1   **Tracing terrestrial versus marine sources of dissolved organic carbon in a coastal bay**

2   **using stable carbon isotopes**

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Abstract

The sources of dissolved organic matter (DOM) in coastal waters are diverse, and they play different roles in the biogeochemistry and ecosystems of the ocean. In this study, we measured dissolved organic carbon (DOC) and nitrogen (DON), δ^{13}C-DOC, and fluorescent dissolved organic matter (FDOM) in coastal bay waters surrounded by heavily industrialized cities (Masan Bay, Korea) to determine the different DOM sources in this region. The surface seawater samples were collected in two sampling campaigns (Aug. 2011 and Aug. 2016). The salinities were in the range of 10–21 in 2011 and 25–32 in 2016. In 2011, excess DOC was observed for higher-salinity (16–21) waters, indicating that the excess source inputs were mainly from marine autochthonous production according to the δ^{13}C-DOC values of −23.7‰ to −20.6‰, the higher concentrations of protein-like FDOM, and the lower DOC/DON (C/N) ratios (8–15). By contrast, the high DOC waters observed in high-salinity waters in 2016 were characterized by low FDOM, more depleted δ^{13}C values of −28.8‰ to −21.1‰, and high C/N ratios (13–45), suggesting that the excess DOC source is from terrestrial C3 plants by direct land-seawater interactions. Our results show that multiple DOM tracers such as δ^{13}C-DOC, FDOM, and C/N ratios are powerful for discriminating the complicated sources of DOM occurring in coastal waters.

1. Introduction

Dissolved organic matter (DOM) plays an important role in biogeochemical cycles (e.g., de-oxygenation, acidification, photochemistry) and ecosystems of the ocean (Hansell and Carlson, 2002). DOM composition depends on its parent organic matter and subsequent biogeochemical processes. DOM in coastal waters originates from various sources including (1) *in situ* production by primary production, exudation of aquatic plants, and their degradation (Markager et al., 2011; Carlson and Hansell, 2015); (2) terrestrial sources by the degradation of soil and terrestrial plant matter (Opsahl and Benner, 1997; Bauer and Bianchi, 2011); and (3) anthropogenic sources (Griffith and Raymond, 2011).

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

The stable carbon isotopic composition of dissolved organic carbon (δ^{13}C-DOC) has been used to distinguish different sources. In general, δ^{13}C values derived from C3 and C4 land plants are in the range of −23‰ – −34‰ and −9‰ – −17‰ (Deines, 1980), respectively, while those derived from marine phytoplankton range from −18 to −22‰ (Kelley et al., 1998; Coffin

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

Masan bay is surrounded by cities with thousands of industrial plants and a population of 1.1 million. In association with large anthropogenic nutrient loading, this area has been recognized as a highly eutrophic embayment (Lee and Min, 1990; Yoo, 1991; Hong et al., 2010). The development of red tides and hypoxic water mass in the bottom layer of the bay has occurred annually in spring and summer (Lee et al., 2009). In addition, there are point sources from sewage treatment plants (STPs), which manage domestic and industrial wastewater from Masan and Changwon cities. Therefore, in this study, we attempted to use δ^{13}C-DOC, FDOM, and DOC/DON ratios to differentiate various sources and characteristics of DOM in Masan bay waters, which may include many different types of terrestrial/anthropogenic and marine sources of DOM.

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2. Materials and methods

2.1 Study site

Masan Bay is located on the southeast coast of Korea with an area of approximately 80 km^2 (Fig. 1). The annual precipitation is approximately 1500 mm, and most of the precipitations occurs in the summer monsoon season. The amount of freshwater discharge into this bay is approximately 2.5×10^8 m^3 yr^{-1} with significant seasonal variation. The tide is semi-diurnal, showing a maximum tidal amplitude of ~1.9 m (average = 1.3 m) during the sampling period. Due to topographic conditions, the current is very weak (2–3 cm s^{-1}), and the residence times of water in the inner bay and in the entire bay are approximately 54 and 23 days, respectively (Lee et al., 2009). In the middle of the bay, an artificial island was constructed in 2015–2016 (Fig. 1) with an area of 0.64 km^2. There is no marsh or wetland habitat. The artificial island may have resulted in changes in water currents, residence times, and biogeochemical conditions.

2.2 Sampling

Sampling was conducted in August 2011 and August 2016 in Masan Bay. Water samples were collected from the surface at 17 sites in 2011 and 10 sites in 2016, from the inner to the outer bay. The bay receives a large amount of freshwater discharge from the northernmost part of the region. The averages of surface water temperature were 30.4 ± 2.3℃ in 2011 and 26.5 ± 0.7℃ in 2016. All water samples were filtered through pre-combusted GF/F filters. Samples for FDOM analysis were stored at 4℃ in pre-combusted amber vials. Samples for DOC, total dissolved nitrogen (TDN), and δ^{13}C-DOC analysis were stored in pre-combusted glass ampoules after acidifying to a pH ~2 with 6 M HCL. Samples analyzed for dissolved

110   inorganic nitrogen (DIN) were stored frozen in a HDPE bottle (Nalgene) prior to analysis.

111

112   *2.3 Analytical methods*

113   The concentrations of DOC and TDN were determined using a high-temperature

114   catalytic oxidation (HTCO) analyzer (TOC-V$_{CPH}$, Shimadzu, Japan). The standardization for

115   DOC analysis was performed using a calibration curve of acetanilide (C:N ratio = 8) in ultra-

116   pure water. The acidified samples were purged with pure air carrier gas for two min to remove

117   dissolved inorganic carbon. Samples were carried into a combustion tube heated to 720 ℃

118   where the DOC was converted quantitatively to CO_2. CO_2 gas was detected by a non-dispersive

119   infrared detector (NDIR). Our DOC and TDN methods were verified using seawater reference

120   samples for DOC of 44–46 μ mol L^{-1} and for TDN of 32–34 μ mol L^{-1}, which were produced

121   by the University of Miami (Hansell's lab) in the USA. Inorganic nutrients were measured

122   using nutrient auto-analyzers (Alliance Instruments, FUTURA+ for 2011 samples and

123   QuAAtro39, SEAL Analytical Ltd. for 2016 samples). Reference seawater materials (KANSO

124   Technos, Japan) were used for the verification of analytical accuracy. DON concentrations

125   were calculated based on the difference between the TDN and DIN concentrations.

126

127   The values of δ^{13}C-DOC were determined using a TOC-IR-MS instrument (Isoprime,

128   Elementar, Germany). The analytical method is the same as that used by Kim et al. (2015) and

129   Lee and Kim (2018). Low carbon water (< 2 μM; University of Miami, Hansell's lab) was

130   measured for blank corrections and used for preparing all standard samples. The blank

131   correction procedure is the same as that reported previously (Panetta et al., 2008; De Troyer et

132   al., 2010). Certified IAEA-CH6 sucrose (International Atomic Energy Agency, −10.45 ±

133   0.03‰) was used for standardization. The standard solution was measured for every ten

134 samples to monitor analyzer drift. Our measured values of δ^{13}C-DOC of the Deep-Sea Water

135 Reference (University of Miami) samples were ±0.3‰ relative to the values provided by

136 Panetta et al. (2008) and Lang et al. (2007).

137

138   FDOM was determined using a spectrofluorometer (FluoroMate FS-2, SCINCO)

139 within two days from the sampling time. EEMs were collected for the emission (Em)

140 wavelength range of 240–600 nm with 2 nm intervals and an excitation (Ex) wavelength range

141 of 240–500 nm with 5 nm intervals. Each sample value was subtracted for the signal of Milli-

142 Q water produced daily to remove Raman scattering peaks. All data were converted to ppb

143 quinine sulfate equivalent (QSE) using a quinine sulfate standard solution dissolved in 0.1N

144 sulfuric acid at Ex/Em of 350/450 nm. EEMs-PARAFAC was performed on MATLAB

145 (R2013a) using a DOMFluor toolbox. We did not correct EEM data for inner filter effects

146 before measurements, because the inner filter effects were found to be negligible for coastal

147 water samples using this instrument (Lee and Kim, 2018).

148

149 **3. Results and Discussion**

150 *3.1 Horizontal distributions of DOM*

151   The salinity of surface seawater in August 2011 ranged from 10 to 21, while the salinity in

152 August 2016 ranged from 25 to 32 (Table 1 and Fig. 2). The concentrations of DOC in both

153 sampling periods ranged from 100 μM to 200 μM (Fig. 2), which fall within the DOC ranges

154 commonly observed in coastal waters (Gao et al., 2010; Osburn and Stedmon, 2011; Kim et al.,

155 2012). The highest concentration of DOC in 2011 (186 μM) was observed at station M4-1 in

156 the middle of the bay, whereas the highest concentration of DOC in 2016 (191 μM) was

157 observed at station M1, which is the innermost station in the bay. DOC concentrations were

158 lowest at the outermost stations in both sampling periods. Concentrations of DON were in the

159 range of 7–24 μM in 2011 and 3–15 μM in 2016, with the highest value at M5-1 in 2011 and

160 at M1 in 2016 (Fig. 2).

161

162 EEM-PARAFAC dataset analyses identified three components in the surface water

163 samples. Based on the excitation-emission peak location (Coble, 2007) and the comparison

164 with data in the OpenFluor (Murphy et al., 2014), Component 1 ($FDOM_M$, Ex = 290–320 nm,

165 Em = 370–420 nm) is associated with a marine humic-like component. Component 2 ($FDOM_H$,

166 Ex = 320–360 nm, Em = 420–460 nm) is associated with a terrestrial humic-like component.

167 Component 3 ($FDOM_P$, Ex = 275–300 nm, Em = 340–360 nm) is associated with a protein-

168 like component, which is a product of microbial processes. We use Component 2 as a

169 representative of terrestrial humic-like FDOM ($FDOM_H$) in this study because there was a good

170 correlation (r^2 =0.95) between Component 1 and Component 2.

171

172 $FDOM_H$ is known to indicate humic substances from terrestrial, anthropogenic, or

173 agricultural sources (Coble, 2007), whereas $FDOM_P$ is likely related to autochthonous or

174 anthropogenic sources (Coble, 1996; Hudson et al., 2007). The intensities of $FDOM_H$ and

175 $FDOM_P$ in 2011 were in the range of 3.6–9.2 ppb QSE and 4–79 ppb QSE, respectively (Fig.

176 3). The intensities of $FDOM_H$ and $FDOM_P$ in 2016 were in the range of 2.7–0.6 ppb QSE and

177 4.8–2.1 ppb QSE, respectively (Fig. 3). An exceptionally higher concentration of $FDOM_P$ was

178 observed at station M4-1 (78 ppb QSE) relative to that of other stations (2–25 ppb QSE) in

179 2011 (Fig. 4d).

180

181 *3.2 Origin of excess DOM*

The plot of DOC against salinity in 2011 showed two different mixing trends. The first slope showed a slight increase in DOC with decreasing salinity toward the innermost stations, including M1, M1-1, and M2 (Fig.4a, Group 1). The source of DOC in these lower salinity stations appears to have originated from land by natural and/or anthropogenic processes. The second trend showed a sharp rise in DOC (excess DOC in 2011) to the maximum at stations with salinities between 18 and 22 (Fig.4a, Group 2), indicating that there are other DOC sources at the high-salinity stations, besides the two end-member mixing. The excess DOC concentrations in higher-salinity waters could have been produced *in situ* by biological production and/or from land sources such as STP. The plot of DOC against salinity showed that DOC in 2016 was in a range similar to that of 2011, although there was much less influence from fresh water (Fig. 4a, Group 3). This plot shows that there was an addition of DOC (excess DOC) in 2016 for high-salinity water in the bay. The source of the excess DOC in this period could be from either biological production or land-seawater interactions. To determine the main sources of the excess DOC using δ^{13}C-DOC, FDOM, and DOC/DON ratios, the excess DOC stations are separated into three groups (Fig. 4a).

Group 1 includes low-salinity water stations (M1, M1-1, M2, M3, M5-1, M5-2, and M5-3) observed in 2011 (Fig. 1). δ^{13}C-DOC values for Group 1 ranged from −25.4‰ to −23.3‰. We plotted a conservative mixing curve of δ^{13}C-DOC for two end-member mixing (Spiker, 1980; Raymond and Bauer, 2001). The assumed end-member values of DOC and δ^{13}C-DOC were 185 μM and −28‰, respectively, for the terrestrial end-member (S=0) and 100 μM and −18‰, respectively, for the marine end-member (S=34). The δ^{13}C-DOC values of Group 1 fit relatively well into this mixing curve (± 1.5‰), indicating that the conservative mixing between the terrestrial C3 land plant (−23‰ to −32‰) in freshwater and the open ocean

206 seawater results in DOC for Group 1. As such, the plot of δ^{13}C-DOC values versus C/N ratios

207 also indicates that the excess DOC of Group 1 is from freshwater DOC (Fig. 5).

208

209 Group 2 includes high-salinity water stations (M4-1, M4-2, M6, M6-1, M7-1, M7-2,

210 M8, M9, and M9-1) observed in 2011 (Fig. 1). The δ^{13}C-DOC values of Group 2 were in the

211 range of −23.3‰ to −20.6‰ and were more enriched than the conservative mixing curve.

212 These values are close to the marine δ^{13}C-DOC values (−22 to −18‰) (Fry et al., 1998), except

213 for one station (M6), in this group (−23.3‰). The δ^{13}C-DOC values of Group 2 suggest that

214 DOM was added *in situ* by biological production in seawater. As such, the plot of δ^{13}C-DOC

215 values versus C/N ratios also indicates that the excess DOC of Group 2 is produced by marine

216 phytoplankton (Fig. 5).

217

218 Group 3 includes high-salinity water stations (M1, M2, M3, M4, M5, M6, and M7)

219 observed in 2016 (Fig. 1). Although all data were collected in the same wet season (August),

220 the salinity ranges of both campaigns were different from those in 2011, with a narrow high

221 salinity range in 2016. The δ^{13}C-DOC values for Group 3 also showed significantly different

222 values relative to those sampled in 2011 (Group 1 and Group 2). The δ^{13}C-DOC values for

223 Group 3 were depleted (−28.8‰ and −21.1‰) relative to the conservative mixing curve (Fig.

224 4b). The plot of δ^{13}C-DOC values versus C/N ratios indicates that the excess DOC of Group 3

225 is from C3 terrestrial plants through direct land-seawater interactions based on the fact that the

226 excess DOC occurred in high-salinity (26–32) waters (Fig. 5).

227

228 FDOM$_H$ showed a significant negative correlation with salinity ($r^2 = 0.89$). The

229 concentrations were highest for Group 1 and lowest for Group 3. This result indicates that

230   humic DOM in this region was mainly from a terrestrial source and behaved conservatively in

231   the freshwater and seawater mixing zone. This trend is commonly observed in coastal waters

232   worldwide (Coble et al., 1998; Mayer et al., 1999). However, the concentration of $FDOM_P$

233   showed no correlation with salinity. In general, $FDOM_P$ shows non-conservative behavior in

234   many estuaries owing to the extra source of DOC produced by *in situ* biological production

235   (Benner and Opsahl, 2001). In the study region, a remarkably high $FDOM_P$ concentration was

236   observed at station M4-1 in 2011, where DOC concentration was highest. This trend also

237   supports the argument based on the δ^{13}C-DOC results, where the main source of DOC at this

238   station is from *in situ* biological production (Twardowski and Donaghay, 2001; Zhang et al.,

239   2009).

240

241   Masan Bay has many potential land sources of DOM from different creeks. In addition,

242   the treated sewage outflow from a STP is located near station M7-1 (Fig. 1). Many studies have

243   been conducted to identify organic pollutants from STP (Kannan et al., 2010; Lee et al., 2011).

244   In our study, however, station M7-1 did not show different DOM characteristics: (1) the

245   concentrations of DOC, $FDOM_H$, and $FDOM_P$ against salinity did not show anomalously

246   higher or lower trends, relative to the other stations nearby. (2) The δ^{13}C-DOC values at M7-1

247   (−20.6‰) were close to the marine values, similar to those in other stations nearby, although

248   they are known to be lighter in some US wastewater treatment plants (−26‰) (Griffith et al.,

249   2009). (3) A fulvic-like peak was not observed, although a significantly higher fulvic-like peak

250   (Ex/Em 320–340 nm/410–430 nm) was observed in treated sewage (Baker and Inverarity,

251   2004). (4) The increase of $FDOM_P$ intensities at stations M7-1 and M7-2 was insignificant

252   relative to those at stations M6-1 and M8, although $FDOM_P$ is often used as a tracer of

253   anthropogenic material including treated effluents (Hudson et al., 2007). Thus, we conclude

254 that the concentration of DOC at station M7-1 was not influenced by STP. This STP appears to

255 reduce TOC concentrations to a level that cannot influence the DOC concentrations resulting

256 from the mixing of other sources, as shown in several other estuaries (Abril et al., 2002).

257 Combining tracers of δ^{13}C-DOC, C/N ratios, and FDOM$_P$, the excess DOC for Group 2

258 occurring in high salinity waters is likely from marine biological production, rather than from

259 STP sources.

260

261 **4. Conclusions**

262  We determined the sources of DOM in 2011 and 2016 using the δ^{13}C-DOC, FDOM,

263 and DOC/DON ratios. The main sources were separated into three groups based on DOC

264 concentrations versus salinity plots. The DOM concentrations in the first group in 2011, which

265 included the lowest salinity waters, were found to be mixtures of terrestrial DOM and open-

266 ocean DOM sources based on the δ^{13}C values of −25.4‰ to −23.3‰ and a good correlation

267 between FDOM$_H$ and salinity. The excess DOC concentrations in the second group in higher

268 salinity waters in 2011 were found to be produced *in situ* by biological production based on

269 more enriched δ^{13}C-DOC values (−22.0‰ to −20.6‰), high FDOM$_P$ concentrations, and low

270 C/N ratios. The excess DOC concentrations in the third group in high salinity waters in 2016

271 seemed to be produced by direct interaction between land and seawater based on more depleted

272 δ^{13}C-DOC values (−28.8‰ and −21.1‰), low FDOM concentrations, and high C/N ratios. Our

273 results show that the combination of multiple DOM tracers, including δ^{13}C-DOC, FDOM, and

274 DOC/DON ratios, is powerful for discriminating the complicated sources of DOM occurring

275 in coastal waters.

276

277 **Data availability**

278 All data used in this paper can be accessed by email to the corresponding author upon request.

279

Author contribution

281 GK conceptualized the study. SL and TK collected the samples. SL performed the analyses. SL and GK wrote the manuscript and all authors contributed to the interpretation and discussion of the results.

284

Competing interests

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

287

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292

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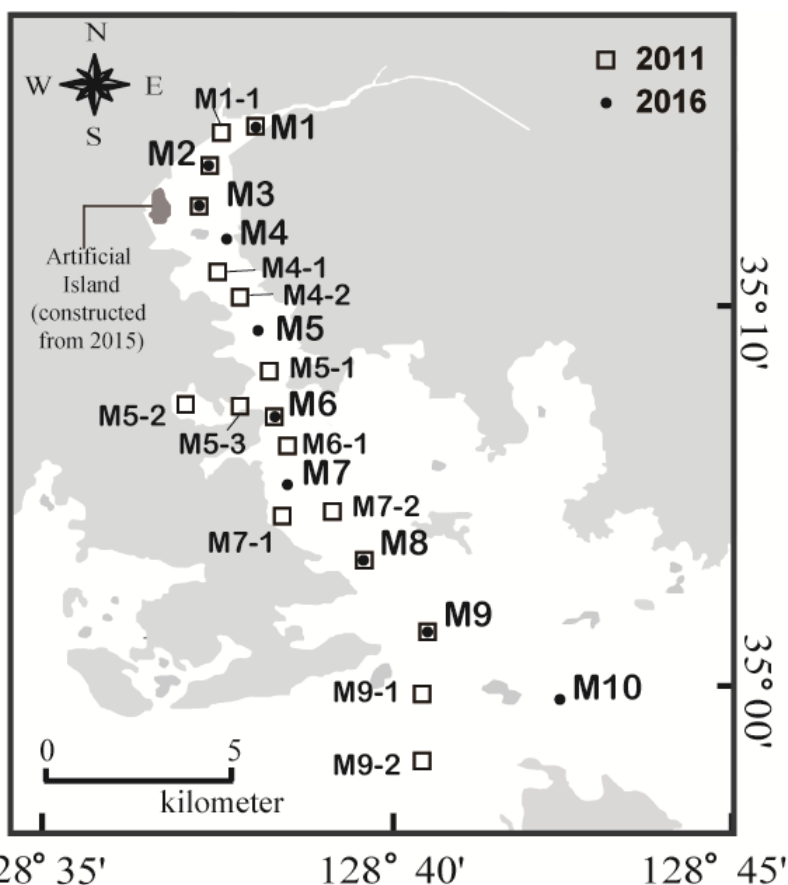
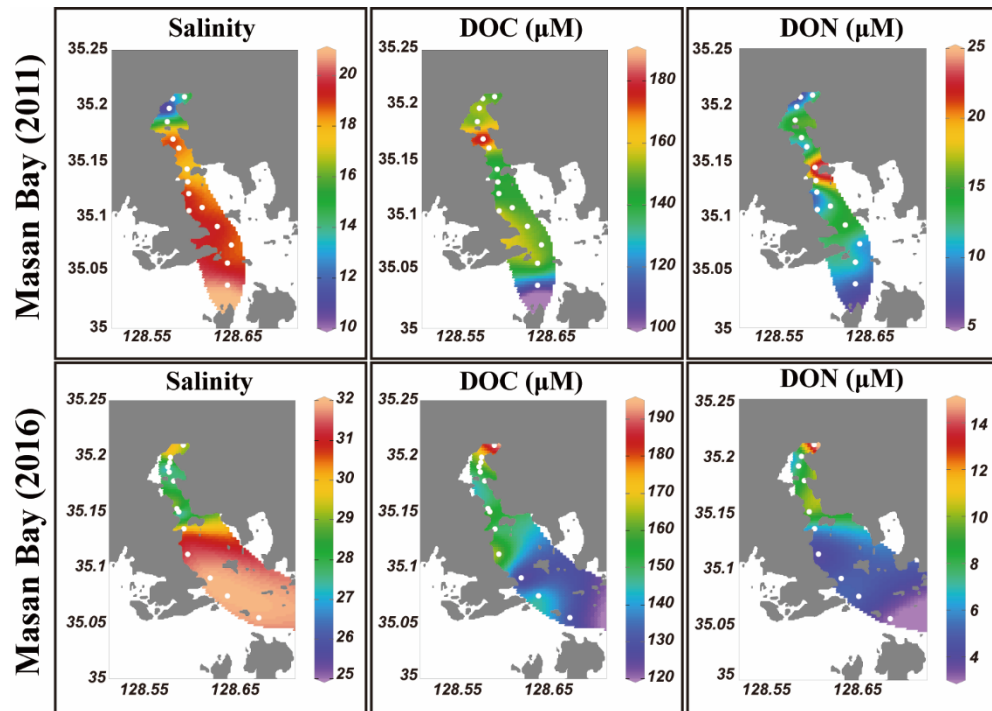
455 **Table 1.** Salinity, DOC, $FDOM_H$, $FDOM_P$, and δ^{13}C-DOC in surface water of Masan Bay in
456 August 2011 and August 2016.

sampling campaign	station	salinity	DOC	$FDOM_H$	$FDOM_T$	δ^{13}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

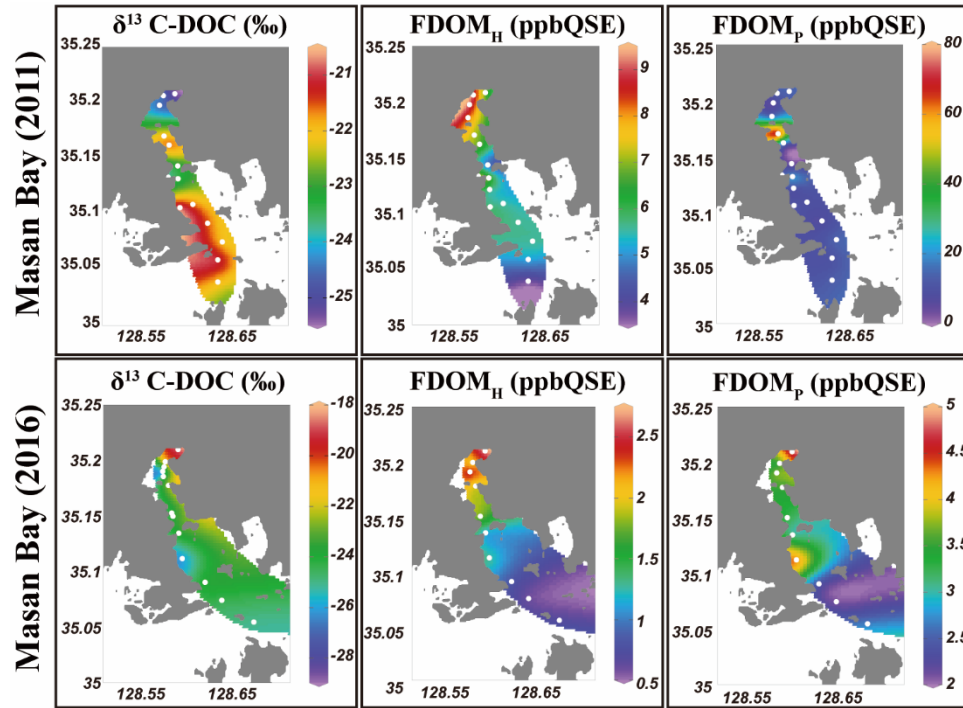
457 n/a = not available.

458

459 **Figure 1.** A map showing the sampling stations for DOC, δ^{13}C-DOC, FDOM, and DOC/DON

460 ratio in Masan Bay, Korea, in 2011 and 2016.

461

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

463 2016.

464

465 **Figure 3.** Surface distributions of δ^{13}C-DOC, FDOM$_H$, and FDOM$_P$ in Masan Bay, Korea, in

466 2011 and 2016.

467

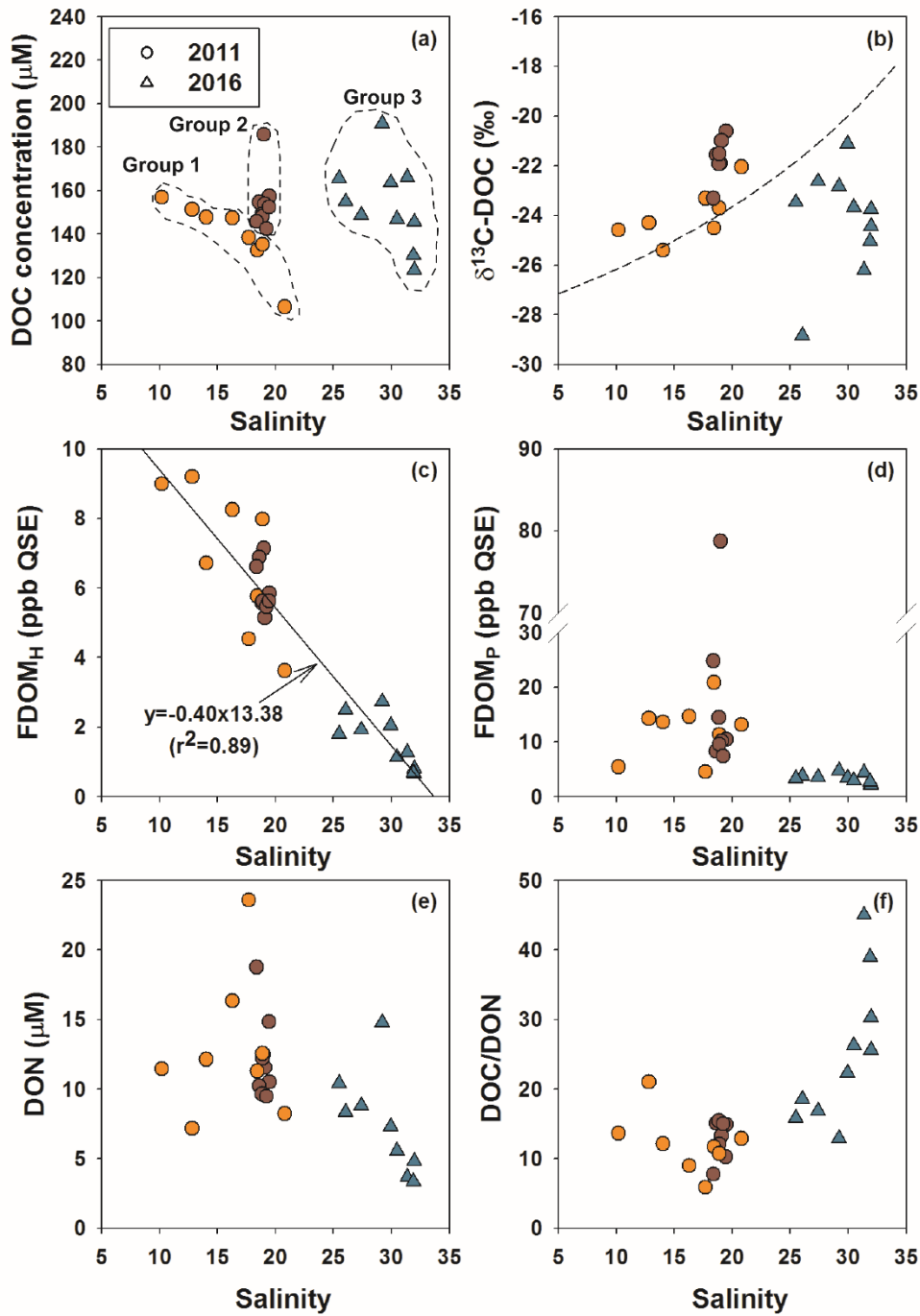



Figure 4. Relationships between salinity versus (a) DOC, (b) δ^{13}C-DOC, (c) FDOM$_H$, (d) FDOM$_T$, (e) DON, and (f) DOC/DON values. The DOC groups are included in the dashed circles. The dashed line (b) represents the binary conservative mixing line for δ^{13}C-DOC between the terrestrial end-member and the marine end-member.

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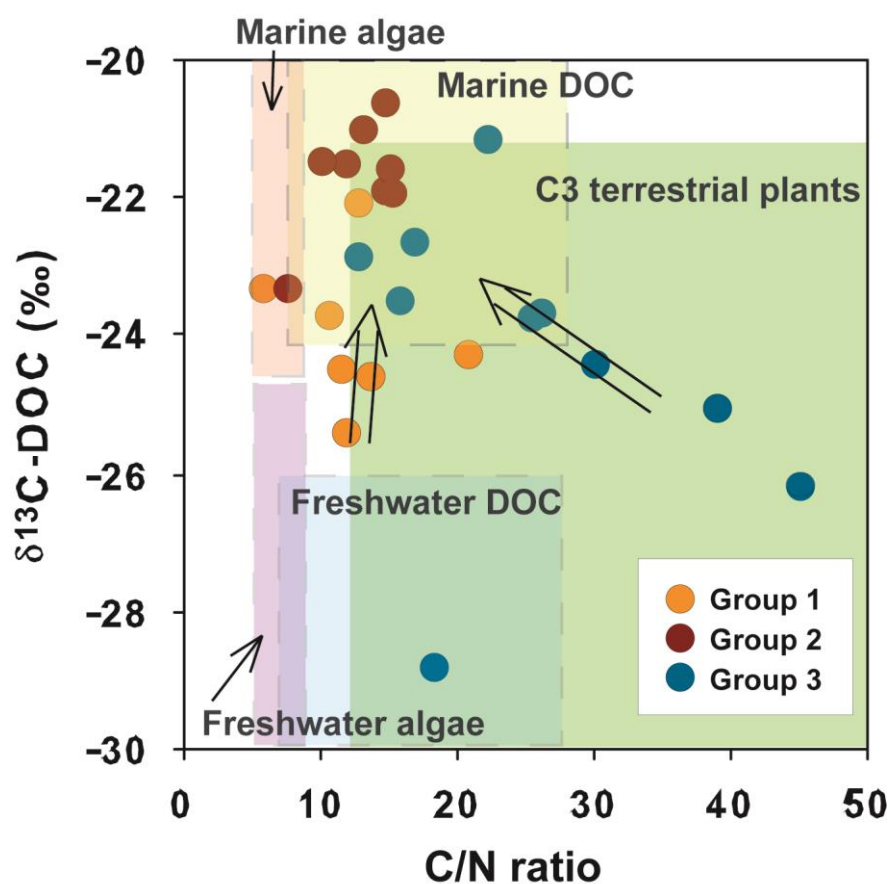
Figure 5. The relationship between DOC/DON ratios and δ^{13}C-DOC values in Masan Bay. The

ranges of DOC/DON ratios and δ^{13}C-DOC values are based on the values reported by Lamb et

al. (2006) and Beaupré (2015).

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