Distribution of Dissolved Inorganic Carbon (DIC) and Its Related Parameters in Seawater of the North Yellow Sea and off the Qingdao Coast in October, 2007

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Abstract  Data on the distribution of dissolved inorganic carbon (DIC) were obtained from two cruises in the North Yellow Sea (NYS) and off the Qingdao Coast (QC) in October, 2007. Carbonate parameters were calculated. The concentrations of DIC are from 1.896 − 2.229 mmolL−1 in the NYS and from 1.939 − 2.032 mmolL−1 off the QC. In the southwest of the NYS, DIC in the upper layers decreases from the north of the SP (Shandong Peninsula) shelf to the center of the NYS; whereas in the lower layers DIC increases from the north of the SP shelf to the center of the NYS and South Yellow Sea. In the northeast of the NYS, DIC in all layers increases from the YR (Yalu River) estuary to the center of the NYS. The distribution of DIC in NYS can be used as an indicator of Yellow Sea Cold Water Mass (YSCWM). Air-sea CO2 fluxes were calculated using three models and the results suggest that both the NYS and the QC waters are potential sources of atmospheric CO2 in October.

Key words  dissolved inorganic carbon; air-sea CO2 flux; North Yellow Sea; Qingdao Coast

1 Introduction

CO2 is biogeochemically important in estuarine and coastal waters. The coastal seas only account for a small fraction (7%) of the ocean but contribute a disproportionately large fraction (15% to 30%) of oceanic primary production (Walsh, 1991; Millero et al., 2006; Wollast, 1998) and strongly affect the global carbon cycle. However, it has been unknown whether the coastal seas act as sinks or sources of atmospheric CO2 (Walsh, 1991; Kempe, 1995; Gattuso et al., 1998; Wollast, 1998). The reason is that there has been a lack of field data on the spatial and temporal variability of dissolved inorganic carbon (DIC) and partial pressure of CO2 (pCO2) in coastal oceans (Bozec et al., 2005).

Since the 1990s, the carbon dioxide system in the China Seas has been studied (Han et al., 1990; Xie and Zhou, 1991; Guo, 1994; Tsunogai et al., 1997, 1999; Zhang et al., 1997, 2000; Peng, 1999; Cai and Wang, 1998; Wang et al., 2002; Shim et al., 2007; Liu et al., 2008). However, these studies mainly concentrated on pH and alkalinity or pCO2. Studies on the distribution of DIC in the North Yellow Sea (NYS) are scarce, so there is a lack of field data of DIC in the NYS. In this paper, DIC is discussed using the data measured from two cruises in the NYS and

Qingdao Coast (QC) in October, 2007. The distributions of carbonate system and air-sea CO2 fluxes are calculated.

2 Experiments

2.1 Experimental Method

The DIC is measured by coulometric method. The DIC of each sample is extracted as CO2 gas by acidification, and then the CO2 gas is quantitatively detected by a coulometer. The carbonate parameters in seawater and air-sea CO2 flux between the surface water and the atmosphere are calculated using temperature, salinity, pH, DIC, the CO2 solubility (Weiss, 1974) and the carbonic acid thermodynamic constants (Mehrbach et al., 1973). The calculations are performed using the following equations:

\[
\begin{align*}
[HCO_3^-] &= TCO_2 \times K_1 \times a_{H^+} / (a_{H_2}^+) ^2 \times K_1 \times a_{H^+} + K_1 \times K_2 \\
[CO_3^{2-}] &= TCO_2 \times K_1 \times K_2 / (a_{H_2}^+) ^2 \times K_1 \times a_{H^+} + K_1 \times K_2 \\
[CO_2] &= TCO_2 \times (a_{H_2}^+) ^2 / (a_{H^+} ^2 \times K_1 \times a_{H^+} + K_1 \times K_2) \\
\ln K_0 &= -58.0931 + 90.5069 \times (100/T) + 22.294 \times \ln(T/100) + 0.027766 - 0.025888 \times (T/100)^2 \times S \\
pCO_2 &= [CO_2] / K_0 \\
F &= K \Delta pCO_2,
\end{align*}
\]

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where \( TCO_2, [HCO_3^-], [CO_3^{2-}] \) and \([CO_2]\) are the concentrations of DIC, HCO_3^-, CO_3^{2-} and CO_2 (including H_2CO_3), respectively; \( K_1 \) and \( K_2 \) are the first and second apparent dissociation constants of carbonic acid in seawater; \( a_{H^+} \) is the activity of \( H^+ \); \( K_0 \) is the CO_2 solubility; \( F \) is the air-sea CO_2 flux with a negative value indicating a net CO_2 invasion into the ocean; \( K \) is the gas transfer velocity, and \( K = k \times K_0 \), \( k \) being the gas exchange coefficient; \( \Delta pCO_2 \) is the difference of \( pCO_2 \) between the surface seawater and the atmosphere.

Partial pressure of atmospheric CO_2 is assumed as 38.5 Pa (380 µatm), which is consistent with the values of Tae-ahn Peninsula (a monitoring station of World Data Center for Greenhouse Gases, about 38.5 Pa in 2003–2004: http://gaw.kishou.go.jp/wdcgg.html). Given that \( K_0 \) is accurately known as a function of salinity and temperature (Weiss, 1974; Wanninkhof, 1992), the accuracy of the estimate of \( F \) mainly depends on the parameterization of \( k \) (Hu and Guan, 2008). Three common models, i.e., the Liss and Merlivat method (Liss and Merlivat, 1986), the Tans method (Tans et al., 1990) and the Wanninkhof method (Wanninkhof, 1992), are chosen to calculate \( k \). The results are as follows: \( k_L < k_W < k_T \); where \( k_W \) is close to the average of \( k_L \) and \( k_T \). These results are consistent with other reports (Wang et al., 2000; Zhang et al., 2000; Shim et al., 2007).

### 2.2 Apparatus and Reagents

CMS014 CO_2 Coulometer and CM5130 Acidification Module are from UIC, Inc. USA. KOH, H_3PO_4 and other reagents are all analytically pure.

### 2.3 Cruise and Sample Collection

The samples were collected from two cruises in the NYS and off the QC in October, 2007. The sampling stations are shown in Fig.1. Seawater samples were collected from the surface, 10 m, 20 m (or 30 m) and the bottom layers and put into 60 mL glass bottles. Then 100 µL saturated HgCl_2 solution was added to each sample in order to terminate all biological activities. The sealed samples were transported to the laboratory for analysis.

![Fig.1 Sampling stations in the NYS and off the QC.](image)

### 3 Results and Discussion

#### 3.1 Distribution of DIC

#### 3.1.1 Horizontal distribution of DIC in seawater of the NYS

The range and average of DIC concentration in seawater of the NYS are listed in Table 1. The distributions of DIC and the normalized total CO_2 (NTCO_2 = TCO_2 \times 35/S) are shown in Fig.2.

Fig.2 shows that the horizontal distribution of DIC in the surface water is different from that in the bottom water. The distribution patterns ofDIC in the upper layers (from surface to 20 m) are similar (Figs.2a–c) and those in the lower layers (below 30 m) are similar (Figs.2d–e). In the northeast of NYS, DIC in all layers increases from the Yalu River (YR) estuary to the center of NYS, which may be due to the freshwater dilution. At the southwest of

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>Range of TCO_2 (mmol L⁻¹)</th>
<th>Average of TCO_2 (mmol L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>surface</td>
<td>1.896 – 2.134</td>
<td>2.013</td>
</tr>
<tr>
<td>10</td>
<td>1.913 – 2.107</td>
<td>2.016</td>
</tr>
<tr>
<td>20</td>
<td>1.949 – 2.130</td>
<td>2.033</td>
</tr>
<tr>
<td>30</td>
<td>1.984 – 2.205</td>
<td>2.075</td>
</tr>
<tr>
<td>bottom</td>
<td>2.019 – 2.229</td>
<td>2.116</td>
</tr>
</tbody>
</table>