Production and Consumption of Carbon Monoxide in Sea Surface Microlayer and the Changes by Increase in Water Temperature

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Introduction

The sea surface microlayer (SML) is defined as less than 1,000-μm thick uppermost layer of the ocean water column. The SML is located at air-sea interface and plays critical roles in global biogeochemical cycles and climate change through the regulation of air-sea gas exchange. The SML forms physically, chemically, and biologically distinct environments compared to the subsurface water (SSW). Interestingly, previous studies have reported significant enrichment of chromophoric dissolved organic matter (CDOM) in the SML although the SML is exposed to the most intense solar radiation in marine environments, which suggests active photochemical processes in the SML by the photodegradation of CDOM. Significant enrichment of bacteria in the SML has also been observed, suggesting active biochemical processes there by bacterial metabolism. Thus, carbon monoxide (CO), mainly produced by the photochemical degradation of CDOM and consumed by aerobic bacterial oxidation in the ocean, was expected to be produced and consumed in the SML actively.
CO concentration regulates the concentrations of various greenhouse gases (GHGs) in the troposphere as an indirect GHG. Generally, because CO in surface waters is supersaturated with respect to its atmospheric concentration, the ocean acts as a source of atmospheric CO. Although high CO production and consumption rates in the SML are expected, they have not been investigated. Further, because the SML is the first in the ocean to receive the increase in water temperature due to global warming, the evaluation of feedback on global warming due to the changes in CO production and consumption rates in the SML by water temperature increase is required to better understand the ocean-climate feedback processes.
Therefore, the present study aimed to clarify the photochemical production and biological consumption of CO in the SML by conducting field investigation. Seawater warming experiments were also carried out to clarify the changes of CO production and consumption in the SML by the increase in water temperature.

Materials & Methods

Monthly surveys were conducted from June 2017 to June 2019 in temperate coastal waters of Sagami Bay, Japan. SML samples were collected using a nylon mesh screen. To estimate photochemical CO production rate, seawater was incubated under the *in situ* water temperature and light conditions. For the estimation of biological CO consumption rate, seawater was incubated at the *in situ* water temperature under the dark condition.
During autumn, winter, spring, and summer, CO production and consumption rates in the SML were estimated as described above except the condition of water temperature. Seawater was incubated at 3°C higher (+ 3°C condition) and the *in situ* water temperature (control condition).

Results & Discussion

In the SML, the light-normalized photochemical CO production rate was relatively high from spring to autumn (3.85 ±3.09 nM [kWh $m^{-2}]^{-1}$) when relatively high CDOM absorbance (0.69 ±0.38 m^{-1}) was

observed. Biological CO consumption rate constant (k_{CO}) in the SML showed relatively high values from spring to autumn (0.060 ±0.010 h^{-1}) during the period of relatively high water temperature (22.3 ±2.7˚C). Significant relationships were observed between CDOM absorbance and the light-normalized CO production rate and between water temperature and k_{CO} in the SML.
The light-normalized CO production rate of the + 3˚C condition was not significantly different from that of the control condition throughout the year. On the other hand, k_{CO} tended to increase with the increase in water temperature during autumn, winter, and spring. Because the stimulation of CO consumption in the SML suppresses CO emission to the atmosphere, the present study suggests that the warming of surface seawater leads to negative feedback on global warming through the changes of CO dynamics in the SML from spring to autumn in temperate coastal waters.

Keywords: Air-sea gas exchange, Sea surface microlayer (SML), Photochemistry, Microbiology, Carbon monoxide (CO), Global warming