



1 **Tracing the sources of dissolved organic carbon occurring in a coastal bay surrounded by**
2 **heavily industrialized cities using stable carbon isotopes**

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4 Shin-Ah Lee^a, Tae-Hoon Kim^b, and Guebuem Kim^{a,*}

5 ^aSchool of Earth and Environmental Sciences/Research Institute of Oceanography, Seoul
6 National University, Seoul 08826, Republic of Korea

7 ^bDepartment of Earth and Marine Sciences, Jeju National University, Jeju, 63243, Republic of
8 Korea

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18 *Corresponding author at: School of Earth and Environmental Sciences, Seoul National
19 University, Seoul 08826, Korea

20 E-mail address: gkim@snu.ac.kr (G.Kim)



21 **Abstract**

22 The sources of dissolved organic matter (DOM) in coastal waters are diverse, and they play
23 different roles in biogeochemistry and ecosystems. In this study, we measured dissolved
24 organic carbon (DOC) and nitrogen (DON), $\delta^{13}\text{C}$ -DOC, and fluorescent dissolved organic
25 matter (FDOM) in coastal bay waters surrounded by heavily industrialized cities (Masan Bay,
26 Korea) to determine the different DOM sources in this region. The surface seawater samples
27 were collected in two sampling campaigns (Aug. 2011 and Aug. 2016). The salinities ranged
28 from 10 to 21 in 2011 and from 25.4 to 32 in 2016. In 2011, the excess DOC was observed for
29 higher-salinity waters (16-21), indicating its main source from marine autochthonous
30 production according to the $\delta^{13}\text{C}$ -DOC values of -23.7‰ to -20.6‰ , higher concentrations of
31 protein-like FDOM, and lower DOC/DON (C/N) ratios. By contrast, the high DOC waters in
32 high-salinity waters of 2016 were characterized by low FDOM, more depleted $\delta^{13}\text{C}$ values of
33 -28.8‰ to -21.1‰ , and high C/N ratios, suggesting that the excess DOC is influenced by
34 direct land-seawater interactions. Our results show that multiple DOM tracers such as $\delta^{13}\text{C}$ -
35 DOC, FDOM, and C/N ratios are powerful for discriminating the complicated sources of DOM
36 in coastal waters.



37 **1. Introduction**

38 Dissolved organic matter (DOM) plays an important role in biogeochemical cycles
39 (e.g., de-oxygenation, acidification, photochemistry) and ecosystems in the ocean (Hansell and
40 Carlson, 2002). DOM composition depends on its parent organic matter and subsequent
41 biogeochemical processes. DOM in coastal waters originates from various sources including
42 (1) *in situ* production by primary production, exudation of aquatic plants, and their degradation
43 (Markager et al., 2011; Carlson and Hansell, 2015); (2) terrestrial sources by the degradation
44 of soil and terrestrial plant matter (Opsahl and Benner, 1997; Bauer and Bianchi, 2011); (3)
45 anthropogenic sources (Griffith and Raymond, 2011). Terrestrial sources are introduced into
46 the ocean via surface runoff, groundwater discharge, and atmospheric deposition.

47

48 Depending on the origin and composition of DOM, behavior and cycling of DOM are
49 different: a labile fraction of DOM is decomposed rapidly through microbially or
50 photochemically mediated processes, whereas refractory DOM is resistant to degradation and
51 can persist in the ocean for millennia. In the coastal ocean, organic matter from terrestrial plant
52 litter or soils appears to be more refractory (Cauwet, 2002) and thus behaves conservatively. In
53 addition, refractory DOM is produced in the ocean by bacterial transformation of labile DOM
54 by reshaping its composition (Tremblay and Benner, 2006; Jiao et al., 2010). However, it is
55 still very difficult to determine the sources and characteristics of DOM in coastal waters.

56

57 The stable carbon isotopes of dissolved organic carbon ($\delta^{13}\text{C}$ -DOC) have been used to
58 distinguish different sources. In general, $\delta^{13}\text{C}$ values derived from C3 and C4 land plants
59 typically range from -23‰ to -34‰ and from -9‰ to -17‰ (Deines, 1980), respectively,
60 while those derived from phytoplankton range from -18 to -22‰ (Kelley et al., 1998; Coffin



61 and Cifuentes, 1999). In addition, the optically active fraction of DOM known as fluorescent
62 DOM (FDOM) have been successfully used for characterizing FDOM (Coble et al., 1990;
63 Coble, 1996). Fluorescence excitation-emission matrices and parallel factor analysis (EEM-
64 PARAFAC) technique has been applied to trace the source of DOM in many estuaries (Chen
65 et al., 2004; Jaffé et al., 2004; Murphy et al., 2008; Huang and Chen, 2009). DOC/DON ratios
66 can also be used to determine the source between allochthonous and autochthonous (Thornton
67 and McManus, 1994; Andrews et al., 1998; McCallister et al., 2006). The C/N ratios of
68 terrestrial organic carbon usually are higher than 12, while those of marine organic carbon from
69 phytoplankton are almost constant ranging from 6 to 8 (Milliman et al., 1984; Lobbes et
70 al., 2000). Thus, multiple DOM tracers are more powerful for discriminating DOM sources in
71 coastal waters where various sources are mixed (Faganeli et al., 1988; Wang et al., 2004;
72 Osburn and Stedmon, 2011; Osburn et al., 2011; Cawley et al., 2012; Pradhan et al., 2014; Ya
73 et al., 2015; Lee and Kim, 2018).

74

75 Thus, in this study, we attempted to use $\delta^{13}\text{C}$ -DOC, FDOM, and DOC/DON ratios to
76 differentiate different sources and characteristics of DOM in coastal bay waters surrounded by
77 heavily industrialized cities.

78

79 **2. Materials and methods**

80 *2.1 Study site*

81 Masan Bay is located on the southeast coast of Korea with an area of approximately
82 80 km² (Fig. 1). The annual precipitation is approximately 1500 mm, most of which occurs in
83 the summer monsoon season. The amount of freshwater discharge into this bay is
84 approximately $2.5 \times 10^8 \text{ m}^3 \text{ yr}^{-1}$ with significant seasonal variation. The tide is strong semi-



85 diurnal, showing a maximum tidal amplitude of ~ 1.9 m (average = 1.3 m) during the sampling
86 period. Because of the topographic condition, the current is very weak ($2\text{--}3\text{ cm s}^{-1}$), and the
87 residence times of water in the inner bay and in the entire bay are approximately 54 and 23
88 days, respectively (Lee et al., 2009). This bay is surrounded by cities with thousands of
89 industrial plants and a population of 1.1 million. This area has been recognized as a highly
90 eutrophic embayment (Lee and Min, 1990; Yoo, 1991; Hong et al., 2010) in Korea owing to
91 the massive discharge of sewage and wastewater into the bay. In the middle of the bay, an
92 artificial island has been constructed since 2015 (Fig. 1) with an area of 0.64 km^2 . The artificial
93 island, which is made up of dredged sediments from the bay floor, may result in changes in
94 water currents, residence times, and biogeochemical conditions.

95

96 *2.2 Sampling*

97 Sampling was conducted in August 2011 and August 2016 in Masan Bay. Water
98 samples were collected from the surface at 17 sites in 2011 and 10 sites in 2016 from the inner
99 to the outer bay. The bay receives a large amount of freshwater discharge from the northernmost
100 part of the region. All water samples were filtered through pre-combusted GF/F filters. Samples
101 for FDOM analysis were stored at 4°C in pre-combusted amber vials. Samples for DOC, TDN
102 and $\delta^{13}\text{C}$ -DOC analysis were stored in pre-combusted glass ampoules after acidifying to $\text{pH} \sim 2$
103 with 6 M HCL. Samples for dissolved inorganic nutrients (DIN) were stored frozen in a HDPE
104 bottle (Nalgene) prior to analysis.

105

106 *2.3 Analytical methods*

107 The concentrations of DOC and TDN were determined by using a high-temperature
108 catalytic oxidation (HTCO) analyzer (TOC-V_{CPH}, Shimadzu, Japan). The standardization for



109 DOC was performed using the calibration curve of acetanilide (C:N ratio = 8) in ultra-pure
110 water. The acidified samples were sparged with pure air carrier gas for two min to remove
111 dissolved inorganic carbon. Samples were carried into a combustion tube heated to 720 °C
112 where the DOC was converted entirely to CO₂. CO₂ gas was detected by a non-dispersive
113 infrared detector (NDIR). Our DOC and TDN method were verified by using seawater
114 reference samples for DOC at 44–46 μ mol L⁻¹ and for TDN at 32–34 μ mol L⁻¹, which were
115 produced by the University of Miami, Florida, USA. Inorganic nutrients were measured with
116 nutrient auto-analyzers (Alliance Instruments, FUTURA+ for 2011 samples and QuAAtro39,
117 SEAL Analytical Ltd. for 2016 samples). Reference seawater materials (KANSO Technos,
118 Japan) were used for analytical accuracy and verification. DON concentrations were calculated
119 based on the difference between TDN and DIN concentrations.

120

121 $\delta^{13}\text{C}$ -DOC signatures were determined using a TOC-IR-MS instrument (Isoprime,
122 Elementar, Germany). The analytical method is the same as Kim et al. (2015) and Lee and Kim
123 (2016). Low carbon water (< 2 μM; University of Miami, Hansell's lab) was measured for the
124 blank corrections and used for preparing all standard samples. The blank correction procedure
125 used a method previously described (Panetta et al., 2008; De Troyer et al., 2010). Certified
126 IAEA-CH6 sucrose (International Atomic Energy Agency, $-10.45 \pm 0.03\text{‰}$) was used for
127 standardization. The standard solution was measured for every ten samples to monitor drifting
128 effects. Also, our measured values of $\delta^{13}\text{C}$ -DOC for the Deep-Sea Water Reference (University
129 of Miami) samples fall within $\pm 0.3\text{‰}$, relative to the values provided by Panetta et al. (2008)
130 and Lang et al. (2007).

131



132 FDOM was determined by using a spectrofluorometer (FluoroMate FS-2, SCINCO)
133 within two days from collection. Emission (Em) spectra were collected between 250 and 500
134 nm at 2 nm intervals at excitation (Ex) wavelengths between 250 and 400 nm at 5 nm intervals.
135 The daily Milli-Q water signals were subtracted from each sample value to remove Raman
136 scattering peaks. All data were converted to ppb quinine sulfate equivalent (QSE) by using a
137 quinine sulfate standard solution in 0.1N sulfuric acid at Ex/Em of 350/450 nm. EEMs-
138 PARAFAC was performed by a MATLAB R2013a program using a DOMFluor toolbox. We
139 did not correct EEM data for inner filter effects before measurement, since inner filter effects
140 were found to be negligible for estuarine water samples using this instrument (Lee and Kim,
141 2018).

142

143 **3. Results and Discussion**

144 *3.1 Horizontal distributions of DOM*

145 The salinity of surface seawater in Aug. 2011 ranged from 10 to 21, while the salinity in
146 Aug. 2016 ranged from 25 to 32 (Table 1 and Fig. 2). The concentrations of DOC in both
147 sampling periods ranged from 100 μM to 200 μM (Fig. 2), which fall within the DOC ranges
148 commonly observed in coastal waters (Gao et al., 2010; Osburn and Stedmon, 2011; Kim et al.,
149 2012). The highest concentration of DOC in 2011 was observed at station M4-1 in the middle
150 of the bay, whereas the highest concentration of DOC in 2016 was observed at station M1,
151 which is the innermost station in this bay. DOC concentrations were lowest at the outermost
152 stations in both sampling periods. Concentrations of DON were in the range of 7–24 μM in
153 2011 and 3–15 μM in 2016, showing the highest value (24 μM) at M5-1 in 2011 and at M1 in
154 2016 (Fig. 2).

155



156 EEMs dataset analyses identified three components for the surface water samples.
157 Based on the excitation-emission peak location, Component 1 (FDOM_H, Ex = 320–360 nm,
158 Em = 420–460 nm) is associated with a humic-like component (C peak) shown by Coble (2007).
159 Component 2 (FDOM_P, Ex = 275–300 nm, Em = 340–360 nm) is associated with a tryptophan-
160 like component (T peak), which is a product of microbial processes. Component 3 (FDOM_M,
161 Ex = 290–320 nm, Em = 370–420 nm) is associated with a marine humic-like component (M
162 peak). We use component 1 as a representative of humic-like FDOM (FDOM_H) in this study
163 since there was a good correlation ($r^2 = 0.95$) between component 1 and component 3.

164

165 FDOM_H is known to indicate humic substances from terrestrial, anthropogenic, or
166 agricultural sources (Coble, 2007), whereas FDOM_P is likely related to anthropogenic and
167 autochthonous sources (Coble, 1996; Hudson et al., 2007). The intensities of FDOM_H and
168 FDOM_P in 2011 were in the range of 3.6–9.2 ppb QSE and 4–79 ppb QSE, respectively (Fig.
169 3). The intensities of FDOM_H and FDOM_P in 2016 were in the range of 2.7–0.6 ppb QSE and
170 4.8–2.1 ppb QSE, respectively (Fig. 3). FDOM_P concentration in 2011 was exceptionally
171 higher at station M4-1 (78 ppb QSE) relative to that of other stations (2–25 ppb QSE) (Fig. 4d).

172

173 3.2 Origin of excess DOM

174 The plot of DOC against salinity in 2011 showed two different mixing trends. The first
175 slope showed a slight increase in DOC with decreasing salinity toward the innermost stations,
176 including M1, M1-1, and M2 (Fig.4a, Group 1). The source of DOC in these lower salinity
177 stations appears to have originated from land by natural and/or anthropogenic processes. The
178 second trend showed a sharp rise in DOC (excess DOC in 2011) to the maximum between
179 salinities of 18 and 22 (Fig.4a, Group 2), indicating that there are other DOC sources at the



180 higher-salinity stations, except for the two end-member mixing. The excess DOC
181 concentrations in higher-salinity waters could have been produced *in situ* by biological
182 production and/or from land sources such as sewage treatment plant (STP). The plot of DOC
183 against salinity showed that DOC in 2016 was in a range similar to that of 2011, although the
184 influence of fresh water was much less (Fig. 4a, Group 3). This plot shows that there was an
185 addition of DOC (excess DOC in 2016) for high-salinity water in the bay. The excess DOC
186 sources in this period could be from either biological production or land-seawater interactions.
187 In order to determine the main sources of these excess DOC using $\delta^{13}\text{C}$ -DOC, FDOM, and
188 DOC/DON ratios, the stations are separated into Group 1, Group 2, and Group 3

189

190 Group 1 includes low-salinity water stations (M1, M1-1, M2, M3, M5-1, M5-2, and
191 M5-3) observed in 2011 (Fig. 1). $\delta^{13}\text{C}$ -DOC values for Group 1 ranged from -25.4‰ to
192 -23.3‰ . We plotted a conservative mixing curve of $\delta^{13}\text{C}$ -DOC for the two end-member mixing
193 equation (Spiker, 1980; Raymond and Bauer, 2001). The end-member values of DOC and $\delta^{13}\text{C}$ -
194 DOC were $185\ \mu\text{M}$ and -28‰ , respectively, for terrestrial end-member ($S=0$) and $100\ \mu\text{M}$ and
195 -18‰ , respectively, for marine end-member ($S=34$). $\delta^{13}\text{C}$ -DOC values for Group 1 fitted
196 relatively well into this mixing curve, indicating that DOC for Group 1 was a conservative
197 mixture of terrestrial C3 land plant (-23‰ to -34‰) in freshwater and open ocean seawater.
198 FDOM_H in Group 1 was relatively higher than the other groups, with a significant linear
199 correlation against salinity ($r^2 = 0.89$). This result indicates that humic materials in this region
200 were mainly from terrestrial sources and behaved conservatively in the course of freshwater
201 and seawater mixing, which is consistent with previous studies for coastal waters (Coble et al.,
202 1998; Mayer et al., 1999).

203



204 Group 2 includes high-salinity water stations (M4-1, M4-2, M6, M6-1, M7-1, M7-2,
205 M8, M9, and M9-1) observed in 2011 (Fig. 1). $\delta^{13}\text{C}$ -DOC values of Group 2 were in the range
206 of -23.3‰ to -20.6‰ , showing much heavier values than the conservative mixing curve.
207 These values are close to the marine $\delta^{13}\text{C}$ -DOC values (-22 to -18‰) (Fry et al., 1998) except
208 for only one station (M6) in this group (-23.3‰). The $\delta^{13}\text{C}$ -DOC values of Group 2 suggest
209 that DOM was added *in situ* by biological production in seawater. In contrast to the good
210 correlation between FDOM_H and salinity for all samples, the concentration of FDOM_P showed
211 no correlation with salinity. In general, FDOM_P showed non-conservative behavior in many
212 estuaries owing to the extra source of DOC produced by *in situ* biological production (Benner
213 and Opsahl, 2001). In the study region, a remarkably high FDOM_P concentration was observed
214 at station M4-1, where DOC concentration was highest. Thus, this source could originate in
215 either anthropogenic source inputs and/or *in situ* production (Twardowski and Donaghay, 2001;
216 Zhang et al., 2009).

217

218 Masan Bay has many potential land sources of DOM from different creeks. In addition,
219 the treated sewage outflow from a STP is located near station M7-1 (Fig. 1). Many studies have
220 been conducted to identify organic pollutants from STP (Kannan et al., 2010; Lee et al., 2011).
221 In our study, however, station M7-1 did not show different DOM characteristics: (1) The
222 concentrations of DOC, FDOM_H , and FDOM_P against salinity did not show anomalously
223 higher or lower trends, relative to the other stations nearby. (2) The $\delta^{13}\text{C}$ -DOC values at M7-1
224 (-20.6‰) are close to the marine values, similar to those in other stations nearby. Although
225 $\delta^{13}\text{C}$ -DOC values in the sewage treatment plant effluents in this region are unknown, they are
226 known to be lighter in some US wastewater treatment plants (-26‰) (Griffith et al., 2009). (3)
227 A fulvic-like peak is not observed, and the increase of FDOM_P intensity at stations M7-1 and



228 M7-2 was insignificant relative to that at stations M6-1 and M8. FDOM_P is often used as a
229 tracer of anthropogenic material including treated effluents (Hudson et al., 2007), together with
230 the fulvic-like peak (Ex/Em 320–340 nm/410–430 nm) (Baker and Inverarity, 2004) which
231 shows significantly higher values in treated sewage. Thus, we conclude that the concentration
232 of DOC at station M7-1 was not influenced by STP. This STP appeared to reduce TOC
233 concentrations to a natural level, as shown in several other estuaries (Abril et al., 2002).
234 Combining the data of $\delta^{13}\text{C}$ -DOC and FDOM_P for Group 2, it is likely from marine biological
235 production, rather than from STP sources.

236

237 Group 3 includes high-salinity water stations (M1, M2, M3, M4, M5, M6, and M7)
238 observed in 2016 (Fig. 1). Although all data were collected in the same wet season (August),
239 the salinity ranges of both campaigns were different from 2011, with a narrow high salinity
240 range in 2016. The $\delta^{13}\text{C}$ -DOC values for Group 3 showed significantly different values relative
241 to those sampled in 2011 (Group 1 and Group 2). The $\delta^{13}\text{C}$ -DOC values for Group 3 were
242 depleted (-28.8‰ and -21.1‰) relative to the conservative mixing curve (Fig. 4b). However,
243 FDOM_H concentrations were much lower than those in 2011. FDOM_P concentrations were also
244 lower within a narrow range. These results suggest that DOC in Group 3 is influenced by
245 terrestrial DOC sources which include lower FDOM. Although the artificial island is made up
246 of marine dredged sediments, it seems to provide more terrestrial components of DOC and
247 lower FDOM, perhaps by including land materials that have less humus.

248

249 No clear relationships were observed between DON and DOC/DON ratios versus
250 salinities in 2011. In general, Group 1 showed higher DON (7–24) and lower C/N ratios (6–
251 21), indicating that the terrestrial DOC from streams included more labile DON, which is



252 bioavailable. By contrast, Group 3 showed lower DON (4–15) but higher C/N ratios (13–45)
253 indicating that they include more refractory DON. In general, DOC/DON ratios range from 6
254 to 8 in the ocean. Thus, these unusually high C/N ratios in DOM seem to be linked to the land
255 materials that have depleted $\delta^{13}\text{C}$ -DOC values. The lower DOC/DON ratios in Group 2 seem
256 to be consistent with DOM production *in situ* by biological production, as indicated by other
257 tracers.

258

259 **4. Conclusions**

260 We determine the sources of DOM in 2011 and 2016 using the $\delta^{13}\text{C}$ -DOC, FDOM, and
261 DOC/DON ratios. The main sources are separated into three groups based on DOC versus
262 salinity plots. The DOM in the first group in 2011, which includes the lowest salinity waters,
263 is found to be a mixture of terrestrial DOM and open-ocean DOM sources based on the $\delta^{13}\text{C}$
264 values of -25.4‰ to -23.3‰ and a good correlation between FDOM_H and salinity. The excess
265 DOC in the second group in higher salinity waters in 2011 is found to be produced *in situ* by
266 biological production based on heavier $\delta^{13}\text{C}$ -DOC values (-22.0‰ to -20.6‰), high FDOM_P ,
267 and low C/N ratio. The excess DOC in the third group in high salinity waters in 2016 seems to
268 be produced by direct interaction between land (the artificial island) and seawater based on
269 lighter $\delta^{13}\text{C}$ -DOC values (-28.8‰ and -21.1‰), low FDOM concentrations, and a high C/N
270 ratio. Our results show that the combination of multiple DOM tracers, including $\delta^{13}\text{C}$ -DOC,
271 FDOM, and DOC/DON ratios, is powerful for discriminating the complicated sources of DOM
272 in coastal waters, which is the critical component of water eutrophication and biogeochemistry.

273

274 **Competing interests**

275 The authors declare that they have no conflict of interest.



276

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283 **References**

284 Abril, G., Nogueira, M., Etcheber, H., Cabeçadas, G., Lemaire, E., and Brogueira, M.:
285 Behaviour of organic carbon in nine contrasting European estuaries, *Estuarine Coastal Shelf*
286 *Sci.*, 54, 241-262, 2002.

287 Andrews, J., Greenaway, A., and Dennis, P.: Combined carbon isotope and C/N ratios as
288 indicators of source and fate of organic matter in a poorly flushed, tropical estuary: Hunts Bay,
289 Kingston Harbour, Jamaica, *Estuarine Coastal Shelf Sci.*, 46, 743-756, 1998.

290 Baker, A., and Inverarity, R.: Protein-like fluorescence intensity as a possible tool for
291 determining river water quality, *Hydrological Processes*, 18, 2927-2945, 2004.

292 Bauer, J. E. and Bianchi, T. S.: Dissolved organic carbon cycling and transformation, in:
293 *Treatise on estuarine and coastal science*, edited by: Wolanski, E. and Mcluski, D. S., 5, 7-67,
294 Academic Press, Waltham, 2011.

295 Benner, R., and Opsahl, S.: Molecular indicators of the sources and transformations of
296 dissolved organic matter in the Mississippi river plume, *Org. Geochem.*, 32, 597-611, 2001.



- 297 Carlson, C. A., and Hansell, D. A.: DOM sources, sinks, reactivity, and budgets, in:
298 Biogeochemistry of marine dissolved organic matter, Elsevier, 65-126, 2015.
- 299 Cauwet, G.: DOM in the coastal zone, Biogeochemistry of marine dissolved organic matter,
300 Elsevier, 579-609, 2002.
- 301 Cawley, K. M., Ding, Y., Fourqurean, J., and Jaffé, R.: Characterising the sources and fate of
302 dissolved organic matter in Shark Bay, Australia: a preliminary study using optical properties
303 and stable carbon isotopes, Mar. Freshwater Res., 63, 1098-1107,
304 <https://doi.org/10.1071/MF12028>, 2012.
- 305 Chen, R. F., Bissett, P., Coble, P., Conmy, R., Gardner, G. B., Moran, M. A., Wang, X., Wells,
306 M. L., Whelan, P., and Zepp, R. G.: Chromophoric dissolved organic matter (CDOM) source
307 characterization in the Louisiana Bight, Mar. Chem., 89, 257-272, 2004.
- 308 Coble, P. G., Green, S. A., Blough, N. V., and Gagosian, R. B.: Characterization of dissolved
309 organic matter in the Black Sea by fluorescence spectroscopy, Nature, 348, 432, 1990b.
- 310 Coble, P. G.: Characterization of marine and terrestrial DOM in seawater using excitation-
311 emission matrix spectroscopy, Mar. Chem., 51, 325-346, 1996.
- 312 Coble, P. G., Del Castillo, C. E., and Avril, B.: Distribution and optical properties of CDOM in
313 the Arabian Sea during the 1995 Southwest Monsoon, Deep Sea Research Part II: Topical
314 Studies in Oceanography, 45, 2195-2223, 1998.
- 315 Coble, P. G.: Marine optical biogeochemistry: the chemistry of ocean color, Chemical reviews,
316 107, 402-418, 2007.



- 317 Coffin, R. B., and Cifuentes, L. A.: Stable isotope analysis of carbon cycling in the Perdido
318 Estuary, Florida, *Estuaries*, 22, 917-926, 1999.
- 319 De Troyer, I., Bouillon, S., Barker, S., Perry, C., Coorevits, K., and Merckx, R.: Stable isotope
320 analysis of dissolved organic carbon in soil solutions using a catalytic combustion total organic
321 carbon analyzer-isotope ratio mass spectrometer with a cryofocusing interface, *Rapid Commun.*
322 *Mass Spectrom.*, 24, 365-374, 2010.
- 323 Deines, P.: The isotopic composition of reduced organic carbon, *Handbook of environmental*
324 *isotope geochemistry*, 329-406, 1980.
- 325 Faganeli, J., Malej, A., Pezdic, J., and Malacic, V.: C: N: P ratios and stable c-isotopic ratios as
326 indicators of sources of organic-matter in the gulf of trieste (northern adriatic), *Oceanolog.*
327 *Acta*, 11, 377-382, 1988.
- 328 Fry, B., Hopkinson, C. S., Nolin, A., and Wainright, S. C.: $^{13}\text{C}/^{12}\text{C}$ composition of marine
329 dissolved organic carbon, *Chem. Geol.*, 152, 113-118, 1998.
- 330 Gao, L., Fan, D., Li, D., and Cai, J.: Fluorescence characteristics of chromophoric dissolved
331 organic matter in shallow water along the Zhejiang coasts, southeast China, *Marine*
332 *environmental research*, 69, 187-197, 2010.
- 333 Griffith, D. R., Barnes, R. T., and Raymond, P. A.: Inputs of fossil carbon from wastewater
334 treatment plants to US rivers and oceans, *Environ. Sci. Technol.*, 43, 5647-5651, 2009.
- 335 Griffith, D. R. and Raymond, P. A.: Multiple-source heterotrophy fueled by aged organic
336 carbon in an urbanized estuary, *Mar. Chem.*, 124, 14-22, 2011.



- 337 Hansell, D. A., and Carlson, C. A.: Biogeochemistry of Marine Dissolved Organic Matter,
338 Academic Press, 2002.
- 339 Hong, S. H., Kannan, N., Jin, Y., Won, J. H., Han, G. M., and Shim, W. J.: Temporal trend,
340 spatial distribution, and terrestrial sources of PBDEs and PCBs in Masan Bay, Korea, Mar.
341 Pollut. Bull., 60, 1836-1841, 2010.
- 342 Huang, W., and Chen, R. F.: Sources and transformations of chromophoric dissolved organic
343 matter in the Neponset River Watershed, Journal of Geophysical Research: Biogeosciences,
344 114, 2009.
- 345 Hudson, N., Baker, A., and Reynolds, D.: Fluorescence analysis of dissolved organic matter in
346 natural, waste and polluted waters—a review, River Research and Applications, 23, 631-649,
347 2007.
- 348 Jaffé, R., Boyer, J., Lu, X., Maie, N., Yang, C., Scully, N., and Mock, S.: Source
349 characterization of dissolved organic matter in a subtropical mangrove-dominated estuary by
350 fluorescence analysis, Mar. Chem., 84, 195-210, 2004.
- 351 Jiao, N., Herndl, G. J., Hansell, D. A., Benner, R., Kattner, G., Wilhelm, S. W., Kirchman, D.
352 L., Weinbauer, M. G., Luo, T., and Chen, F.: Microbial production of recalcitrant dissolved
353 organic matter: long-term carbon storage in the global ocean, Nat. Rev. Microbiol., 8, 593-599,
354 2010.
- 355 Kannan, N., Hong, S. H., Yim, U. H., Kim, N. S., Ha, S. Y., Li, D., and Shim, W. J.: Dispersion
356 of organic contaminants from wastewater treatment outfall in Masan Bay, Korea, Toxicology
357 and Environmental Health Sciences, 2, 200-206, 2010.



- 358 Kelley, C. A., Coffin, R. B., and Cifuentes, L. A.: Stable isotope evidence for alternative
359 bacterial carbon sources in the Gulf of Mexico, *Limnol. Oceanogr.*, 43, 1962-1969, 1998.
- 360 Kim, T.-H., Waska, H., Kwon, E., Suryaputra, I. G. N., and Kim, G.: Production, degradation,
361 and flux of dissolved organic matter in the subterranean estuary of a large tidal flat, *Mar. Chem.*,
362 142, 1-10, 2012.
- 363 Kim, T. H., Kim, G., Lee, S. A., and Dittmar, T.: Extraordinary slow degradation of Dissolved
364 Organic Carbon (DOC) in a cold marginal sea, *Sci. Rep.*, 5, 13808, doi:10.1038/srep13808,
365 2015.
- 366 Lang, S. Q., Lilley, M. D., and Hedges, J. I.: A method to measure the isotopic (^{13}C)
367 composition of dissolved organic carbon using a high temperature combustion instrument, *Mar.*
368 *Chem.*, 103, 318-326, 2007.
- 369 Lee, C.-W., and Min, B.-Y.: Pollution in Masan Bay, a matter of concern in South Korea, *Mar.*
370 *Pollut. Bull.*, 21, 226-229, 1990.
- 371 Lee, H. J., Hong, S. H., Kim, M., Ha, S. Y., An, S. M., and Shim, W. J.: Tracing origins of
372 sewage and organic matter using dissolved sterols in Masan and Haengam Bay, Korea, *Ocean*
373 *Sci. J.*, 46, 95-103, 2011.
- 374 Lee, S.-A., and Kim, G.: Sources, fluxes, and behaviors of fluorescent dissolved organic matter
375 (FDOM) in the Nakdong River Estuary, Korea, *Biogeosciences*, 15, 1115-1122, 2018.
- 376 Lee, Y.-W., Hwang, D.-W., Kim, G., Lee, W.-C., and Oh, H.-T.: Nutrient inputs from submarine
377 groundwater discharge (SGD) in Masan Bay, an embayment surrounded by heavily
378 industrialized cities, Korea, *Sci. Total Environ.*, 407, 3181-3188, 2009.



- 379 Lobbes, J. M., Fitznar, H. P., and Kattner, G.: Biogeochemical characteristics of dissolved and
380 particulate organic matter in Russian rivers entering the Arctic Ocean, *Geochim. Cosmochim.*
381 *Acta*, 64, 2973-2983, 2000.
- 382 Markager, S., Stedmon, C. A., and Søndergaard, M.: Seasonal dynamics and conservative
383 mixing of dissolved organic matter in the temperate eutrophic estuary Horsens Fjord, *Estuarine*
384 *Coastal Shelf Sci.*, 92, 376-388, 2011.
- 385 Mayer, L. M., Schick, L. L., and Loder, T. C.: Dissolved protein fluorescence in two Maine
386 estuaries, *Mar. Chem.*, 64, 171-179, 1999.
- 387 McCallister, S. L., Bauer, J. E., Ducklow, H. W., and Canuel, E. A.: Sources of estuarine
388 dissolved and particulate organic matter: a multi-tracer approach, *Org. Geochem.*, 37, 454-468,
389 2006.
- 390 Milliman, J. D., Qinchun, X., and Zuosheng, Y.: Transfer of particulate organic carbon and
391 nitrogen from the Yangtze River to the ocean, *Am. J. Sci.*, 284, 824-834, 1984.
- 392 Murphy, K. R., Stedmon, C. A., Waite, T. D., and Ruiz, G. M.: Distinguishing between
393 terrestrial and autochthonous organic matter sources in marine environments using
394 fluorescence spectroscopy, *Mar. Chem.*, 108, 40-58, 2008.
- 395 Osburn, C. L., and Stedmon, C. A.: Linking the chemical and optical properties of dissolved
396 organic matter in the Baltic-North Sea transition zone to differentiate three allochthonous
397 inputs, *Mar. Chem.*, 126, 281-294, 10.1016/j.marchem.2011.06.007, 2011.
- 398 Osburn, C. L., Wigdahl, C. R., Fritz, S. C., and Saros, J. E.: Dissolved organic matter
399 composition and photoreactivity in prairie lakes of the US Great Plains, *Limnol. Oceanogr.*, 56,
400 2371-2390, 2011.



- 401 Panetta, R. J., Ibrahim, M., and Gélinas, Y.: Coupling a High-Temperature Catalytic Oxidation
402 Total Organic Carbon Analyzer to an Isotope Ratio Mass Spectrometer To Measure Natural-
403 Abundance $\delta^{13}\text{C}$ -Dissolved Organic Carbon in Marine and Freshwater Samples, *Anal. Chem.*,
404 80, 5232-5239, 2008.
- 405 Pradhan, U., Wu, Y., Shirodkar, P., Zhang, J., and Zhang, G.: Sources and distribution of organic
406 matter in thirty five tropical estuaries along the west coast of India-a preliminary assessment,
407 *Estuarine Coastal Shelf Sci.*, 151, 21-33, 2014.
- 408 Raymond, P. A., and Bauer, J. E.: DOC cycling in a temperate estuary: a mass balance approach
409 using natural ^{14}C and ^{13}C isotopes, *Limnol. Oceanogr.*, 46, 655-667, 2001.
- 410 Spiker, E.: The Behavior of ^{14}C and ^{13}C in Estuarine Water-Effects of In situ CO_2 Production
411 and Atmospheric Exchange, *Radiocarbon*, 22, 647-654, 1980.
- 412 Thornton, S., and McManus, J.: Application of organic carbon and nitrogen stable isotope and
413 C/N ratios as source indicators of organic matter provenance in estuarine systems: evidence
414 from the Tay Estuary, Scotland, *Estuarine Coastal Shelf Sci.*, 38, 219-233, 1994.
- 415 Tremblay, L., and Benner, R.: Microbial contributions to N-immobilization and organic matter
416 preservation in decaying plant detritus, *Geochim. Cosmochim. Acta*, 70, 133-146, 2006.
- 417 Twardowski, M. S., and Donaghay, P. L.: Separating in situ and terrigenous sources of
418 absorption by dissolved materials in coastal waters, *Journal of Geophysical Research: Oceans*
419 (1978–2012), 106, 2545-2560, 2001.
- 420 Wang, X.-C., Chen, R. F., and Gardner, G. B.: Sources and transport of dissolved and
421 particulate organic carbon in the Mississippi River estuary and adjacent coastal waters of the
422 northern Gulf of Mexico, *Mar. Chem.*, 89, 241-256, 2004.



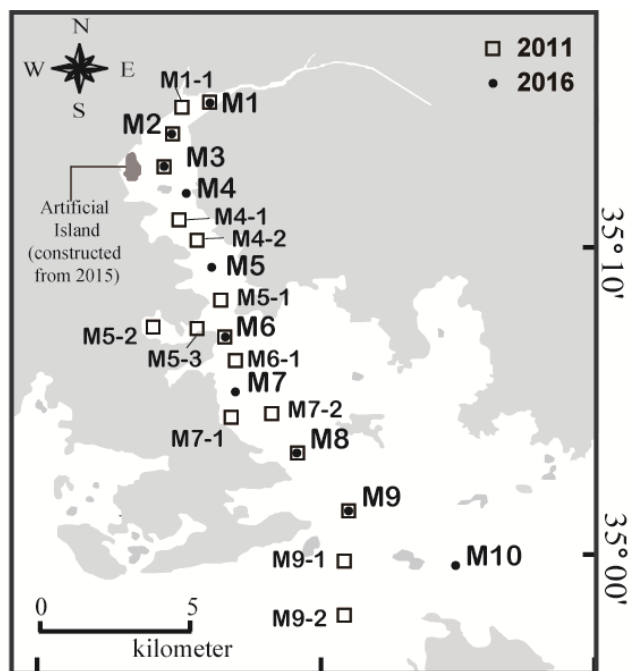
- 423 Ya, C., Anderson, W., and Jaffé, R.: Assessing dissolved organic matter dynamics and source
424 strengths in a subtropical estuary: Application of stable carbon isotopes and optical properties,
425 Cont. Shelf Res., 92, 98-107, 2015.
- 426 Yoo, K.: Population dynamics of dinoflagellate community in Masan Bay with a note on the
427 impact of environmental parameters, Mar. Pollut. Bull., 23, 185-188, 1991.
- 428 Zhang, Y., van Dijk, M. A., Liu, M., Zhu, G., and Qin, B.: The contribution of phytoplankton
429 degradation to chromophoric dissolved organic matter (CDOM) in eutrophic shallow lakes:
430 field and experimental evidence, water research, 43, 4685-4697, 2009.



431 **Table 1.** Salinity, DOC, FDOM_H, FDOM_P, and $\delta^{13}\text{C}$ -DOC in surface water of Masan Bay in
 432 August 2011 and August 2016.

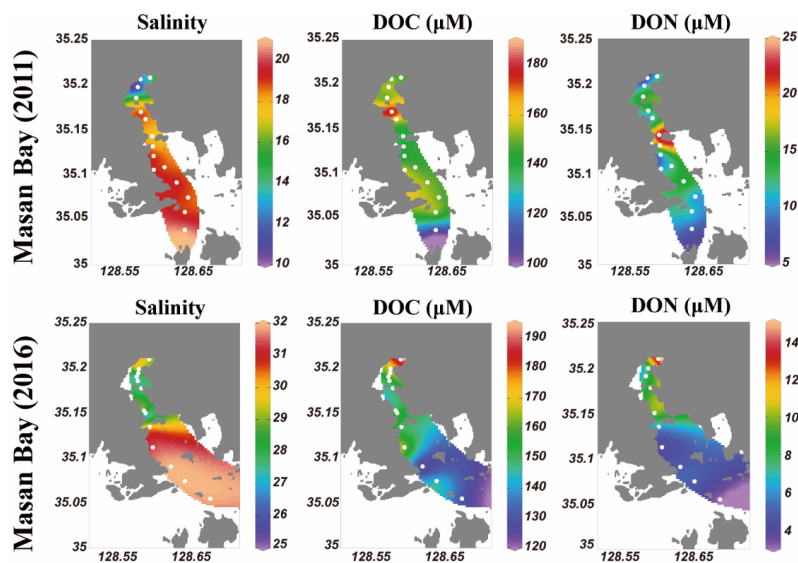
sampling campaign	station	salinity	DOC	FDOM _H	FDOM _T	$\delta^{13}\text{C}$ - DOC	DON	DOC/DON
			μM	ppbQSE	ppbQSE	‰	μM	
Aug. 2011	M1	14.0	148	6.7	13.6	-25.4	12	12
	M1-1	12.8	151	9.2	14.3	-24.3	7	21
	M2	10.2	157	9.0	5.4	-24.6	11	14
	M3	16.3	147	8.2	14.7	n/a	16	9
	M4-1	19.0	186	7.1	78.7	-21.9	13	15
	M4-2	18.6	155	6.9	8.3	-21.6	10	15
	M5-1	17.7	138	4.5	4.5	-23.3	24	6
	M5-2	18.4	133	5.8	20.9	-24.5	11	12
	M5-3	18.9	135	8.0	11.3	-23.7	13	11
	M6	18.4	146	6.6	24.8	-23.3	19	8
	M6-1	19.2	142	5.5	7.4	n/a	9	15
	M7-1	19.5	157	5.8	10.5	-20.6	11	15
	M7-2	18.9	148	5.6	9.6	-21.5	12	12
	M8	19.5	152	5.6	7.6	-21.5	15	10
	M9	18.8	149	5.6	14.5	-21.9	10	15
M9-1	19.1	154	5.1	10.2	-21.0	12	13	
M9-2	20.8	106	3.6	13.1	-22.0	8	13	
Aug. 2016	M1	29.2	191	2.7	4.8	-22.8	15	13
	M2	29.9	164	2.0	3.4	-21.1	7	22
	M3	26.0	155	2.5	3.8	-28.8	8	19
	M4	27.4	149	1.9	3.5	-22.6	9	17
	M5	25.5	165	1.8	3.3	-23.5	10	16
	M6	30.5	147	1.1	3.0	-23.7	6	26
	M7	31.4	166	1.3	4.4	-26.2	4	45
	M8	32.0	123	0.8	2.3	-23.7	5	26
	M9	32.0	146	0.6	2.1	-24.4	5	30
	M10	31.9	130	0.7	2.7	-25.0	3	39

433 n/a = not available.



434 128° 35' 128° 40' 128° 45'

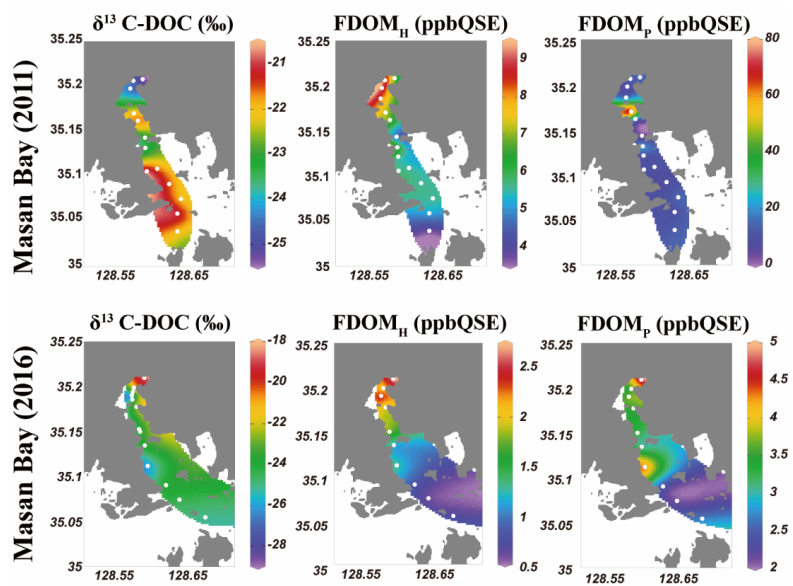
435 **Figure 1.** A map showing the sampling stations for DOC, $\delta^{13}\text{C}$ -DOC, FDOM, and DOC/DON
436 ratio in Masan Bay, Korea, in 2011 and 2016.



437

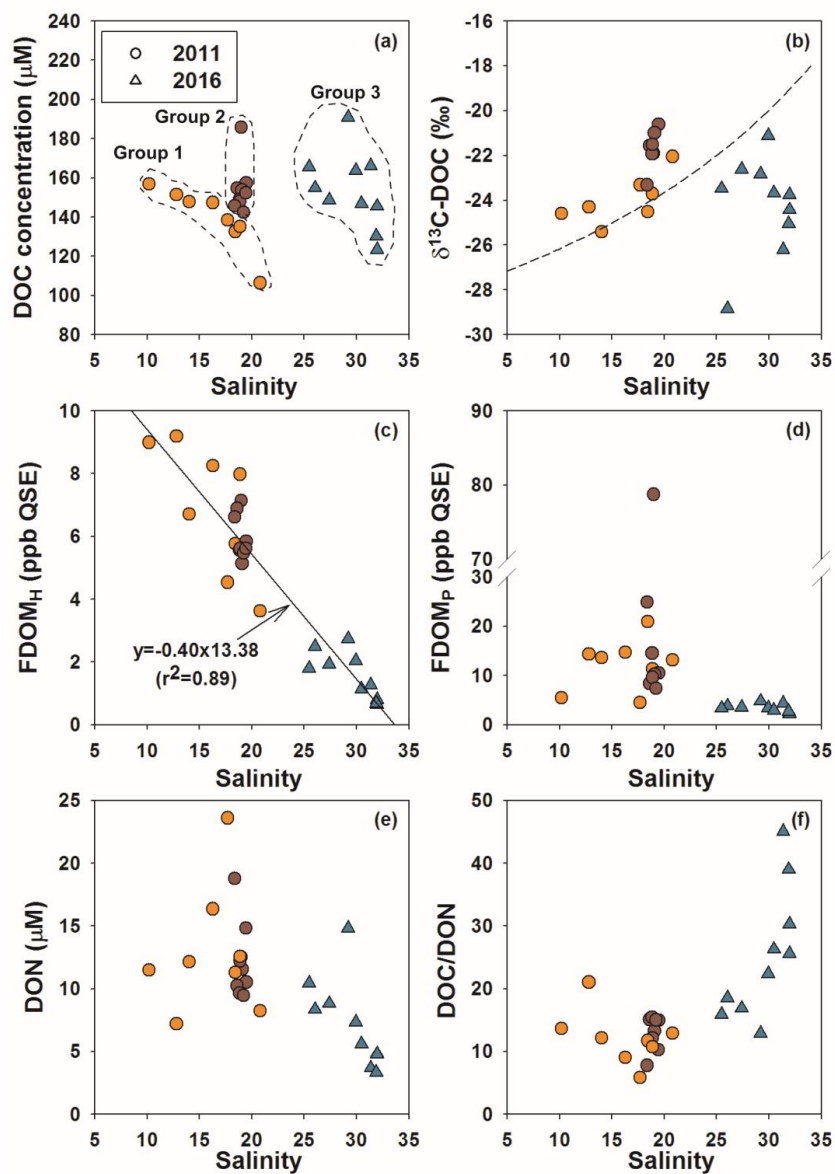
438 **Figure 2.** Surface distributions of salinity, DOC, and DON in Masan Bay, Korea, in 2011 and

439 2016.



440

441 **Figure 3.** Surface distributions of $\delta^{13}\text{C-DOC}$, FDOM_H , and FDOM_P in Masan Bay, Korea, in
442 2011 and 2016.



443

444 **Figure 4.** Relationships between salinity versus (a) DOC, (b) $\delta^{13}\text{C-DOC}$, (c) FDOM_H , (d)
445 FDOM_T , (e) DON and (f) DOC/DON values. The DOC groups are included in the dashed
446 circles. The dashed line (b) represents the binary conservative mixing line for $\delta^{13}\text{C-DOC}$
447 between the terrestrial end-member and the marine end-member.