Enrichment of organic matter and microorganisms in the sea surface microlayer of temperate coastal waters and its roles in air-sea gas exchange

温帯沿岸域の海面ミクロ層における有機物・微生物の集積と
大気－海洋間のガス交換における役割

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SYNOPSIS

海洋の最表層 1 mm 未満の層である海面ミクロ層は、大気と海洋の境界に位置しており、大気－海洋間のガス交換を通して生物地球化学的物質循環や気候変動に重要な役割を果たしていると考えられている。本研究では、温帯沿岸域の海面ミクロ層における有機物・微生物の集積とその大気－海洋間のガス交換における役割を明らかにすることを目的とし、相模湾沿岸の海面ミクロ層における、有機物濃度・微生物現存量の季節性（Study 1）および光化学的・生物学的に生成・消費される一酸化炭素（CO）の動態（Study 2）を調査した。Study 1 では、海面ミクロ層における有機物（溶存態・懸濁態有機炭素、有色溶存態有機物［CDOM］、透明細胞外ポリマー粒子）濃度および微生物（植物プランクトン、細菌、ナノ鞭毛藻・虫）現存量が年間を通して海面直下（水深 0.5 m）よりも有意に高く、春季（2014 年 4 月、2015 年 5 月）に大きく増加した。これは、外部からの無機栄養塩（リン酸塩）の負荷により海面ミクロ層において植物プランクトンブルームが起こったためであると考えられ、温帯沿岸域の海面ミクロ層における化学的・生物学的要因の季節性が示された。Study 2 では、海面ミクロ層において、培養期間中の太陽放射照度で標準化した CO 生成速度は CDOM の集積が見られた春季から秋季（2017 年 6 月−11 月、2018 年 3 月−6 月）に比較的高い値（3.85 ± 3.09 nM [kWh m^{-2}]$^{-1}$）を示し、CO 消費速度定数は高水温期の春季から秋季（2017 年 6 月−11 月、2018 年 5 月−6 月）に比較的高かった（0.060 ± 0.010 h^{-1}）。また、海洋－大気 CO フラックス（F）は海面直下における CO 濃度と同様に変動したが、海面ミクロ層では春季（2017 年 6 月）の植物プランクトンブルーム時に CO 濃度が大きく増加し（15.0 nM）、海面ミクロ層における植物プランクトン由来の有機物の集積により大気－海洋間のガス交換が抑制されることが示唆された。海面ミクロ層における CO の生成・消費および大気への放出の滞留時間（それぞれ τ_{prod}, τ_{cons}, $\tau_{sea\text{-}air}$）を比較したところ、τ_{cons}（13.5−27.8 h）は $\tau_{sea\text{-}air}$（0.003−0.079 h）よりもはるかに高く、海面ミクロ層における生物学的 CO 消費は大気－海洋間の CO 交換を考慮する上で無視できることが示唆された。しかし、τ_{prod}（0.36−11.5 h）は夏季（2017 年 8 月）に $\tau_{sea\text{-}air}$ と比較的同等の値（$\tau_{sea\text{-}air}/\tau_{prod}$ = 21.9%）を示し、海面ミクロ層における光化学的 CO 生成は太陽放射照度と生物生産が高く、風速が低い夏季に F を高めることが示唆された。

Keywords: Sea surface microlayer (SML), Temperate coastal water, Seasonality, Phytoplankton bloom, Organic matter, Microorganism, Air-sea gas exchange, Carbon monoxide (CO)

Introduction

The sea surface microlayer (SML) is defined as less than 1,000-µm uppermost layer of the ocean water column (Liss & Duce 1997). Because the SML is located at the interface between the atmosphere and the ocean, the SML plays critical roles in global biogeochemical cycles and climate change through the regulation of the air-sea exchange of relatively insoluble, climate-related gases (Cunliffe et al. 2013).

The SML is exposed to the most intense solar radiation, especially, ultraviolet radiation, and subject to the largest magnitude of salinity change due to precipitation in the ocean. Further, previous studies have reported significantly higher organic matter concentration and microbial abundance in the SML than in the subsurface water (SSW), usually at 0.5–1 m, of various oceanic areas (e.g. Joux et al. 2006). The enrichment of organic matter and microorganisms in the SML results from higher production in the SML than in the SSW and/or upward transport in the water column through passive adsorption on rising bubbles and buoyant particles such as transparent exopolymer particles (TEPs) (Liss & Duce 1997), which rapidly form aggregates with organic particles and microbial cells (Azetsu-Scott & Passow 2004). Thus, the SML forms physically, chemically, and biologically distinct environments compared to the SSW.

Conrad & Seiler (1988) conducted air-sea gas exchange experiments under the controlled turbulent condition and found significant difference between the air-sea and sea-air gas transfer velocity (k_w) of atmospheric trace gases such as methane and carbon monoxide (CO). This result indicates that gases can be produced and/or consumed enough to change k_w while they pass through the SML via molecular diffusion. Salter et al. (2011) experimentally showed significant decrease in k_w even at high wind speed in artificially surfactant-covered waters compared to natural areas, which indicates the suppression of air-sea gas exchange by organic film formed in the SML. These studies suggest that chemical and biological reactions and the accumulation of organic matter in the SML are required to be considered in addition to wind condition to estimate k_w and subsequently calculate air-sea gas flux accurately as pointed out by Cen-Lin & Tzung-May (2013).

Interestingly, Obernosterer et al. (2008) showed that chromophoric dissolved organic matter (CDOM) was significantly enriched in the SML which receives the highest light intensity, indicating active photochemical reactions in the SML. Further, previous studies have reported significant enrichment of bacteria in the SML, which indicates active biochemical reactions by bacteria there. Based on these studies, CO was suggested to be most actively produced and/or consumed in the SML among climate-related, atmospheric trace gases because CO was mainly produced by the photochemical

degradation of CDOM and consumed by biological oxidation by bacteria.

Temperate coastal waters are one of the most productive areas in the ocean. In the water column, the seasonal patterns of vertical structure, chemical distribution, and biological productivity are clearly observed (Sugai et al. 2016). Seasonal events such as phytoplankton blooms during spring are also expected to occur in the SML, and the enrichment of organic matter and microorganisms in the SML may also show seasonality. However, the seasonality in chemical and biological parameters in the SML of temperate coastal waters has never been investigated, and time-series investigation at the same sampling station is required to provide information on dynamic and complex interactions in the SML (Cunliffe et al. 2013).

Therefore, the objective of the present study was to clarify the enrichment of organic matter and microorganisms in the SML of temperate coastal waters and its roles in the air-sea exchange of CO. First, the seasonal variations in organic matter concentration and microbial abundance and relationships between them in the SML and SSW were investigated by a two-year monthly field survey (Study 1). Then, a one-year monthly field survey and incubation experiments were conducted to investigate CO production and consumption in the SML and SSW and evaluate their significance in air-sea CO exchange (Study 2). The formation, chemical and biological characteristics, and biogeochemical roles of the SML in temperate coastal waters are discussed.

Materials and Methods

Study 1. Seasonal variation in the enrichment of organic matter and microorganisms in the SML

Surveys were conducted monthly for two consecutive years from September 2013 to September 2015 at Station M (120 m depth, 35°09'45"N, 139°10'00"E), located 2 km northeast off the Manazuru Peninsula, in coastal waters of Sagami Bay, Japan. SML samples were taken using a nylon mesh screen (nylon diameter: 430 μm, mesh size: 1.25 mm) (Garrett 1965) to effectively collect dissolved and particulate materials with a wide range of sizes during a relatively short period (Agogué et al. 2004). The thickness of the collected SML was calculated to be 380 ± 9 μm. SSW samples were taken at 0.5 m depth using a horizontal Niskin bottle.

Water temperature, salinity, inorganic nutrients such as phosphate (PO_4), dissolved organic carbon (DOC), the absorption coefficient of CDOM at 320 nm (a_{CDOM} [320]), particulate organic carbon (POC), TEPs, chlorophyll (chl.) *a*, bacterial abundance, and autotrophic and heterotrophic nanoflagellate (ANF and HNF, respectively) abundance were measured. Wind speed data were obtained from the Japan Meteorological Agency. The extent of enrichment in the SML was numerically expressed as enrichment factors (EFs), defined as the ratio of a value in the SML to that in the SSW (e.g. Joux et al. 2006).

Study 2. CO production and consumption in the SML and emission to the atmosphere

Surveys were conducted monthly for a year from June 2017 to June 2018 at the same sampling station as Study 1. A nylon mesh screen was used again to reduce unavoidable CO loss from SML samples during samplings (Yang et al. 2001).

In addition to parameters measured in Study 1, solar irradiance, dissolved CO concentration ([CO]), photochemical CO production rate, and biological CO consumption rate constant (k_{CO}) were measured. [CO] was measured by headspace analysis and GC-FID analysis (e.g. Ohta 1997). Photochemical CO production rate and k_{CO} were estimated by incubating seawater in quartz bottles for 2–12 h at the *in situ* water temperature under the natural light and dark conditions, respectively (e.g. Xie et al. 2005). [CO] was determined using the Bunsen solubility coefficient of CO (Wiesenburg & Guinasso 1979). Sea-air CO flux (F) was calculated by $F = k_w (C_{sw} - C_{eq})$ where C_{sw} and C_{eq} are [CO] in the SSW and in seawater equilibrated with the atmospheric [CO], respectively. k_w was determined using wind speed and water temperature according to a wind-driven turbulent model (e.g. Nightingale et al. 2000). The turnover time of photochemical CO production (τ_{prod}), biological CO consumption (τ_{cons}), and sea-air CO emission ($\tau_{sea\text{-}air}$) in the SML were calculated by τ_{prod} = [CO] / photochemical CO production rate, $\tau_{cons} = 1 / k_{CO}$, and $\tau_{sea\text{-}air}$ = [CO] in the SML × SML thickness / F, respectively (e.g. Yang et al. 2001).

Results and Discussion

Study 1. Seasonal variation in the enrichment of organic matter and microorganisms in the SML

During the study period, DOC (Wilcoxon signed-rank test, $p < 0.001$), a_{CDOM} (320) ($p < 0.001$), POC ($p < 0.001$), TEPs ($p < 0.001$), chl. *a* ($p < 0.05$), ANF abundance ($p < 0.001$), bacterial abundance ($p <$

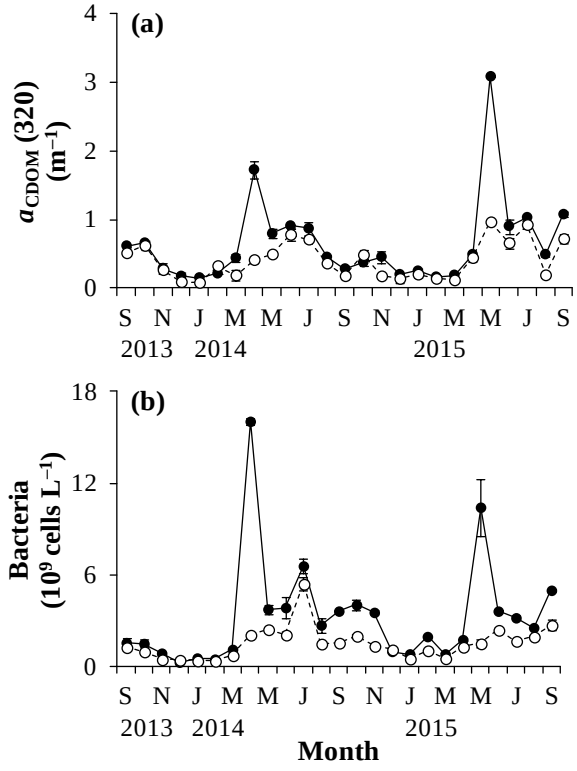

Fig. 1. Seasonal variations in (a) the absorption coefficient of chromophoric dissolved organic matter at 320 nm (a_{CDOM} [320]) and (b) bacterial abundance in the surface microlayer (closed circles) and subsurface water (open circles) from September 2013 to September 2015 (Sugai et al. 2018)

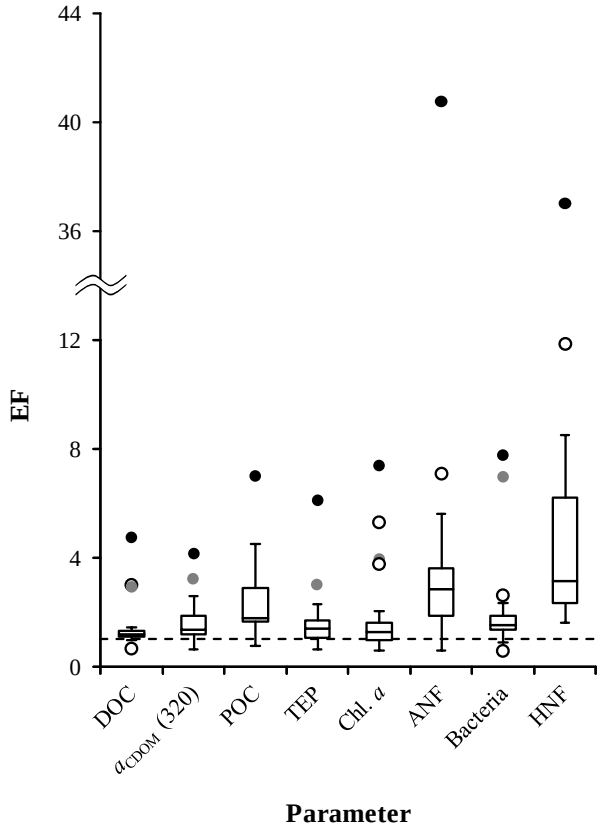

Fig. 2. Enrichment factors (EFs) of organic matter concentration and microbial abundance. Closed black circles, closed gray circles, and open circles represent outliers in April 2014, May 2015, and the other months, respectively. Dashed line indicates EF = 1

0.001), and HNF abundance ($p < 0.001$) in the SML were all significantly higher compared to the SSW (Fig. 1) (Sugai et al. 2018). Seasonally, the values in the SML and thus the EFs of these chemical and biological parameters particularly increased during spring (in April 2014 and May 2015) except for POC and flagellate abundance in May 2015 (Fig. 2).

During the study period except in April 2014 and May 2015, the mean EFs of chemical and biological parameters were within ranges reported by previous studies (e.g. Joux et al. 2006). During the period, each chemical and biological parameter in the SML and SSW was significantly positively correlated, which shows that organic matter concentration and microbial abundance in the SML varied similarly to those in the SSW. Because no significant relationship was observed between the EFs of TEP concentration and other chemical and biological parameters except chl. *a*, significant enrichment of organic matter and microorganisms in the SML during the period possibly resulted from a combination of higher production in the SML and upward transport in the water column through passive adsorption on rising bubbles and buoyant particles other than TEPs.

In April 2014 and May 2015, the EFs of chemical and biological parameters except for POC and flagellate abundance in May 2015 showed high values enough to be comparable with those reported by Wurl et al. (2011), conducted in visible slick areas, and Nakajima et al. (2013), conducted in coral reef waters. Because the ratio of TEP to POC concentrations, used to examine the possibility of the upward transport of TEP aggregates in the water column, was not high in the SSW in April 2014 (1.20 mg X_{eq} mgC^{-1}) and May 2015 (1.10 mg X_{eq} mgC^{-1}) compared to other months (1.09 ± 0.59 mg X_{eq} mgC^{-1}), the possibility was unlikely. Interestingly, relatively high PO_4 concentration, which is enough to relieve the nutrient limitation of phytoplankton during spring, was observed in the SML in April 2014 (0.61 µM) and May 2015 (0.52 µM) despite much lower values in the SSW (0.02 µM and 0.05 µM, respectively). The *in situ* field investigation and bioassay experiments by Fujiki et al. (2004) indicated the limitation of phytoplankton growth by PO_4 unavailability in coastal waters of Sagami Bay. These facts suggest that organic matter and microorganisms showed particular enrichment in the SML in April 2014 and May 2015 due to phytoplankton blooms in the SML induced by the external supply of PO_4. Further, the particular enrichment was maintained probably by the formation of the viscous, stable SML due to the accumulation of TEPs without the disruption of the SML by wind-induced wave mixing at wind speed of 3.8 m s^{-1} in April 2014 and 2.8 m s^{-1} in May 2015.

Study 2. CO production and consumption in the SML and emission to the atmosphere

Photochemical CO production rate normalized by the integrated solar irradiance during the incubation period in the SML was relatively high from spring to autumn (3.85 ± 3.09 nM h^{-1}) and significantly higher compared to the SSW (1.22 ± 0.65 nM h^{-1}) during the period (Paired *t*-test, $p < 0.01$) (Table 1). On the other hand, no significant difference was observed between the CO production rate in the SML (0.84 ± 0.31 nM h^{-1}) and SSW (0.65 ± 0.60 nM h^{-1}) during winter ($p = 0.41$). The CO production rate (y) was significantly positively correlated with a_{CDOM} (320) (x) both in the SML (y =

Table 1. Photochemical carbon monoxide (CO) production rate normalized by the integrated solar irradiance during the incubation period (CO prod. rate/light) and biological CO consumption rate constant (k_{CO}) in the surface microlayer (SML) and subsurface water (SSW) from June 2017 to June 2018

Month	CO prod. rate/light (nM [kWhm^{-2}]$^{-1}$)		k_{CO} (h^{-1})	
	SML	SSW	SML	SSW
Jun 2017	10.5	2.22	0.064	0.094
Jul	2.49	0.90	0.064	0.085
Aug	7.58	2.14	0.074	0.092
Sep	3.43	1.29	0.063	0.081
Oct	5.51	1.98	0.067	0.058
Nov	1.61	0.68	0.042	0.071
Dec	1.20	1.33	0.037	0.031
Jan 2018	0.65	0.46	0.068	0.045
Feb	0.68	0.18	0.043	0.012
Mar	1.22	0.48	0.062	0.018
Apr	1.24	0.63	0.036	0.019
May	2.28	0.91	0.057	0.057
Jun	2.65	1.00	0.048	0.056

6.60 x − 0.58, $p < 0.001$) and SSW ($y = 2.99\ x + 0.06$, $p < 0.01$). This result indicates that photochemical CO production is mainly regulated by light intensity and CDOM absorbance. The slope of the relationship in the SML (6.60) was higher than that in the SSW (2.99), which indicates higher photochemical degradability of CDOM in the SML under more intense light condition. Both in the SML and SSW, a_{CDOM} (320) (y) showed a significant positive relationship with not salinity ($p = 0.28$ and 0.24, respectively) but chl. a (x) ($y = 0.271$ ln $[x] + 0.477$, $p < 0.001$ and $y = 0.143\ x + 0.165$, $p < 0.01$, respectively). This result indicates that CDOM was mainly derived from autochthonous phytoplankton, and the difference between the relationships in the SML and SSW was probably due to more active photodegradation of CDOM in the SML under more intense light condition.

k_{CO} in the SML was relatively high from spring to autumn (0.060 ± 0.010 h^{-1}) and significantly lower compared to the SSW (0.074 ± 0.016) during the period ($p < 0.05$) (Table 1). In contrast, significantly higher k_{CO} was observed in the SML (0.049 ± 0.015 h^{-1}) than in the SSW (0.025 ± 0.013 h^{-1}) from winter to spring ($p < 0.05$). These results indicate that biological CO consumption in the SML was inhibited by relatively strong solar radiation from spring to autumn as reported by Tolli & Taylor (2005), and that the photoinhibition was alleviated under relatively weak light condition from winter to spring. k_{CO} (y) showed a significant positive correlation with water temperature (x) both in the SML ($y = 0.0018\ x + 0.0209$, $p < 0.05$) and SSW ($y = 0.0061\ x$ − 0.0662, $p < 0.001$). This result indicates that the activity of CO-oxidizing bacteria was mainly regulated by water temperature. The difference in the slopes of the relationship in the SML (0.0018) and SSW (0.0061) was probably due to different community structure of CO-oxidizing bacteria as reported by Cunliffe et al. (2008).

No significant difference was observed between [CO] in the SML (3.53 ± 3.61 nM) and SSW (3.59 ± 2.63 nM) during the study period ($p = 0.95$). In June 2017, [CO] in the SML was much higher (15.0 nM, 16,650% supersaturation) compared to other months (2.58 ± 1.14 nM). Interestingly, particularly high concentrations of chl. a (43.4 μg L^{-1}) and TEPs (2.25 mg X_{eq} L^{-1}) were also observed in June 2017. These results indicate that CO emission to the atmosphere was suppressed in June 2017 by the accumulation of biogenic surfactants in the SML derived from phytoplankton as reported by Salter et al. (2011). Under such a condition, the estimation of k_w and subsequently the calculation of F based on wind speed only can be erroneous. During the study period except in June 2017, the EF of [CO] (y) showed a significant negative relationship with [CO] in the SSW (x) ($y = 1.74\ e^{-0.213\ x}$, $p < 0.05$). This result indicates that large difference in air-sea [CO] increases CO loss from the SML as reported for dimethylsulfide by Yang et al. (2001). F ranged from 8.55 nmol m^{-2} h^{-1} in January 2018 to 574 nmol m^{-2} h^{-1} in April 2017. F was significantly positively correlated with [CO] in the SSW ($r = 0.925$, $n = 13$, $p < 0.001$) rather than k_w ($r = 0.767$, $n = 13$, $p < 0.01$).

During the study period, τ_{cons} (13.5–27.8 h) was three–four orders of magnitude higher than $\tau_{sea\text{-}air}$ (0.003–0.079 h), and the highest $\tau_{sea\text{-}air}/\tau_{cons}$ was only 0.58% in August 2017. This result suggests that biological CO consumption in the SML is not significant and can be ignored in air-sea CO exchange. On the other hand, although τ_{prod} (0.36–11.5 h) was one–three orders of magnitude higher than $\tau_{sea\text{-}air}$ during the study period, τ_{prod} (0.36 h) can be relatively comparable to $\tau_{sea\text{-}air}$ (0.079 h) in August 2017 with $\tau_{sea\text{-}air}/\tau_{prod}$ of 21.9%. In August 2017, moderate solar irradiance (205 W m^{-2} h^{-1}) and relatively high a_{CDOM} (320) (1.22 m^{-1}) probably due to relatively high chl. a (6.41 μg L^{-1}) were observed in addition to relatively low wind speed (1.1 m s^{-1}). These results suggest that photochemical CO production in the SML is significant in air-sea CO exchange and enhance F under intense light, active biological production, and weak wind conditions during summer. Thus, under such conditions, photochemical CO production in the SML must be considered to estimate k_w and subsequently F. Further, the comparison among τ_{prod}, τ_{cons}, and $\tau_{sea\text{-}air}$ indicates that CO loss by emission to the atmosphere largely dominates over that by biological consumption and that only photochemical production cannot counteract the CO loss to maintain the balance of CO in the SML, which suggests the overestimation of F and the importance of another source of CO in the SML such as gas transfer from the underlying water.

Conclusions

This study clarified the seasonality in chemical and biological parameters in the SML of temperate coastal waters. The enrichment of organic matter and microorganisms in the SML was particularly high during spring probably due to phytoplankton blooms there induced by the external supply of inorganic nutrients (PO_4). During a phytoplankton bloom in the SML, particularly high [CO] was observed in the SML, which indicates the suppression of air-sea gas exchange by the accumulation of biogenic surfactants in the SML. Whereas biological CO consumption can be ignored in air-sea CO exchange, photochemical CO production can enhance F under intense light, active biological production, and weak wind conditions during summer. Therefore, the present study suggests that, in temperate coastal waters, the accumulation of organic matter during spring and photochemical CO production during summer in the SML must be considered in air-sea gas exchange model to estimate k_w and subsequently calculate F accurately.

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