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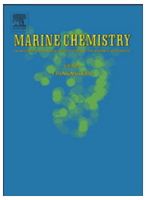

Distribution, flux and photoproduction of carbon monoxide in the Bohai and Yellow Seas

Bao-Zhen Zhao [a,b], Gui-Peng Yang [a,b,*], Huixiang Xie [c], Xiao-Lan Lu [a,b], Jian Yang [a,b]

[a] *Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, Ocean University of China, Qingdao 266100, China*
[b] *College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266100, China*
[c] *Institut des sciences de la mer de Rimouski, Université du Québec à Rimouski, Rimouski, Québec G5L 3A1, Canada*

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ABSTRACT

The distribution, sea-to-air flux, and photoproduction of carbon monoxide (CO) were determined in the Bohai Sea (BS) and the Yellow Sea (YS) during September, 2010. The concentrations of CO in the surface water varied from 0.09 to 6.81 nmol L^{-1} with an average of 1.05 nmol L^{-1}. Surface water at most sampling stations was supersaturated with CO with a mean saturation factor of 2.3. The hourly and daily sea-to-air fluxes of CO were estimated to be 76.6 nmol m^{-2} h^{-1} and 0.65 μmol m^{-2} d^{-1}, respectively. By extrapolation, the emission of CO from the study area accounted for 0.1% of the global oceanic emission. Coupled optical–photochemical modeling based on measured spectral CO apparent quantum yields arrived at a total CO photoproduction of 78.5 Gg CO-C yr^{-1} in the study area. Using CO as a proxy for dissolved inorganic carbon and biolabile carbon photoproducts, the total photomineralization rate of dissolved organic matter was estimated to be 2.4 Tg C yr^{-1}, representing 2.0% of the primary production in the study area. Our results show that photomineralization is a relatively small but significant term in the organic carbon cycle of coastal waters.

1. Introduction

Carbon monoxide (CO) has long been of biogeochemical interest because of its key role in regulating atmospheric concentration of hydroxyl radicals (•OH) (Derwent, 1995; Thompson, 1992; Yang et al., 2010). About 90% of atmospheric CO reacts with •OH to form carbon dioxide (CO_2) (Fichot and Miller, 2010), which as a greenhouse gas contributes most to the global warming. Simultaneously, the reaction of •OH with methane, which is another more efficient greenhouse gas, is a major pathway to remove the •OH from the atmosphere. Through competition for atmospheric •OH, CO indirectly affects the concentration of atmospheric methane and thus acts as an indirect greenhouse gas (Evans and Puckrin, 1995; Thompson, 1992).

The ocean has long been recognized as a source of atmospheric CO (Stubbins et al., 2006a; Yang et al., 2010; 2011), albeit with large uncertainties in its source strength. Marine emissions of CO are poorly defined and become increasingly controversial. The estimates of CO emissions made during the last several decades span two orders of magnitude, ranging from 4 to 600 Tg CO-C yr^{-1} (Bates et al., 1995; Conrad et al., 1982; Erickson, 1989; Khalil and Rasmussen, 1990; Prather et al., 2001; Stubbins et al., 2006a; Zuo and Jones, 1995). Little consideration of coastal and estuary areas, whose role on the global CO emission should not be neglected (Day and Faloona, 2009; Yang et al., 2011; Zafiriou et al., 2008), increases the uncertainty of CO emission in marine environments.

CO is the second most abundant inorganic carbon product of chromophoric dissolved organic matter (CDOM) photochemistry (Miller and Zepp, 1995; Mopper and Kieber, 2000). The direct evidence for a major photochemical CO source in seawater came from observations of a pronounced diurnal cycle in sea-surface CO concentrations. CO concentration in seawater shows complex spatial and temporal variations as a result of interactions among photoproduction (Yang et al., 2011; Zafiriou et al., 2003; Zuo and Jones, 1995) and microbial consumption (Xie et al., 2005; Yang et al., 2010; Zafiriou et al., 2003), air–sea gas exchange (Bates et al., 1995; Stubbins et al., 2006a; Yang et al., 2010; Zuo and Jones, 1995) and physical mixing (Gnanadesikan, 1996; Johnson and Bates, 1996). Estimates of global open-ocean CO photoproduction cover an enormous range (30–820 Tg CO-C yr^{-1}) (Moran and Zepp, 1997; Valentine and Zepp, 1993; Zuo and Jones, 1995), with a relatively precise amount of 30–70 Tg CO-C yr^{-1} (Fichot and Miller, 2010; Stubbins et al., 2006b; Zafiriou et al., 2003). Moreover, CO has been suggested as a key proxy to evaluate the photoproduction of CO_2 and biolabile organic carbon (Miller and Zepp, 1995; Miller et al., 2002; Mopper and Kieber, 2000), which together account for the majority of CDOM photodegradation products (Stubbins et al., 2006b). Thus a more precise quantification of CO photoproduction rates becomes increasingly important, particularly in coastal waters where only a few

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[*] Corresponding author at: College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266100, China. Tel.: +86 532 66782686; fax: +86 532 66782657.
E-mail address: gpyang@ouc.edu.cn (G.-P. Yang).

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studies on CO photoproduction have been conducted (Day and Faloona, 2009; Yang et al., 2011; Zhang and Xie, 2012).

The Bohai Sea (BS) is a semi-enclosed shelf sea of the northwest Pacific Ocean, with a surface area of 7.7×10^4 km^2 and an average depth of 18.7 m. The area with a depth of less than 30 m constitutes 95% of the total area of the sea (Mao et al., 2008). The Yellow Sea (YS) is commonly considered to be among the broadest marginal seas in the world (Yang et al., 2003). It is a semi-enclosed sea of the northwest Pacific Ocean with a surface area of 38×10^4 km^2 and an average depth of 44 m, surrounded by the west coast of the Korean Peninsula and the east coast of China and connected to the East China Sea (ECS) in the south and to the BS in the north (Sun, 2006).

To date, only a few studies have been conducted regarding CO in China's marginal seas. Lu et al. (2010b) determined the concentrations of CO in the North Yellow Sea (NYS) by headspace analysis. Yang et al. (2010 and 2011) reported distribution, flux, photoproduction, and biological consumption of CO in the YS and the ECS. In this study we present data of CO from seawater and atmosphere samples covering almost the entire area of the BS and YS (Fig. 1A). The objectives of this study are to understand the spatial distributions of CO, estimate the CO emission into the atmosphere, and quantify the photoproduction of CO in the BS and YS.

2. Methods

2.1. Sampling

Samples were collected in the BS and YS on board the R/V "*Dong Fang Hong 2*" during September 8–22, 2010. The locations of sampling stations are shown in Fig. 1A.

The surface seawater samples were taken with 12-L Niskin bottles deployed on standard conductivity–temperature–depth (CTD) rosettes. Fifty-milliliter acid-cleaned glass syringes fitted with a three-way Teflon valve were used to sub-sample the Niskin bottles, following the procedures recommended by Zafiriou et al. (2008) to minimize sampling artifacts. Once collected, the samples were immediately analyzed for CO surface concentration ($[CO]_{surf}$).

To minimize the influence of ship emissions, atmospheric CO samples were collected on the top deck of the ship, facing the wind, with 50 mL gastight glass syringes when the ship was decelerating. Then the samples were analyzed for CO atmospheric concentration ($[CO]_{atm}$).

Samples for dissolved organic carbon (DOC) and chlorophyll *a* (Chl-*a*) were immediately filtered through glass-fiber filters (Whatman GF/F, precombusted at 500 °C for 3 h). The filtrate for the analyses of DOC was collected into the precombusted 40 mL glass vials and stored at −20 °C. The filters were stored at −20 °C for the analysis of Chl-*a*.

Samples for determining the apparent quantum yields (AQYs) of CO photoproduction were sequentially passed through 0.8-μm and 0.2-μm polyethersulfone membrane filters contained in an ArcoPak™ 500 Capsule filtration unit (Pall, USA), transferred into acid-cleaned 5-L clear glass bottles, and stored in the dark at 4 °C. After the cruise, the samples were brought back to a land-based laboratory in Qingdao and irradiated within two months of sample collection.

2.2. Irradiation

Samples were re-filtered with 0.2-μm polyethersulfone membranes (Pall, USA), purged in the dark with CO-free air to minimize background CO concentration, and then siphoned into gastight quartz-windowed cells. The cell was filled from the bottom and overflowed with ~50 mL of sample before closing. The samples were aligned vertically in a black, temperature-regulated aluminum block holder and irradiated at a constant temperature (24 ± 0.1 °C) using a SUNTEST CPS solar simulator equipped with a 1.5-kW xenon lamp (Atlas, Germany). Successive Schott long band-pass cutoff filters of WG280, WG295, WG305, WG320, WG345, GG395, GG435 and GG495 (numbers are nominal 50% transmission cutoff wavelengths) were placed at the base of the irradiation chamber to obtain eight spectral treatments (Johannessen and Miller, 2001; Zhang et al., 2006). Spectral irradiance under each cutoff filter was measured with an ILT-900R UV–VIS spectroradiometer (International Light Technologies, USA). Parallel incubations in the dark were conducted to correct for potential dark production of CO.

2.3. Analysis

Both atmospheric and water samples were analyzed using a modified ta3000 reduction gas analyzer (Trace Analytical, Ametek, USA). Water samples were preprocessed using a headspace method before analysis (Lu et al., 2010b; Xie et al., 2002). Briefly, 6 mL of high-purity nitrogen was introduced into the sample-filled syringe with 44 mL of seawater. The syringe was shaken for 5 min at a constant rotational velocity ($120\ r\ min^{-1}$) and then the equilibrated headspace air was injected into the 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). Atmospheric samples were directly injected into the analyzer for quantification. The system was calibrated with a gaseous CO standard (nominal concentration: 0.993 ppm by volume in nitrogen; analytical accuracy: ±5%, State Center for Standard Matter, China). The CO standard was approved by China State Bureau of Technical Supervision and was a certified reference material with a standard reference material no. 060152.

Absorbance spectra of CDOM were recorded from 200 to 800 nm at 1-nm increments using a UV-2550 UV–VIS spectrometer (Shimadzu) fitted with 10 cm quartz cells and referenced to Milli-Q water. A baseline correction was applied by subtracting the absorbance value averaged over a 5-nm interval around 685 nm from all the spectral values (Babin et al., 2003). Absorption coefficients (*a*) were calculated as:

$$a = \frac{2.303 \times A}{r} \tag{1}$$

where *A* is the absorbance, and *r* is the cell's light path length in meters.

The concentration of dissolved organic carbon (DOC) was measured using a TOC-V_{CPH} carbon analyzer (Shimadzu, Japan) calibrated with potassium biphthalate. The DOC consensus reference materials (CRM) from the Hansell Laboratory (University of Miami, USA) were used as reference materials. The relative standard deviation was less than 2%.

The concentration of Chl-*a* was fluorometrically measured with a F-4500 fluorescence spectrophotometer (Hitachi, Japan) after filtration of 300 mL of seawater onto Whatman GF/F glass fiber filter and extraction in 90% acetone according to Parsons et al. (1984).

Wind speeds were measured at a height of 10 m with a 27600-4X ship-borne weather instrument (Young, USA).

2.4. Calculation

2.4.1. CO flux

According to Xie et al. (2002), CO concentration in the initial surface seawater samples, $[CO]_{surf}$ ($nmol\ L^{-1}$), could be calculated as:

$$[CO]_{surf} = pm_a(\beta pV_w + V_a)/(RTV_w) \tag{2}$$

where m_a is the equilibrated headspace mixing ratio (ppbv); β ($(mL\ CO)(mL\ H_2O)^{-1}\ atm^{-1}$) is the Bunsen solubility coefficient of CO, which is a function of temperature and salinity (Wiesenburg and Guinasso, 1979); *p* is the atmospheric pressure (atm); V_w is the water sample size (mL); V_a is the volume of the headspace air (mL); *R* is the gas constant ($0.08206\ atm\ L\ mol^{-1}\ K^{-1}$), and *T* is the temperature (K).