Diurnal, seasonal, and spatial variations and flux of carbon monoxide in Jiaozhou Bay, China

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A B S T R A C T

Four cruises were conducted in Jiaozhou Bay from January to November in 2008 to study carbon monoxide (CO) distribution, diurnal variation, seasonal variation, and sea-to-air flux. Surface water CO concentration exhibited strong diurnal variations at an anchor station in both April and November, with highest CO concentration 3–5 times higher than minimum values. Diurnal variation (sampling time) exerts an overall pattern on CO distribution, spatially distributed factors impose extra influence. High CO concentrations and fluxes were observed in the eastern, northern, and western parts of the bay, which are close to areas of estuaries, dense population, and high industrialization, reflecting the impact of human activities on CO distribution. Both surface water CO concentrations and sea-to-air fluxes showed seasonal variations, with the highest values in summer and the lowest values in winter. Sea-to-air CO flux in Jiaozhou Bay ranged from 0 to 34.66 μmol m⁻² d⁻¹ with a mean flux of 4.96 μmol m⁻² d⁻¹.

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1. Introduction

Atmospheric CO is a major sink of tropospheric hydroxyl radical with a radiative forcing potential of approximately two times of CO₂ (Forster et al., 2007). The reaction of CO with hydroxyl radical affects the oxidation capacity of the atmosphere, and thus can influence the concentrations of some greenhouse gases such as methane. Therefore, atmospheric CO acts as both a direct and an indirect greenhouse gas (Thompson, 1992; Derwent et al., 1995). Previous studies showed that dissolved CO in surface seawater was typically supersaturated with respect to atmospheric equilibrium (Lamontagne et al., 1971; Stubbins et al., 2006; Zafiriou et al., 2008; Day and Falloona, 2009; Yang et al., 2010, 2011; Zhao et al., 2015), indicating the ocean, coastal, and estuary areas, as a whole, being a source of atmospheric CO. Global oceanic CO emissions have been estimated to range from 4 to 600 Tg CO-C yr⁻¹ during the last several decades, the huge variability of CO emission could possibly be due to high diurnal, seasonal, and spatial variations that introduce uncertainty when extrapolating data measured at sparse locations to global ocean (Conrad et al., 1982; Erickson, 1989; Khalil and Rasmussen, 1990; Bates et al., 1995; Zuo and Jones, 1995; Stubbins et al., 2006). To our knowledge, by far there have been only a few publications reporting CO seasonal variation.

CO in seawater is mainly produced through photo-oxidation of colored dissolved organic matter (CDOM) (Zhang and Xie, 2012; Powers and Miller, 2015), and is lost through microbial consumption and sea-to-air emissions (Bates et al., 1995; Xie et al., 2005; Zafiriou et al., 2003; Yang et al., 2010). The complexity of source and sink with chemical, biological, and physical interactions leads to diverse spatial and temporal CO distributions. Sea-surface CO concentrations show a strong diurnal cycle with the maximum in early afternoon and the minimum before dawn as the result of temporal variability of the marine source-sink terms, particularly the photochemical source (Conrad et al., 1982; Day and Falloona, 2009; Johnson and Bates, 1996; Stubbins et al., 2006; Yang et al., 2010, 2011; Zafiriou et al., 2008). As a principal loss term, biological consumption is an important and essential parameter for modeling the biogeochemical behavior of CO in the upper ocean (Zafiriou et al., 2003; Xie et al., 2005; Zhang et al., 2005; Day and Falloona, 2009).

In recent years, there have been several studies reporting CO distribution, sea-to-air flux, microbial consumption, and photosynthesis in China’s marginal seas (Yang et al., 2010, 2011; Zhang et al., 2011; Wang et al., 2015; Zhao et al., 2015). There are no data about CO distribution, flux, and microbial consumption in Jiaozhou bay, a typical semi-enclosed eutrophic bay in China. This study represents the first attempt to carry out in situ measurements of surface water CO in Jiaozhou Bay.

KEYWORDS: Atmospheric CO; CO distribution; diurnal variation, seasonal variation, and sea-to-air CO flux; Jiaozhou Bay; CO concentration.

1 The first and second authors contributed equally to the paper.
during four cruises in 2008. The primary objectives of this work were: 1), to track seasonal variations of CO concentration, and to explore factors that may affect the variations; 2), to examine diurnal variation and horizontal distribution of CO; 3), to estimate the sea-to-air fluxes of CO in Jiaozhou bay.

2. Materials and methods

2.1. Study area

Jiaozhou Bay (35.97°–36.30°N, 120.07°–120.38°E) is the largest semi-enclosed water body along the Southern Yellow Sea and is situated in the western part of the Shandong Peninsula, northern China (Song, 2010). It is surrounded by Qingdao city and has an area of about 390 km² with an average depth of about 6–7 m and a maximum depth of about 70 m in a narrow channel close to the mouth directly affected by strong tidal currents (Liu et al., 2008). More than ten small seasonal rivers carrying various amounts of water enter into the bay. The largest river is the Daguhe River with an annual average runoff of $7.235 \times 10^8$ m³ (Fu et al., 2007). Other rivers, such as the Lincunhe River, the Haibohe River, and the Loushanhe River, pass through the urban area and bring industrial and human waste from Qingdao city into the bay (Yan et al., 2001). With rapid economic and social developments of the surrounding regions, the bay is greatly influenced by human activities, leading to increasing amount of discharge of industrial, agricultural, and aquaculture waste (Zhang et al., 2013; Liang et al., 2015). Thus, the characteristic of the water in the bay differs significantly from that of the ocean water.

2.2. Sampling

Four cruises were conducted in Jiaozhou Bay in January, April, July, and November in 2008, respectively. The sample locations are shown in Fig. 1. There were 18 stations in each survey. Samples were collected and analyzed between 08:00 to 16:00 local time except for samples at the diurnal variation site where we sampled every 3 h. Surface seawater samples (usually 0–1 m) were collected using 2.5 L Niskin bottles deployed on standard conductivity-temperature-depth (CTD) rosettes. Subsamples were transferred into a 50-mL dry, acid-cleaned glass syringe fitted with a three-way Teflon valve that was used to sub-sample from the Niskin bottles (Zafiriou et al., 2008). Once collected, samples were immediately (<5 min) analyzed for CO concentration ([CO]surf).

Chlorophyll a samples were collected by filtering surface seawater through glass-fiber filters (Whatman GF/F, precombusted at 500 °C for 3 h), and samples were stored at −20 °C until analyses.

2.3. Analytical procedures

Water samples were immediately analyzed after collection using a modified ta3000 reduction gas analyzer (Trace Analytical, Ametek, USA). Specifically, CO in water was extracted using the headspace method as described in Xie et al. (2002) and Lu et al. (2010). Briefly, in a sampling syringe, we mixed 44 mL of seawater and 6 mL of high-purity nitrogen, which is purified with an external purifier (PS2-GC50-R/N, SAES, USA) to remove potential CO. The syringe is shaken for 5 min at a constant rotational velocity (120 r min⁻¹) and then the equilibrated headspace air is injected into a modified ta3000 gas analyzer through a syringe filter holder (Millipore) that contained a water-impermeable 0.2 μm Nuclepore Teflon filter to prevent liquid water from entering the chromatographic columns of the analyzer (Xie et al., 2002). The headspace system’s blank is as low as 0.02 nmol L⁻¹. The system was calibrated with a gaseous CO standard (nominal concentration: 0.993 ppm by volume in nitrogen; analytical accuracy: ±5%, DaTe®, Dalian, China). The CO standard was approved by China State Bureau of Technical Supervision and was a certified reference material No. 060152. The relative standard deviation of this analysis method was <4.4% and the detection limit was 0.02 nmol L⁻¹ (Lu et al., 2010).

Chl a on GF/F was extracted in 90% acetone according to Parsons et al. (1984). Its concentration was fluorometrically determined with an F-4500 fluorescence spectrophotometer (Hitachi, Japan).

Fig. 1. CO spatial distributions in four seasons. Numbers in each figure represent Station number. Color and marker size represent CO concentration. Same color scale and size scale are used in all figures.
2.4. Calculations

Briefly, CO concentration in the original seawater ([CO]_{surf}) is calculated based on Xie et al. (2002) as follows:

\[ [\text{CO}]_{\text{surf}} = p m_a (\beta p V_w + V_a) / RT V_w, \]

where \( p \) is atmospheric pressure (atm) of dry air; \( m_a \) is equilibrated headspace mixing ratio (ppbv); \( \beta \) (ml CO mL^{-1} H2O atm^{-1}) is the Bunse sen solubility coefficient of CO, and is a function of temperature and salinity (Wiesenburg and Guinasso, 1979); \( V_w \) and \( V_a \) are volume of water sample and headspace air (ml), respectively; \( R \) is the gas constant (0.08206 atm L mol^{-1} K^{-1}), and \( T \) is temperature (K).

Sea-to-air fluxes of CO (\( F \)) were calculated using the following equation:

\[ F = k ([\text{CO}]_{\text{surf}} - [\text{CO}]_{\text{eq}}), \]

where [CO]_{eq} is dissolved CO concentration with respect to in situ atmospheric CO concentration and is calculated using the following equation:

\[ [\text{CO}]_{\text{eq}} = ([\text{CO}]_{\text{atm}} \times \beta) / M, \]

where [CO]_{atm} is atmospheric CO mixing ratio (ppbv). \( M \) is the molar volume of CO (25.094 L mol^{-1}) at standard temperature and pressure (Lide, 1992; Stubbins et al., 2006); and \( k \) is the gas transfer coefficient (m h^{-1}) and calculated following the method described by Nightingale et al. (2000). The coefficient \( k \) was adjusted by (Sc/660)^{-0.5} where \( Sc \), the Schmidt number for CO in seawater, was calculated using the equation from Zafiriou et al. (2008).

\[ Sc = -0.0553 t^3 + 4.3825 t^2 - 140.07 t + 2134, \]

where \( t \) is temperature in Celsius degrees. In this study, we used site specific temperature for each site.

3. Results and discussion

Seasonal variations of sea surface temperature (SST), sea surface salinity (SSS), and Chl \( a \), along with CO concentration are presented in Fig. 2. Error bars are standard deviations. As can be seen, SST and Chl \( a \) show strong seasonal variations. SSS displays the lowest value in summer, comparable values in the other three seasons. Chl \( a \) concentrations exhibit two high peaks in July (13.23 \( \mu g \) L^{-1}) and January (8.59 \( \mu g \) L^{-1}). This was consistent with the results of Li et al. (2005) and Wu et al. (2004), who found the two-peak pattern during 2001 to 2004 in the bay, respectively. In addition, according to Wang and Hou (2006), the highest monthly-accumulated ultraviolet radiation in July was about 10 times higher than that in January, and 3 and 6 times higher than those in April and November, respectively.

3.1. Diurnal variations

CO diurnal variations in the surface seawater were investigated at an anchor station (Station 9, Fig. 1), which was visited every 3 h in April and November. CO concentrations exhibited clear diurnal variations in both seasons with maximum concentrations 3–5 fold higher than minimum values. As shown in Fig. 3, the highest CO concentrations were usually found at 13:00–14:00 (local time) and minimal concentration of CO occurred before dawn. CO concentrations showed small variability during nighttime, and a relatively large variability during day time. In addition, it can also be seen from Fig. 3 that CO concentrations in April were higher than those in November, corresponding to CO seasonal variations as discussed in Section 3.3. When plotted against sampling time, CO concentration shows general diurnal variations in January, April, and November despite being sampled at different locations as shown in Fig. 4, which indicates that diurnal variation imposes an overall pattern. Outliers (unexpected high or low values on a diurnal curve) in Fig. 4 represent spatial variations that will be discussed in Section 3.2.

CO diurnal variation and afternoon peak were intensively reported by other researchers (Bullister et al., 1982; Conrad et al., 1982; Jones, 1991; Ohta, 1997; Stubbins et al., 2006; Day and Falloona, 2009; Yang et al., 2010, 2011; Wang et al., 2015). Among these observations, the variation factors were different, such as Jones (1991) (2–20), Stubbins et al. (2006) (5–7), Yang et al. (2010) (4–8), Yang et al. (2011) (5–6), and Wang et al. (2015) (8–14). The variation factors in this study were lower than these observations in general. It has been argued that CO diurnal variation in euphotic ocean water was a product of photochemical CO production from CDOM, microbial oxidation, and sea-to-air flux (Conrad et al., 1982). The strong UV radiation in noon inhibits bacteria CO consumption, but promotes photochemical production. Therefore, CO concentration builds up and shows an early afternoon peak (Tolli and Taylor, 2005). Note that Jiaozhou Bay is a tidally active location with currents. It is worth exploring whether changing of mixed layer depth is a factor causing CO diurnal variations. Based on salinity and temperature profiles (Yang and Wu, 1999), there is no apparent stratification except in summer season. Therefore, diurnal variations observed at anchor station were not caused by mixed layer depth variation.

3.2. Spatial distribution of CO

Horizontal distributions of surface water CO concentrations ([CO]_{surf}) for the four cruises are shown in Fig. 1. As we discussed in last section, sampling time imposes a general influence on CO concentration, whose variations can be simply caused by sampling time. However, when the outliers in Fig. 4 are picked out and are corresponded to sampling locations, clear variations due to sampling location appear. Specifically, in January the two stations with low [CO]_{surf} and sampled after 1200 are Stn. 16 and 17. In April, the two unexpected low [CO]_{surf} were found at Stn.15 and 16. In November, stations with unexpected high [CO]_{surf} are Stn. 5 and 10, which were sampled after 1600 and before 1100, respectively, unexpected low are Stn. 16, 17, 18. From Fig. 1, it is easy to locate stations with unexpected low [CO]_{surf} at the mouth of the Bay, where water exchange between the Yellow Sea and the Bay is intensive. In addition, water depth at these stations is much deeper than that at stations inside the Bay, thus deep mixing can partially contribute to low surface CO concentration. On the other hand, stations with unexpected high [CO]_{surf} are near coastal lines, especially Stn. 5 and 10 showing unexpected high [CO]_{surf} in both July and November are at the estuaries of Licunhe and Haibohe, respectively. Compared with other cruises, CO distribution showed less spatial variations in July. For the summer season, the sampling time ranged from 9:00 to 18:00,
during which period, in middle latitude Northern hemisphere, the change of light intensity is not as much as other seasons. In addition, a storm two days before the cruise might have exerted extra influence on CO distribution.

3.3. Seasonal variations

Surface water CO concentrations ranged from 0.32 to 12.22 nmol L\(^{-1}\) for all the samples, with an average of 3.08 nmol L\(^{-1}\). In general, CO concentrations in the Bay were comparable to those in marginal seas of China and shelf sea areas affected strongly by human activity (Table 1). Average [CO\(_{\text{surf}}\)] of each cruise along with ancillary data are shown in Fig. 2. The maximum average concentration was 5.34 ± 2.34 nmol L\(^{-1}\) in July probably corresponding to strong radiation, followed by April (2.85 ± 2.32 nmol L\(^{-1}\)), January (2.12 ± 1.31 nmol L\(^{-1}\)), and the minimum average concentration was 2.00 ± 1.81 nmol L\(^{-1}\) in November. One-way ANOVA analysis conducted using Matlab routine anova1 indicates that seasonal variation is significant (\(p \ll 0.01\)).

Seasonal variations of [CO\(_{\text{surf}}\)] may be related to the changes of general oceanographic properties. High temperature, strong light, and high levels of CDOM would promote CO production in seawater (Conrad et al., 1982; Zhang et al., 2006). We thus conducted a multi-linear Pearson correlation analysis.
analysis towards CO and oceanography properties (salinity, temperature, Chlorophyll a, and wind speed at 10 m) using a Matlab built-in function “corr(X)” to find out which property(ies) can influence CO distribution. The correlation coefficients are shown in Table 2, and plots are shown in Fig. 5. As can be seen, these properties show different extent of correlations with CO in different seasons. Chl a had strong correlation with CO in January (p < 0.01), and when all seasons’ data were combined (p = 0.01). However, in individual month April, July, and November, the correlations are weak (p > 0.1). SST was negatively correlated with [CO]surf in January (p < 0.01), April (p < 0.01), and November (p < 0.01) (Table 2), implying a direct impact of river runoff on CO concentration. SST in April and November, positive correlation in April (p < 0.01) and negative correlation in November (p < 0.05). In the studies of Yang et al. (2011) and Zhao et al. (2015), there were no significant correlation observed between SST and [CO]surf. These studies suggested that it is difficult to evaluate the effect of water temperature on [CO]surf, especially in the complex environmental conditions in coastal waters. Wind speed shows negative correlation with CO in January (p ≈ 0.01), but no correlation was found for other seasons. In the month of July, none of the properties had a significant relationship with CO, which probably indicated that properties, such as illumination and CDOM concentration, that can potentially influence CO concentration had not been taken into consideration. In addition, the storm as we mentioned before could also perturbed the correlations in July.

3.4. Sea-to-air gas exchange and its seasonal variations

Compared with atmospheric CO mixing ratio, CO in surface sea water is always supersaturated. In this study, CO saturation factor was derived from [CO]surf divided by [CO]a. Eq. The mean saturation factors of CO were 2.9, 7.1, 14.0, and 3.8 in January, April, July, and November, respectively. Variation of CO saturation factors was a combination effect of CO variations in seawater and atmosphere, the latter of which, unfortunately, were not measured in situ. Instead, seasonal data (680 ppbv, 439 ppbv, 497 ppbv, and 587 ppbv for Jan. Apr. Jul. and Nov., respectively)

<table>
<thead>
<tr>
<th>Table 1</th>
<th>[CO]surf,and Flux in this study compared with other papers. Data in parentheses represent average values with standard deviations.</th>
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<tbody>
<tr>
<td>Region</td>
<td>Time</td>
</tr>
<tr>
<td>Scheldt Estuary</td>
<td>All year</td>
</tr>
<tr>
<td>California upwelling</td>
<td>All year</td>
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<tr>
<td>Beaufort sea</td>
<td>Spring</td>
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<td>Sagami Bay</td>
<td>Jul.</td>
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<tr>
<td>Southern Yellow Sea and the East China Sea</td>
<td>Nov.</td>
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<tr>
<td>East China Sea and the Yellow Sea</td>
<td>Apr., May.</td>
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<tr>
<td>Southern Yellow Sea</td>
<td>Jul., Aug.</td>
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<tr>
<td>Jiaozhou Bay</td>
<td>Jan.</td>
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<td></td>
<td>Apr.</td>
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<td></td>
<td>Jul.</td>
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<tr>
<th>Table 2</th>
<th>Pearson correlation coefficients of multi-linear regression analyses between [CO]surf and oceanographic parameters in Jiaozhou Bay during the four cruises. The numbers in parentheses are corresponding “r” values.</th>
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<tbody>
<tr>
<td>[CO]surf</td>
<td>Chl a</td>
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<tr>
<td>Jan.</td>
<td>CO</td>
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<tr>
<td>Apr.</td>
<td>CO</td>
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<td>Jul.</td>
<td>CO</td>
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<td>Nov.</td>
<td>CO</td>
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<tr>
<td>All</td>
<td>CO</td>
</tr>
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measured in 2009 over Jiaozhou Bay were used. The seasonal atmospheric CO mixing ratios used are consistent with the expectation that CO mixing ratio is high in winter due to shallow atmospheric boundary layer and high anthropogenic input due to coal burning for heating. Even the lowest CO mixing ratio in April is ~3 times higher than the open ocean value (151 ppbv, Stubbs et al., 2006), demonstrating anthropogenic influence on atmospheric CO mixing ratio. Sea-to-air emission, which is minor compared to other CO sources (e.g. photochemical production in the troposphere and forest fire), can be suppressed by the high atmospheric CO mixing ratios.

Overall, based on the above atmospheric CO mixing ratio, [CO]_{surf} were supersaturated compared with atmospheric CO mixing ratios during four cruises at most stations (about 92%), demonstrating that the Jiaozhou Bay was a net source of atmospheric CO during studied time. The mean saturation factors of CO in this study were comparable to the results of China’s marginal seas, such as Yang et al. (2010) (0.58 to

![Graphs showing CO concentration versus Chl a and salinity for different months.](image)

**Fig. 5.** CO concentration versus ancillary parameters.
15.42 in November), Wang et al. (2015) (0.54 to 25.90 in July, 1.12 to 174.3 in August), and Zhao et al. (2015) (0.3 to 11.0 in September).

Estimated sea-to-air fluxes of CO throughout the year range from 0 to 34.66 $\mu$mol m$^{-2}$ d$^{-1}$ with a mean flux of 4.96 $\mu$mol m$^{-2}$ d$^{-1}$, and exhibited considerable spatial variability. Seasonal emission rates of CO in the Bay were calculated using average daily fluxes ($\mu$mol m$^{-2}$ d$^{-1}$).

Based on average seasonal CO emission rates, the corresponding percentages were 11.3%, 22.0%, 57.0%, and 9.7% for winter, spring, summer, and autumn, respectively. Considering the total area of 390 km$^2$ of Jiaozhou Bay (Liu et al., 2008), the annual emission of CO was estimated to be 0.008 Gg CO-C. We are obliged to point out that this estimation probably represents a high end estimation, since all samples were collected

**Fig. 5 (continued)**.
and measured during daytime when CO concentration was high in a diurnal cycle. CO fluxes in summer and spring accounted for most part of annual emission. In general, CO sea-to-air fluxes of the Bay were consistent with those of coastal sea and bays in previous studies (Table 2).

4. Conclusions

The study reported the first in situ measurements of CO distribution and sea-to-air flux in the Jiaozhou Bay in different seasons. [CO]_{air} showed significant seasonal variations with the highest mean concentration recorded in summer and the lowest in winter. [CO]_{air} showed a strong diurnal variation no matter at the anchor station or all samples combined for each cruise. Diurnal variation exerts an overall pattern for CO distribution. During a diurnal variation, maximum [CO] values are 3–5 fold higher than minimum values with the peaks observed in the early afternoon (about 13:00–14:00). Beyond diurnal variation, surface CO also displays spatial variation, with high values near coastal line and low values at the mouth of the bay. Jiaozhou Bay was a net atmospheric source in 2008 and the annual emission of CO was estimated to be 0.008 Gg CO-C.

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References


Day, D.A., Falona, I., 2009. Carbon monoxide and chromophoric dissolved organic matter concentration recorded in summer and the lowest in winter. [CO]_{sea} also displays spatial variation, with high values near coastal line and low values at the mouth of the bay. Jiaozhou Bay was a net atmospheric CO source in 2008 and the annual emission of CO was estimated to be 0.008 Gg CO-C.


