温帯沿岸域の海面ミクロ層における一酸化炭素（CO）動態
Dynamics of carbon monoxide (CO) in the sea surface microlayer of temperate coastal waters

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Introduction

In the atmosphere, carbon monoxide (CO) is one of the dominant sinks of hydroxyl radical which regulates the concentration of greenhouse gases (GHGs) such as methane and ozone. Thus, CO is considered as an indirect GHG (Thompson 1992). Generally, CO concentration dissolved in the surface ocean was supersaturated compared to the atmospheric concentration, and the ocean is a source of atmospheric CO (Conrad et al. 1982). In the surface ocean, CO is primarily produced by the photochemical degradation of chromophoric dissolved organic matter (CDOM) and lost by biological oxidation and sea-air gas exchange (Zafiriou et al. 2003).

Sea-air gas exchange is mainly constrained by molecular diffusion in the water-side diffusive sublayer (Upstill-Goddard et al. 2006), and the sublayer is known as the sea surface microlayer (SML), defined as the less than 1-mm uppermost layer of the ocean water column (Liss & Duce 1997). Previous studies indicated that microbial activity in the SML changes the sea-air gas transfer velocity of atmospheric trace gases (Conrad & Seiler 1988). Thus, it is essential to understand the production and consumption of the gases in the SML.

Due to intense solar radiation and the accumulation of CDOM and microorganisms (Sugai et al. in press), the photochemical production and biological consumption of CO in the SML may be more active compared to the subsurface water (SSW). Therefore, the objective of the present study is to clarify the production and consumption of CO in the SML.

Materials & Methods

The present study was conducted at St. M (120 m depth) in Sagami Bay, Japan. The SML (380 ±9 μm thickness) and SSW (0.5 m depth) samples were collected using a mesh screen and horizontal Niskin bottle, respectively (Garrett 1965). Dissolved CO concentration, photochemical CO production rate, and first-order biological CO consumption rate constant (k_{CO}) as well as water temperature, salinity, wind velocity, solar radiation, dissolved organic carbon concentration, the absorption coefficient of CDOM at wavelength λ ($a_{CDOM}(\lambda)$), bacterial abundance, and chlorophyll *a* (chl. *a*) concentration were measured. Sea-air CO flux was estimated as k_w (CO_{sw} –$CO_{eq.}$) where k_w is gas transfer velocity calculated according to Nightingale et al. (2000), CO_{sw} is CO concentration in seawater, and $CO_{eq.}$ is CO concentration in seawater equilibrated with the atmospheric concentration calculated following Wiesenburg & Guinasso (1979).

Results & Discussion

CO concentration ranged from 0.82 to 14.9 nM (mean 3.60 nM) in the SML and from 0.41 to 7.55 nM (mean 2.88 nM) in the SSW. Sea-air CO flux was 7.01–498 nmol m^{-2} h^{-1}. Sea-air turnover time in the SML, calculated using CO concentration in the SML, SML thickness, and sea-air CO flux, varied from 0.01 to 0.11 h.

During the study period, a_{CDOM} (320) was significantly higher in the SML relative to the SSW ($p < 0.05$). CO production rate was higher in the SML (3.44–8.93 nM h^{-1}) than in the SSW (1.26–2.23 nM h^{-1}) during summer. Significant positive correlations were observed between a_{CDOM} (320) and CO production rate both in the SML ($p < 0.01$) and SSW ($p < 0.01$). a_{CDOM} (320) showed significant relationship with chl. *a* concentration both in the SML ($p < 0.001$) and SSW ($p < 0.05$), which indicates that CDOM was mainly derived from phytoplankton. Photochemical turnover time in the SML, calculated using CO concentration and production rate in the SML, ranged from 0.34 to 10.3 h. Because photochemical turnover time in the SML was largely higher than sea-air turnover time, this study indicates that CO in the SML was primarily supplied from the SSW.
No significant difference was observed between k_{CO} in the SML and SSW during the study period ($p = 0.46$). Biological turnover time in the SML, calculated using k_{CO}, varied from 6.67 to 21.7 h, which was largely higher than sea-air turnover time in the SML. Therefore, the present study indicates that CO in the SML was primarily lost by sea-air gas exchange.

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