replaced by the initial TCO₂ value in the present-day sea surface (TCO₂^0 present) by subtracting a constant quantity, i.e. TCO₂^0 preind = TCO₂^0 present – C. Here C represents the quantitative change in surface TCO₂ between present-day and the pre-industrial times. Assuming that the deep water has not been affected by the anthropogenic CO₂ input, C was determined as the difference between TCO₂^0 present and TCO₂^0 in the deep water. In the calculations, all quantities except AOU were normalized to a salinity of 35. TCO₂^0 present and TA^0 were given by linear functions of potential temperatures formulated from the temperature relationships of TCO₂ and TA at the present-day sea surface.

4.2 Major problems with the previous method

4.2.1 Mixing of water masses

One of the major problems in this method is the mixing of the original water parcel with seawater of different origin and with different initial values (Shiller, 1981). In previous studies, to minimize the mixing problem, TCO₂ and TA were normalized to salinity and then correlated with temperature. Generally, sea-surface TCO₂ has a negative correlation with temperature because the solubility of CO₂ is higher at lower temperatures. If we can formulate salinity-normalized values of both TCO₂ and TA at the sea surface in single linear functions with temperature, mixing will not introduce errors into the calculations.

Chen (1982) formulated temperature relationships for both TCO₂^0 present and TA^0 in the North Pacific based on observational data from the Geochemical Ocean Section Study (GESECS) in 1973 and 1974. Those temperature relationships reflect a complex interplay of many factors, such as biological activity, air-sea gas exchange and temperature change, and thus probably have large spatial variations. If we can determine the mixing ratio and the appropriate initial concentrations of all the end-members, the back-calculation method will provide reliable estimates of excessTCO₂. However, the lack of knowledge...
about the mixing process and the origin of water masses has made it difficult to determine appropriate $T\text{CO}_2^0$ and $T\text{A}^0$ for many regions of the oceans.

4.2.2 Summer-winter incompatibility in temperature relationships of surface $T\text{CO}_2$ and $T\text{A}$

To estimate excess $T\text{CO}_2$ by the back-calculation method, we must determine the initial concentrations of end-members in pre-industrial times as a linear function of temperature. In previous studies, most data used in determining the relationship between surface $T\text{CO}_2$ and temperature were collected during summer conditions because observations during winter are difficult due to rough weather conditions, especially in high latitude areas. As research in this field progressed, some researchers (Takahashi et al., 1993; Inoue et al., 1995) reported that the relationship between surface $T\text{CO}_2$ and temperature in the surface mixed layer of the North Pacific had a large seasonal variation. The sinking water should reflect the condition in winter because vertical mixing is enhanced by diminishing of the seasonal thermocline during winter. Therefore, to estimate the excess $T\text{CO}_2$ correctly, the relationship between temperature and surface $T\text{CO}_2$ should be determined based on the winter condition. The seasonal change in this relationship has probably provided a large systematic error in previous estimates. We plotted $T\text{CO}_2$ against temperature at the sea surface (<100 m depth) in the northern part of the North Pacific subtropical gyre (NPSG) between 42°N and 21°N along 175°E during both spring and summer (Fig. 3). The least-squares fit lines for each condition are also shown in Fig. 3, together with the relationship that Chen (1982) suggested for the northwestern Pacific. Although some bias probably exists among those data since we did not apply any corrections to them, the considerable difference in the slopes of the least-squares fit lines implies that the results of this method will contain a large systematic error unless the seasonal changes in surface waters are taken into account.

4.2.3 Determining appropriate initial concentrations in the pre-industrial times

Another point at issue is the shift in values of surface $T\text{CO}_2$ caused by the increase in atmospheric $\text{CO}_2$ fugacity ($f\text{CO}_2$). We computed $T\text{CO}_2$ values for two $f\text{CO}_2$ values, 360 and 280 µatm, with a constant $T\text{A}$ of 2300 µeq·kg$^{-1}$ and salinity of 35, assuming equilibrium between seawater and the atmosphere, and plotted them against temperature (Fig. 4). The difference between the $T\text{CO}_2$ values calculated for the two different $f\text{CO}_2$ values is also shown in Fig. 4. The results of the computation suggest that warmer water can take up more $\text{CO}_2$ than colder water as atmospheric $f\text{CO}_2$ increases. When atmospheric $f\text{CO}_2$ increases from 280 to 360 µatm, seawater at 25°C absorbs about 9 µmol·kg$^{-1}$ more $\text{CO}_2$ than at 10°C. This

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**Fig. 3.** Seasonal variation of (a) $T\text{A}$ and (b) $T\text{CO}_2$ observed above a depth of 100 m. Solid circles represent the data obtained during summer observations; open circles are the data obtained during spring observations. The solid line represents the least-square fit line based on summer data; the dotted line represents that based on spring data; the hashed line was suggested by Chen (1982).

**Fig. 4.** (a) $T\text{CO}_2$ calculated from $T\text{A}$ of 2300 µeq·kg$^{-1}$ and salinity of 35 psu for two different $f\text{CO}_2$ values, 280 and 360 µatm. (b) The difference between $T\text{CO}_2$ calculated for $f\text{CO}_2$ at 280 and 360 µatm.
effect was not addressed in the previous method (e.g. Chen, 1982). It therefore provided systematic errors in estimates of excess TCO$_2$.

4.3 The improved method

Although the previous back-calculation method has provided a general approximation of TCO$_2$ increases over broad areas of the oceans, many details of the TCO$_2$ increase are still uncertain because of the problems mentioned above. By focusing on a limited area, we attempted to provide more reasonable estimates of TCO$_2$ increase. First, we chose an area of water in which complications caused by the mixing of different water masses were negligible. Second, we determined the appropriate relationships for the study area between TCO$_2^{0}$$_{\text{preind}}$ and TA$^{0}$ in winter and temperature. Third, we evaluated the degree of air-sea CO$_2$ disequilibrium in winter and reconstructed TCO$_2^{0}$$_{\text{preind}}$ by using a correction for air-sea disequilibrium. Finally, we estimated excess TCO$_2$ by the improved method.

4.3.1 Choosing the study area

The water in a region of the ocean where the potential temperature-versus-salinity diagram (T-S diagram) is linear, is generally formed by simple mixing of two end-members; nonlinear effects resulting from the mixing of different water masses can be ignored. There is thus no need to normalize both TCO$_2$ and TA to salinity. If we know the appropriate values of TCO$_2^{0}$$_{\text{preind}}$ and TA$^{0}$ of the end-members in pre-industrial times, we can estimate excess TCO$_2$ in the water using Eq. (1). The T-S diagram for the north-south section between 48°N and 15°S along 175°E is shown in Fig. 5. In one area (Table 1), the T-S relationship was almost linear and this area was chosen for study.

Generally, the depth of the surface mixed layer reaches a maximum of around 100 m in winter. Hence, the water above that depth should have exchanged CO$_2$ in the winter just before the observations. Accordingly, we divided the study area into two parts at a depth of 102 m. The T-S diagrams of these areas are shown in Fig. 6. The relationship between potential temperature and salinity agreed almost perfectly with a single mixing line all over the study area and there was no difference between the upper and lower parts. Thus, we considered that the water in the whole area was formed by simple mixing of the common end-members and was not affected by seasonal heating. Hereinafter, we use the term “remnant water” to refer to the upper part of the area.

![Fig. 5. T-S diagrams for the water observed during cruise NH94-1.](image-url)
4.3.2 Determination of initial TA and TCO$_2$

In seawater, chemical changes resulting from biological activities affect the value of TA. TA can be expressed as follows:

$$\text{TA} = \text{TA}^0 + \Delta \text{TA}_{\text{Carb}} - \Delta \text{NO}_3$$

where $\Delta \text{TA}_{\text{Carb}}$ is the change in TA induced by production and dissolution of CaCO$_3$; and $\Delta \text{NO}_3$ is the net change in NO$_3$, as the result of production and remineralization of organic matter. To determine $\text{TA}^0$ from observed TA, corrections using both $\Delta \text{TA}_{\text{Carb}}$ and $\Delta \text{NO}_3$ are necessary.

If the stoichiometric ratio of NO$_3$ to O$_2$ during photosynthesis and remineralization is constant within a region, we can determine $\Delta \text{NO}_3$ as the product of the stoichiometric ratio and AOU. Here, we can determine $\Delta \text{NO}_3$ as follows:

$$\Delta \text{NO}_3 = R_{\text{N/O}} \cdot \text{AOU}$$

where $R_{\text{N/O}}$ is the NO$_3$-to-O$_2$ stoichiometric ratio. We used the ratio of 16±1:170±10 given by Anderson and Sarmiento (1994).

The production rate of CaCO$_3$ shells is generally less than 10% of the net primary production rate (Takahashi et al., 1993). Because net primary production remains at a low level in the NPSG throughout the year, we assumed that the effect of CaCO$_3$ production on TA change was negligible in the study area. However, because the seawater is supersaturated with respect to CaCO$_3$, dissolution of CaCO$_3$ does not occur above a depth of 300 m. We plotted $(\text{TA} + \Delta \text{NO}_3)$ against potential temperature (Fig. 7). From the fact that there was no obvious difference between $(\text{TA} + \Delta \text{NO}_3)$ in the remnant water and the water below it, we inferred that we could neglect the effect of the production and dissolution of CaCO$_3$ in the study area. Therefore, $\text{TA}^0$ can be expressed as follows:

$$\text{TA}^0 = \text{TA} + R_{\text{N/O}} \cdot \text{AOU}.$$  \hspace{1cm} (4)

As a logical consequence, the plots for remnant water in Fig. 7 represent the relationship between temperature and $\text{TA}^0$ in the winter just before the observations. $\text{TA}^0$ increases linearly with temperature. Since temperature in this region has a positive linear correlation with salinity, the linear $\text{TA}^0$-temperature relationship is due to the fact that TA is a major component of seawater and that the ratio of TA to salinity is nearly constant (Millero et al., 1998).

Although the input of anthropogenic CO$_2$ affects the degree of disequilibrium between TCO$_2$ and CaCO$_3$ in the surface water, TA would not be affected by the resulting change in surface TCO$_2$ because the water is highly supersaturated with respect to CaCO$_3$ (Gruber et al., 1996). Therefore, the $\text{TA}^0$-temperature relationship should not change with time.

### Table 1. The sampling locations that we choose to calculate excess TCO$_2$ in this study.

<table>
<thead>
<tr>
<th>Latitude ($\degree$N)</th>
<th>Sampling date</th>
<th>Depth (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>42$\degree$N</td>
<td>5/30/1994</td>
<td>102</td>
</tr>
<tr>
<td>40$\degree$N</td>
<td>5/30/1994</td>
<td>49–150</td>
</tr>
<tr>
<td>37$\degree$N</td>
<td>5/29/1994</td>
<td>21–304</td>
</tr>
<tr>
<td>33$\degree$N</td>
<td>5/27/1994</td>
<td>50–303</td>
</tr>
<tr>
<td>30$\degree$N</td>
<td>5/26/1994</td>
<td>76–304</td>
</tr>
<tr>
<td>27$\degree$N</td>
<td>5/25/1994</td>
<td>10–303</td>
</tr>
<tr>
<td>23$\degree$41′N</td>
<td>5/22/1994</td>
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<td>4/20/1994</td>
<td>102–305</td>
</tr>
<tr>
<td>19$\degree$N</td>
<td>4/21/1994</td>
<td>126–302</td>
</tr>
<tr>
<td>16$\degree$N</td>
<td>4/22/1994</td>
<td>254–303</td>
</tr>
</tbody>
</table>
Following the procedure of Chen and Pytkowicz (1979), we represented TCO$_2$ as follows:

$$\text{TCO}_2 = \text{TCO}_2^0 + \Delta \text{TCO}_{2,\text{org}} + \Delta \text{TCO}_{2,\text{carb}} \quad (5)$$

Assuming that the stoichiometric ratio in the study area is uniform and constant with time, we determined $\Delta \text{TCO}_{2,\text{org}}$ as the product of the CO$_2$-to-O$_2$ stoichiometric ratio and AOU. As mentioned above, the effect of the production and the dissolution of CaCO$_3$ is negligible in this region. Consequently, we calculated TCO$_2^0$ as follows:

$$\text{TCO}_2^0 = \text{TCO}_2 - R_{\text{C/O}} \cdot \text{AOU} \quad (6)$$

where $R_{\text{C/O}}$ is the CO$_2$-to-O$_2$ stoichiometric ratio. We used the ratio of 117±14:170±10 given by Anderson and Sarmiento (1994). TCO$_2^0$ in the remnant water should represent surface TCO$_2$ in the winter just before the observations; therefore we can regard it as TCO$_2^0$ present.

### 4.3.3 Determination of sea-surface fCO$_2$ in winter

When both temperature and salinity are known, we can calculate fCO$_2$ in the water (fCO$_2$ water) from TCO$_2$ and TA using apparent equilibrium constants for the carbonate system.

Both TA$^0$ and TCO$_2$ present were determined from the observations in the remnant water. Thus, we could determine the values of surface fCO$_2$ water (fCO$_2$ water$^0$) in the winter just before the observations. We represent them below as fCO$_2$ water present$^0$. We plotted fCO$_2$ water present against potential temperature (Fig. 8). Since CO$_2$ fugacity in the atmosphere (fCO$_2$ atm) at the time of observations was about 360 µatm, the plot implies that the level of fCO$_2$ water present$^0$ was lower than that of present-day fCO$_2$ atm all over the study area. However, there were broad minima of fCO$_2$ water present$^0$ in the temperature range 15°C to 20°C. These features are consistent with observations (Takahashi et al., 1993; Inoue et al., 1995), which supports the validity of our procedure for calculating fCO$_2$ water present$^0$.

### 4.3.4 Determining TCO$_2^0$ preind

To reconstruct TCO$_2^0$ preind, we first determined sea surface fCO$_2$ in the winter of pre-industrial times. We introduced a coefficient D as follows:

$$\text{fCO}_2^0_{\text{water}} = D \cdot \text{fCO}_2^0_{\text{atm}} \quad (7)$$

where coefficient D is a measure of air-sea CO$_2$ disequilibrium. Assuming that D is constant with changes in fCO$_2$ atm (discussed below), we determined fCO$_2$ water$^0$ from appropriate values of fCO$_2$ atm at present and at pre-industrial times as follows:

$$\text{fCO}_2_{\text{water}}^0_{\text{preind}} = D \cdot \text{fCO}_2_{\text{atm}}^0_{\text{preind}} = \left(\frac{\text{fCO}_2_{\text{water}}^0_{\text{present}}}{\text{fCO}_2_{\text{atm}}^0_{\text{present}}} \right) \cdot \text{fCO}_2_{\text{atm}}^0_{\text{preind}} \quad (8)$$

where fCO$_2$ water$^0_{\text{preind}}$ and fCO$_2$ atm$^0_{\text{preind}}$ are pre-industrial values of fCO$_2$ water$^0$ and fCO$_2$ atm, respectively. Consequently, we could determine TCO$_2^0$ preind thermodynamically by using TA$^0$ and fCO$_2$ water$^0_{\text{preind}}$. In this paper we use values of 360 µatm for fCO$_2$ atm$^0_{\text{present}}$ and 280 µatm for fCO$_2$ atm$^0_{\text{preind}}$ (Neftel et al., 1985; Friedli et al., 1986). We calculated D from fCO$_2$ water$^0_{\text{present}}$ and fCO$_2$ atm$^0_{\text{present}}$ (Fig. 9). Then we calculated TCO$_2$ preind of the remnant water thermodynamically and plotted the values against potential temperature (Fig. 10).

The validity of the assumption that D is constant with change in fCO$_2$ atm requires discussion. Seasonal variation of fCO$_2$ water$^0$ in the NPSG was discussed in detail by Inoue et al. (1995), who stated that, in general, temperature change is the dominant factor in determining seasonal variations of fCO$_2$ water$^0$. If the seasonal variation in fCO$_2$ water$^0$ is controlled only by temperature and the annual mean value of fCO$_2$ water$^0$ is equal to that of fCO$_2$ atm, Eq. (8) gives a good approximation of fCO$_2$ water$^0$ preind with an error of less than 1 µatm. Inoue et al. (1995) suggested that the effect of mixing dynamics...
and biological activity in determining seasonal variation in $f_{\text{CO}_2,\text{water}}$ is negligible south of 18°N in the western North Pacific (132°E to 142°E). In that region, we could determine $f_{\text{CO}_2,\text{water}}^{\text{preind}}$ by Eq. (8). However, they also suggested that mixing dynamics and biological activity play a relatively more important role in determining seasonal change in $f_{\text{CO}_2,\text{water}}$ north of 19°N. In such cases, values of $f_{\text{CO}_2,\text{water}}^{\text{preind}}$ determined by Eq. (8) probably contain some uncertainty.

Inoue et al. (1995) estimated that the annual growth rate of $f_{\text{CO}_2,\text{water}}$ was 1.8 ± 0.6 μatm north of 15°N, based on observations during 1984 to 1993. This rate was equal to that of $f_{\text{CO}_2,\text{atm}}$ during the same period. Assuming that $f_{\text{CO}_2,\text{water}}$ has increased with the same growth rate as $f_{\text{CO}_2,\text{atm}}$ since the Industrial Revolution, we determined $f_{\text{CO}_2,\text{water}}^{\text{preind}}$ by subtracting a constant quantity from $f_{\text{CO}_2,\text{water}}$ present as follows:

$$f_{\text{CO}_2,\text{water}}^{\text{preind}} = f_{\text{CO}_2,\text{water}}^{\text{present}} - (f_{\text{CO}_2,\text{atm},\text{present}} - f_{\text{CO}_2,\text{atm},\text{preind}}). \quad (9)$$

We calculated $T_{\text{CO}_2}^{\text{preind}}$ thermodynamically, based on Eq. (9), and plotted the values against potential temperature together with those based on Eq. (8) (Fig. 10). $T_{\text{CO}_2}^{\text{preind}}$ values based on Eq. (9) were lower than those based on Eq. (8) throughout the temperature range, and the difference between them was about 7 μmol·kg⁻¹ on average. Consequently, values of excess$T_{\text{CO}_2}$ estimated using data from Eq. (9) are about 7 μmol·kg⁻¹ higher than those based on Eq. (8). This difference is sufficiently large in comparison with excess$T_{\text{CO}_2}$ signals of 40 to 50 μmol·kg⁻¹ to demonstrate the importance of determining the effect of air-sea disequilibrium. According to Inoue et al. (1995), the growth rate of $f_{\text{CO}_2,\text{water}}$ has considerable spatial variability. Incorporation of the effect of air-sea disequilibrium in determining $T_{\text{CO}_2}^{\text{preind}}$ is a subject that requires further study. In the following discussion, we use values of $T_{\text{CO}_2}^{\text{preind}}$ based on Eq. (8).

We formulated the relationship between $T_{\text{CO}_2}^{\text{preind}}$ and potential temperature (Fig. 10) in the remnant water as follows:

$$T_{\text{CO}_2}^{\text{preind}} = 2051 - 5.89 \theta \ (±7) \quad (10)$$

where $\theta$ represents the potential temperature. The number in parentheses gives one standard deviation of the least-squares fit line of the equation.

### 4.3.5 Determining excess$T_{\text{CO}_2}$

Using the back-calculation method, excess$T_{\text{CO}_2}$ is normally determined from Eq. (1). As mentioned above, chemical changes induced by production and dissolution of CaCO₃ were negligible in the study area above a depth of 300 m between 42°N and 21°N. Thus, we rewrote Eq. (1) for the area as follows:

$$\text{excess}T_{\text{CO}_2} = T_{\text{CO}_2} - R_{\text{C/O}} \cdot \text{AOU} - T_{\text{CO}_2}^{\text{preind}} \quad (11)$$

Salinity normalization was not performed, since the water in the study area was generated from simple mixing.

### 5. Results and Discussion

#### 5.1 Vertical distribution of $T_{\text{CO}_2}$ and $T_{\text{CO}_2}^0$

The vertical profiles of $T_{\text{CO}_2}$ and $T_{\text{CO}_2}^0$ between 42°N and 21°N are shown in Fig. 11. Since the solubility of CO₂ is higher in colder water, the values of $T_{\text{CO}_2}$ and $T_{\text{CO}_2}^0$ are all greater at high latitudes. Supersaturation of dissolved oxygen due to both local heating and photosynthesis causes $T_{\text{CO}_2}^0$ to exceed $T_{\text{CO}_2}$ near the surface at all stations. Since both these effects were negligible below a depth of about 100 m, $T_{\text{CO}_2}$ exceeded $T_{\text{CO}_2}^0$ at all stations due to the addition of $T_{\text{CO}_2}$ from remineralization of organic matter. The difference between $T_{\text{CO}_2}$ and $T_{\text{CO}_2}^0$ increases with depth because the deeper water is older, and hence contains more $T_{\text{CO}_2}$ as remineralization of organic matter has proceeded for longer.

#### 5.2 Distribution of excess$T_{\text{CO}_2}$

The vertical distributions of excess$T_{\text{CO}_2}$ are shown in Fig. 12. We excluded data below the isopycnal horizon of $\sigma_θ = 26.3$, since water below this horizon would not outcrop in the NPSG. The error bar in the profile of excess$T_{\text{CO}_2}$ represents the errors in the formulation of $T_{\text{CO}_2}^{\text{preind}}$ using Eq. (11), in the stoichiometric ratios and in the $T_{\text{CO}_2}$ measurement; however, it does not include the error in the coefficient D in Eq. (8) because we cannot quantify the error in D from the existing information. The vertical distribution of excess$T_{\text{CO}_2}$ calculated by our improved method reflects not only the change of $f_{\text{CO}_2,\text{atm}}$
but also the variation in water temperature as mentioned in the previous section. To recognize the effect from the change of \( f_{\text{CO}_2, \text{atm}} \), we calculated the difference between \( \text{TCO}_2^0 \) for the two different \( f_{\text{CO}_2, \text{atm}} \) values of 360 µatm and 280 µatm with potential temperature, \( T^0 = 4.32 \theta + 2207 \), based on Fig. 7) and \( D = (1.20 - 3.51 \times 10^{-2} \theta + 9.93 \times 10^{-4} \theta^2) \), based on Fig. 9) and indicated them together with excess\( \text{TCO}_2 \). Hereafter, we call this value excess\( \text{TCO}_2^{360} \). The difference between excess\( \text{TCO}_2 \) and excess\( \text{TCO}_2^{360} \) should be greater in older water.

Between 40°N and 33°N, excess\( \text{TCO}_2 \) was at almost the same level as excess\( \text{TCO}_2^{360} \) throughout the depth range due probably to strong vertical mixing in the high latitudes and the horizontal transport of young water. South of 30°N, the water below a depth of 100 m contained less excess\( \text{TCO}_2 \) than in the north. The strong density gradient in the low latitudes probably reduced the vertical transport of excess\( \text{TCO}_2 \) there. Since the subsurface water in that region flowed southward, the more southerly water was older and hence contained less excess\( \text{TCO}_2 \) than did more northerly water.

We also calculated excess\( \text{TCO}_2 \) by the previous method (Chen, 1982). We used \( R \) in Eq. (1) and the temperature relationship between \( T^0 \) and \( \text{TCO}_2^0 \) present of Chen (1982). We determined \( \text{TCO}_2^0 \) preind by subtracting a constant quantity from \( \text{TCO}_2^0 \) present, i.e. \( \text{TCO}_2^0 \) preind = \( \text{TCO}_2^0 \) present – C. The value we assigned to C was that giving an average value of zero for \( \text{TCO}_2^0 \) present at the bottom of the AOU maximum at 30°N, 23°41′N and 21°N during the NH94-1 cruise. Hereinafter, we represent this value as excess\( \text{TCO}_2^{\text{Chen}} \). In the previous back-calculation method, even if the observed values of \( \text{TCO}_2 \) and \( T^0 \) contain some bias, it would not affect the compatibility of the results calculated from different datasets because the bias would be canceled when determining C.

The value of excess\( \text{TCO}_2 \) was smaller than excess\( \text{TCO}_2^{\text{Chen}} \) at all locations. The difference between them was larger in the north and was about 20 µmol·kg\(^{-1}\) north of 33°N. One possible source of this large difference in excess\( \text{TCO}_2 \) is a difference between the water masses at the surface and at depth. In the previous method, we determined excess\( \text{TCO}_2^{\text{Chen}} \) as the difference \( \text{TCO}_2^0 - \text{TCO}_2^0 \) present observed at any location from that observed in the deep layer. The deep water below the AOU maximum comes from the Southern Ocean. Therefore, the relationships of \( \text{TCO}_2^0 \) present and \( T^0 \) with temperature possibly differ from those at the surface of the North Pacific. That difference can cause significant error in excess\( \text{TCO}_2 \) in the upper layer. Another possibility is that the relationships of \( T^0 \) and
Anthropogenic CO$_2$ Calculation

TCO$_2$$_0$ present with temperature used in the previous method contain errors due to summer-winter incompatibility. The magnitude of these errors may possibly amount to more than 20 $\mu$mol·kg$^{-1}$, judging from Fig. 3.

Adding to these sources of error, the effect of the variable change in surface TCO$_2$ against changes in fCO$_2$,atm (Fig. 4), would also contribute to uncertainty in the method.

5.3 Uncertainty in the estimation

5.3.1 Uncertainty in estimating the stoichiometric ratio

In this study, we assumed that the stoichiometric ratio during photosynthesis, respiration and remineralization was constant and uniform in the study area, and used the ratio P:N:C:O$_2$ = 1:16±1:117±14:170±10 given by Anderson and Sarmiento (1994). This ratio differs from the well-known ratio of 1:16:106:138 suggested by Redfield et al. (1963). Takahashi et al. (1985) estimated this stoichiometric ratio along two isopycnal surfaces in the Atlantic and Indian oceans and suggested a ratio of 1:16:103:172 or 1:16:140:172. The difference between these ratios provides some uncertainty in the estimation of excessTCO$_2$. Since the effects of photosynthesis and remineralization are small in remnant water, the uncertainty in the stoichiometric ratio probably gives negligible errors in determining TA$^0$ and TCO$_2$$_0$. However, the remineralization of organic matter does significantly affect TCO$_2$ of water at depth. In the study area, AOU had a maximum value of around 100 $\mu$mol·kg$^{-1}$; hence, $\Delta$TCO$_2$,org calculated using the ratio of Anderson and Sarmiento (1994) was about 8 $\mu$mol·kg$^{-1}$ lower than that based on the ratio of Redfield et al. (1963) at a maximum. The estimated values of excessTCO$_2$ will directly reflect this uncertainty in $\Delta$TCO$_2$,org.

5.3.2 Internal errors in the thermodynamic calculations

In the computational scheme, we used the apparent constants recommended by DOE (1991) to calculate fCO$_2$,water present from TA$^0$ and TCO$_2$$_0$ present, and then calculated TCO$_2$$_0$ preind from fCO$_2$,water preind and TA$^0$. Some doubt has been expressed about the accuracy of these calculations using apparent constants (Goyet et al., 1991). Noticeable differences between computed and observed values of fCO$_2$ have been reported. The degree of difference varies with temperature. However, in our computational scheme, most of the systematic error generated in the calculation of fCO$_2$,water present with TA$^0$ and TCO$_2$$_0$ present is canceled out in the calculation of TCO$_2$$_0$ preind from fCO$_2$,water preind and TA$^0$. Hence, any error in the thermodynamic calculations would have an insignificant effect on the results.

Fig. 12. Vertical distribution of excessTCO$_2$. Dashed line indicates excessTCO$_2$$_{Chen}$. Open circles indicate excessTCO$_2$$_{Chen}$. 
6. Summary

We have improved the back-calculation method for estimating the oceanic anthropogenic CO$_2$ content based on NOPACCS 1994 data in the North Pacific. In NPSG, we found an area in which the complications of watermass mixing were negligible. We determined the relationships of TA and TCO$_2$ with temperature at the surface of this area in present-day winter. We evaluated the degree of disequilibrium in CO$_2$ between atmosphere and surface water, and reconstructed the value of TCO$_2$ at the sea surface in the pre-industrial times using a correction for air-sea disequilibrium. The difference in TCO$_2$ between the pre-industrial times and the present-day represents the TCO$_2$ increase resulting from the anthropogenic CO$_2$ input. Although the spatial coverage was limited, our method provides useful information about the distribution of anthropogenic carbon in one area. We found, however, some remaining problems that cause systematic error in estimating the anthropogenic TCO$_2$ content by our method.

The improved method gave results that differ significantly from those calculated by the previous method. Our results, in an area north of 33°N, were nearly 20 μmol·kg$^{-1}$ lower than those obtained by the previous method and imply that, by optimizing the method to a specified region, the improved back-calculation method can provide more reliable estimates than the previous method. The strategy we used in this study will be helpful in estimating the TCO$_2$ increase in other regions of the oceans. More reliable estimation of the fCO$_2$ in surface water in pre-industrial times will be a subject of further intensive studies.

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References


