Distribution and sea-to-air exchange of carbon monoxide in surface microlayer and subsurface seawater in the eastern marginal seas of China

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Abstract

Sea-surface microlayer (SML) is the boundary interface between the atmosphere and ocean, exhibiting an enrichment of dissolved organic matter (DOM) and participating in sea-to-air gas exchange. However, how DOM enrichment in the SML controls the flux of several gases in sea-to-air exchange remains poorly understood. In our study, incubation experiments and in-situ investigation in the eastern marginal seas of China were conducted to determine the distribution of carbon monoxide (CO) and its production and consumption rates in the SML during winter. Chromophoric DOM (CDOM) (92%) and fluorescent DOM (FDOM) (92%) were frequently enriched in the SML during winter, and the enrichment of CO was lower than the enrichments of CDOM and FDOM. CO ranged from 0.48 to 2.81 nmol L^{-1} (1.22 ± 0.85 nmol L^{-1}) and 0.50 to 3.61 nmol L^{-1} (1.54 ± 1.61 nmol L^{-1}) in the subsurface layer (SSW) and the SML, respectively, with higher concentration observed in the SML due to CDOM enrichment. Enrichment in the SML was expressed as enrichment factors (EFs) defined as the ratio of values in the SML to those in the SSW. Although CO, CDOM and FDOM concentrations decreased from in-shore regions to open oceans, higher enrichment factors (EFs > 2) of CO and CDOM and FDOM in the SML were generally observed in the off-shore areas. Considering the photoproduction rate (mean value: 12.41 nmol L^{-1} d^{-1}) of CO in the SML was significantly higher than that in the SSW (10.32 nmol L^{-1} d^{-1}), the enrichment and the concentration of CO in the SML showed a diurnal variation, with the higher values observed in the early afternoon. The flux of CO exhibited a significantly negative correlation with the CDOM absorption coefficient at 254 nm and marine-humic-like FDOM in the SML, suggesting that elevated DOM could stimulate the

photoproduction of CO, but may also decrease sea-to-air CO exchange in the SML. Given the importance of the organic-rich SML as a diffusion layer in the air–sea exchange of climate-relevant gases and heat, understanding the layer's enrichment processes is crucial.

1. Introduction

Carbon monoxide (CO) is an indirect greenhouse gas, and it plays an important role in atmospheric chemistry (Nguyen et al., 2020). It is the predominant sink of hydroxyl radical (OH•, Conte et al., 2019; Cordero et al., 2019), which oxidizes pollutants and greenhouse gases (such as CH_4) emitted to the atmosphere by human activities (Nguyen et al., 2020). The photodegradation of dissolved organic matter (DOM) is thought to be the main source of CO in the ocean (Stubbins et al., 2006), and the ocean acts as a net source of atmospheric CO (Mopper and Kieber, 2002). In addition, direct production of CO by phytoplankton has been observed in laboratory experiments (Troxler et al., 1972; Gros et al., 2009) and dark/thermal production was also inferred from modeling at Bermuda Atlantic Time Series (BATS, Kettle, 2005), and from incubations of water samples from the Delaware Bay (Xie et al., 2005) and St Lawrence estuary (Zhang et al., 2008). Microbial consumption and sea-to-air fluxes (Doney et al., 1995; Song et al., 2015) of CO are considered the primary sinks of oceanic CO (Zafiriou et al., 2003). The average annual sea-to-air flux accounted for 10% of the global CO sinks estimated by Zafiriou et al. (2003), Conte et al. (2019) and Yang et al. (2024). In the ocean, CO acts as a microbial energy source that supports food webs, a link in carbon cycling that connects surface and deep waters, and a modulator

of oxygen cycles. With increasing concern about atmospheric pollution and the potential role of CO, a primary goal of studying oceanic CO concentrations is to evaluate its long-term stability and distribution trends in the marine boundary layer (Conte et al., 2019; Xu et al., 2023), where the ocean and atmosphere exchange momentum, heat, moisture, and gases.

The ocean surface layer plays a vital role in climate change through the sea-to-air exchange of greenhouse gases. The sea-surface microlayer (SML) is located at the sea-to-air interface and is considered to play a critical role in global biogeochemical cycles and climate change by regulating the sea-to-air exchange of gases and aerosol particles (Liss and Duce, 1997; Cunliffe et al., 2013). In addition, SML is exposed to the most intense solar radiation of any seawater layer, especially ultraviolet (UV) light, and shows significantly higher colored dissolved organic matter (CDOM) concentration and microbial abundances compared to the subsurface layer (SSW, Obernosterer et al., 2006; Obernosterer et al., 2008; Wurl et al., 2009; Yang et al., 2022). For decades, articles have emphasized the presence and enrichment of organic matter and gases (CO and DMS) in the SML (Liss and Duce, 1997; Orellana et al., 2011; Ma and Yang, 2023; Sugai et al., 2020), but it remains unclear how this is maintained whilst CO is lost to the atmosphere.

The role and response of the SML, along with the complex interplay of biological, geochemical, and physical processes, govern the transfer of CO from the SSW, where it can either be consumed by bacteria or released into the atmosphere. Generally, the sea-to-air flux is estimated from CO concentration in sea surface waters (2 to 10 m),

but there is evidence that biogeochemical processes within the SML may also affect the CO flux (Sugai et al., 2020). CDOM enrichment in the SML relative to the SSW has been reported, with an enrichment factor (EF) range of 0.4 to 6.7 (Huang et al., 2015; Shaharom et al., 2018; Yang et al., 2022), and mediates all mass transfer across the SML (Rickard et al., 2019 and 2022). Although intense solar radiation and enrichment of DOM may promote CO photoproduction involving SML (Cunliffe et al., 2013; Pereira et al., 2018; Sugai et al., 2021), and likely modify sea-to-air gas transfer velocity (k_w) of CO and other gases (Pereira et al., 2018). However, CO-related data from the SML is especially scarce, and the fate of CO in the SML remains unknown, because of the sampling limitation (Engel et al., 2017). Our study hypothesized that SML-specific environmental changes (i.e., enrichment processes and biogeochemical processes) and the abundance and composition of DOM in the eastern marginal seas of China influence the rate of sea-to-air CO exchange, and they contribute to the formation of the marine boundary layer involved in atmospheric chemistry and climate regulation.

2. Materials and Methods

2.1 Study Area

The Yellow Sea (YS) and the East China Sea (ECS) are marginal seas of the western Pacific Ocean with complicated hydrological characteristics and are substantially affected by the Yellow Sea Cold Water Mass (YSCWM), the Kuroshio Current, and the coastal currents (Fig. 1). The YSCWM is a low-temperature (< 10°C) and high-salinity (32.0–33.0) water mass. Seawater in the Kuroshio presents high

106 temperatures (20–29°C), high salinities (34.2–34.8), and low suspended particulate
107 concentrations (SPC) (< 2 mg L^{-1}) (Yang et al., 2022). The Changjiang River
108 contributed more than 80% of the total freshwater inflow to the YS and the ECS (Wang
109 et al., 2020). In addition, the atmospheric circulation in the study area was generally
110 governed by the East Asian monsoon, with strong northerly winds prevailing from
111 September to April. Low pressure over the northwestern Pacific Ocean produced
112 offshore winds that transported continental air masses into the study area (Li et al.,
113 2019). This interaction significantly influences the hydrological conditions, circulation
114 structures, material exchange, ecological environment, and the biogeochemical
115 processes of CO and DOM in the region (Chen, 2009; Yu et al., 2025; Zhang et al.,
116 2007).

117 *2.2 Sampling and analysis*

118 We collected 52 paired SML and SSW water samples in the YS and ECS aboard
119 the R/V "*Dong Fang Hong 3*" from 28 December 2019 to 16 January 2020. There were
120 38 sampling stations during the daytime (7: 00-19: 00) and 32 sampling stations during
121 the nighttime (19: 00-7: 00, Table S1). SSW samples were collected at 2–5 m depth
122 using 24 × 10 L Niskin bottles mounted on a rosette equipped with a conductivity–
123 temperature–depth (CTD) profiler. SML sampling used a Garrett Screen (Garrett, 1965;
124 Chen et al., 2016; Ma and Yang, 2023) (mesh: 16 mm, wire diameter: 0.36 μm; effective
125 surface area: 2.025 cm^2) according to standard procedures (Pereira et al., 2016;
126 Sabbaghzadeh et al., 2017) when seawater conditions were calm. While SML integrity

is disrupted by a moving vessel, or when sampling from its stern (Cunliffe and Wurl, 2014; Wurl et al., 2016), the SML can be successfully sampled from a vessel's bow while on-station (Sabbaghzadeh et al., 2017) with the ambient waterflow toward the RV (Cunliffe and Wurl, 2014). The sampling distance is at a certain distance (5 ~ 8 m) where the CTD sampler was deployed, and both SSW and SML CO did not change during the sampling. We therefore adopted this procedure, hand-deploying the Garrett Screen over the bow on the crest of a wave (Cunliffe and Wurl, 2014) and further minimizing potential contamination (engines off, wheelhouse and afterdeck downwind) (Pereira et al., 2016).

A TA3000R trace gas analyzer (Ametek, USA) was used to measure CO concentrations in the atmosphere and seawater with a lower detection limit of 10 ppbv. Before analysis, the instrument was calibrated using a CO standard gas (nominal concentration: 100 ppbv in zero-grade air; analytical accuracy: ± 2%, State Center for Standard Matter, China). The calibration was repeated every six hours during measurements. Atmospheric CO samples ($[CO]_{atm}$, ppbv) were collected about 10 m above sea level using a 10 mL gas-tight syringe (VICI, USA) and were obtained by injecting atmospheric samples directly into the instrument through a PTFE hydrophobic filter membrane (Millipore, USA, atmospheric CO samples were filtered for dust/aerosol particles) into the TA3000R trace gas analyzer for determination. To minimize the influence of ship emissions, $[CO]_{atm}$ samples were collected from the highest deck of the ship (~10 m), facing the wind, with 8 mL gastight glass syringes when the ship was decelerating. CO in seawater was measured using the headspace

equilibrium method (Xie et al., 2002), wherein a 50 mL sample bottle was filled with seawater sample and sealed (as above), and then an equivalent amount of the seawater sample was replaced with 8 mL of ultrahigh-purity N_2 using a gas-tight syringe. The samples were then shaken at 300 r min^{-1} for 5 min to ensure that the nitrogen-filled headspace in the bottle reached gas-liquid equilibrium before 6 mL of the equilibrated gas was extracted using a gas-tight syringe and injected through a PTFE hydrophobic filter membrane (Millipore, USA) into the TA3000R trace gas analyzer for determination (the PTFE filter membranes were set up to prevent the potential entry of liquid water). The measured equilibrated headspace mixing ratio of CO (ppbv) was corrected using the saturated water vapor pressure and standard atmospheric pressure (Stubbins et al., 2006) and then converted to obtain the concentration of dissolved CO (nmol L^{-1}) in seawater. The method's lower detection limit was 0.02 nmol L^{-1}, with an analytical accuracy of better than 10%.

CO data from the SML samples is scarce. The SML samples were collected in 500 mL brown sample bottles. The screen was held level and dipped into the sea surface, moved laterally to sample from an undisturbed film, and then withdrawn slowly from the surface. Repeated dipping (11 times, 600 mL) was conducted until the desired volume was collected (the depths of the SML samples ranged within 100–500 μm, Garrett, 1965). The screening method is often applied during field studies because of its relative quickness and large sample volume compared to other techniques (Chen et al., 2016). CO in seawater samples was collected and measured first on board, immediately after collection. A comparison showed that screen-collected samples

171 usually exhibit greater microlayer enrichment of gas than the plate-collected samples,
172 indicating that the screen sampler might be more effective for in-situ measurements
173 (Yang et al., 2001). Although established sampling techniques of the SML (Garrett
174 screen and glass plate) are associated with high losses for the volatile trace gases (Engel
175 et al., 2017). As the Garrett screen is widely used and can collect a large number of
176 SML samples in the short term (Turner and Liss, 1985; Walker et al., 2016; Yang et al.,
177 2001), we chose the Garrett screen.

178 CDOM, DOC, and Chl-*a* samples were filtered using 0.7 μm glass fiber filters
179 (GF/F, Whatmann) and the filtrates were transferred to 60- and 40-mL brown glass
180 bottles (pre-cleaned and pre-combusted) for later CDOM and DOC analyses. All
181 samples were frozen (−20°C) and protected from light. Upon arriving at the land
182 laboratory, samples were analyzed as soon as possible. Sea-surface temperature and
183 salinity were obtained from the sensors on the Seabird 911 CTD rosette. Seawater
184 temperature and salinity in the SML were measured *in situ* using a pre-calibrated multi-
185 parameter water quality probe (AP-5000, Aquaread Co., UK). Meteorological data (e.g.,
186 wind speed and air temperature, ~ 10 m) were recorded simultaneously by a ship-borne
187 weather instrument (Li et al., 2019, Table S1). Net solar radiation is the balance
188 between all incoming and outgoing radiant energy fluxes at the Earth's surface. Our
189 ocean surface net solar radiation was measured and recorded using a net radiometer
190 (Table S1). Ocean surface net solar radiation is significant in research on the Earth's
191 heat balance systems, sea-to-air interactions, and other applications.

192 *2.3 Photoexposure experiments*

193 The in-situ natural sunlight incubation experiment was conducted to estimate the
194 CO photoproduction rates in different seawater layers. SSW and SML samples for
195 photochemical incubation were collected from stations B1 and C4, as well as E2, FJ5,
196 P1, and P7, located in the YS and the ECS, respectively (Fig. 1). SML and SSW (5 m
197 below seawater surface) samples (SSW: 2 L; SML: 500 mL) were passed through a
198 0.22 μm PES filters (Pall Corp. Port Washington, NY, USA) immediately to remove
199 the majority of the bacteria and was then placed in an acid-washed and pre-combusted
200 quartz tubes (120 mL, acid-washed and pre-combusted) in a natural sunlight incubation
201 and sealed without headspace or air bubbles. Photo incubation experiments were
202 conducted on the ship immediately after sample collection. To measure the
203 photoproduction at solar radiation production rates of CO, the quartz tubes were treated
204 as follows: (1) uncovered quartz tubes exposed to full-spectrum irradiation; (2) quartz
205 tubes wrapped in multiple layers of aluminum foil to eliminate all light transmission.
206 Treatment (2) was subtracted from light-exposed treatments to remove the fraction of
207 CO produced by dark production. The quartz tubes were positioned under the in-situ
208 irradiation source to maximize the exposure of the sample; the water depth in each tube
209 was 5 cm (i.e., the diameter of the tube). SML and SSW quartz tubes were irradiated
210 for 4 hours and were exposed to direct solar irradiation while being held in a water bath
211 with circulating seawater. The change in the CO photoproduction with time can be seen
212 as a constant due to the relatively small amount of total radiation during the short
213 exposure time.

214 *2.4 Microbial consumption and dark production experiments*

215 Six stations were selected to determine the microbial consumption rates of CO
216 (YS: stations A1, B1, and C4; ECS: stations E2, T2, and S6). CO concentrations in
217 seawater samples were measured immediately after collection from the SSW and the
218 SML and used as background values. Seawater was used to fill 1 L glass syringes
219 equipped with a 3-way nylon valve, which were pre-cleaned with 10% HCl-Milli-Q
220 water and Milli-Q water until free of headspace, and wrapped with aluminum foil. The
221 syringes were immersed in a shallow tank of flowing water that was continuously
222 pumped from the sea to maintain the temperature of the incubation experiments equal
223 to that of the ambient surface seawater. Each sampling series consisted of 4–5 points,
224 and the data from each series were fitted exponentially to determine the consumption
225 rate constant (k_{bio}). The turnover time of the photochemical production (τ_{prod}) and
226 biological consumption (τ_{cons}) in the SML (SSW) was calculated by the following
227 equations (Doney et al., 1995; Jones and Amador, 1993):

228 $$\tau_{prod} = [CO] \text{ in SML} / \text{photochemical CO production rate in SML} \quad (1)$$

229 $$\tau_{cons} = [CO] \text{ in SML} / k_{bio} \text{ in SML} \quad (2)$$

230 The dark production incubations were used to eliminate the effect of dark
231 production from the microbial CO consumption measurements. According to Zhang et
232 al. (2008), the dark production is the abiotic dark production. Seawater was first filtered
233 through 0.2 μm polyethersulfone membranes and bubbled with CO-free gas (ultrahigh-
234 purity N_2, China) to reduce the background CO values before being put into the 1 L
235 syringes as previously described. Then syringes were rinsed with the sample water and

then overflowed with the sample twice their volumes before they were closed without headspace. All incubations were conducted in duplicate, and wrapped in multiple layers of aluminum foil, and placed in the same incubator environment. Samples were collected at 0, 0.5, 1, 2, and 4 h during incubation. CO incubation experiment was performed under the same conditions as the CO degradation processes according to the method of Xie et al. (2005) and Xu et al. (2023).

2.5 Calculation of sea-to-air flux of CO

The two-layer model proposed by Liss and Merlivat (1986) was used to calculate the instantaneous sea-to-air flux of CO according to the following equation:

$$F = k([CO]_{surf} - [CO]_{eq}) \quad (3)$$

Where F refers to the sea-to-air flux of CO (nmol m^{-2} h^{-1}), and k is the gas transfer coefficient (cm h^{-1}) as a function of wind speed u (m s^{-1}) and the Schmidt number of CO (Sc). In this paper, we used empirical formula E2011 (Edson et al., 2011), which applies to wind speeds from 0 to 18 m s^{-1} (Wind speed ranged from 0.68 m s^{-1} to 12.00 m s^{-1}), to calculate the gas transfer coefficient as follows:

$$k = (0.029u^3 + 5.4)\,(Sc/660)^{-1/2} \quad (4)$$

The Schmidt number of CO was referenced from the research of Zafiriou et al. (2008):

$$Sc = -0.0553t^3 + 4.3825t^2 - 140.07t + 2134 \quad (5)$$

where t is seawater temperature (°C).

256 $[CO]_{surf}$ represents the concentration of CO in the initial SML and SSW seawater, calculated
257 by the following equation:

258 $$[CO]_{surf} = pm_a (\beta p V_w + V_a)/(RTV_w) \quad (6)$$

259 Where *P* is the standard atmosphere pressure (atm) and m_a represents the concentration
260 of CO in the headspace when the sample reaches equilibrium. β is the Bunsen solubility
261 coefficient which is dependent on salinity and temperature (Wiesenburg and Guinasso,
262 1979). *Vw* and *Va* are the volumes of seawater and headspace in the sample bottle,
263 respectively. *T* is temperature (in Kelvin) and *R* is the gas constant with the value of
264 0.08206 atm L (mol K)$^{-1}$.

265 The daily fluxes (μmol m^{-2} d^{-1}) of CO in the YS and the ECS were calculated
266 using the method reported by Stubbins et al. (2006) and Yang et al. (2011), based on
267 the hourly flux (μmol m^{-2} h^{-1}). These hourly fluxes were examined on the scale of
268 individual days by plotting hourly fluxes against the time of day. Days without full
269 coverage of diurnal variations were discarded, leaving 4 days of data in the final
270 analysis. The area under each daily curve was calculated (OriginPro 8.0) to give daily
271 CO emissions.

272 *2.6 Determination of CDOM absorption*

273 The Napierian absorption coefficients of CDOM ($a_{CDOM}(\lambda)$ (m^{-1})) were calculated
274 as follows:

275 $$a_{CDOM}(\lambda) = 2.303\ A_{CDOM}(\lambda)/L \quad (7)$$

Where $A_{CDOM}(\lambda)$ is the absorbance of the sample at wavelength λ; and L is the cell pathlength of the quartz cuvette in meters (0.1 m, Stedmon and Markager, 2003). CDOM absorption $a_{CDOM}(254)$ is an effective proxy for dissolved organic carbon (DOC) and chlorophyll-*a* (Chl-*a*) concentrations in the eastern marginal seas of China (Yang et al., 2021).

The spectral slope of the absorption spectrum was obtained by nonlinear fitting of the absorption coefficient according to the following equation (Stedmon and Markager, 2003):

$$a_{CDOM}(\lambda) = a_{CDOM}(\lambda_0)\exp[-S(\lambda - \lambda_0)] + K \quad (8)$$

Where $a_{CDOM}(\lambda)$ and $a_{CDOM}(\lambda_0)$ are the Napierian absorption coefficients at wavelengths λ and λ_0; λ_0 is the reference wavelength (440 nm); S is the spectral slope of the absorption spectrum; and K represents the background parameters with CDOM removed (Yang et al., 2022). The specific UV absorbance ($SUVA_{254}$) can be used to measure aromaticity (Weishaar et al., 2003) and molecular weight (Chowdhury, 2013) of DOM, with higher values generally indicative of higher aromaticity. $SUVA_{254}$ is calculated by dividing the absorbance at 254 nm by DOC. Detailed Chl-*a*, DOC, fluorescence DOM (FDOM), dissolved oxygen (DO), and wavelength (λ)-dependent absorption coefficients of CDOM ($a_{CDOM}(\lambda)$) were determined in the laboratory using published techniques. See supplementary information (Section S1) for analytical details.

295 *2.7 Statistical analyses*

296 The correlation coefficient (r) and probability (p) values were used to assess the
297 goodness of fit. The correlation matrix, analysis of variance, and principal components
298 analysis were performed with SPSS version 18.0 (SPSS Inc., Chicago, IL, USA) to
299 examine potential relationships between CO, DOM parameters, and environmental
300 factors. P values < 0.05 were considered significant. Shapiro-Wilk tests (Table S2,
301 supplementary information) indicated that the data were normally distributed for DOC
302 in the SSW ($p = 0.258$), but not for $[CO]_{SSW}$, $[CO]_{SML}$, $a_{CDOM}(254)$ in the SSW and
303 SML, and DOC in the SML ($p < 0.001$ for all). Therefore, all data were analyzed
304 consistently using non-parametric Kruskal-Wallis and Dunn-Bonferroni post-hoc tests.
305 Pearson's product-moment correlation was used to identify relationships between
306 parameters and was calculated at a 95% confidence level.

307 **3. Results**

308 *3.1 Environmental Factors and CO Concentration in the SSW and the SML*

309 Surface water temperature increased from 2.08°C at YS station H12 to 23.8°C at
310 ECS station E7 (mean value: 11.85 ± 4.53°C, Fig. 2). Surface salinity increased from
311 28.85 at Changjiang River Estuary (CRE) station E1 to 34.62 at ECS station E7 (32.35
312 ± 1.17, Fig. 2). Wind speed during sampling ranged from 0.68 m s^{-1} at station H9 to
313 12.00 m s^{-1} at station FJ1 (6.09 ± 2.50 m s^{-1}). The integrated net solar irradiance (14.09

± 114.64 kW m^{-2}) during the in-situ incubation ranged from −111.8 kW m^{-2} at YS station H5 to 417.9 kW m^{-2} at ECS station F4 (Table S1).

During the study period, $[CO]_{SSW}$ was particularly high at the station F4 (3.61 nmol L^{-1}, sampling time: 12: 43) in the SML and relatively high at the station P6 (2.81 nmol L^{-1}, sampling time: 14: 36) in the SSW (Fig. 2). The maximum $[CO]_{SML}$ was observed during daytime, but the minimum $[CO]_{SML}$ was observed during nighttime (station E2: 0.59 nmol L^{-1}, sampling time: 22: 22, Fig. 3). No significant difference was observed between [CO] in the SML (1.54 nmol L^{-1}) and the SSW (1.23 nmol L^{-1}) ($n = 52$, $p = 0.11$, Wilcoxon signed-rank test). [CO] mean value in the YS (SSW: 1.23 ± 0.40 nmol L^{-1}; SML: 1.54 ± 0.68 nmol L^{-1}) was similar to the concentration observed in the ECS (SSW: 1.23 ± 0.45 nmol L^{-1}; SML: 1.55 ± 0.92 nmol L^{-1}) between the SML and the SSW, respectively. $a_{CDOM}(254)$ in the YS (SSW: 3.59 ± 0.89 m^{-1}; SML: 4.78 ± 0.85 m^{-1}) was higher than that in the ECS (SSW: 1.64 ± 0.72 m^{-1}; SML: 4.70 ± 3.35 m^{-1}) in both the SML and the SSW. $a_{CDOM}(254)$ in the SML (4.74 ± 2.50 m^{-1}) showed relatively higher values compared to the SSW (2.52 ± 1.26 m^{-1}) during winter. The stronger negative linear relationship observed between salinity and $a_{CDOM}(254)$ was observed in the SSW ($r = -0.716$, $n = 52$, $p < 0.01$), where the influence of terrestrial input in this water layer was higher than that in the SML ($r = -0.038$, $n = 52$).

3.2 Variations in parallel factor analysis (PARAFAC)-derived fluorescent DOM components and factors controlling the composition of the fluorescent components

The three fluorescent DOM components were determined statistically by conducting Parallel factor analysis (PARAFAC) of the samples (Table S3; Fig. S1; Supplementary Information 1.2). Component C1 was apparent with excitation and emission peaks at 275 nm and 335 nm, respectively, and was likely a tryptophan-like peak T (Yamashita et al., 2017). C2 exhibited excitation/emission (E_x/E_m) maxima at 350 nm/455 nm and similar to peak C derived from terrestrial humic sources (Coble and Paula, 2007). Peak C has often been observed in various coastal (Coble, 1996) and oceanic environments (Yamashita et al., 2017). C3 appeared as a fluorophore with E_x/E_m wavelengths of 320 nm/390 nm and was similar to marine humic-like components from coastal environments (Yamashita and Jaffé, 2008).

3.3 Variation and enrichment of CO, CDOM, DOC, and FDOM in the SML

[CO] showed relatively higher mean value in the SML, where its EFs ranged from 0.34 to 3.6 and it had a mean EFs value of 1.3 ± 0.7 (Fig. 3). The absorption of CDOM and the fluorescence intensity of FDOM components in the SML were positively correlated with their respective SSW values (Fig. S2), indicating that transport of DOM from the SSW to the SML is an important pathway. Up to 92% of CDOM samples were enriched in the SML, with the average EF value of $a_{CDOM}(254)$ of 2.2 ± 1.2, ranging between 0.4 and 6.7. The EFs of C3, C1 and C2 were 1.6 ± 0.7, 1.4 ± 0.6, and 1.3 ± 0.5, respectively. The EFs of CO, CDOM, and DOC in the SML were generally higher in

353 the ECS than those in the YS· (Fig. 2 and Fig. S3). Furthermore, relatively higher
354 CDOM absorption slope mean values ($S_{275\text{-}295}$ and S_R) were observed in the SML (SSW:
355 $S_{275\text{-}295}$: 0.0206 ± 0.0068 and S_R: 1.48 ± 0.49; SML: $S_{275\text{-}295}$: 0.0210 ± 0.0055 and S_R:
356 1.53 ± 0.22), indicating that CDOM in the SML experienced more significant
357 photodegradation than that in the SSW. The EF of CO in the daytime (1.5 ± 0.8, 7: 00-
358 19: 00) was 1.6 times higher than that in the nighttime (0.9 ± 0.3, 19: 00-7: 00) (Fig.
359 3b)). The EF of CDOM in the daytime (2.3 ± 11.4) was 1.1 times higher than that in
360 the nighttime (2.1 ± 0.9) (Fig. 3b)). In addition, $[CO]_{SSW}$ in the daytime (1.39 ± 0.47
361 nmol L^{-1}) was 1.3 times higher than that in the nighttime (1.05 ± 0.22 nmol L^{-1}) and
362 $[CO]_{SML}$ in the daytime (1.88 ± 0.77 nmol L^{-1}) was 2.0 times higher than that in the
363 nighttime (0.95 ± 0.29 nmol L^{-1}).

364 *3.4 Variation of sea-to-air flux of CO*

365 The atmospheric mixing ratios ($[CO]_{atm}$) of the eastern marginal seas of China
366 ranged from 239 to 900 ppbv, with an average of 602 ± 164 ppbv (n = 69; Fig. 2) during
367 winter. $[CO]_{atm}$ measured at station A1 in the YS (the highest concentration) was nearly
368 4 times higher than that measured at station T2 in the ECS (the lowest concentration).
369 YS showed higher CO mixing ratios (mean value: 423 ppbv in 2007; 657 ppbv in 2019)
370 than ECS (mean value: 252 ppbv in 2007; 476 ppbv in 2019) in this study and a previous
371 study (Yang et al., 2010), indicating that $[CO]_{atm}$ was relatively higher in the YS than
372 the ECS. Generally, $[CO]_{atm}$ showed a significant decreasing trend from the northern to
373 the southern regions in the eastern marginal seas of China (Fig. 2).

The instantaneous sea-to-air fluxes of CO ranged from −1.75 to 39.78 nmol m^{-2} h^{-1} in the SML (4.96 ± 7.35 nmol m^{-2} h^{-1}) and from −0.04 to 34.18 nmol m^{-2} h^{-1} in the SSW (7.40 ± 7.31 nmol m^{-2} h^{-1}). Higher fluxes mostly occurred in the southernmost part of the survey area in the ECS (Fig. 2). Although the concentrations of $[CO]_{atm}$ in the northern region (YS) were generally higher than those in the southern region (ECS), the sea-to-air fluxes of CO in the SML in the southern region (6.94 ± 9.61 nmol m^{-2} h^{-1}) were 3.5 times higher than that in the northern region (1.97 ± 2.11 nmol m^{-2} h^{-1}), indicated that the sea-to-air flux of CO did not followed $[CO]_{atm}$ shown in Fig. 2.

3.5 CO production and consumption

The photoproduction rate of CO (K_{photo}) under solar irradiance ranged from 0.71 to 1.05 nmol L^{-1} h^{-1} (0.86 ± 0.12 nmol L^{-1} h^{-1}) and 0.71 to 1.27 nmol L^{-1} h^{-1} (1.03 ± 0.16 nmol L^{-1} h^{-1}) during the in-situ incubation experiments in the SSW and the SML, respectively, as shown in Fig. 4a) and Table S4. The mean value of K_{photo} in the SML was slightly higher than that in the SSW, but the τ_{prod} was lower in the SML (1.35 h) than in the SSW (1.22 h). In addition, a significant relationship was observed between the light-normalized CO production rates between the SML and the SSW ($r = 0.408$, $p < 0.01$, $n = 6$) during winter. The dark production rates of CO (k_{dark}) ranged from −0.01 to 4.81 nmol L^{-1} d^{-1}, with a mean value of 1.25 ± 2.34 nmol L^{-1} d^{-1} in the SSW (Table S3). However, no significant dark production was observed in the SML water samples, which indicated that dark production may be the main factor controlling CO concentrations in deeper seawater.

The microbial consumption rates of CO in the SML varied greatly (0.18 ± 0.05 nmol L^{-1} h^{-1}), higher than the average in the SSW (0.13 ± 0.03 nmol L^{-1} h^{-1}) (Fig. 4b). CO photoproduction rates were 5.7 times higher than CO consumption rates in the SML, and CO photoproduction rates were 6.6 times higher than CO consumption rates in the SSW. The turnover times driven by microorganism (τ_{bio}), i.e., the reciprocal of k_{bio}, were 8.9 ± 2.9 h and 11.9 ± 5.4 h in the SML and the SSW, respectively. τ_{bio} in the SML and the SSW ranged between 1.43 and 3.78 d^{-1} (2.76 ± 0.80 d^{-1}) and between 1.17 and 3.48 d^{-1} (2.46 ± 0.88 d^{-1}), respectively, higher than those observed in the Arctic marginal sea (0.96 ± 0.29 d^{-1}; Xie et al., 2005), but lower than those in the Northwest Atlantic Ocean (6.24 ± 5.76 d^{-1}; Xie et al., 2005) and the China shelf sea (4.80 ± 1.82 d^{-1}; Zhang et al., 2019). The maximum k_{bio} value appeared at the near-shore station B1 and the minimum value at the offshore station S6 in the SML (Table S3). Thus, the bacterial consumption rate constant of CO was low in oligotrophic open ocean regions but higher in productive coastal areas. Since the CO photoproduction rate in the SSW at the near-shore station B1 was lower than that of the near-shore station E2 and its CO consumption ability was much stronger, the seawater concentration of CO at coastal station E2 (1.62 nmol L^{-1}) was higher than that at coastal station B1 (1.51 nmol L^{-1}).

3.6 Primary factors controlling the distribution of the optical parameters of DOM and CO and their EFs

Negative relationships were observed between salinity and $a_{CDOM}(254)$ (SSW: $p < 0.01$, $r = -0.715$, $n = 62$; SML: $p = -0.045$, $n = 52$), $a_{CDOM}(355)$ (SSW: $p < 0.01$, $r =$

−0.622; SML: r = −0.146), and the C1 (SSW: $p < 0.01$, r = −0.758; SML: r = −0.158), C2 (SSW: $p < 0.01$, r = −0.341; SML: r = −0.106), and C3 (SSW: $p < 0.01$, r = −0.851; SML: r = −0.154) components in SSW and SML (Table 1). High and low fluorescence levels of these three components were usually found at sites with low and high salinities, respectively (Fig. 2). These results indicated that riverine inputs mainly determined the distributions of CDOM and FDOM. $a_{CDOM}(254)$ and all three fluorescence components were also positively correlated with $SUVA_{254}$ (Table 1), indicating that CDOM showed higher aromaticity and humification in the eastern marginal seas of China. In addition, we observed a significant positive relationship between $a_{CDOM}(254)$ and Chl-*a* in the SSW ($p < 0.01$, r = 0.333, n = 62), suggesting that phytoplankton biomass and biological processes played an essential role in generating new CDOM and controlling the distribution of CDOM in winter.

Although significant CO production via CDOM photodegradation has been recorded in estuarine systems (Stubbins et al., 2011), no significant relationships were observed between [CO] and $a_{CDOM}(254)$ in either the SSW or the SML in our study regions. $a_{CDOM}(254)$ ($p < 0.01$, r = −0.419) and the marine humic-like C3 ($p < 0.01$, r = −0.201) were both negatively correlated with the flux of CO in the SML (Fig. 5a and b). The flux of CO was positively related to temperature ($p < 0.01$, r = 0.511) and salinity ($p < 0.01$, r = 0.338) in the SSW (Fig. 5), but the EF of CO showed no significant relationship with surface water temperature, salinity, or mean wind speed during sampling (Fig. 5d and 5f).

4. Discussion

4.1 CO and DOM distribution and enrichment in the SML

[CO] showed great seasonal and diel variability, as well as variability between ocean regions. $[CO]_{SSW}$ mean value in the YS in January 2020 (1.23 ± 0.40 nmol L^{-1}) was higher than in September 2010 (1.05 nmol L^{-1}, Zhao et al., 2015). $[CO]_{SSW}$ mean value in the ECS during winter (1.23 ± 0.45 nmol L^{-1}) was also higher than in October 2021 (0.97 ± 0.86 nmol L^{-1}, Yang et al., 2024). Globally, $[CO]_{SSW}$ mean value (1.23 nmol L^{-1}) in the eastern marginal seas of China was similar to that observed in the Bohai Sea and the YS during autumn (Zhang et al., 2019, 1.22 nmol L^{-1}) and the Arctic waters of the Amundsen Gulf (Beaufort Sea) in September/October (Xie et al., 2009, 0.17–1.34 nmol L^{-1}), but was relatively lower than the Eastern Indian Ocean (Xu et al., 2023, 1.92 nmol L^{-1}). The Eastern Indian Ocean, on the other hand, had a salinity of approximately 34 and a relatively high temperature (around 29°C) in autumn 2020 (Xu et al., 2023). Tropical and subtropical open ocean regions were generally less affected by terrestrial influences compared to estuarine, coastal and high-latitude areas. CO production and fluxes normalized to discharge are usually higher in warmer waters (Kieber et al., 2014), presumably also partly due to temperature controls on dissolution (Johnson et al., 1996). Therefore, the relatively higher concentration of $[CO]_{SSW}$ in the open ocean (ECS) might be characterized by the relatively high seawater temperature and/or strong production processes during our sampling period.

Our results showed that there was no significant enrichment of CO in SML during the investigation, and CO enrichment in SML only occurred at 25 stations. Earlier studies have shown that the diurnal variation of $[CO]_{SSW}$ in sea surface concentration, which was first noted in the Atlantic Ocean by Swinnerton et al. (1970), with a characteristic minimum just before dawn and a maximum in the early afternoon. This cycle was subsequently observed in other expeditions in both the Pacific and Atlantic Oceans (Matsueda et al., 2000; Rhee, 2000; Ren et al., 2010; Yang et al., 2010; Yang et al., 2011). Here, $[CO]_{SSW}$, $[CO]_{SML}$ and the EFs of CO also showed strong diurnal fluctuations (Fig. 3, Section 3.1 and 3.3). Significant positive relationships were observed between the EFs of CO and the net solar irradiance (Table 3), likely resulting from the sunlight-induced photochemical production of CO during daytime and the stronger microbial consumption at night. The higher EF values of CO also occurred in the daytime (Fig. 3b), suggesting that sufficient light and higher temperatures combined to facilitate the photoproduction of CO and its enrichment in the SML.

CO, CDOM, and FDOM were more frequently enriched in the ECS (Fig. 2). DOC and CDOM decreased from coastal regions to the open ocean, and decreased from the northern sampling area (the YS) to the southern sampling area (the ECS) in both the SSW and the SML (Fig. 2), which was likely due to the input from the land-based sources (Yang et al., 2022). Moreover, atmospheric deposition of organic carbon and nutrients was found to peak in winter over the coastal ECS (Wang et al., 2019). Although the source of CDOM originated from allochthonous terrestrial sources in the ECS and the YS (Yang et al., 2021), the sink of CDOM in the ECS was more dominated

by photochemical degradation processes (Zhu et al., 2018). The EF of marine humic-like Component 3 was significantly higher than the other fluorescence components (1.6 vs. 1.4 and 1.3), indicating that in-situ autochthonous DOM was more strongly enriched in the SML than terrestrial DOM. Thus, CO, CDOM, and FDOM were more frequently enriched in the open ocean (ECS), which was attributed mainly to the significant local photoproduction. Further, one note of the study of gases in the SML is that gases supersaturated with respect to their atmospheric concentrations, including CO, are inevitably lost from SML samples during sampling, depending on environmental conditions such as water temperature and wind. For example, in case of dimethylsulfide (DMS), a volatile gas with large concentration difference between the atmosphere and the ocean, Yang et al. (2001) and Yang and Tsunogai (2005) showed about 50–70% and 60% (mean) of loss from SML samples collected using a mesh screen at 0–15°C and at a water temperature of 10°C and wind speed of 4 m s^{-1}, respectively. A mesh screen was also used in this study, and parameters such as $[CO]_{SML}$ and the EF of CO may have been underestimated.

4.2 Photochemical and dark CO production and biological CO consumption in the SML and the SSW

Photochemical CO production is the most active in the SML, the mean photoproduction rate of CO in the SML was 1.1 times higher than that in the SSW in the eastern marginal seas of China. CO in our study region showed a longer turnover time than the findings of Sugai et al. (2021) in Sagami Bay, Japan (τ_{prod} = 0.09 h), which

is probably due to the relatively low photochemical CO production rate in the SML and/or the higher photochemical degradability of CDOM in the SML under more intense light conditions in our study region.

The turnover times driven by sea-to-air exchange were much longer than those of microbial consumption, about 219 h and 1029 h in the SSW and SML, respectively. This indicated that microbial removal of CO was much faster than sea-to-air exchange, which may make the latter a subordinate pathway for CO removal in our study regions. Relatively higher microbial consumption rate of CO in marine systems has been historically attributed to higher Chl-*a*, but lower salinity level (Xie et al., 2009; Yang et al., 2010; Xu et al., 2023). In addition, the heterotrophic bacterial abundance in the SML was ~ 7.5 times greater than in the SSW and the ECS in March 2017 (Sun et al., 2020). The SML is an aggregate-enriched biofilm environment with distinct microbial communities, the diversity of which can differ significantly from underlying waters (Liss and Duce, 2005; Cunliffe et al., 2013). This higher abundance of bacteria could result in the rapid consumption of CO, along with a wide variety of other organic substances in the SML. Moreover, elevated nutrient concentrations can stimulate the growth of phytoplankton, biological activity, and subsequently lead to abundant primary production in the SML (Yang et al., 2022). Therefore, compared to the SSW, the elevated DOM concentrations and bacteria abundances could enhance the influences of photoproduction and microbial consumption on CO cycling processes in the SML.

4.3 Implications of CO sea-to-air exchange and emission to the atmosphere

Based on the areas of the ECS (7.7×10^5 km^2) and YS (3.8×10^5 km^2) and their respective CO sea-to-air fluxes, the releases of CO from the ECS and YS to the atmosphere were estimated to range from 3 to 230 Mg CO-C month^{-1} (Mg = 10^6 g) and from –0.2 to 880 Mg CO-C month^{-1}, with averages of 70 Mg CO-C month^{-1} and 10 Mg CO-C month^{-1}, respectively. Clearly, the average annual release of CO to the atmosphere in the ECS was much higher (nearly 7 times) than in the YS. Yang et al. (2010) suggested that $[CO]_{SSW}$ was the main factor affecting the sea-to-air flux of CO, but $[CO]_{SSW}$ in the ECS was similar to that in the YS. The lower temperatures and especially reduced wind speeds may hinder its outgassing to the atmosphere. The higher $[CO]_{atm}$ at the northern stations (the YS) was representative of the regionally polluted continental outflow air mass due to the anthropogenic activity in East Asia. Therefore, $[CO]_{atm}$ values in the YS were heavily dependent on land anthropogenic input, but in the ECS, the distribution of $[CO]_{atm}$ was more dependent on the sea-to-air flux of CO.

As noted above, the most probable sources of CO in the SML of these sea regions are in-situ photoproduction from DOM and/or vertical export through underlying SSW water. Actually, surface-active surfactants are ubiquitous and accumulate in the uppermost < 1000 μm in seawater (Rickard et al., 2019), where they slow the rate of gas exchange between seawater and air (Cunliffe et al., 2013). Although surfactants represent only a fraction of the dissolved organic matter pool, Rickard et al. (2022) observed that the first-order estimates of the potential suppression of the gas transfer velocity (*kw*) by photo-derived surfactants were 12.9%–22.2% in coastal North Sea

543 water. The highest SML enrichments in surfactants have been seen in low productivity,
544 oligotrophic regions away from terrestrial influences, where surfactant concentrations
545 in SSW are generally low (Wurl et al., 2016). Pereira et al. (2018) also noted that the
546 observed reduction in the air-to-sea CO_2 exchange in the Atlantic Ocean was due to
547 biological surfactants acting as physical barriers and altering turbulent transfer near the
548 water surface. Therefore, the relatively lower fluxes of CO observed in the YS may
549 indicate that seawater contains lots of DOM (surfactants) in the SML. Despite the clear
550 importance of surfactants at the sea-to-air interface, we did not conduct surfactant-
551 specific analyses due to the analytical limitations. In our experiments, the CO flux
552 varied by 131% in winter. The negative correlations between $a_{CDOM}(254)$ and the sea-
553 to-air flux of CO, and between marine humic-like C3 and the sea-to-air flux of CO
554 suggested that CDOM concentration may reduce the CO sea-to-air gas exchange rate
555 in our study regions (Fig. 5a and 5b). In addition, low wind speeds may lead to high
556 DOM enrichment, but in the meantime give rise to low sea-to-air fluxes as well.
557 Therefore, due to the complexity of the DOM pool in the SML and its may result in
558 decreased sea-to-air flux of CO, more measurements are needed to validate our
559 conceptual model and provide a better understanding of the flux measurements of CO
560 in the SML.

561 During our study period (winter), surface seawater temperature showed substantial
562 spatial fluctuations (from 2.08°C in the YS to 23.80°C in the ECS) due to the broad
563 investigation range. In our previous manuscript (Yang et al., 2022), we observed that
564 the relatively higher enrichment of nutrients in summer which could enhance

phytoplankton growth and promote DOM production in the SML; and stronger enrichment and photochemical processes occur in the SML, resulting in the relatively accelerated enrichment of more marine local production DOM in the SML than the SSW. During warm seasons, stronger light and temperature may change the relative importance of light production, microbial production and DOM (surfactants) composition and inhibition of CO flux. Therefore, DOM inhibits CO flux still requires further verification in other seasons and regions.

4.4 Modeling of CO dynamics in the SML and the SSW

All sources and sinks, including photoproduction and dark production, microbial consumption and sea-to-air emission, should be considered in estimating CO dynamics in the SML and SSW (Fig. 6). The effective solar illumination period of each day was approximately 12 h, and based on this the average photoproduction rates in the SML and the SSW were calculated to be 12.41 ± 1.87 nmol L^{-1} d^{-1}, 10.32 ± 1.48 nmol L^{-1} d^{-1}, respectively. In the SSW, the ratio of photoproduction to dark production (1.88 ± 2.89 nmol L^{-1} d^{-1}) was about 4:1, and dark production accounted for about 15% of the total production. No dark production of CO was observed in the SML. CO photoproduction was lower in deeper water, while dark production was higher. The calculated contribution of dark production to CO production in this study was similar to that for the St. Lawrence estuary (14%; Zhang and Xie, 2012) but much lower than for the Eastern Indian Ocean (20%; Xu et al., 2023). These were because dark production needs to be given more weight in estimating its contribution to the total production of

586 CO in the deeper waters of the ocean than in estuaries (Xu et al., 2023). The total
587 removal rates of CO were about 2.64 nmol L^{-1} d^{-1} and 2.88 nmol L^{-1} d^{-1} in the SSW and
588 the SML, respectively, including the microbial consumption rates of 2.46 ± 0.88 nmol
589 L^{-1} d^{-1} and 2.76 ± 0.80 nmol L^{-1} d^{-1} in the SSW and the SML, respectively. The sea-to-
590 air exchange rates were 0.18 ± 0.18 nmol L^{-1} d^{-1} in the SSW and 0.12 ± 0.18 nmol L^{-1}
591 d^{-1} in the SML. The turnover of CO occurred faster in the SML environment than in the
592 SSW (~ 1.2 times). Microbial consumption was the primary sink of CO, accounting for
593 about 95% of CO removal, indicating that the biogeochemical cycling of CO is almost
594 entirely contained within seawater and only a small amount of CO is released into the
595 atmosphere (Xie et al., 2005; Yang et al., 2010; Zhang et al., 2019; Xu et al., 2023).
596 The production rates of CO in both SML and SSW significantly exceed the loss rates,
597 this could lead to the accumulation of CO in these systems. Therefore, CO balance in
598 the ECS and YS indicated that the underlying loss of CO (via sea-to-air flux and
599 biodegradation) was slower than the production of CO in the SML, therefore, a positive
600 CO balance was maintained in the SML.

601 The average annual photoproduction, microbial consumption, and sea-to-air flux
602 of CO in the SSW were about 3.02, 1.58, and 0.04 Gg CO-C $month^{-1}$, respectively,
603 based on the area of the survey region (~ 1.2 × 10^6 km^2, SSW ~ 10 m). Conte et al.
604 (2019) used the NEMO-PISCES model combined with original ocean CO data
605 collected worldwide over the last 50 years, ultimately estimating that global emissions
606 of CO to the atmosphere were 4.0 Tg CO-C yr^{-1} (Tg = 10^{12} g). Based on our data, we
607 estimated the contribution of China's eastern marginal seas to global marine CO

608 emissions via sea-to-air flux to be ~ 0.3‰, and the YS and the ECS occupy 2.7‰ of
609 the global ocean area. The simulated surface CO concentrations and sea-to-air fluxes
610 based on our measured values were much smaller than those simulated by Erickson
611 (1989). In our study, CO produced can be rapidly consumed by microorganisms and
612 only a small fraction was released into the atmosphere, which may explain why the
613 relative contribution of the eastern marginal seas of China to atmospheric CO was much
614 lower than the global level.

615 Notably, the enrichment of CO in the SML was more common during the daytime
616 when photochemical processes were more active, but natural sunlight can inhibit the
617 microbial consumption of CO. CO was maximal in the SML, leading to the significant
618 enrichment and supersaturation. CDOM in the SML experienced more significant
619 photodegradation than that in the SSW, as can be seen in Section 3.3. Moreover,
620 researchers assumed that biological, chemical and physical processes in the SML are
621 controlled by changes in DOM concentration at this uppermost thin boundary layer
622 between the ocean and the atmosphere (Cunliffe et al., 2013). We found that
623 autochthonous humic-like DOM was more enriched in the SML than terrestrial DOM,
624 indicating that it could be an indispensable part of CO photoproduction (Yang et al.,
625 2022). Solar irradiance was positively related to the EFs of CO (Table 3), suggesting
626 that the integrated solar irradiance influenced CO enrichment in the SML. Moreover,
627 we did discover the potential for CDOM accumulation in the SML to prevent CO
628 emissions into the atmosphere (Section 4.3). Therefore, CDOM accumulation and the

production rates of CO in the SML significantly exceed the loss rates, which could lead to the significant accumulation of CO in the SML, especially in the daytime.

5. Conclusions

This study is the first comprehensive analysis of CO distribution, loss, and production in both the SML and SSW, as well as sea-to-air CO flux in the ECS and YS during winter. $[CO]_{SSW}$, $[CO]_{SML}$, CDOM, FDOM, and DOC generally decreased from coastal regions toward the open ocean. However, the EFs of CO, CDOM, FDOM, and DOC were significantly higher in offshore areas, indicating that stronger enrichment and/or production processes in the SML are more common in open waters than nearshore. CDOM absorption slope mean values ($S_{275\text{-}295}$ and S_R) showed that CDOM in the SML experienced more extensive photodegradation than in the SSW. Notably, the EF of the marine humic-like component C3 was significantly higher than other fluorescence components, suggesting that in-situ autochthonous DOM was more strongly enriched in the SML compared to terrestrial DOM. Significant negative correlations were observed between $a_{CDOM}(254)$ and sea-to-air CO flux, as well as between sea-to-air CO flux and humic-like C3 in the SML, indicating that the open sea had lower CDOM concentrations but greater suppression of CO gas transfer compared to nearshore waters. This suggests that DOM enrichment may influence CO emissions to the atmosphere in the SML. The diurnal variability in CO EF and $[CO]_{SML}$ indicates that in-situ photoproduction processes are vital in shaping CO distribution within the SML. Our results demonstrate a complex interaction between DOM enrichment and

sea-to-air CO fluxes in the SML, which should be incorporated into future carbon budget models for more accurate assessments of carbon cycling in marine environments.

Author contribution

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Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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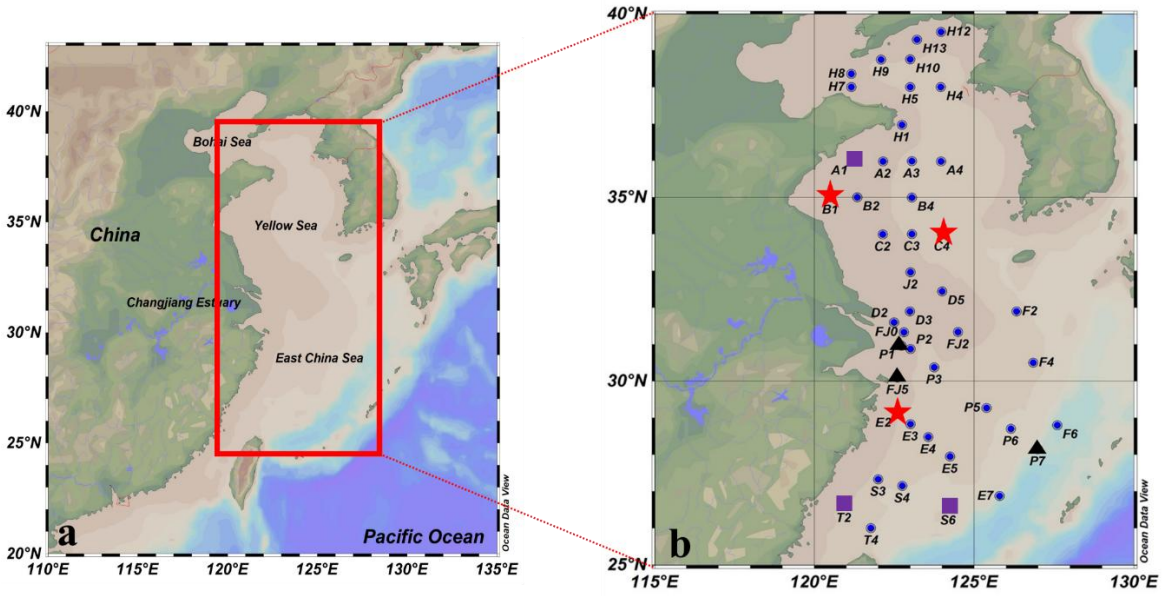
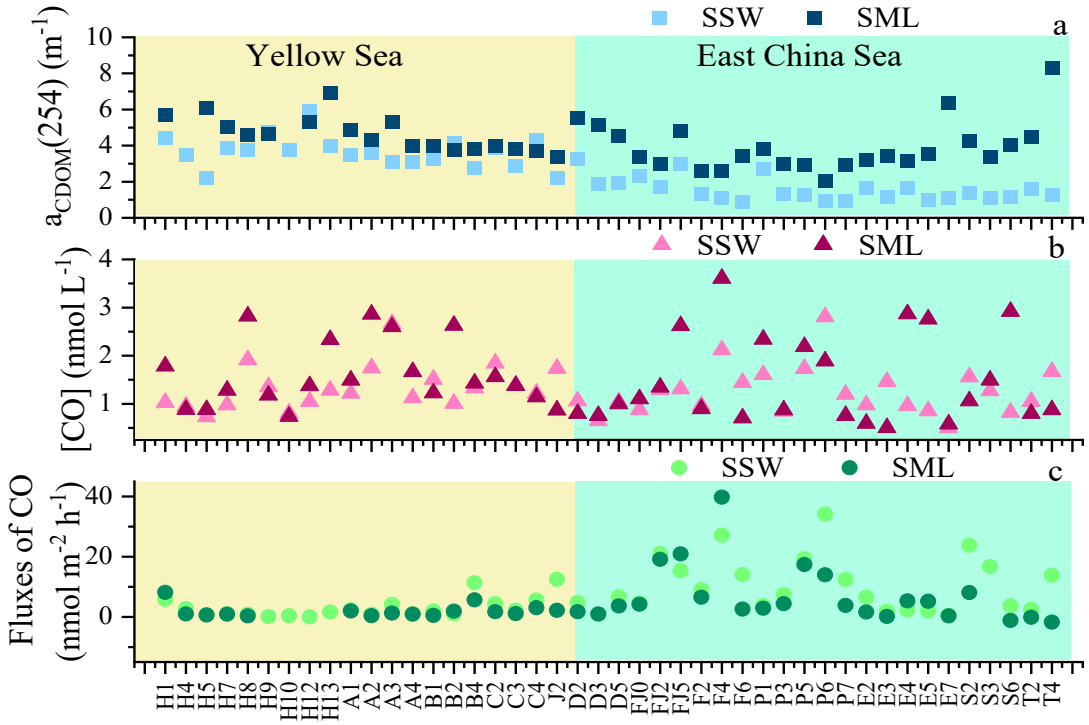


Fig. 1. Map of sampling stations in the East China Sea and the Yellow Sea during winter. Red box represented photochemical incubation experiment stations, and the purple rhomboid represented biological consumption experiment stations.

■: Stations for CO microbial consumption incubation experiments; ▲: Stations for CO photochemical production incubation experiments; ★: Station for both CO microbial consumption and photochemical production incubation experiments; ●: Stations only for seawater sampling.



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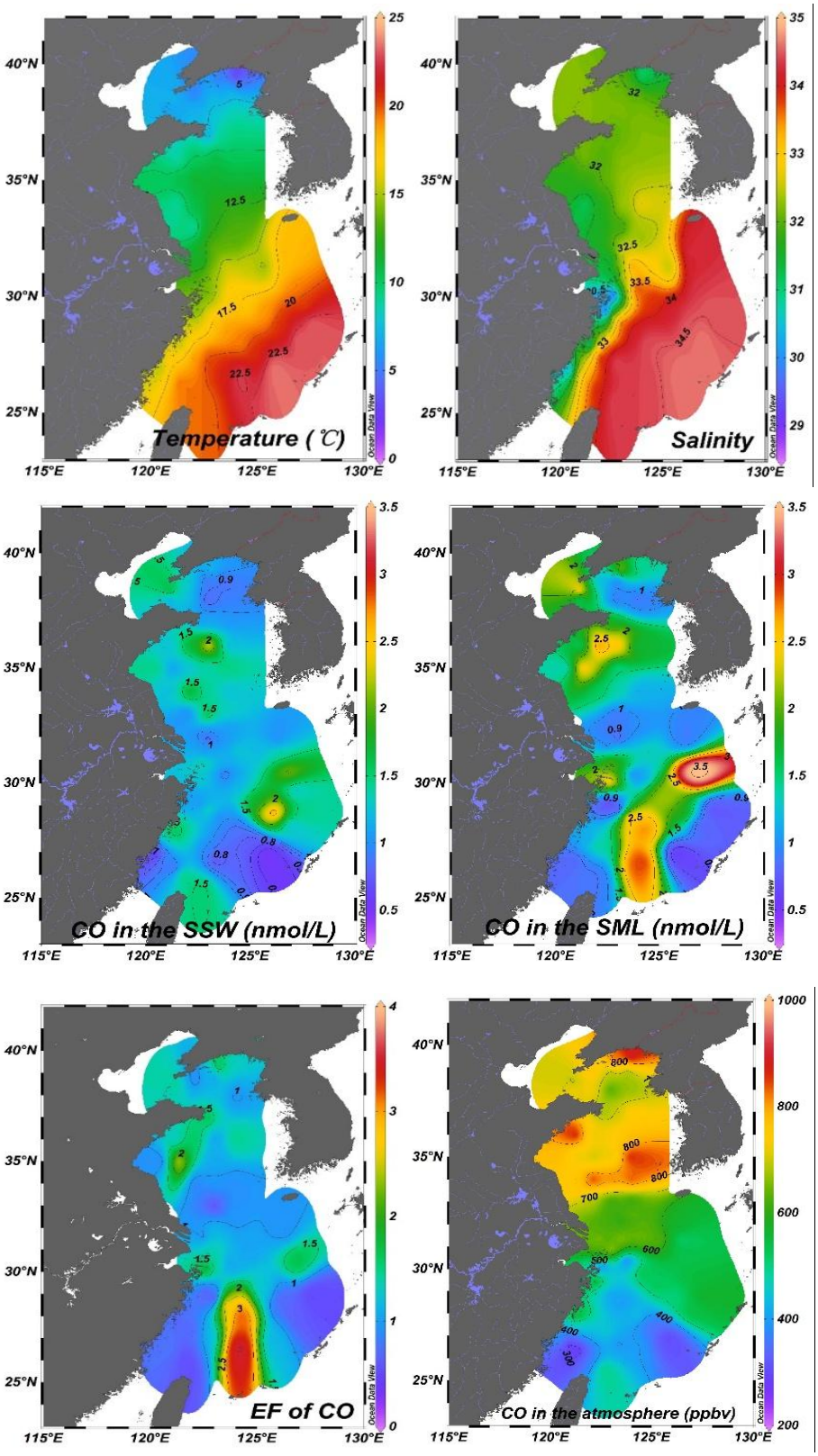

Temperature (℃)
Salinity
CO in the SSW (nmol/L)
CO in the SML (nmol/L)
EF of CO
CO in the atmosphere (ppbv)
40°N
35°N
30°N
25°N
115°E
120°E
125°E
130°E
Ocean Data View

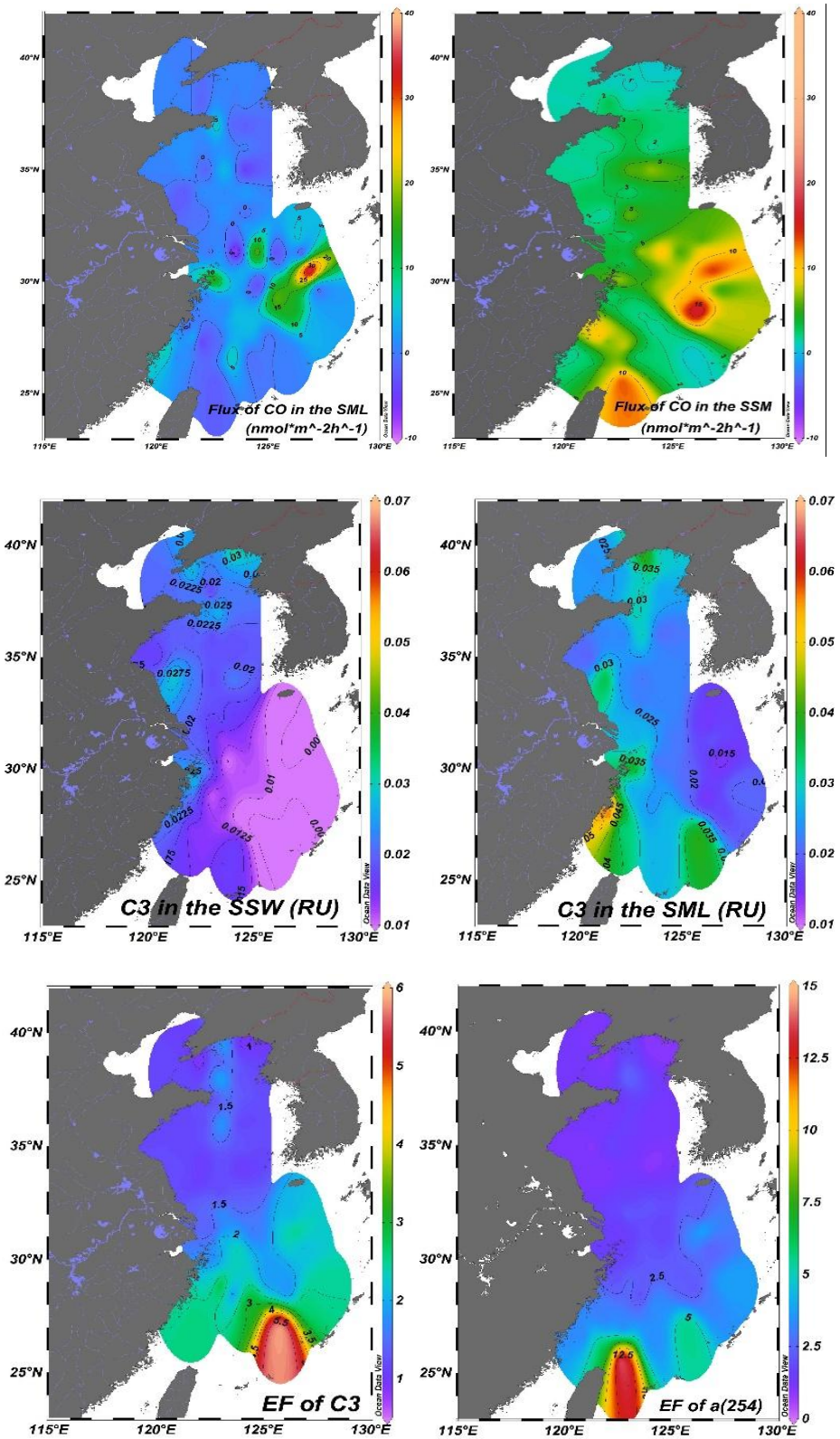


Fig. 2. $a_{CDOM}(254)$ values in the SSW and the SML (a); CO concentrations in the SSW and the SML (b); The flux of CO in the SSW and the SML (c); Spatial distributions of temperature and salinity, CO and the marine-like fluorescence C3 in the SSW and the SML; CO in the atmosphere, and the enrichment factors of CO and the marine-like fluorescence C3 in the SML in the East China Sea

and the Yellow Sea in January 2020 (d). The concentration profiles of CO in the SSW resemble those of CO in the SML, which is evidence for a biogeochemically very stable environment.

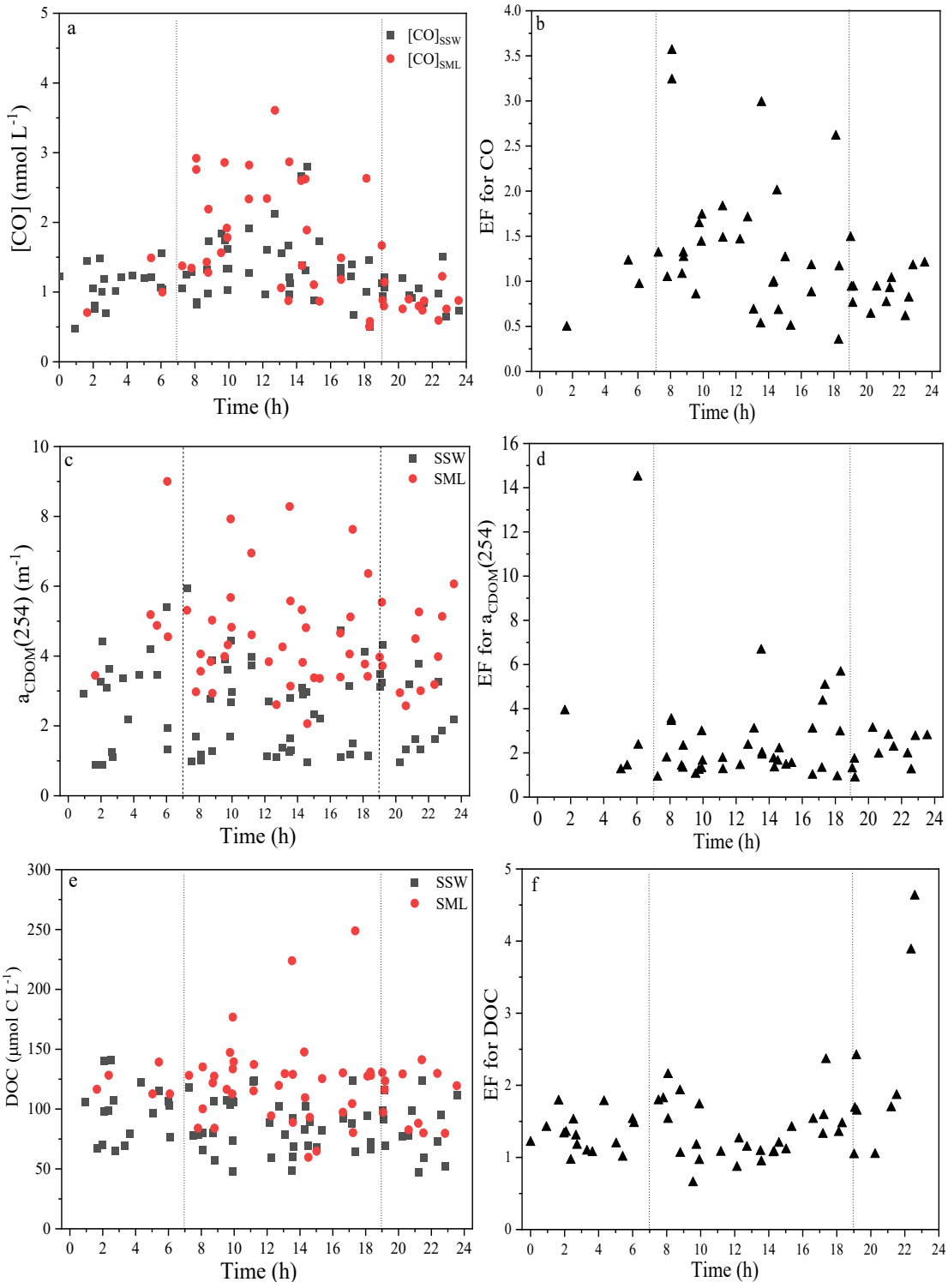


Fig. 3. Variations in the $[CO]_{SML}$, $[CO]_{SSW}$, $a_{CDOM}(254)$, and DOC, EFs of [CO], $a_{CDOM}(254)$, and DOC with the sampling time at each station.

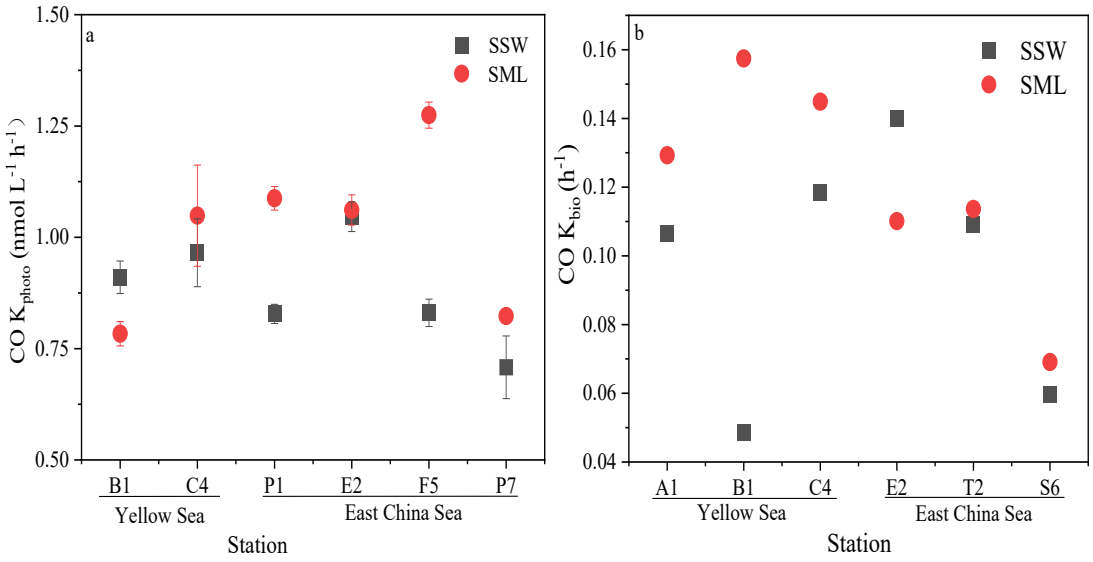
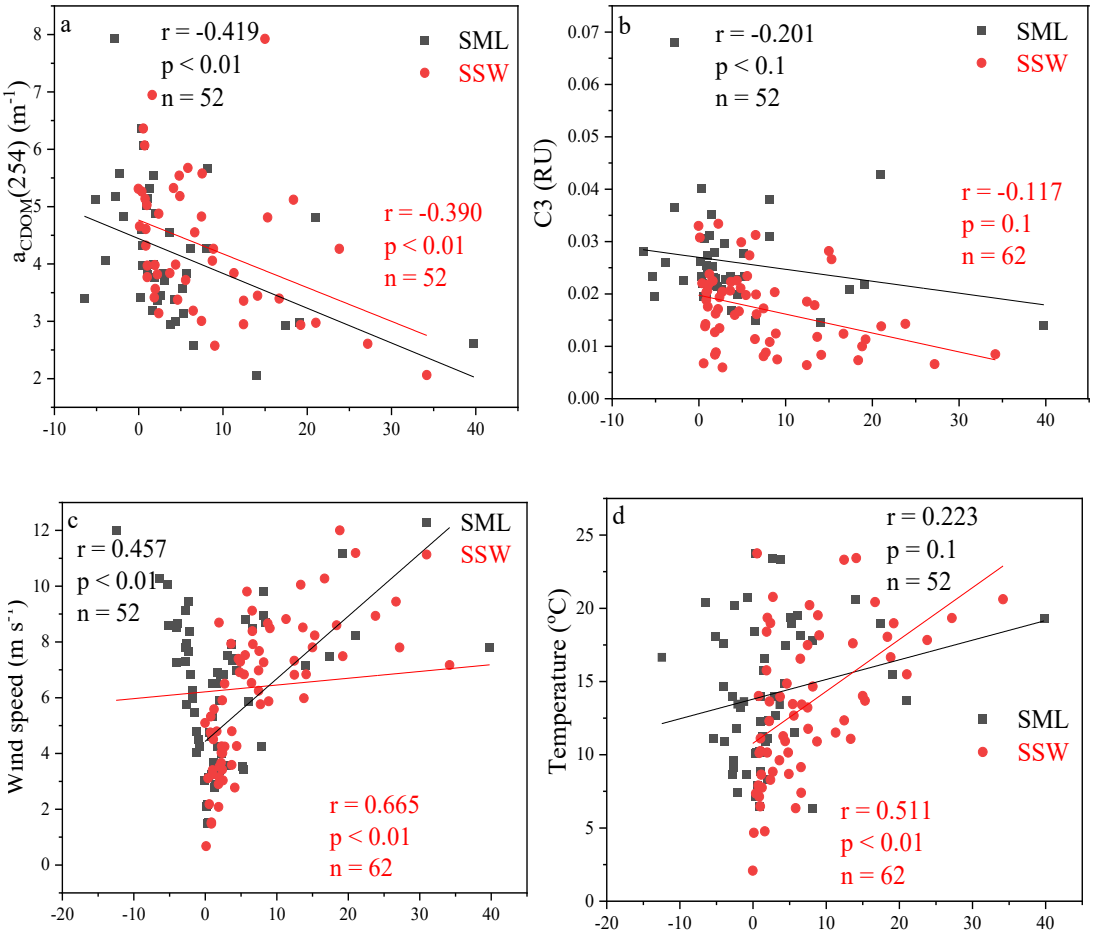


Fig. 4. Variations in photochemical CO production rate of CO (K_{photo}) in the SML (red) and the SSW (black) (a)). Variations in microbial consumption rate constants of CO (K_{bio}) in the SML (red) and the SSW (black). Data are presented as mean values and error bars represent the standard deviation of duplicate samples.



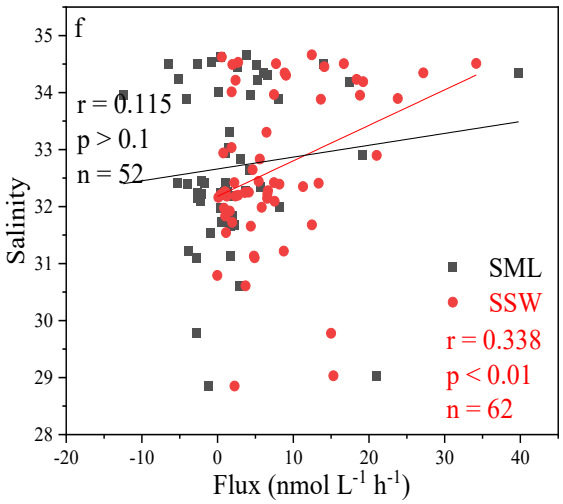


Fig. 5. Correlations between the instantaneous sea-to-air fluxes of CO (Flux) in the SSW and the SML with $a_{CDOM}(254)$, marine humic-like C3, wind speeds, temperature, and salinity in the East China Sea and the Yellow Sea during winter.

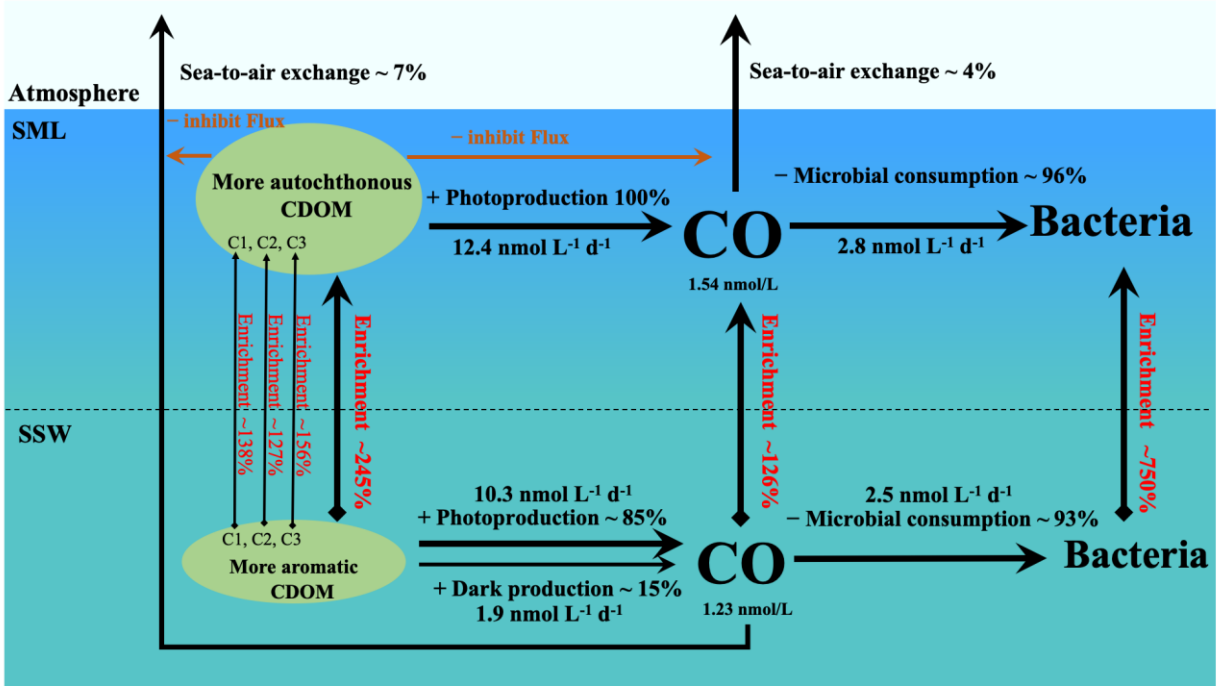


Fig. 6. Budget model of CO transformation in the SML and the SSW in the eastern marginal seas of China during winter. (Bacterial enrichment was calculated by Sun et al., 2020).

Table 1 Correlation coefficients between [CO], CDOM optical parameters, DOC, Chl-*a*, O_2, salinity, and temperature in SSW a) and SML b).

a)

	$[CO]_{ssw}$	Temperature	Salinity	O_2	$a_{CDOM}(254)$	$a_{CDOM}(330)$	$a_{CDOM}(355)$	C1	C2	C3	DOC	Chl-*a*	$SUVA_{254}$	$S_{275-295}$	$S_{350-400}$
Temperature	-0.001														
Salinity	0.017	0.699**													
O_2	-0.072	-0.977**	-0.723**												
$a_{CDOM}(254)$	-0.029	-0.907**	**-0.716****	0.876**											
$a_{CDOM}(330)$	-0.118	-0.783**	**-0.690****	0.758**	0.939**										
$a_{CDOM}(355)$	-0.151	-0.717**	**-0.622****	0.690**	0.894**	0.990**									
C1	0.008	-0.591**	**-0.758****	0.596**	**0.675****	0.680**	0.632**								
C2	0.053	-0.324*	**-0.341****	0.286*	**0.533****	0.592**	0.599**	0.759**							
C3	-0.049	-0.788**	**-0.851****	0.779**	**0.894****	0.887**	0.838**	0.891**	0.665**						
DOC	0.008	-0.598**	-0.239	0.583**	**0.532****	0.394**	0.354**	0.241	0.146	0.323*					
Chl-*a*	0.109	-0.357**	-0.092	0.415**	**0.333****	0.235	0.208	0.104	0.159	0.215	0.348**				
$SUVA_{254}$	-0.081	-0.676**	-0.705**	0.654**	**0.824****	**0.860****	**0.831****	**0.653****	**0.560****	**0.853****	-0.006	0.134			
$S_{275-295}$	0.045	0.100	0.099	-0.092	-0.204	-0.385**	-0.448**	-0.197	-0.241	-0.269*	-0.009	0.084	-0.241		
$S_{350-400}$	-0.001	0.009	-0.060	0.044	-0.095	-0.214	-0.279*	0.009	-0.103	-0.043	-0.088	0.026	-0.050	0.867**	
S_R	0.059	0.346**	0.421**	-0.429**	-0.254*	-0.220	-0.134	-0.343**	-0.104	-0.393**	-0.087	-0.148	-0.316*	-0.506**	-0.645**

*Correlation is significant at the 0.05 level (two-tailed).

**Correlation is significant at the 0.01 level (two-tailed). N = 44.

b)

	$[CO]_{sml}$	Temperature	Salinity	SML $a_{CDOM}(254)$	SML $a_{CDOM}(330)$	SML $a_{CDOM}(355)$	SML C1	SML C2	SML C3	SML DOC	SML $SUVA_{254}$	SML $S_{275-295}$	SML $S_{350-400}$
Temperature	-0.032												
Salinity	-0.098	0.699**											
SML $a_{CDOM}(254)$	-0.137	-0.037	-0.045										
SML $a_{CDOM}(330)$	-0.119	-0.113	-0.135	**0.948****									
SML $a_{CDOM}(355)$	-0.143	-0.114	-0.146	**0.901****	0.989**								
SML C1	-0.095	0.158	-0.156	**0.711****	0.504**	0.434**							
SML C2	-0.217	0.089	-0.106	**0.670****	0.675**	0.673**	0.702**						
SML C3	-0.060	0.092	-0.154	**0.823****	0.622**	0.541**	0.938**	0.703**					
SML DOC	-0.018	0.136	0.174	**0.898****	0.783**	0.705**	0.572**	0.280	0.665**				
SML $SUVA_{254}$	-0.063	-0.250	-0.439**	0.136	0.303*	0.376**	0.240	**0.501****	0.262	-0.272			
SML $S_{275-295}$	0.254	0.241	0.223	0.040	-0.217	-0.318*	0.323*	-0.056	0.336*	0.216	-0.409**		
SML $S_{350-400}$	0.270	0.112	0.082	0.136	-0.090	-0.187	0.385**	0.047	0.427**	0.244	-0.281	0.968**	
SML S_R	-0.288	0.231	0.213	-0.248	-0.057	0.044	-0.276	0.029	-0.339*	-0.296*	0.167	-0.726**	-0.776**

*Correlation is significant at the 0.05 level (two-tailed).

**Correlation is significant at the 0.01 level (two-tailed). N = 44.

Table 2 Correlation coefficients between EFs of CO, DOM absorption, DOC, three fluorescence components, temperature, salinity, and wind speed.

	EF of CO	EF of DOC	EF of $a_{CDOM}(254)$	EF of $a_{CDOM}(330)$	EF of $a_{CDOM}(355)$	EF of C1	EF of C2	EF of C3	Temperature	Salinity	Wind speed
EF of DOC	-0.098										
EF of $a_{CDOM}(254)$	-0.067	0.867**									
EF of $a_{CDOM}(330)$	-0.111	0.726**	0.912**								
EF of $a_{CDOM}(355)$	-0.124	0.556**	0.752**	0.945**							
EF of C1	0.081	0.731**	0.898**	0.753**	0.619**						
EF of C2	-0.084	0.149	0.586**	0.600**	0.580**	0.486**					
EF of C3	-0.022	0.796**	0.935**	0.830**	0.714**	0.964**	0.502**				
Temperature	0.037	**0.363****	**0.528****	**0.533****	**0.456****	**0.617****	**0.296***	**0.604****			
Salinity	0.006	**0.289***	**0.478****	**0.493****	**0.427****	**0.500****	**0.268**	**0.491****	0.699**		
Wind speed	-0.177	0.008	0.186	0.159	0.161	-0.130	-0.006	-0.105	0.129	0.052	
Solar irradiance	**0.409****	-0.024	-0.051	-0.082	-0.050	0.022	-0.139	0.002	0.160	0.157	0.104

*Correlation is significant at the 0.05 level (two-tailed).

**Correlation is significant at the 0.01 level (two-tailed). N = 44.