

1 **Spatial-temporal distribution, photoreactivity and environmental**
2 **control of dissolved organic matter in the sea-surface microlayer of**
3 **the eastern marginal seas of China**

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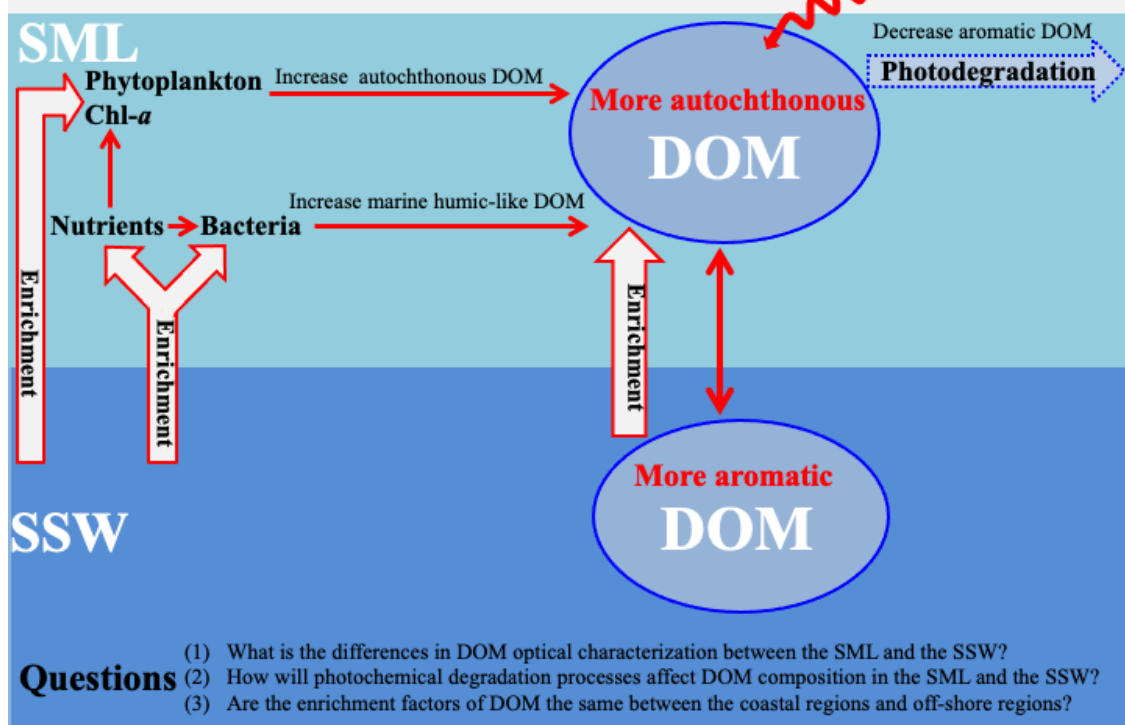
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Scientific hypothesis

The stronger photochemical reactions and enrichment processes could influence the composition difference of DOM between the SML and the SSW.



12

13

Graphical Abstract

14 **Abstract**

15 As the boundary interface between the atmosphere and ocean, the sea-surface microlayer (SML)
16 plays a significant role in the biogeochemical cycles of dissolved organic matter (DOM) and
17 macronutrients in marine environments. In our study, the optical properties of DOM were compared
18 between the SSW and the SML during spring, summer and winter in the East China Sea (ECS) and the
19 Yellow Sea (YS), photoexposure experiments were design to compare photochemical degradation
20 processes of DOM between the SML and the SSW. Chromophoric DOM (CDOM), fluorescent DOM,
21 dissolved organic carbon, chlorophyll *a*, picoplankton, nutrients, and bacteria were frequently enriched
22 in the SML. The enrichment factors (EFs) of tryptophan-like component 4 was significantly higher
23 than other fluorescence components; the longer wavelength absorption values of CDOM showed
24 higher EFs in the SML, and the more significant relationship between CDOM and Chl-*a* in the SML,
25 indicating that autochthonous DOM was more strongly enriched in the SML than the terrestrial DOM.
26 We find that higher EFs were generally observed in the SML in the off-shore regions than in the
27 coastal regions, and CDOM in the SML is photobleached less after relatively strong irradiation, as also
28 indicated by the lower percentages of humic-like DOM and lower specific UV absorbance values
29 ($SUVA_{254}$) in the SML than the subsurface water (SSW). Compared to the SSW, the elevated nutrients
30 may stimulate phytoplankton growth, biological activity and then production of abundant fresh
31 autochthonous DOM in the SML. Our results revealed a new enrichment model and the more
32 autochthonous properties of DOM in the SML than the SSW for exploring the oceanic air-sea layer
33 environment.

34

35 **Keywords:** Sea-surface microlayer; Dissolved organic matter; Photochemical degradation;

36 Enrichment processes; Eastern marginal seas of China

37 **1 Introduction**

38 The sea-surface microlayer (SML) is the boundary interface between the atmosphere and the
39 ocean, which covers about 70% of the Earth's surface. SML is physicochemically distinct from
40 subsurface water (SSW, depth 3 ~ 5 m) and is characteristically enriched with phytoplankton,
41 chlorophyll, particulate carbon, dissolved organic matter (Hardy 1982; Hardy and Apts, 1989), and
42 biogenic organic compounds, such as lipids, proteins, and polysaccharides ((Liss and Duce, 1997; Liss
43 and Duce, 2005). With a total thickness ranging between 1 μm and 1000 μm , the SML remains present
44 in wind speeds of up to 13 m s^{-1} (Sabbaghzadeh et al., 2017). A variety of processes contribute to the
45 formation of the SML in aquatic systems, these include but are not limited to, scavenging by rising
46 bubbles, atmospheric deposition, dissolved organic matter (DOM) photochemical degradation and
47 transformation, secretion, and biodegradation by organisms living within the microlayer (Neuston),
48 and migration of motile organisms into the SML (Aller et al., 2005; Wotton and Preston, 2005). The
49 SML is a very dynamic interface (Cunliffe et al., 2013), the impact of changes in UV radiation on
50 air-sea fluxes in the SML of important trace gases will need to be assessed. In addition, another
51 uncertainty is whether photochemical reactions on the SML affect the flux of volatile species at the
52 air-sea interface (Blough, 1997). Therefore, the role of the microlayer in oceanic emissions is not well
53 understood and fundamental advance in understanding its properties are needed.

54 The processes leading to the enrichment of DOM in the SML are not solely controlled by changes
55 in the DOM concentration at the sea surface microlayer, but are more complex (Mustaffa et al., 2018).
56 Because of its unique position at the air-sea interface, the biological and photochemical reactions of
57 DOM in the SML could strongly impact the biogeochemical cycling of biologically important

58 elements, for example, via the conversion of DOM into volatile species such as carbonyl sulfide
59 (OCS), which influence the atmospheric chemistry and climate (Mopper et al., 2002). Air-sea gas
60 exchanges of trace gases (e.g., CO, OCS, dimethylsulfide (DMS), and alkyl nitrates gases) can also be
61 greatly influenced by biological and photochemical reactions at the sea surface (Blough, 1997).

62 Optical measurements of absorbance and fluorescence have been applied to track DOM
63 variability in aquatic ecosystems (McKnight et al., 2001; Zepp et al., 2004; Coble, 2007). The fraction
64 of DOM that absorbs light in the ultraviolet and visible ranges of the electromagnetic spectrum and the
65 fraction that exhibits a blue fluorescence are known as chromophoric DOM (CDOM) and fluorescence
66 DOM (FDOM), respectively, and their relative compositions can provide information differentiating
67 between autochthonous and allochthonous sources (Coble, 1996; McKnight et al., 2001; Stedmon et
68 al., 2007). Photolysis of DOM promotes the formation of low-molecular-weight compounds,
69 increasing the bioavailability of biologically refractory materials and facilitating carbon uptake by
70 microbes (Kieber et al., 1989). Indices based on optical measurements of absorbance and fluorescence
71 are commonly used to track DOM composition and infer DOM processing due to their low analytical
72 cost and high throughput relative to molecular level analyses (Coble, 2007; Fellman et al., 2010;
73 Gabor et al., 2014). Recent studies have mainly focused on using the characteristics of CDOM as
74 indicators of the sources and degradation states of DOM (Massicotte et al., 2017) in the SSW, and its
75 vertical distribution in estuaries and open oceans (Yamashita et al., 2017; Margolin et al., 2018). In
76 addition, Mustafa et al. (2018 and 2017) observed that FDOM enrichment in the SML in the coastal
77 regions and open Atlantic Ocean, and FDOM is frequently enriched during upwelling events in the
78 Baltic Sea.

79 Even though there are many studies that have documented the enrichment in DOM (e.g. amino

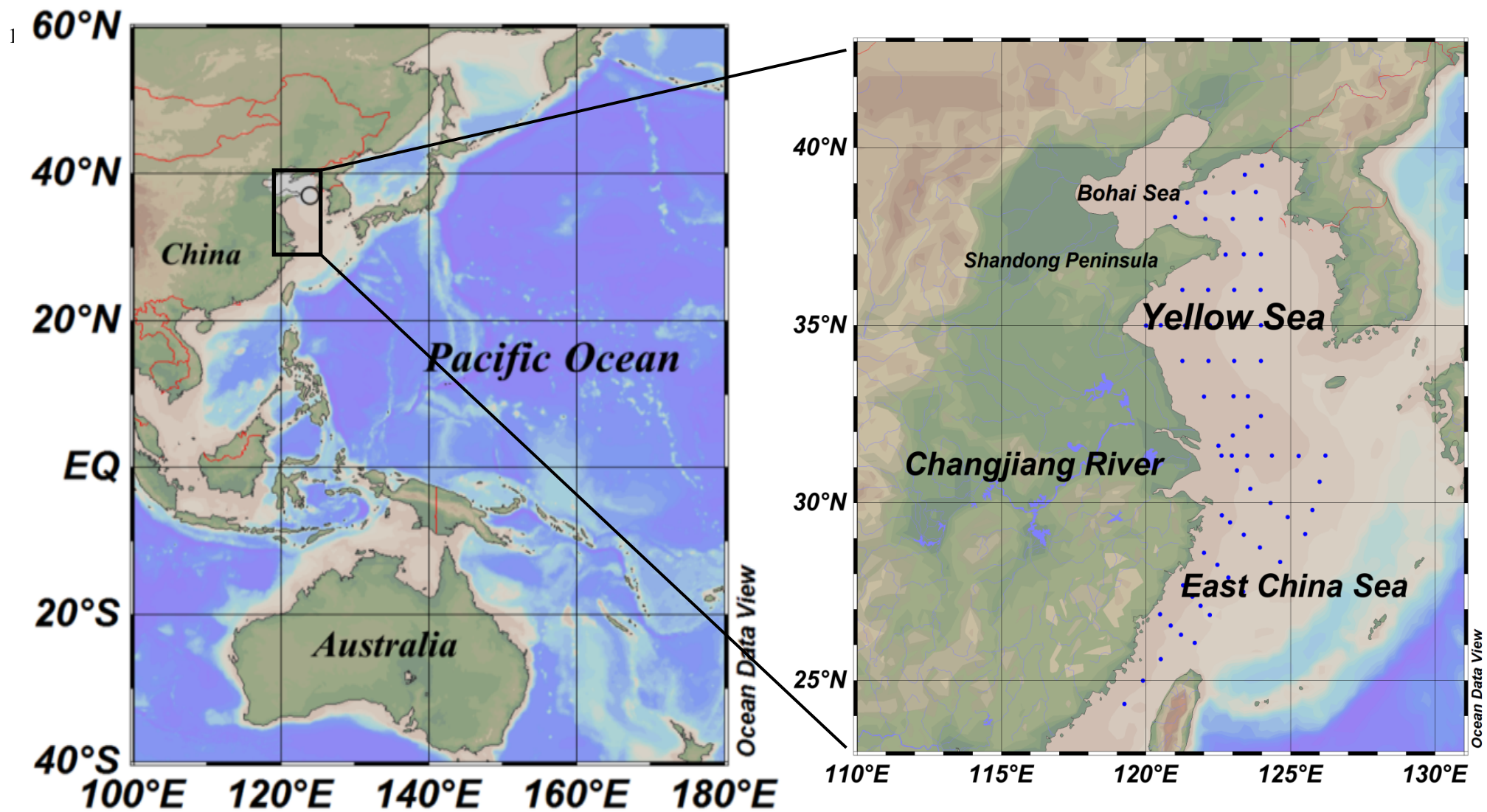
80 acids; carbohydrates) and inorganic nutrients in the SML relative to the SSW (Orellana et al., 2011;
81 Chen et al., 2016), the differences in organic matter composition between the SML and SSW, the
82 different enrichment factors of DOM in the SML between the coastal regions and the off-shore regions,
83 and how do photochemical degradation activities regulate DOM concentration in the SML need more
84 thorough discussion. Here, we investigated the concentration and composition of DOM in the SML
85 relative to the SSW and the responses of DOM to photoexposure. We hypothesized that the
86 photochemical reactions and enrichment processes could influence the composition difference of
87 DOM between the SML and the SSW, and greater solar exposure in the SML than in the SSW would
88 enhance the mineralization of DOM. To test these hypotheses, our study was designed to answer the
89 questions: (1) What is the differences in optical characterization of DOM between the SML and the
90 SSW? (2) [Are the enrichment factors \(EFs\) of DOM the same between the coastal regions and](#)
91 [off-shore regions?](#) (3) How will photochemical degradation processes affect DOM composition in the
92 SML and the SSW? We, therefore, compared the optical properties of DOM between the SSW and the
93 SML, and EFs of CDOM, FDOM components, dissolved organic carbon (DOC), chlorophyll-*a* (Chl-*a*),
94 nutrients, and bacterial abundance from the coastal waters to open ocean in the eastern marginal seas
95 of China (including the East China Sea (ECS) and the Yellow Sea (YS)) during spring of 2017 and
96 2019, summer of 2018, and winter of 2019; discuss how the composition of accumulated DOM was
97 affected by environmental conditions (wind speed and salinity) within the SML; and conducted
98 photoexposure experiments to compare photochemical degradation processes of DOM between the
99 SML and the SSW.

100

101 **2 Materials and methods**

102 2.1 Study Area

103 Four cruises were conducted during the four seasons, specifically, from: 27 March to 15 April
104 2017 (R/V “*Dong Fang Hong 2*”), 26 June to 19 July 2018 (R/V “*Dong Fang Hong 2*”), March 2019
105 (R/V “*Zheyu No. 2*”), and 28 December 2019 to 16 January 2020 (R/V “*Dong Fang Hong 3*”). The
106 station locations are shown in [Fig. 1](#). In spring, summer, and winter, SML samples were collected in
107 the YS and the ECS, which are shallow seas located almost entirely on the continental shelf in the
108 western Pacific Ocean where there is strong interaction between land and sea.



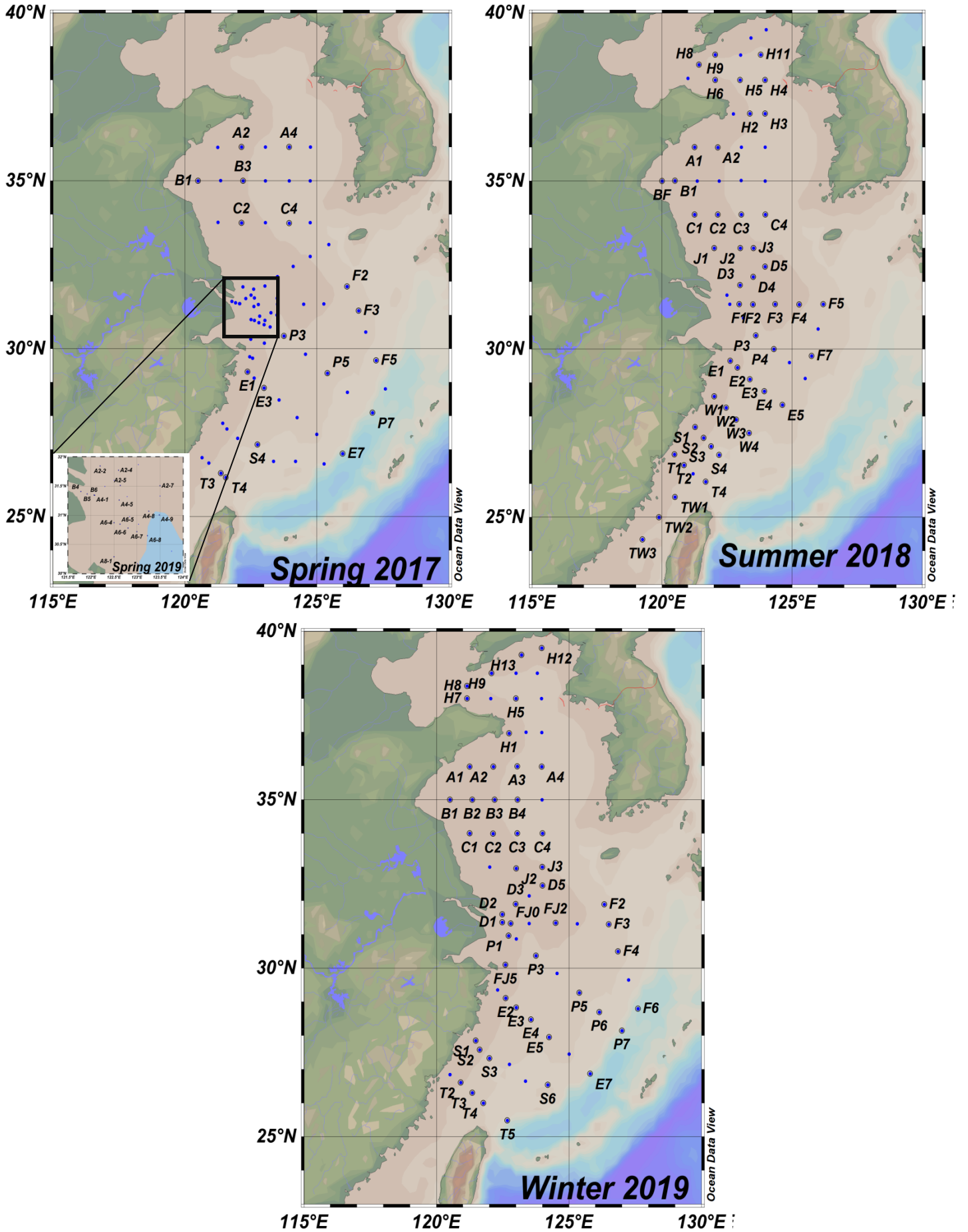


Fig. 1 Map of sampling stations.

112 2.2 Sampling

113 We collected 220 paired SML and SSW water samples. SSW samples were collected at 2–5 m
114 depth using 24 × 10-L Niskin bottles mounted on a rosette equipped with a
115 conductivity-temperature-depth (CTD) profiler. The SML samples were collected using the screen
116 sampling technique (Chen et al., 2016; Garrett, 1965) and were taken directly from the ship's bow
117 when conditions were calm. A screen sampler with a 1.6 mm mesh of stainless steel wire on a 40 cm ×
118 40 cm stainless steel frame was used. The SML samples were collected in 500 mL brown sample
119 bottles. The screen was held level and dipped into the sea surface, moved laterally in order to sample
120 from an undisturbed film, and then withdrawn slowly from the surface. Repeated dipping was
121 conducted until the desired volume was collected (11 times, 600 ml; the thickness of the SML sample
122 is nearly 300 ~ 1000 μm). The screen method is often applied during field studies because of its
123 relatively short sampling time and large sample volume compared to other techniques (Momzikoff et
124 al., 2004; Chen et al., 2016). Immediately after collection, samples were filtered using 0.7 μm glass
125 fiber filters (GF/F, Whatmann) and the filtrates were transferred to 60 mL and 40 mL brown glass
126 bottles (pre-cleaned and pre-combusted) for later CDOM and DOC analyses. All samples were frozen
127 (-20°C) and protected from light, and upon arriving at the land laboratory, were analyzed as soon as
128 possible. Sea surface temperature and salinity were obtained from a Seabird 911 CTD Rosette.
129 Meteorological data (e.g., wind speed and air temperature) were recorded simultaneously by a
130 ship-borne weather instrument (Li et al., 2019).

131 2.3 Photoexposure experiment

132 SSW and SML water samples were collected in July 2018 at stations A3, BF, and H10 as well as
133 D2 and F6 located in the YS and the ECS, respectively. Samples (SSW: 2L; SML: 500 mL) were

134 immediately passed through 0.22 μm PES filters (Pall Corp. Port Washington, NY, USA) to remove
135 the majority of bacteria, placed in acid-washed and pre-combusted brown glass bottles and stored at
136 4°C. Similarly, filtered samples from each site were placed in five 80 mL optically transparent quartz
137 tubes (acid-washed and pre-combusted) and sealed without headspace or air bubbles to measure the
138 effect of light exposure. The quartz tubes were positioned on their sides under the irradiation source to
139 maximize the exposure of the sample; the water depth in each tube was 5 cm (i.e. the diameter of the
140 tube). Both sets (SML and SSW) were irradiated for 6, 12, 24, 50, and 88 h (25°C) in a GLZ-C
141 Quantum Sensor (Top Cloud-Agri Instrument, Zhejiang, China) solar simulator. All samples for DOC
142 concentration measurements were acidified to approximately pH 2.0 with high purity HCl and
143 analyzed within 7 d, and absorbance spectra and fluorescence excitation emission matrices (EEMs)
144 were run on non-acidified samples within 3 d of sampling (4°C and dark).

145 *2.4 Analytical measurements*

146 *Determination of the CDOM absorption coefficient*

147 Absorption spectra were determined using a UV-visible spectrophotometer (UV-2550 bi-channel;
148 Shimadzu, Tokyo, Japan) equipped with two 10 cm path-length quartz cuvettes. Sample absorbance
149 was automatically corrected for the absorbance of Milli-Q water. Absorbance scans ranged from 200 to
150 800 nm, with a spectral resolution of 1 nm. The absorption coefficient of CDOM was calculated
151 according to equation (1):

$$152 \quad a(\lambda) = 2.303A(\lambda)/l \quad (1)$$

153 where, $A(\lambda)$ is the absorbance at wavelength λ ; and l is the path length of the quartz cuvette in meters.

154 The spectral slope of the CDOM absorption curve (S) was calculated according to a non-linear
155 regression over the 275–295 nm and 350–400 nm wavelength range, according to:

$$156 \quad a(\lambda) = a(\lambda_0)\exp[S(\lambda_0 - \lambda)] + K \quad (2)$$

157 where, $a(\lambda)$ is the absorption coefficient at wavelength λ ; $a(\lambda_0)$ is the absorption at the reference

158 wavelength λ_0 of 440 nm; S is the spectral slope; and K is a background parameter that accounts for
159 baseline shifts or attenuation due to factors other than CDOM. S was measured in the wavelength
160 ranges of 275–295 nm ($S_{275-295}$, nm^{-1}) and 350–400 nm ($S_{350-400}$, nm^{-1}). $S_{275-295}$ is used to characterize
161 DOM, with high values generally indicative of low-molecular-weight DOM that are linked to
162 photochemical modification (Helms et al., 2008; Ortega-Retuerta et al., 2009). The spectral slope ratio
163 (S_R) was defined as the ratio of the two spectral slopes, $S_{275-295}$ to $S_{350-400}$. S_R is also a sensitive
164 indicator of photochemically induced changes in the molecular weight within the CDOM pool, with
165 increases in S_R suggesting stronger photochemical degradation (Helms et al., 2008; Ortega-Retuerta et
166 al., 2009). We used the absorption coefficient at 254 nm ($a(254)$) to determine the concentration and
167 distribution of CDOM in the SML from the eastern marginal seas of China. The specific UV
168 absorbance ($SUVA_{254}$) can be used to measure aromaticity (Weishaar et al., 2003) and molecular
169 weight (Chowdhury, 2013) of DOM, with higher values generally indicative of higher aromaticity.
170 $SUVA_{254}$ is calculated as dividing the absorbance at 254 nm by DOC.

171 *EEMs and determination of the CDOM fluorescence index*

172 EEMs were obtained using a F-4500 fluorescence spectrophotometer with a 1 cm quartz cuvette
173 (Shimadzu) (Hoge et al., 1993). The emission spectra were scanned every 5 nm from 250 nm to 550
174 nm, and at the excitation wavelengths between 200–400 nm at 5 nm intervals, with 5 nm slit widths
175 for the excitation and emission modes. The FL Toolbox, which was developed by Wade Sheldon
176 (University of Georgia) for MATLAB, was used to remove the Rayleigh and Raman scattering peaks
177 using the Delaunay triangulation method (Zepp et al., 2004). The fluorescence intensities of the
178 samples were corrected with Milli-Q water blank EEMs and then normalized to the water Raman
179 integrated area maximum fluorescence intensities ($Ex/Em = 350 \text{ nm}/365\text{--}430 \text{ nm}$, 5 nm bandpass)
180 (Coble et al., 1998; Singh et al., 2010). Raman units (RU) (Stedmon et al., 2007; Singh et al., 2010)
181 were used as the units for the Raman peak areas of water when the excitation wavelength of 350 nm
182 was used for correction. EEMs were modeled using PARAFAC in MATLAB 7.5 with the DOMFluor

183 toolbox (Stedmon and Bro, 2008).

$$X_{ijk} = \sum_{n=1}^F a_{in} b_{jn} c_{kn} + \varepsilon_{ijk} \quad (3)$$

184
185 where X_{ijk} is the fluorescence intensity of the i th sample at the k th excitation and j th emission
186 wavelengths; a_{in} is directly proportional to the concentration (scores) of the n th fluorophore in the i th
187 sample; b_{jn} and c_{kn} are the estimates of the emission and excitation spectra (loadings) of the n th
188 fluorophore at wavelengths j and k , respectively; F is the number of components (fluorophores); and
189 ε_{ijk} represents the unexplained variability of the model (Singh et al., 2010). Split-half analysis
190 validation was used to determine the number of fluorescent components. The fluorescence intensity of
191 each fluorescent component was evaluated (Fig. S2, Supporting Information, Table 1).

192 *Determination of DOC, chlorophyll-a, heterotrophic bacterial abundance, dissolved oxygen, and*
193 *other parameters*

194 Concentrations of DOC were determined using the Shimadzu TOC-V_{CPH} total organic carbon analyzer
195 with an injection volume of 80 μ L. The accuracy of the test was ensured by measuring a deep seawater
196 reference (Hansell Laboratory, University of Miami) every 10 samples. [Two forms of reference water](#)
197 [have been developed for DOC analysis. Deep-ocean water, collected at 2600 m in the Sargasso Sea](#)
198 [and containing biologically refractory DOC, as well as low carbon water for testing instrument blanks](#)
199 [are available to the U.S. and international communities of aquatic chemists \(Hansell, 2013\).](#) The Chl- a
200 concentration was determined by a fluorescence spectrophotometer (7200-000, Turner Designs, CA)
201 after extraction in 90% acetone based on the procedure of Parsons et al. (1984). DO was determined
202 by iodination using the Winkler titration method (Carpenter, 1964), the endpoint was determined using
203 starch as a visual indicator. Salinity and temperature data were collected in situ by a
204 conductivity-temperature-depth sensor. All phytoplankton samples were enumerated in triplicate
205 according to Specification for Oceanographic Survey (State Bureau of Technical Supervision Bureau,
206 1992). Nutrient species concentrations were determined using an automatic analyzer (QuAatro, Seal
207 Analytical, Germany) (Grasshoff et al., 2007). [All phytoplankton samples were enumerated in](#)
208 [triplicate according to Specification for Oceanographic Survey \(State Bureau of Technical Supervision](#)
209 [Bureau, 1992\).](#) Heterotrophic bacterial abundance was measured by flow cytometry (Beckman Coulter
210 FC500-MPL) as described by Marie et al. (1997).

211

212 *Enrichment factors*

213 The enrichment factor (EF) in the SML is defined as follows

$$214 \quad EF = C_M / C_S \quad (4)$$

215

216 where C_M is the concentration of any substance in the SML; and C_S is its concentration in the SSW. If

217 the EF of a substance is greater than 1.0, that substance is considered enriched, if it is less than 1.0, it

218 is considered depleted (Chen et al., 2016).

219 *2.5 Statistical analyses*

220 The correlation coefficient (R) and probability (P) values were used to evaluate the

221 goodness-of-fit. The correlation matrix, analysis of variance, and principal components analysis were

222 conducted with SPSS version 18.0 (SPSS Inc., Chicago, IL, USA) to determine the possible

223 relationships between the DOM parameters and environmental factors. A P -value ≤ 0.05 was

224 considered significant. Regression analyses between the optical parameters of DOM and several

225 biogeochemical parameters in the SSW and the SML samples were performed in the Table S1 and the

226 Table S2, respectively.

227 **3. Results and discussion**

228 *3.1 Distribution and chemical characterization of DOM in the SSW of the eastern marginal seas of*

229 *China*

230 The surface distributions of salinity, temperature, CDOM, DOC, Chl- a , and several optical

231 parameters in the study area during spring, summer and winter are shown in Fig. S3 (SSW)-S4 (SML)

232 (Supporting Information). There was a strong south-to-north temperature gradient, with warmer waters

233 in the ECS and cooler waters in the YS. Lower salinities were observed in the Changjiang Estuary and
234 coastal waters. The lowest mean wind speed was observed in the summer of 2018 (Table 2). In spring
235 and summer, the bacterial abundances were lower in the YS (spring mean concentration: 2.26×10^8
236 cells/L; summer mean concentration: 3.79×10^8 cells/L) than in the ECS (spring mean: 2.98×10^8
237 cells/L; summer mean: 7.64×10^8 cells/L), indicating that the warmer southern ECS had stronger
238 biological activity in the SSW.

239 The $a(254)$ value ranged from 1.08 to 19.28 m^{-1} in the SML and from 0.82 to 14.23 m^{-1} in the
240 SSW during these three seasons. $a(254)$ values in the Changjiang Estuary (spring: station D1 (4.13
241 m^{-1}); summer: station D2 (3.98 m^{-1}); winter: station D1 (3.14 m^{-1})) and the northern YS (spring: station
242 A2 (4.26 m^{-1}); summer: station H11 (5.37 m^{-1}); winter: station H12 (5.95 m^{-1})) were generally higher
243 than other stations. CDOM absorption values and DOC concentrations were decreased from the
244 inshore to the offshore stations (Fig. S3 c-d)). There were significantly negative linear correlations
245 between salinity and $a(254)$ in all cruises in the SSW ($p < 0.01$, Fig. 3), especially in the ECS,
246 implying that freshwater run-off and seawater mixing played a more important role in determining
247 CDOM distributions in the SSW. The strongest negative linear relationship observed between salinity
248 and $a(254)$ was observed in winter when the influence of terrestrial input in this study region was
249 maximal. In addition, SUVA_{254} ranged from 0.51 to 8.39 $\text{L mg C}^{-1} \text{m}^{-1}$ in the SML. In comparison with
250 the SML, the SSW exhibited lower variability in SUVA_{254} values from 0.63 to 5.39 $\text{L mg C}^{-1} \text{m}^{-1}$, with
251 higher values at the northern YS stations and Changjiang Estuary coastal stations (Fig. S3k)).
252 According to the SUVA_{254} trends observed by Massicotte et al. (2017), the DOM composition we
253 observed in the SSW of the Changjiang Estuary ecosystem were more similar to the DOM measured in
254 freshwater ecosystems than in the ocean. SUVA_{254} underwent a sharp decrease from the Changjiang

255 Estuary ecosystem to the southeastern ECS, suggesting that aromatic and/or highly conjugated DOM
256 moieties were degraded along the aquatic continuum from the Changjiang Estuary to the open ocean.
257 Higher $S_{275-295}$ values were also observed in some off-shore stations (Fig. S4i)). These comparisons
258 showed that the DOM pools of the Changjiang Estuary contained molecules that were more
259 HMW-DOM and contained more aromatic compounds, CDOM in the SSW of the southeastern ECS,
260 which was derived predominantly from an autochthonous origin (phytoplankton production and
261 bacterial activity), clearly showed the presence of organic matter freshly released into sea (Yang et al.,
262 2020). The detail of mixing behavior, biological and photolytic degradation of dissolved organic
263 matter in the East China Sea and the Yellow Sea were discussed in our previous paper (Yang et al.,
264 2020).

265

266 *3.2 Fluorescence signature and factors controlling the composition of FDOM components in the SSW*
267 *and the SML*

268 FDOM properties can be used as the sensitive indicator of DOM processing and water mass. Four
269 fluorescent components were identified by PARAFAC analysis with the DOM Fluor toolbox in
270 MATLAB 7.5 (Stedmon and Bro, 2008), hereafter named C1, C2, C3, and C4 (Fig. S2). The
271 humic-like C1 and C3 were categorized as two traditional types of humic-like fluorescent components
272 (Coble 1996). Component 1 had primary fluorescence excitation and emission peaks at 345 nm and
273 455 nm, respectively, which was similar to terrestrial humic-like fluorophores in the visible region
274 (peak C) (Osburn et al., 2012). Relative to C1, the fluorescence of C3 was blue-shifted and had
275 fluorescence peaks at 385 nm emission and 315 nm excitation. The microbial humic-like component
276 had a relatively shorter emission peak wavelength compared to the terrestrial humic-like PARAFAC

277 components previously identified in the open ocean (Catala et al., 2015). C2 exhibited Ex/Em maxima
278 at 255 nm/310 (375) nm, which could be considered tyrosine-like fluorescence (Stedmon et al., 2003)
279 and attributed to autochthonous and/or microbial FDOM. C4 had an excitation range of 280 nm with
280 an emission peak at 335 nm, which corresponded to peak T of the amino-acid-like fluorescence of
281 tryptophan, likely derived from in situ primary autochthonous substances and other fresh biological
282 sources (Coble, 1996). The tryptophan-like C4 and the humic-like C1 and C3 in the SSW were all
283 negatively correlated with salinity ($P < 0.01$, Table S1), but increased with the increasing DO level.
284 These suggested that water mixing and microbial activity were important factors in determining
285 geographical distributions of FDOM in the SSW (Breitburg, et al., 2018; Yamashita et al., 2017;
286 Galgani and Engel, 2016). Moreover, the geographical distribution of humic-like C1 and protein-like
287 components were more similar to that of the Chl-a concentration in the SML (Fig. 4 a, b, d). Such
288 relationships suggested that the production of protein-like and humic-like FDOM with phytoplankton
289 production and decay in the SML.

290 FDOM enrichment in the SML of all stations ranged between 0.5 and 11 ($n = 225$) and FDOM
291 was more frequently enriched (C1: 89.6%; C2: 73.2%; C3: 91.8%; C4: 93.4% of all samples) than
292 CDOM. The fluorescence intensity of the components in the SML samples decreased in the following
293 order: tryptophan-like > tyrosine-like > terrestrial humic-like > marine humic-like; whereas those in
294 the SSW samples decreased in the order: tyrosine-like > tryptophan-like > marine humic-like >
295 terrestrial humic-like. The tryptophan-like component (C4) was mostly enriched in the SML samples
296 with a median EF = 2.2 and a range from 0.2 and 8.0. The EF of C4 was clearly higher than other
297 components in all seasons (Fig. 6b)), especially in summer, and the FDOM composition in the SML
298 revealed a relatively higher proportion of autochthonous tryptophan-like FDOM than the SSW. It has

299 also been broadly recognized that tryptophan-like C4 in the particulate fraction is related to recent
300 primary production (Brym et al., 2014; Yamashita, 2014) and that phytoplankton excrete
301 tryptophan-like fluorophores (Romare-Castillo et al., 2010). Together, as already emphasized
302 previously, the variation observed for FDOM can be more related to that of Chl-*a* in the SML, these
303 observations suggested that the DOM enriched in the SML was made up of a relatively higher
304 proportion of marine autochthonous DOM than the SSW.

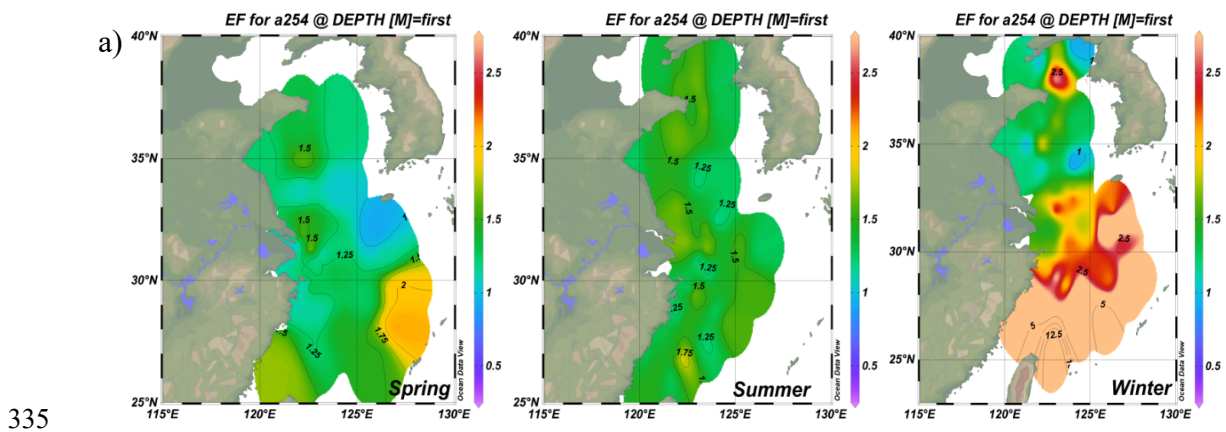
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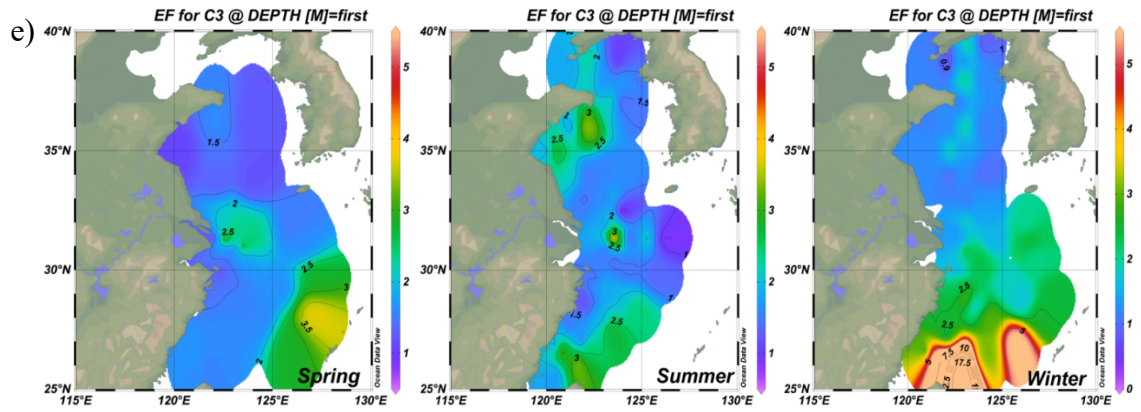
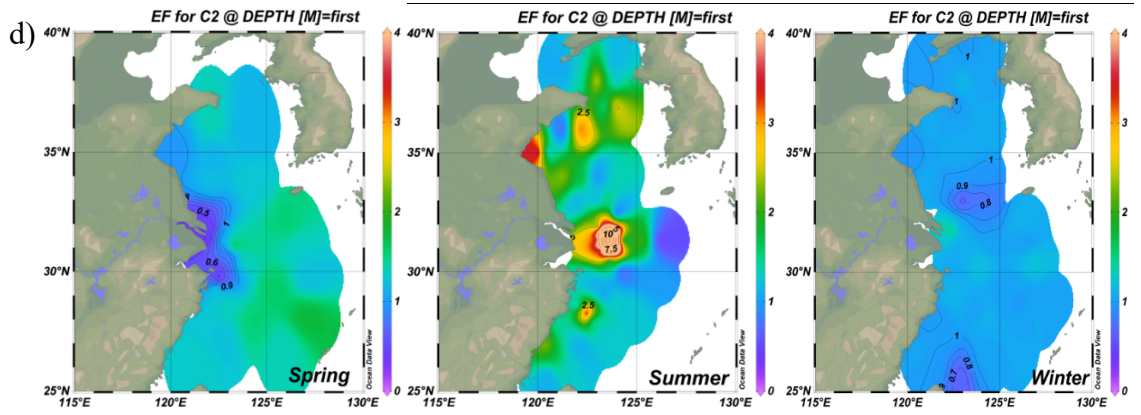
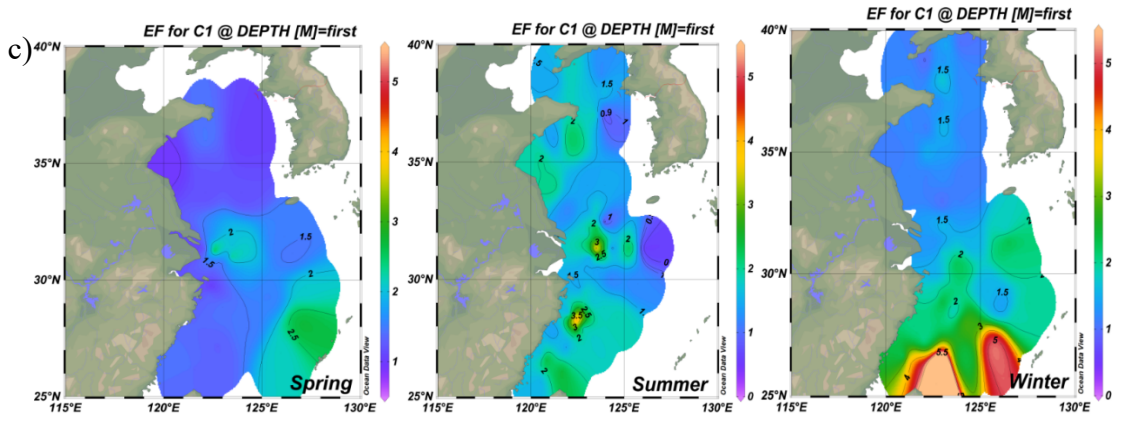
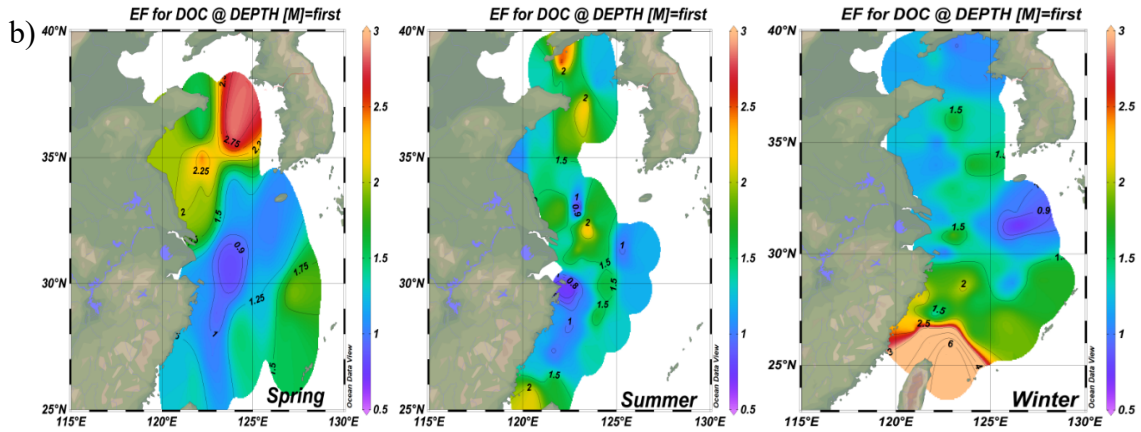
306 *3.3 DOM and biogenic molecules accumulation in the SML*

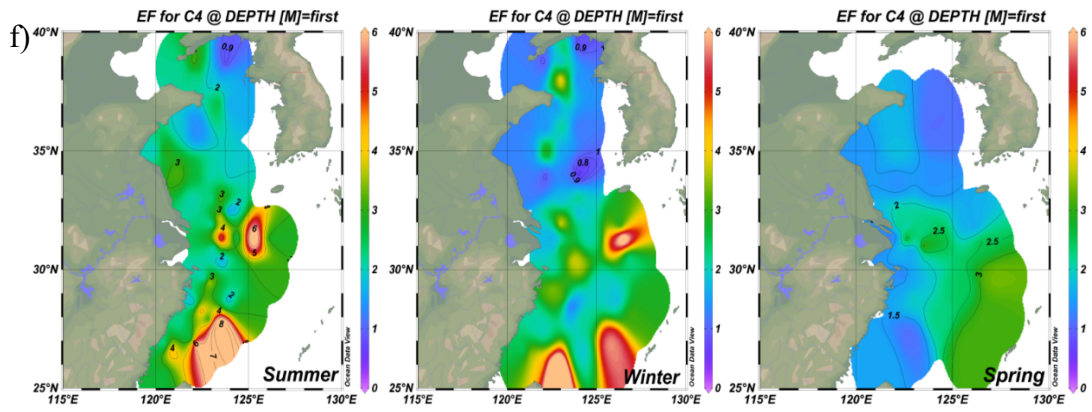
307 Up to 88% of our CDOM samples were enriched in the SML, with the median EF for a(254) of
308 1.3, ranging between 0.4 and 6.7. Concentrations of CDOM, FDOM, nutrients, bacterial abundance,
309 and Chl-*a* in the SML were correlated with their respective SSW concentrations (Fig. 5),
310 demonstrating that transport from the SSW to the SML is an important pathway. Furthermore, the
311 relatively higher CDOM absorption enrichment value in the SML were found at longer wavelengths
312 (Fig. 6a) EF of a(355) > EF of a(254)). Marine DOM usually has higher absorption slope than
313 terrestrial DOM, and the higher slope (no matter it is S₃₂₀₋₄₁₂ or S₂₇₅₋₂₉₅), marine production of DOM
314 had the largest influence on the CDOM absorption properties in the longer wavelength range (Danhiez
315 et al., 2017) (S₃₂₀₋₄₁₂: DOM marine origin VS. S₂₇₅₋₂₉₅: terrestrial DOM).

316 Galgani and Engel (2016) also observed that amino acid-like fluorophores were highly enriched
317 in the SML, not only due to their amphiphilic properties, but also due to their local production in the
318 SML. Therefore, the marine local production might significantly affect the composition of DOM in the
319 SML. Additionally, the nutrients showed significantly higher EFs (NO₃⁻: 3.41 ± 6.08, *n* = 41; NO₂⁻:
320 3.57 ± 5.54, *n* = 52; PO₄³⁻: 2.13 ± 2.74, *n* = 68; and SiO₃²⁻: 6.53 ± 13.67, *n* = 13) than biological and
321 DOM parameters in the SML. The strong correlation between the SML and SSW concentrations of

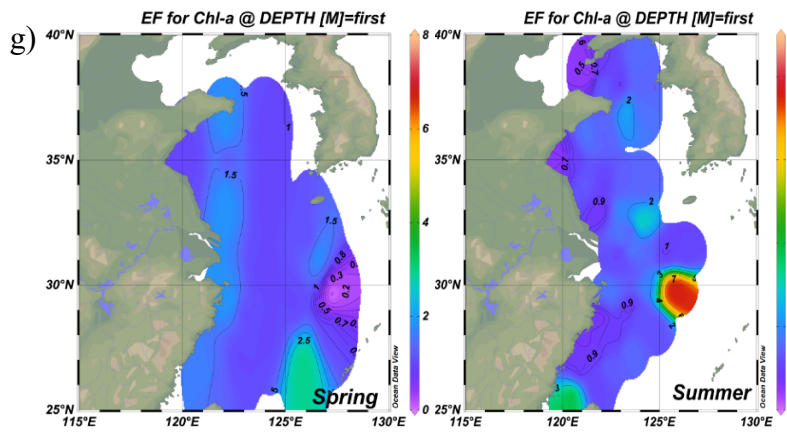
322 NO_2^- , NO_3^- , and SiO_3^{2-} (Fig. 5) showed that the similar fundamental drivers are probably at work in
 323 both compartments for these nutrients. For example, dissolved substances, particles, and
 324 microorganisms were brought to the interface by simple diffusion, rising bubbles (Jarvis, 1967),
 325 convection, and upwelling from sediments and subsurface water, and at the same time, the microlayer
 326 is also a sink for fallout from the atmosphere (Duce et al., 1976). In addition, we also observed the
 327 significant positive relationship between $a(254)$ and Chl- a ($R = 0.662$, $P < 0.01$) in the SML during
 328 spring, and the positive relationship between the EF of PO_4^{3-} and the EF of Chl- a ($R = 0.319$, $P = 0.01$,
 329 Table 3). These observations indicated that spatial variation of CDOM concentrations were related to
 330 Chl- a in the SML. The enrichment of inorganic nutrients would be an important factor influencing the
 331 production and composition of phytoplankton-produced DOM (Carlson and Hansell, 2003) in the
 332 SML. Therefore, phytoplankton growth, primary productivity rate, biological activity and marine
 333 autochthonous DOM production would all be enhanced by the enriched nutrients in the SML.
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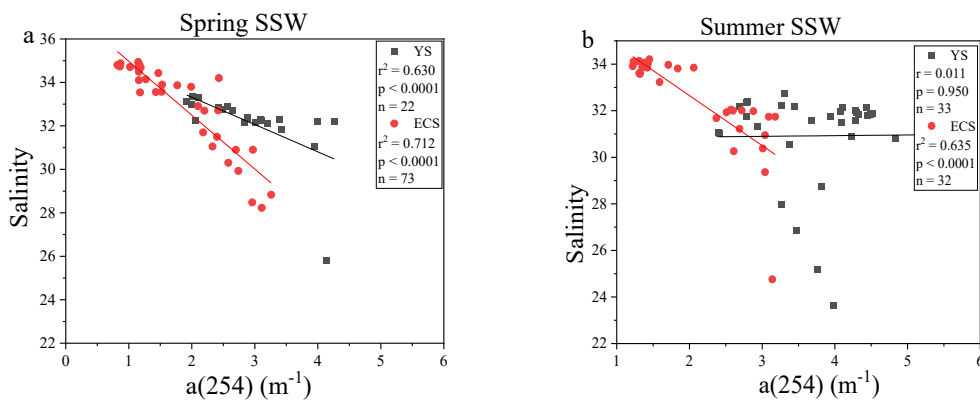


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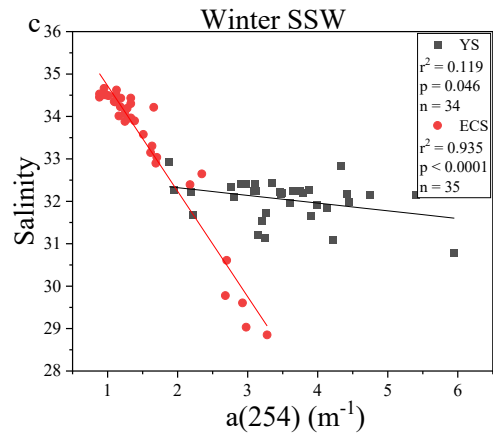


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342 Fig. 2. Distributions of enrichment factors of CDOM, DOC, Chl-*a*, and four fluorescence components
 343 in the surface microlayer water during spring, summer, and winter. Increasing DOM yields were
 344 significant in coastal regions in all seasons, but the higher enrichment factors (EFs) were more
 345 pronounced in off-shore regions.



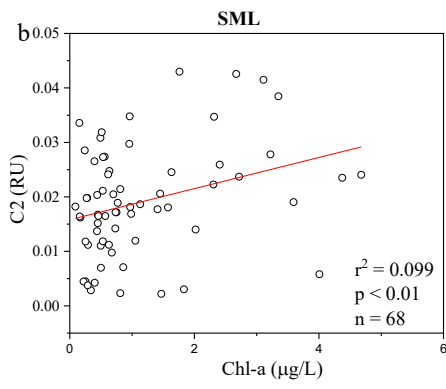
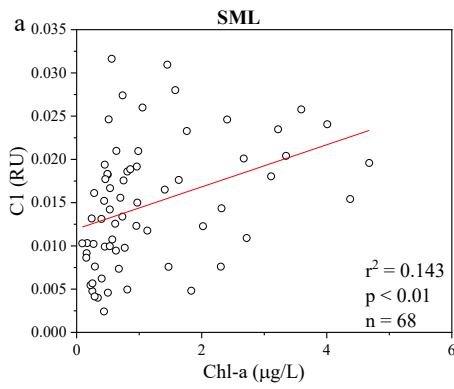
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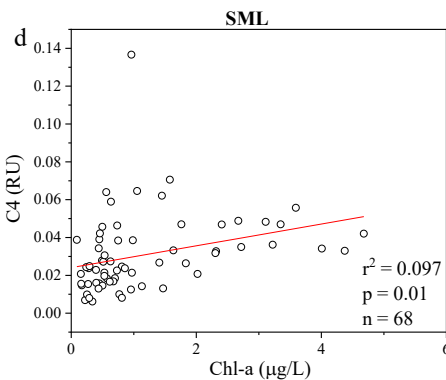
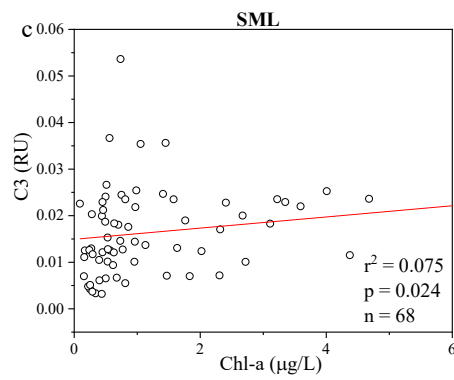
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348 Fig. 3. Relationships between $a(254)$ and salinity in the subsurface water (SSW) in the East China Sea
 349 (ECS) and the Yellow Sea (YS) during spring, summer and winter.
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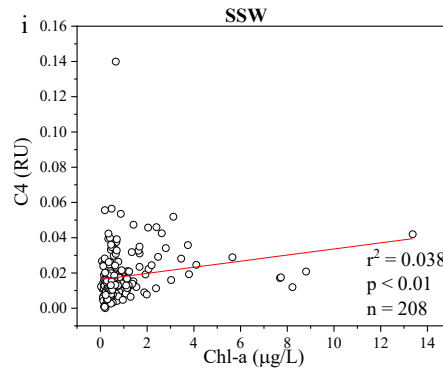
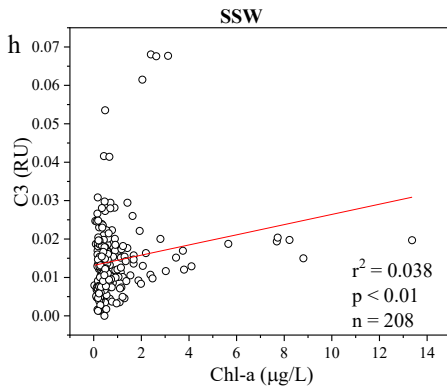
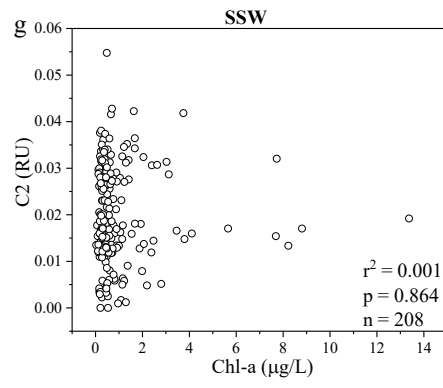
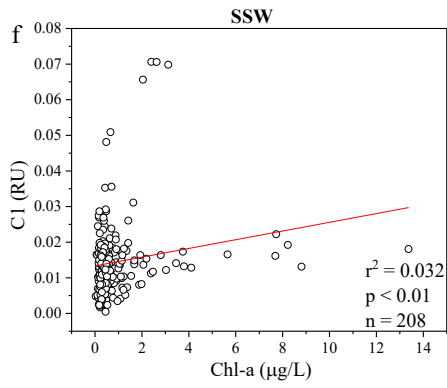
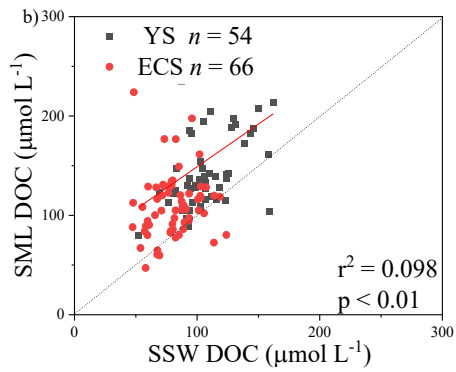
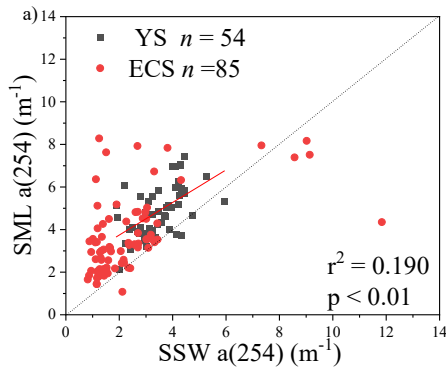
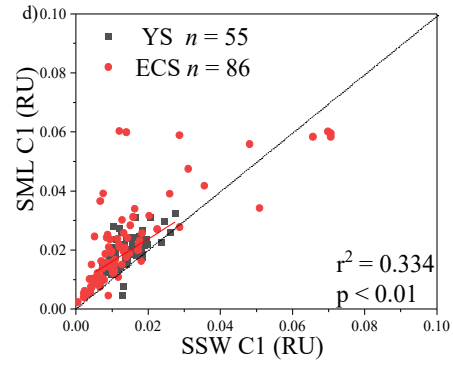
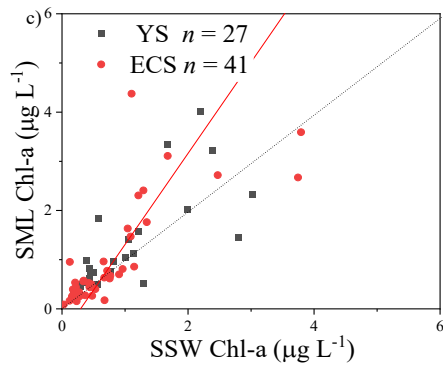


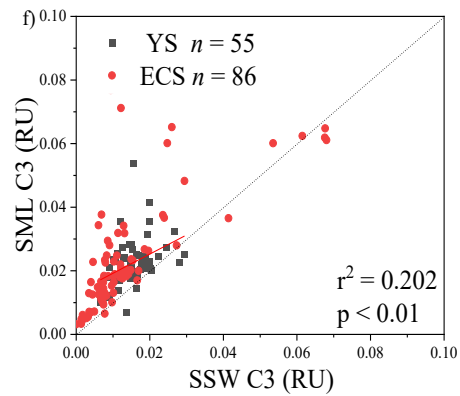
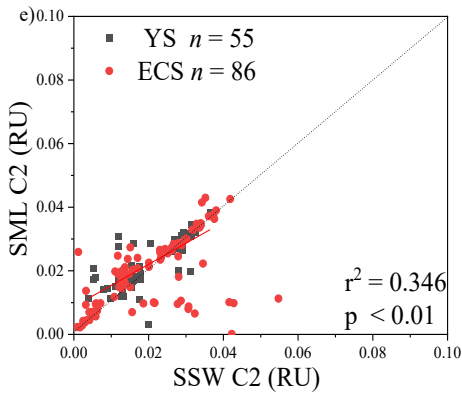
Fig. 4. Relationships between a(254), four fluorescence components and Chl-a in the sea-surface microlayer (SML) (a-d) and in the SSW (f-i).



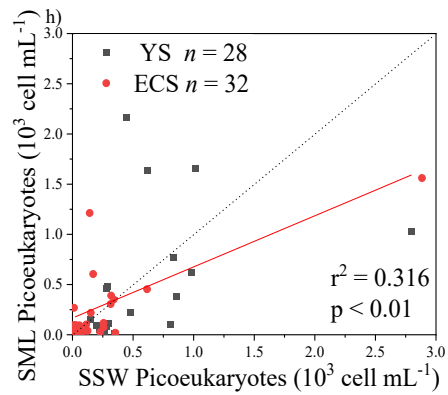
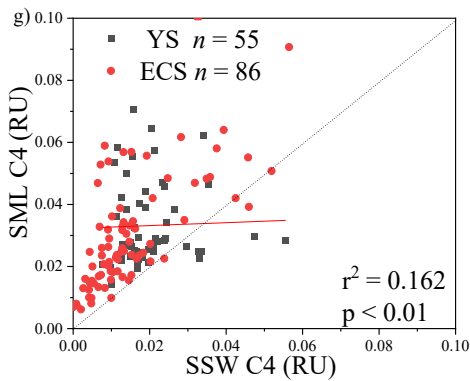
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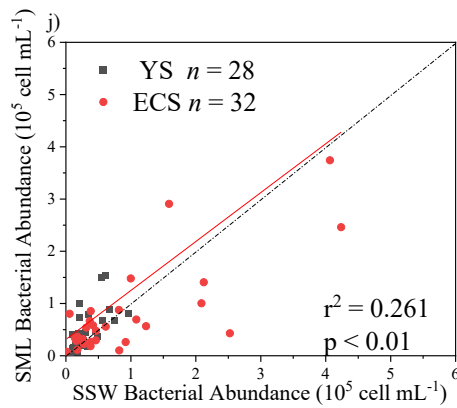
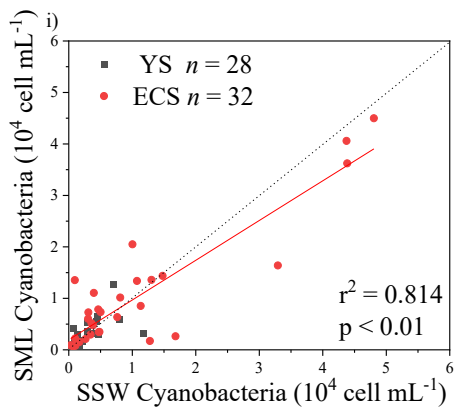
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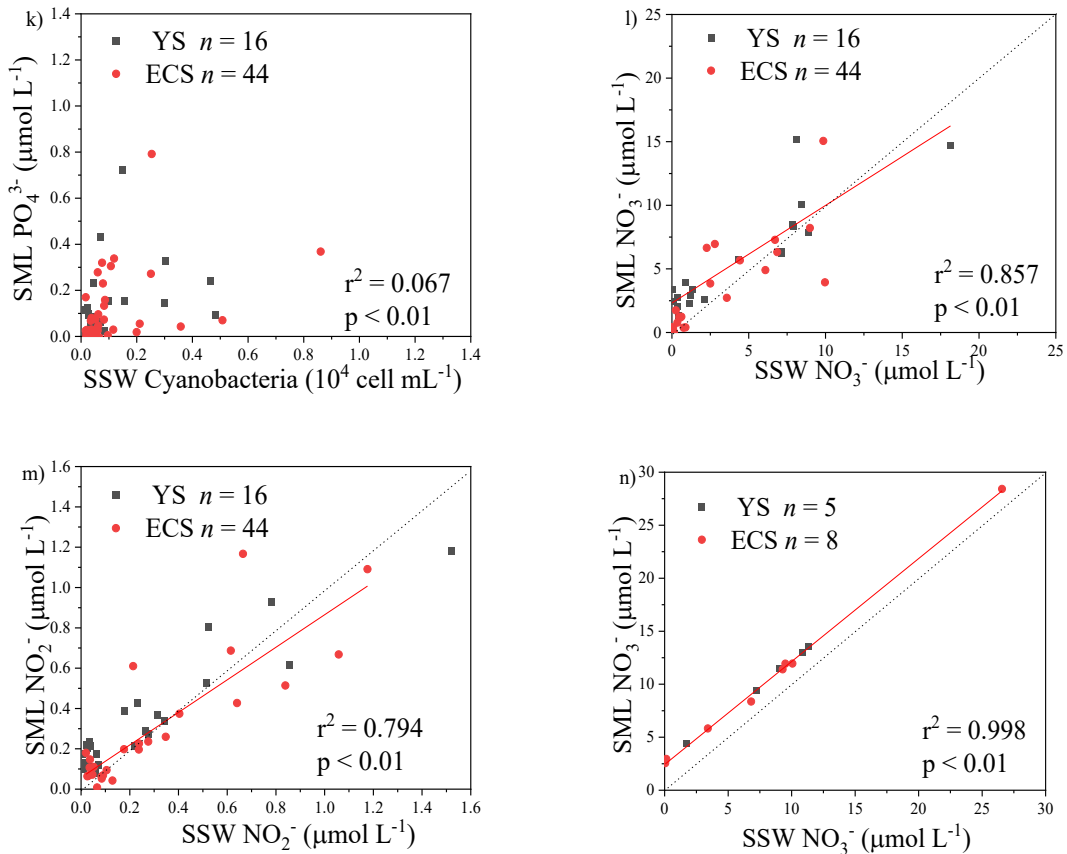


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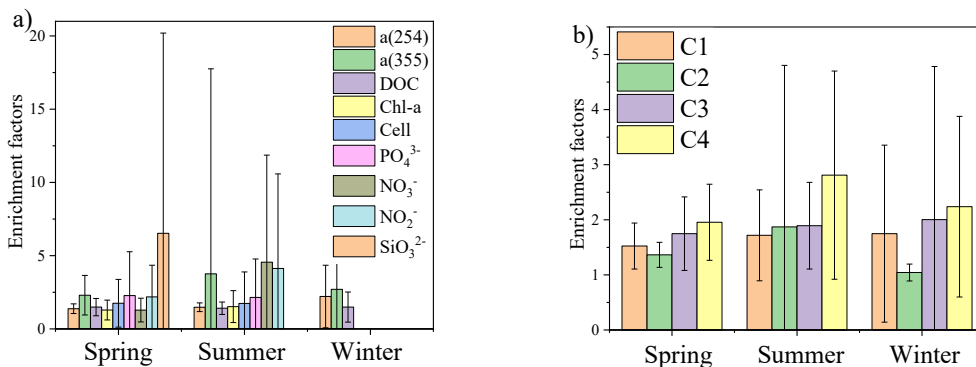
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Fig. 5. Correlations between the microlayer CDOM, DOC, Chl-*a*, four fluorescence components concentrations, cyanobacteria, phytoplankton biomass, nutrients and bacterial abundance, and their subsurface water concentrations. The dashed lines correspond to the 1:1 lines, and the full lines are the regression models. (All DOM spectroscopic parameters sample were analyzed in spring, summer and winter; Chl-*a* was determined in spring, summer, and summer; cyanobacteria, phytoplankton biomass, nutrients and bacterial abundance were determined in spring and summer.).



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Fig. 6. Mean enrichment factor of a_{CDOM} (254 nm and 355 nm), DOC, Chl-*a*, nutrients (PO_4^{3-} ; NO_3^- ; NO_2^- , SiO_3^{2-}), and four fluorescence components during spring, summer, and winter.

374 3.4 Wind speed influencing the enrichment of DOM optical properties

375 The wind speeds during our observations ranged from 0.2 to 14.9 m s⁻¹. We divided them into
376 three different wind regimes: low (0.0–2.0 m s⁻¹), moderate (2.0–10.0 m s⁻¹), and high (10.0–14.9 m
377 s⁻¹). Although the EFs of DOC and Chl-*a* were negatively correlated with wind speed (DOC: $P = 0.002$;
378 Chl-*a*: $P = 0.042$), the EFs of CDOM and FDOM were not. During the low wind regime, no
379 significant relationships were apparent between wind speed and either EFs of CDOM or FDOM,
380 CDOM and FDOM were consistently enriched, with EFs ranging from 1.0 to 2.2, and a mean $a(254)$
381 EF value of 1.3 ($n = 20$). However, the EFs during moderate winds had larger variability and ranged
382 from 0.9 to 14.5, with a mean EF value of 1.6 ($n = 143$), and during high winds they ranged from 0.6
383 to 1.8, with a lower mean EF value of 1.1 ($n = 18$). In addition, depleted levels of CDOM ($EF < 1$)
384 occurred at frequencies of 5.6%, 9.1%, and 20.0% during low, moderate, and high wind regimes,
385 respectively. Therefore, although lower wind speeds and ascending bubbles might further promote the
386 transportation of organic materials from the underlying waters, DOM enrichments were still observed
387 at wind speeds up to > 10 m s⁻¹. Reinthaler et al. (2008) also reported that higher enrichment was
388 found at higher wind speeds. During moderate to high wind regimes, breaking waves not only can
389 disrupt the surface film and physically drive DOM back into the bulk water, but also facilitate the
390 formation of the SML as rising bubble plumes transported DOM to the surface, resulting in wider
391 ranges of EFs (Frew et al., 2004). Higher wind speed does enhance mixing (Reinthaler et al., 2008),
392 which can arguably favour transport of nutrients and DOM from the SSW equally (Wurl et al., 2011).
393 Although wind speed appear to play an important role in the enrichment of surface-active DOM, the
394 chemical composition of the SML influence its stability. For example, enrichments of sulphate
395 half-ester groups in the SML (Wurl and Holmes, 2008) could increase stability because these groups
396 can influence the intrinsic viscosity of marine polymers (Nichols et al., 2005) and sulphur-containing

397 algal carbohydrates are less soluble and hydrolysable (Kok et al., 2000). Sampling needs to be
398 performed on the leeward side of the boat with the boat moving into the wind to avoid contamination.
399 Although some disturbance of SML integrity was produced by the ship's movement and potential
400 contamination at high wind speeds and tidal mixing. It has long been known that the SML reforms
401 rapidly following physical disruption (Dragcevic and Pravdic, 1981). Rapid SML recovery occurs
402 because SML organics dispersed by breaking waves readily reabsorb to the surfaces of rising bubbles
403 generated by the same breaking waves (Woolf, 2005). Enrichment processes and biochemical
404 processes of organic substances in the marine environment are all likely to be the more important
405 contributors of DOM to the SML in our study regions.

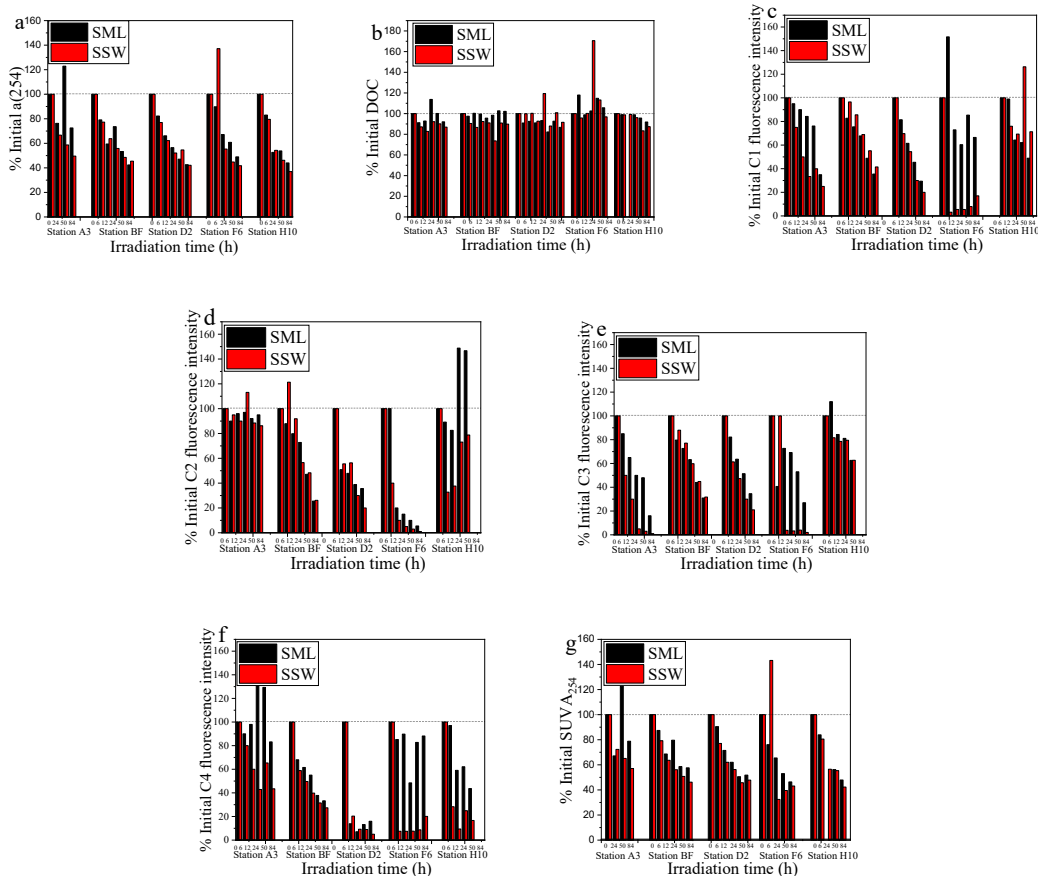
406 *3.5 Photochemical degradation of DOM in the SSW and the SML*

407 Photobleaching is one of the major mechanisms determining the geographical distributions of
408 chromophoric and fluorescent DOM in the ocean (Helms et al., 2008; Brinkmann et al., 2003; Siegel
409 et al., 2005). The average SUVA₂₅₄ values in SSW were generally higher than those in the SML in our
410 study regions (SSW: 2.45 ± 0.91 L mg-C⁻¹ m⁻¹ vs. SML: 2.39 ± 1.34 L mg-C⁻¹ m⁻¹), and the most
411 obvious distinction happened in summer (Table 2). These indicated that although CDOM
412 concentration in the SSW was lower than that in the SML, CDOM in the SSW has a higher degree of
413 aromaticity compared to the SML. Thus we performed photochemical incubation experiments to
414 confirm whether photochemical reactions influenced the differentiated aromaticity and photo-reactive
415 features of DOM between the SML and the SSW.

416 After 88 h of exposure, the a(254) values were only 49.6%, 45.5%, 42.1%, 41.8% and 37.0% of
417 the initial values at stations A3, BF, D2, F6, and H10 in the SSW, and 72.5%, 42.4%, 42.6%, 49.0%
418 and 44.0% of the initial values at stations A3, BF, D2, F6, and H10 in the SML, respectively. Overall,

419 a(254) and SUVA₂₅₄ decreased by $49.9 \pm 12.8\%$ and $43.0 \pm 15.5\%$, respectively, in the SML, and by
420 $56.8 \pm 4.7\%$ and $56.0 \pm 10.2\%$, respectively in the SSW. Therefore, stimulated solar UV exposure
421 caused a larger decrease in DOM absorbance in the SSW than the SML (Fig. 7). The relatively rapid
422 decrease of SUVA₂₅₄ in the SSW indicated a more rapid conversion of DOM to less humic-type
423 materials than in the SML. Although photodegradation causes CDOM absorption to decrease, DOC is
424 not sensitive to photodegradation in our photodegradation experiments, implying that the light
425 exposure preferentially removed the colored DOM rather than the non-colored DOM (Bittar et al.,
426 2015). All incubation samples were not contaminated, both measurement and analytical errors will let
427 DOC data exceed 100%. Approximately 65% of FDOM was lost during the irradiation experiment,
428 except in the case of the tyrosine-like component 2 from the SML at the station H10, which increased
429 slightly. Photoproduction of tyrosine-like components has been previously reported by Zhu et al.
430 (2017), who suggested that the photochemical degradation of CDOM contributed to the release small
431 amounts of tyrosine-like fluorophores. The tryptophan-like C4, humic-like C1 and C3 were more
432 photodegraded in the SSW than in the SML (Fig. 7c, e, f). For example, C1, C3 and C4 show a
433 marked decrease in the SSW at the off-shore station F6. Because of the origin of CDOM at the station
434 F6 remote from the direct terrestrial influence, the majority of CDOM at the station F6 was thought to
435 be a by-product of net primary production. The present results showed that a large fraction of the total
436 CDOM in the SSW at the off-shore station F6 is still potentially sensitive to photooxidation. As
437 already referred previously, CDOM in the SSW showed higher SUVA₂₅₄ values, and higher
438 percentages of humic-like DOM than in the SML. Therefore, the photochemically mediated shifts in
439 DOM in the SSW were more pronounced than those in the SML in our incubation experiments, in
440 terms of both absorption and fluorescence values.

441 This heterogeneity in the EFs and photochemical reactivities of FDOM components can be
442 related to the chemical and structural nature, such as molecular weight, aromaticity or humification of
443 FDOM enrichment processes. Hydrophilic, carboxylic acid-bearing DOM moieties are preferentially
444 degraded by simulated sunlight (Brinkmann et al., 2003). The largest fractions of photolabile DOM are
445 made up of aromatic carbon rings or high double bond equivalent molecules (Kujawinski et al., 2004;
446 Gonsior et al., 2009). The humic-like C1 and C3, all of which exhibited significantly positive
447 relationships with $SUVA_{254}$ (< 0.001 , Table 1) and shown higher aromaticity, were more prone to
448 photochemical degradation (Fig. 7c, e, and f). The tyrosine-like C2, as compared to other
449 protein-like compounds, is generally considered more labile and susceptible to bacterial cycling and
450 rapid consumption by microbiota (Medeiros et al., 2015). The SML experiences the most intense solar
451 radiation, especially ultraviolet (UV) light (Obernosterer et al., 2005). Photochemical degradation may,
452 therefore, be a sink for aromaticity fluorescent components in the SML, and be a source for the
453 tyrosine-like C2. In addition, Blough (1997) discovered that photochemical production rates in the
454 SML should lead to the more rapid oxidative turnover of materials at the interface and potentially to
455 reactions and processes not observed in bulk waters. Therefore, differences in $SUVA_{254}$ values and
456 photoreaction behavior between the SSW and the SML may also reflect that DOM in the SML was
457 already photobleached, which resulted in the decrease of DOM aromaticity, CDOM in the SSW
458 appeared to be more susceptible to photochemical degradation than CDOM in the SML. Together,
459 photo-irradiation have the significant influence on the accumulation of protein-like DOM and
460 depletion of aromatic organic compounds in the SML, and organic carbon might have undergone a
461 more rapid cycling in the SML than the SSW.



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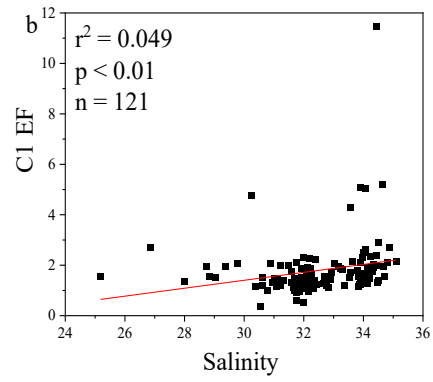
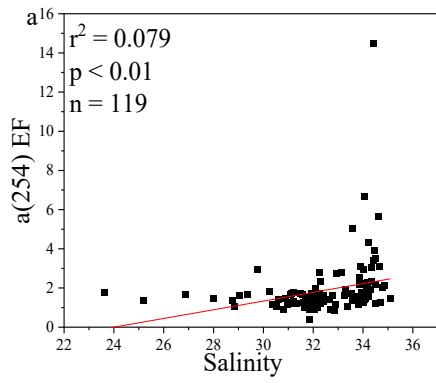
465 **Fig. 7.** Changes in ratios of a(254), DOC, SUVA₂₅₄ and four fluorescence components intensities
 466 to initial values for both SML and SSW sample.

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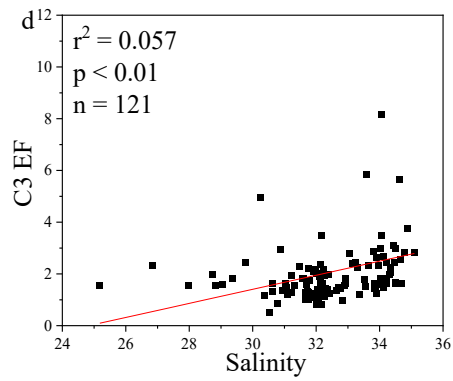
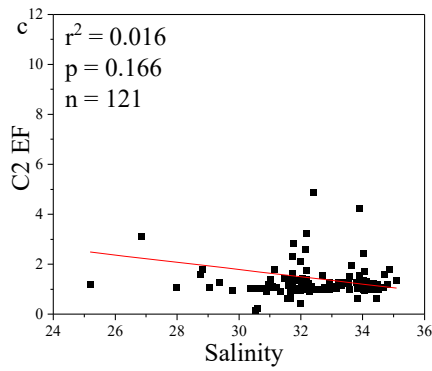
468 *3.6 Variations in the enrichment factors of CDOM, DOC, FDOM along the coastal regions to ocean*

469 The concentrations of a(254) and DOC decreased from the coastal regions to the open ocean, and
 470 decreased from the northern part of the sampling area (the YS) to the southern part of the sampling
 471 area (the ECS) in both the SSW and the SML (Fig. S3 c-d) and Fig. S4 a-b)). However, CDOM and
 472 FDOM were more frequently enriched in the ECS (CDOM: 93% of all samples; FDOM: 72–94% of
 473 all samples) than that in the YS (CDOM: 86% of all samples; FDOM: 70–92% of all samples). The
 474 higher EF values for CDOM, FDOM, DOC, Chl-*a*, nutrients, and cell were generally observed in the
 475 ECS (Fig. 2). Lower EFs and EFs < 1, which indicate a depletion of CDOM in the SML, were usually
 476 observed at short distances from the coast (Fig. 2) with lower salinity. The salinity during our

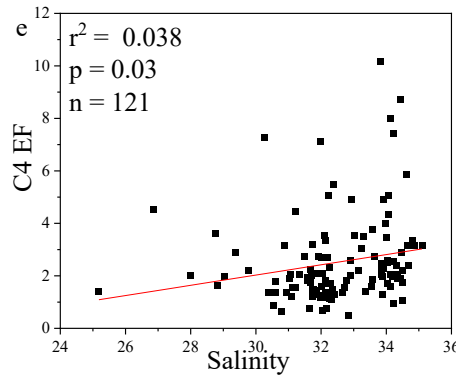
477 observations ranged from 23.6 to 35.1. Although CDOM and FDOM concentration negatively
478 correlated with salinity, the EFs of CDOM and FDOM were weakly positive related with salinity (Fig.
479 8). The EFs of Chl-*a* and nutrient were also higher in the southeastern ECS (Fig. 2 and Fig. S5), where
480 sufficient light and higher temperature combined to facilitate primary production and higher
481 contributions of autochthonous materials to DOM. DOM in the SSW of the southern ECS was more
482 dominated by marine autochthonous materials in our previous discussion (Yang et al., 2020). The
483 Changjiang River discharges enormous amounts of N and P into the ECS (Liu et al., 2018), but
484 phosphorus is generally the major limiting element for phytoplankton growth in the ECS (Liu et al.,
485 2016). Thus the difference in EFs of CDOM and Chl-*a* between YS and the ECS, and between the
486 coast and off-shore regions is likely due to the significantly nutrients enrichment in the SML in the
487 off-shore regions. In winter, we observed especially higher EF values for CDOM and FDOM in the
488 southern ECS (Fig. 2a-f)). With wind from the northwest (Weng et al., 2011), biologically essential
489 trace elements and anthropogenic emissions are carried from the land and can enter the ocean via the
490 SML by wet or dry deposition. The EFs of humic-like C1 and C3 were relatively high in winter (Fig.
491 6b)), probably due to the input from atmospheric deposition during winter, and the relatively low
492 CDOM concentrations in bulk water. Atmospheric deposition of organic carbon and nutrients were
493 found a peak in winter over the coastal ECS (Wang et al., 2019). We suggested that the EFs of CDOM
494 and FDOM increased from the coastal regions to the open ocean, and increased from the YS to the
495 ECS were likely due to the enrichment of enough nutrients in the SML in the open ocean promote
496 phytoplankton biomass and DOM production.



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Fig. 8. Relationships between salinity and EFs of a(254), Chl-a, DOC, and four fluorescence components.

502 The SML is an aggregate-enriched biofilm environment with distinct microbial communities,
503 where the diversity of microorganisms can differ significantly from those of underlying waters (Liss
504 and Duce, 2005; Cunliffe et al., 2013), the heterotrophic bacterial abundance in the SML was ~ 7.5
505 fold greater than those in the SSW in the ECS during our spring cruise (Sun et al., 2020). Here, EFs
506 showed a greater presence of bacteria and marine protein-like DOM in the SML than that in the SSW,
507 while the protein-like DOM was linked to microbial utilization and degraded faster than the humic-like
508 substances (Yang et al., 2017; Jørgensen et al., 2011). Therefore, compared to coastal waters that have
509 larger terrestrial DOM and nutrients inputs, CDOM shown higher EFs in off-shore regions where
510 DOM in the SSW is mostly of marine autochthonous origin with higher temperatures and stronger
511 biological activity. The significantly higher abundance of cells, phytoplankton, nutrients, and
512 protein-like DOM in the SML supported microbial activities, and further contributing to the local
513 release of marine extracellular DOM directly from microbes in the SML in the off-shore regions.
514 When exposed to higher light intensities (summer), obviously enhance mineralization of DOM in the
515 SML, and relatively less photochemical degradation in SSW could result in lower percentage of
516 aromatic DOM in SML than the SSW. We concluded that SML CDOM dynamics can be expressed as
517 a complex balance among enrichment process, primary production and photochemical destruction.
518 Thus, higher EF of DOM in the SML in off-shore regions are likely supported by a favorable
519 combination of: 1) deposition and accumulation of amphiphilic compounds, 2) importance of bubble
520 for upward transport of DOM and enrichment in SML, and 3) new production of DOM within the
521 SML as a consequence of higher nutrients enrichment and the primary production.

522

523 **4. Conclusions**

524 This study has provided the first data set that considers the distributions of CDOM, FDOM, DOC,
525 Chl-*a*, nutrients, and bacterial abundances in the SML and SSW of the ECS and the YS during spring,
526 summer, and winter. We have observed that the CDOM distribution related variability in primary
527 production in the SML. Furthermore, we have demonstrated that localized and stronger photochemical
528 oxidation may be responsible for the decrease in the aromaticity of the DOM in the SML, due to
529 enhanced transformation or removal of terrestrial DOM, compared with the SSW. We also
530 demonstrated that in off-shore seawaters away from terrigenous influence, the EFs of CDOM, DOC,
531 FDOM and Chl-*a* in SML tend to be higher in off-shore regions than those in coastal regions, because
532 of the relatively higher enrichment of nutrients which could enhance phytoplankton growth and
533 promoted plant production and DOM production in the SML. Multiple observations of spatial
534 distributions, seasonal variations, chemical compositions, and photochemical reactions of CDOM in
535 the SML have supported the hypothesis that stronger enrichment and photochemical processes occur in
536 the SML in ocean, resulting in relatively accelerated enrichment of more marine local production
537 DOM in the SML than the SSW.

538

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547

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Table 1 Spectral characteristics of the four fluorescent components identified by the PARAFAC

modal in this study, compared with those previously identified.

| Component | $E_{X_{max}}$ (nm) | $E_{M_{max}}$ (nm) | Coble (1996) | Comparison with other studies using PARAFAC | Description and probable source |
|-----------|-----------------------|-----------------------|---------------------------|---------------------------------------------------|-------------------------------------------------------------------------------|
| C1 | 345 | 455 | peak C 320-360/420-480 | Osburn et al. (2012) | Terrestrial-like humic substances |
| C2 | 255 | 310 (375) | peak A 230-260/380-460 | Stedmon et al. (2003) | Tyrosine-like or marine humic-like substances |
| C3 | 315 | 385 | peak M 290-310/370-420 | Stedmon and Markager (2005) | Marine humic-like substances (biological degradation) |
| C4 | 280 | 335 | peak T 270-280/340-350 | Coble (1996) | Tryptophan-like; Non-Humic-like; Biological production in the water column |

Table 2 Average temperature, salinity, wind speed, CDOM $a(254)$, DOC, Chlorophyll- a (Chl- a), dissolved oxygen (DO), $S_{275-295}$, S_R , and $SUVA_{254}$ of the SSW and SML in the YS and ECS during spring, summer, and winter.

| | Water layer | Spring | | Summer | | Winter | |
|--------------------------------------------------------|-------------|--------|--------|--------|--------|---------|--------|
| | | mean | SD | mean | SD | mean | SD |
| Temperature ($^{\circ}\text{C}$) | SSW | 14.0 | 4.91 | 24.0 | 3.66 | 14.0 | 5.23 |
| Salinity | SSW | 32.5 | 1.92 | 31.7 | 2.17 | 32.7 | 1.41 |
| Wind Speed (m s^{-1}) | SSW | 5.98 | 2.86 | 5.47 | 2.51 | 6.09 | 2.52 |
| DO (mg L^{-1}) | SSW | 6.44 | 0.85 | 7.57 | 1.07 | 8.32 | 0.99 |
| Chl- a ($\mu\text{g L}^{-1}$) | SSW | 1.26 | 2.38 | 1.13 | 1.48 | 0.42 | 0.25 |
| | SML | 1.63 | 3.66 | 1.28 | 1.13 | no data | |
| DOC ($\mu\text{mol L}^{-1}$) | SSW | 91.3 | 25.7 | 109.4 | 33.55 | 88.4 | 22.51 |
| | SML | 132.9 | 77.4 | 145.7 | 49.8 | 131.3 | 91.1 |
| $a(254)$ (m^{-1}) | SSW | 3.20 | 2.49 | 3.10 | 1.34 | 2.52 | 1.26 |
| | SML | 3.70 | 1.98 | 4.05 | 1.66 | 4.74 | 2.50 |
| $S_{275-295}$ (nm^{-1}) | SSW | 0.0201 | 0.0049 | 0.0188 | 0.0035 | 0.0207 | 0.0068 |
| | SML | 0.0222 | 0.0073 | 0.0178 | 0.0021 | 0.021 | 0.0055 |
| S_R | SSW | 1.723 | 1.026 | 1.731 | 1.557 | 1.521 | 0.52 |
| | SML | 1.095 | 0.218 | 1.361 | 0.296 | 1.416 | 0.214 |
| $SUVA_{254}$ ($\text{L mg-C}^{-1} \text{m}^{-1}$) | SSW | 2.067 | 0.664 | 2.244 | 0.671 | 3.008 | 0.949 |
| | SML | 1.911 | 0.768 | 1.951 | 0.359 | 2.992 | 1.034 |

Table 3 Correlation coefficients between EF of DOM optical properties, Chl-*a*, DOC, PO₄³⁻, NO₃⁻, NO₂⁻, SiO₃²⁻, Cyanobacteria, Picophytoplankton, Bacterial abundance.

| | EF of a(254) | EF of DOC | EF of Chl- <i>a</i> | Ef of C1 | EF of C2 | EF of C3 | EF of C4 | EF of PO ₄ ³⁻ | EF of NO ₃ ⁻ | EF of NO ₂ ⁻ | EF of SiO ₃ ²⁻ | EF of Cyanobacteria | EF of picophytoplankton |
|--------------------------------------|-----------------|--------------|------------------------|---------------|---------------|---------------|-------------|----------------------------------------|---------------------------------------|---------------------------------------|-----------------------------------------|------------------------|----------------------------|
| EF of DOC | 0.185 | | | | | | | | | | | | |
| EF of Chl- <i>a</i> | 0.092 | 0.021 | | | | | | | | | | | |
| EF of C1 | .336** | 0.047 | -0.119 | | | | | | | | | | |
| EF of C2 | 0.163 | 0.073 | -0.017 | .635** | | | | | | | | | |
| EF of C3 | .413** | 0.179 | -0.096 | .907** | .557** | | | | | | | | |
| EF of C4 | .319** | 0.021 | 0.011 | .574** | .368** | .628** | | | | | | | |
| EF of PO ₄ ³⁻ | 0.129 | 0.267 | .319* | 0.131 | -0.037 | 0.139 | 0.087 | | | | | | |
| EF of NO ₃ ⁻ | -0.065 | -0.054 | 0.235 | -0.037 | -0.044 | -0.027 | -0.053 | 0.26 | | | | | |
| EF of NO ₂ ⁻ | 0.15 | 0.208 | .307* | 0.142 | -0.017 | 0.192 | 0.035 | .571** | 0.271 | | | | |
| EF of SiO ₃ ²⁻ | .634* | 0.004 | 0.074 | 0.122 | -0.101 | 0.305 | 0.151 | 0.205 | -0.118 | -0.141 | | | |
| EF of Cyanobacteria | 0.091 | -0.017 | 0.028 | -0.027 | -0.105 | -0.047 | -0.052 | 0.218 | 0.027 | .755** | -0.286 | | |
| EF of Picophytoplankton | .347** | 0.0281 | 0.252 | -0.067 | -0.082 | -0.077 | 0.025 | 0.218 | -0.08 | 0.113 | -0.327 | 0.081 | |
| EF of Bacterial abundance | -0.036 | -0.069 | -0.063 | -0.061 | 0.004 | 0.014 | -0.093 | -0.12 | -0.026 | -0.073 | -0.099 | .730** | -0.064 |

** Correlation is significant at the 0.01 level (two-tailed)

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