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Carbon monoxide distribution and microbial consumption in the Southern Yellow Sea

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ABSTRACT

Two cruises were conducted in the Southern Yellow Sea (SYS) in late July and early August 2008 to study marine carbon monoxide (CO) distribution, sea-to-air flux, and microbial consumption. Surface water dissolved CO showed an apparently higher average concentration (31.9% higher) during the second cruise than during the first cruise. Surface water CO concentrations were found to follow an apparent diurnal variation, during which CO concentrations varied by a factor of 8–14. Atmospheric CO mixing ratios ranged from 194 to 596 ppbv with an average of 390 ppbv for the first cruise, and from 53 to 238 ppbv with an average of 124 ppbv for the second one. Average sea-to-air CO fluxes (W92) were estimated to be 4.58 μmol m^{-2} d^{-1} and 0.08 μmol m^{-2} d^{-1} for the first and second cruise, respectively. Incubation experiments were conducted at 12 stations during the second cruise; results showed that surface-water microbial CO consumption rate constants (K_{co}) ranged from 0.07 to 0.83 h^{-1}, with an average of 0.33 h^{-1}. Microbial CO uptake typically followed first-order reaction kinetics at most of the studied stations.

1. Introduction

Atmospheric CO plays an important role in controlling atmospheric oxidation capacity through its reaction with hydroxyl radical (OH) (Derwent, 1995), thus imposes an impact on other reduced species, such as methane (Crutzen and Zimmermann, 1991; Thompson, 1992). CO oxidation in conjunction with the reduction of NO_x has an influence on the abundance of tropospheric ozone that is a potential greenhouse gas and atmospheric oxidant (Dignon and Hameed, 1985; Stubbins et al., 2006). The major source of oceanic CO is *in-situ* photolysis of colored dissolved organic matter (CDOM); and its sink includes microbial consumption, sea-to-air exchange (Conrad and Seiler, 1980, 1982; Bates et al., 1995), and vertical mixing (Kettle, 1994, 2005; Najjar et al., 1995; Gnanadesikan, 1996; Johnson and Bates, 1996; Stubbins et al., 2006).

The ocean, as a whole, is a source of atmospheric CO. Carbon monoxide (CO) in seawater has been studied intensively worldwide: from initial laboratory experiments (Swinnerton et al., 1968; Xie et al., 2002), sea-to-air flux estimates (Stubbins et al., 2006; Yang et al., 2010, 2011), to the mechanisms of biological consumption (Xie et al., 2005; Zhang et al., 2008), and photoproduction (Zhang et al., 2006; Yang et al., 2011). However, there are only a few papers reporting CO distribution, and biological CO consumption in marginal seas around China. The objective of this study is to supply CO data to the global CO biogeochemical cycle database.

The Yellow Sea (YS) is divided into northern YS and southern YS (SYS) by a line between Chengshanjiao in Shandong Peninsula and Jangsan point in Korean Peninsula. The bathymetry along the western coasts (China side) in the SYS is characterized by a wide shallow water, Subei Bank (Lü et al., 2010). The SYS has a total surface area of 30.9 $\times$ 10^4 km^2 and an average depth of 46 m. The hydrographic character of this region is mainly defined by a circulation system that includes the Yellow Sea Cold Water Mass, the Yellow Sea Warm Current, and the Yellow Sea Coastal Currents on the western side (Feng et al., 1999; Yuan et al., 2008). With the Jiaozhou Bay and the Haizhou Bay located on the west of the SYS, the SYS is not only one of the most concentrated regions of human activities and economic development, but also an intense

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interaction zone of land, sea, and atmospheric processes. Owing to its shallow depth, the SYS has no deep-water mass exchange, leading to relatively poor self-purification ability and hydrological conditions, which makes the SYS a quite complicated area.

In this paper, we reported the distribution of CO in surface water and in the atmosphere of the SYS in July and August 2008.

2. Material and methods

2.1. Sampling

The studied area in the SYS is presented in Fig. 1. A total of 55 sea surface samples were collected on board R/V "*Dong Fang Hong 2*" during two cruises conducted respectively in July 22–26 and August 5–14, 2008. Water samples were collected using 12-L Niskin bottles mounted on a Seabird CTD-Sonde Rosette supplying salinity, temperature, and depth data. Blanks of our sampling bottles were estimated to be at picomolar levels due to the fact that the bottles were held in a waterproof shelter that provided a low-light environment to ensure the Niskin bottles' acceptability (Zhang et al., 2006; Xie et al., 2009). Atmospheric CO samples were collected on the top deck of the ship (10 m above sea level) with a 50-ml dry, acid-cleaned, and gastight glass-only syringe when the ship was underway. In this way, the exhausts of the ship would not significantly contaminate the atmospheric CO samples.

2.2. CO analysis and incubation

Both atmospheric and seawater CO samples were immediately (normally less than half an hour) analyzed onboard after collection following the methods described in Xie et al. (2002) and Lu et al. (2010). Briefly, water samples were transferred from Niskin bottles into 50-ml acid-cleaned glass-only syringes using a Teflon tube coupled with a three-way Nylon valve. Sampling syringes were rinsed with sample water for three times, including one bubble-free flushing, before the final drawing. Surface water samples (average depth: 0.5 m) were analyzed as soon as being sampled with no delay to avoid any possible production or consumption. A precise ratio between sample water and CO-zero headspace air was set using a device described in Xie et al. (2002). Phase equilibration was established by shaking the sampling syringe for 4 min with a shaker (GJ-8175, Feihuang®, Guangdong, China). After that, headspace sample was injected into a RGA3 reduction gas analyzer (Trace Analytical Model ta3000R Gas Analyzer, Ametek®, USA). A 0.2 μm Nuclepore Teflon water-impermeable (13-mm diameter) filter fitted in a filter holder (Millipore®) was used here to prevent any liquid water from being injected into the analyzer. Atmospheric samples were injected into the analyzer immediately after sampling. Calibration was conducted every few hours with a commercial standard CO gas (nominal concentration: 299 ppbv in zero-grade air, analytical accuracy: ±5%, DaTe®, Dalian, China) that was a certified reference material with the standard reference material No. 060152, and was approved by China State Bureau of Technical Supervision.

In the incubation experiments, surface-water was incubated in a 200 ml acid-cleaned Al-foil wrapped all-glass syringe at a temperature ±1 °C of surface water temperature. A 50 ml acid-cleaned glass syringe was used to get sub-samples from the 200 ml incubation syringe. The first sample was sampled and measured immediately after each incubation; and the second one was analyzed half an hour later after the first sample. The following sub-samples were analyzed at appropriate intervals depending on CO consumption rate. The method precisions for repeated analyses of water samples, atmospheric samples, and incubation samples were about 5%, 3%, and 7%, respectively, in routine sample analysis.

Water temperature and salinity data were obtained from the CTD. Wind speeds were measured at a height of 10 m by ship-borne weather instrument (27600-4X, Young®, US).

2.3. Calculation of CO flux

Sea-to-air CO fluxes were calculated according to the gas exchange model of Liss (1973), which assumes that sea-to-air flux (F) is proportional to the product of the concentration difference ($C_{obs}-C_{eq}$) across the air-sea interface and a transfer velocity (k):

$$F = k \times (C_{obs} - C_{eq})$$

where the transfer velocity k was calculated using the quadratic k/wind speed relationship established by Wanninkhof (1992) (W92), and was adjusted by multiplying $(Sc_{CO}/660)^{-0.5}$, where Sc_{CO} is the Schmidt number for CO. The Sc_{CO} in seawater was calculated according to Zafiriou et al. (2008):

$$Sc_{CO} = -0.0553T^3 + 4.3825T^2 - 140.07T + 2134$$

where T is temperature in Celsius degree. C_{obs} is the observed concentration of dissolved CO, which is calculated according to Xie et al. (2002). Briefly, the initial CO concentration ($\{CO\}_{eq}$ in ml CO/ml H_2O) is calculated, assuming a mass balance:

$$\{CO\}_{eq} = 10^{-6} \times m_a \times (\beta \times p \times V_w + V_a)/V_w$$

where m_a is equilibrated headspace mixing ratio (ppmv); β is the Bunsen solubility coefficient of CO, which varies as a function of temperature and salinity (Wiesenburg and Guinasso, 1979); p is atmospheric pressure (atm) of dry air; V_w is the volume of water sample (ml); V_a is the volume of the headspace air (ml). C_{obs} (nM) is calculated using the following equation:

$$C_{obs} = 10^9 \times p \times \{CO\}_{eq} \Big/ (R \times T)$$

where R is the gas constant (0.08206 atm L mol^{-1} K^{-1}); and T is the temperature (K).

C_{eq} is the air-equilibrated seawater CO concentration.

$$C_{eq} = (CO_a \times \beta)/M$$

where CO_a is the CO mixing ratio of the atmosphere (ppbv); M is the molar volume of CO at standard temperature and pressure, 25.094 L mol^{-1} (Lide, 1992; Stubbins et al., 2006).

3. Results and discussion

3.1. Atmospheric CO

Atmospheric CO mixing ratios in the investigated area ranged from 194.8 to 596.9 ppbv with an average of 390.4 ppbv for the first cruise, which was higher than those reported in the literature. For instance, Yang et al. (2010) reported that average CO mixing ratio was 297 ppbv in the overlapped study area in November 2007. Lam et al. (2000) reported that average CO mixing ratio in autumn was 313 ppbv at their monitoring site Cape D'Aguilar (22.2°N, 114.3°E, 60 m above sea level). Stubbins et al. (2006) found that mean CO mixing ratio was 151 ppbv over the ocean from Montevideo, Uruguay (35°S, 55°W) to Grimsby, UK (54°N, 0°W) in April and May 2000. The higher atmospheric CO mixing ratio observed during the