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# Tracing terrestrial versus marine sources of dissolved organic carbon in a coastal bay 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), the stable carbon isotopic composition of dissolved organic carbon ($\delta^{13}$C-DOC), and fluorescent dissolved organic matter (FDOM) in coastal bay waters surrounded by large cities (Masan Bay, Republic of Korea) to determine the different DOM sources in this region. The surface seawater samples were collected in two sampling campaigns (August 2011 and August 2016). The salinities were in the range of 10–21 in 2011 and 25–32 in 2016. In 2011, excess DOC was observed in high-salinity (16–21) waters; the excess DOC source was found to be mainly from marine autochthonous production according to the $\delta^{13}$C-DOC values ($-23.7$ ‰ to $-20.6$ ‰), the higher concentrations of protein-like FDOM, and the lower DOC/DON (C/N) ratios (8–15). In contrast, excess DOC observed in high-salinity waters in 2016 was characterized by low FDOM, more depleted $\delta^{13}$C values ($-28.8$ ‰ to $-21.1$ ‰), and high C/N ratios (13–45), suggesting that the source of excess DOC is terrestrial $C_3$ plants by direct land–seawater interactions. Our results show that multiple DOM tracers such as $\delta^{13}$C-DOC, FDOM, and C/N ratios are powerful for determining different 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, and 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 aquatic plant 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 such as industrial, agricultural, and domestic sewage (Griffith and Raymond, 2011).

Depending on the origin and composition of DOM, its behavior and cycling are different; the labile fraction of DOM decomposes 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 the bacterial transformation of labile DOM, which reshapes 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.

There are many approaches to distinguish the source of DOM in coastal areas using various tracers (Faganeli et al., 1988; Benner and Opsahl, 2001; Chen et al., 2004; Baker

and Spencer, 2004; Cawley et al., 2012; and Lee and Kim, 2018). The stable carbon isotopic composition of dissolved organic carbon ($\delta^{13}$C-DOC) has been used to distinguish different sources. In general, $\delta^{13}$C values derived from $C_3$ and $C_4$ land plants are in the range of $-23$‰ to $-34$‰ and $-9$‰ to $-17$‰ (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) has been successfully used for characterizing DOM (Coble et al., 1990; Coble, 1996). The fluorescence excitation–emission matrices and parallel factor analysis (EEMs–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; and Murphy et al., 2008). Dissolved organic carbon (DOC) and nitrogen (DON) ratios, DOC/DON, are often used to differentiate allochthonous versus autochthonous sources. 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). However, the interpretation of the isotopic ratio from a bulk sample in complex coastal environments is somewhat complicated by the overlap of isotopic ranges. Thus, several studies have used $\delta^{13}$C-DOC combined with FDOM (Osburn and Stedmon, 2011; Osburn et al., 2011; Ya et al., 2015; and Lu et al., 2015) or carbon isotope ratios combined with the C/N ratio (Thornton and McManus, 1994; Andrews et al., 1998; Wang et al., 2004; McCallister et al., 2006; and Pradhan et al., 2014) to discriminate different sources of DOM in estuarine and coastal waters. As far as we know, these three tracers have not yet been used together to determine DOM sources in coastal waters.

Our study aimed to discriminate between DOM sources in coastal waters, where various sources are present, using $\delta^{13}$C-DOC, FDOM, and DOC/DON ratios together. Masan Bay is surrounded by cities with thousands of industrial plants and a population of 1.1 million people. In association with large anthropogenic nutrient loading, this area has been recognized as a highly eutrophic embayment (Lee and Min, 1990; Yoo, 1991; and Hong et al., 2010). Red tides and a hypoxic water mass in the bottom layer of the bay have occurred annually in spring and summer (Lee et al., 2009). In addition, there are potential point sources from sewage treatment plants (STPs) which manage domestic and industrial wastewater from the cities of Masan and Changwon. Lee et al. (2011) revealed the origins of sewage and organic matter using dissolved sterols in Masan Bay. They reported that the water samples from creeks, the inner bay, and a nearby STP were affected by sewage sources. Oh et al. (2017) showed that the excess DOC in bay water is produced by phytoplankton production. Therefore, Masan Bay is a suitable place to test the applicability of these multiple tracers in order to determine different DOM sources in other coastal regions around the world.

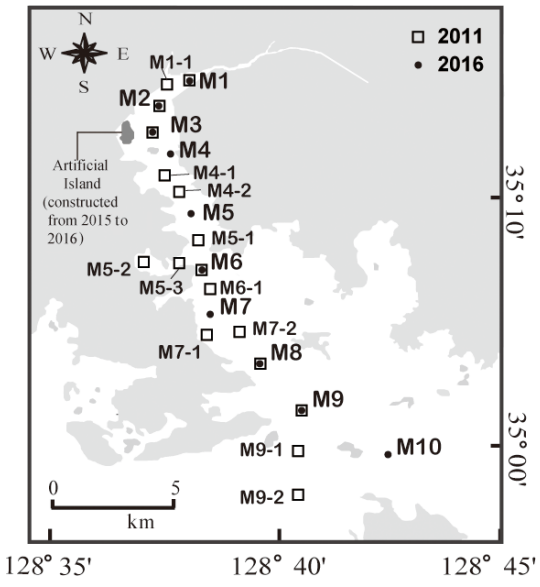


**Figure 1.** A map showing the sampling stations for DOC, $\delta^{13}$C-DOC, FDOM, and the DOC/DON ratio in Masan Bay, Republic of Korea, in 2011 and 2016.

## 2 Materials and methods

### 2.1 Study site

Masan Bay is located on the southeast coast of the Republic of Korea with an area of approximately 80 km$^2$ (Fig. 1). The annual precipitation is approximately 1500 mm, and most of the precipitation occurs in the summer monsoon season. The amount of freshwater discharge into this bay is approximately $2.5 \times 10^8$ m$^3$ yr$^{-1}$, with significant seasonal variation. The tide is semidiurnal, showing a maximum tidal amplitude of $\sim$ 1.9 m (average amplitude = 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 d, 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$^2$. 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. The bay receives a large amount of freshwater discharge from the northernmost part of the region. The average surface water tempera-

tures were $30.4 \pm 2.3$ °C in 2011 and $26.5 \pm 0.7$ °C in 2016. All water samples were filtered through pre-combusted glass fiber filters (GF/F, Whatman). Samples for FDOM analysis were stored at 4 °C in pre-combusted amber vials. Samples of DOC, total dissolved nitrogen (TDN), and $\delta^{13}$C-DOC analysis were stored in pre-combusted glass ampoules after acidifying to a pH of $\sim 2$ with 6 M HCl. Samples analyzed for dissolved inorganic nitrogen (DIN) were stored frozen in a HDPE bottle (Nalgene) prior to analyses.

### 2.3 Analytical methods

The concentrations of DOC and TDN were determined using a high-temperature catalytic oxidation (HTCO) analyzer (TOC-$V_{CPH}$, Shimadzu, Japan). The standardization for DOC analysis was performed using a calibration curve of acetanilide (C/N ratio = 8) in ultra-pure water. The acidified samples were purged with pure air carrier gas for 2 min to remove dissolved inorganic carbon. Samples were carried into a combustion tube heated to 720 °C where the DOC was converted quantitatively to $CO_2$. $CO_2$ gas was detected by a nondispersive infrared detector (NDIR). Our DOC and TDN methods were verified using deep seawater reference samples, 44–46 µmol $L^{-1}$ for DOC and 32–34 µmol $L^{-1}$ for TDN, which were produced by the University of Miami (Hansell Organic Biogeochemistry Lab, USA). Inorganic nutrients were measured using nutrient auto-analyzers (FUTURA+, Alliance Instruments, for 2011 samples; QuAAtro39, SEAL Analytical Ltd., for 2016 samples). Reference seawater materials (KANSO Technos, Japan) were used for the verification of analytical accuracy. DON concentrations were calculated based on the difference between the TDN and DIN concentrations.

The values of $\delta^{13}$C-DOC were determined using a TOC–IRMS instrument (IR-MS from Isoprime, UK coupled with a Vario TOC cube from Elementar, Germany). The analytical method is the same as that used by Kim et al. (2015) and Lee and Kim (2018). Low carbon water ($< 2$ µM; University of Miami, Hansell Organic Biogeochemistry Lab) was measured for blank corrections and used for preparing all standard samples. The blank correction procedure is the same as that reported previously (Panetta et al., 2008; De Troyer et al., 2010). Certified IAEA-CH-6 sucrose (International Atomic Energy Agency; $-10.45 \pm 0.03$ ‰) was used for standardization. The standard solution was measured every 10 samples to monitor the drifting effect. Our measured values of $\delta^{13}$C-DOC in the deep seawater reference (University of Miami) samples were ±0.3 ‰ relative to the values provided by Panetta et al. (2008) and Lang et al. (2007).

FDOM was determined using a spectrofluorometer (FluoroMate FS-2, SCINCO) within 2 d of the sampling time. EEMs were collected for the emission (Em) wavelength range of 240–600 nm with 2 nm intervals and an excitation (Ex) wavelength range of 240–500 nm with 5 nm intervals. Each sample value was subtracted from the signal of Milli-Q water produced daily to remove Raman scattering peaks. All data were converted to quinine sulfate units (QSU) using a quinine sulfate standard solution dissolved in 0.1 N sulfuric acid at Ex/Em of 350/450 nm. We did not correct EEM data for inner filter effects before measurements, because the inner filter effects were found to be negligible for coastal water samples using this instrument (Lee and Kim, 2018). EEMs–PARAFAC was performed in MATLAB (R2013a) using a DOMFluor toolbox, and the three components (C1–C3) were validated by split-half analysis (Figs. S1 and S2 in the Supplement).

## 3 Results and discussion

### 3.1 Horizontal distributions of DOM

The salinity of surface seawater in August 2011 ranged from 10 to 21, while the salinity in August 2016 ranged from 25 to 32 (Table 1 and Fig. 2). The concentrations of DOC in both sampling periods ranged from 100 to 200 µM (Fig. 2), which fall within the DOC ranges commonly observed in coastal waters (Gao et al., 2010; Osburn and Stedmon, 2011; and Kim et al., 2012). The highest concentration of DOC in 2011 (186 µM) was observed at station M4-1 in the middle of the bay, whereas the highest concentration of DOC in 2016 (191 µM) was observed at station M1, which is the innermost station in the bay. DOC concentrations were lowest at the outermost stations in both sampling periods. Concentrations of DON were in the range of 7–24 µM in 2011 and 3–15 µM in 2016, with the highest value at station M5-1 in 2011 and at M1 in 2016 (Fig. 2).

EEMs–PARAFAC dataset analyses identified three components in the surface water samples. EEMs contour plots and split-half validation results for three components are shown in the Supplement (Figs. S1 and S2). Based on the comparison with data in the OpenFluor (Murphy et al., 2014), Component 1 ($FDOM_H$; Ex/Em = 322/405 nm) is associated with a terrestrial humic-like component (Liu et al., 2019; Dalmagro et al., 2019; and Chen et al., 2016). Component 2 ($FDOM_M$; Ex/Em = 386/450 nm) is also associated with an allochthonous humic-like component (Wünsch et al., 2017). Component 3 ($FDOM_P$; Ex/Em = 280/330 nm) is associated with a protein-like component, which is a product of microbial processes (Liu et al., 2019; Murphy et al., 2011; and Osburn et al., 2011). We use Component 1 as a representative of terrestrial humic-like FDOM ($FDOM_H$) in this study because there was a significant correlation ($r^2 = 0.95$) between Component 1 and Component 2.

$FDOM_H$ is known to indicate humic substances from terrestrial, anthropogenic, or agricultural sources (Coble, 2007), whereas $FDOM_P$ is likely related to autochthonous or anthropogenic sources (Coble, 1996; Hudson et al., 2007). The intensities of $FDOM_H$ and $FDOM_P$ in 2011 were in the range of 3.6–9.2 and 4–79 QSU, respectively (Fig. 3). The inten-

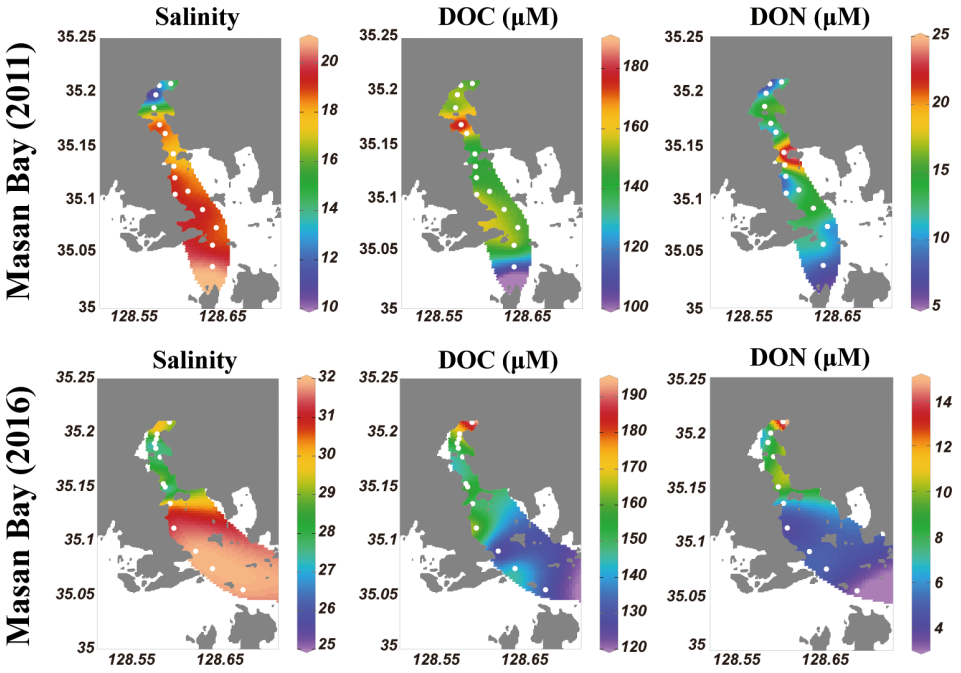


**Figure 2.** Surface distributions of salinity, DOC, and DON in Masan Bay, Republic of Korea, in 2011 and 2016.

sities of $FDOM_H$ and $FDOM_P$ in 2016 were in the range of 2.7–0.6 and 4.8–2.1 QSU, respectively (Fig. 3). An exceptionally high concentration of $FDOM_P$ was observed at station M4-1 (78 QSU) relative to that of other stations (2–25 QSU) in 2011 (Fig. 4d).

### 3.2 Origin of excess DOM

The plot of DOC versus salinity in 2011 (Fig. 4a) shows two different mixing trends. The first slope shows a slight increase in DOC with decreasing salinity toward the innermost stations, including M1, M1-1, and M2 (Fig. 4a, Group 1). The second trend is a sharp rise in DOC (excess DOC in 2011) to the maximum value 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 source mixing. The plot of DOC versus salinity shows that DOC in 2016 was in a range similar to that of 2011, although there was much less influence from freshwater (Fig. 4a, Group 3). This plot shows that there was additional DOC (excess DOC) in 2016 in the high-salinity water in the bay. The potential sources of excess DOC occurring in this bay water may include terrestrial freshwater from creeks, STP water, direct land–seawater interaction, and in situ biological production. The creek water may also include various anthropogenic sources (i.e., industrial, agricultural, and domestic sewage) as well as natural land sources. There are no salt-marsh or wetland habitats in Masan Bay. To determine the main sources of the excess DOC using $\delta^{13}$C-DOC, FDOM, and DOC/DON ratios, the stations with excess DOC are separated into three groups (Group 1, Group 2 in 2011, and Group 3 in 2016) (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). $\delta^{13}$C-DOC values from Group 1 ranged from −25.4 ‰ to −23.3 ‰. We plotted a conservative mixing curve of $\delta^{13}$C-DOC for two end-member source mixing (Spiker, 1980; Raymond and Bauer, 2001). The assumed end-member values of DOC and $\delta^{13}$C-DOC were 185 µM and −28 ‰ (Raymond and Bauer, 2001), respectively, for the terrestrial end-member ($S = 0$) and 100 µM and −18 ‰ (Kelley et al., 1998), respectively, for the marine end-member ($S = 34$). The $\delta^{13}$C values from Group 1 fall on the mixing line or are slightly heavier than the mixing line, within 1.5 ‰, indicating conservative mixing between the terrestrial $C_3$ land plants (−23 ‰ to −32 ‰; Deines, 1980) in freshwater and open-ocean seawater. The slightly heavier values could be produced by in situ biological production during the mixing processes. As such, the plot of $\delta^{13}$C-DOC values versus C/N ratios also indicates that the excess DOC in Group 1 is from freshwater DOC (Fig. 5a).

Group 2 includes high-salinity water stations (M4-1, M4-2, M6, M6-1, M7-1, M7-2, M8, M9, and M9-1) observed in 2011 (Fig. 1). The $\delta^{13}$C-DOC values from Group 2 were in the range of −23.3 ‰ to −20.6 ‰ and were more enriched than the conservative mixing curve. These values are close to the marine $\delta^{13}$C-DOC values (−22 ‰ to −18 ‰) (Fry et al., 1998), except for one station (M6), in this group (−23.3 ‰). The $\delta^{13}$C-DOC values from Group 2 suggest that excess DOM was added in situ by biological production in

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

| Sampling | Station | Salinity | DOC (μM) | $FDOM_H$ (QSU) | $FDOM_P$ (QSU) | $\delta^{13}$C-DOC (‰) | DON (μM) | DOC/DON |
|---|---|---|---|---|---|---|---|---|
| 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 | NA | 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 | NA | 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 |

NA: not available.

seawater. As such, the plot of $\delta^{13}$C-DOC values versus C/N ratios also indicates that the excess DOC of Group 2 is produced by marine phytoplankton (Fig. 5a).

Group 3 includes high-salinity water stations (M1, M2, M3, M4, M5, M6, and M7) observed in 2016 (Fig. 1). Although all data were collected in the same wet season (August), the salinity ranges from both campaigns were different from those in 2011, with a narrow high-salinity range in 2016. The $\delta^{13}$C-DOC values from Group 3 also show significantly different values relative to those sampled in 2011 (Group 1 and Group 2). The $\delta^{13}$C-DOC values from Group 3 were depleted (−28.8 ‰ and −21.1 ‰) relative to the conservative mixing curve (Fig. 4b). The plot of $\delta^{13}$C-DOC values versus C/N ratios indicates that the excess DOC in Group 3 is from C3 terrestrial plants through direct land–seawater interactions (including the possible sources from a newly built artificial island), based on the fact that the excess DOC occurred in high-salinity (26–32) waters (Fig. 5a).

$FDOM_H$ had a significant negative correlation with salinity ($r^2 = 0.89$). The concentrations were highest for Group 1 and lowest for Group 3. This result indicates that humic DOM in this region was mainly from a terrestrial source and behaved conservatively in the freshwater and seawater mixing zone. This trend is commonly observed in coastal waters worldwide (Coble et al., 1998; Mayer et al., 1999). However, the concentration of $FDOM_P$ had no correlation with salinity. In general, $FDOM_P$ shows nonconservative behavior in many estuaries owing to the extra source of DOC produced by in situ biological production (Benner and Opsahl, 2001). In the study region, a remarkably high $FDOM_P$ concentration was observed at station M4-1 in 2011, where the DOC concentration was highest. This trend also supports the argument that, based on the $\delta^{13}$C-DOC results, the main source of DOC at this station is from in situ biological production. We observed the decoupling of DOC and $FDOM_H$ because $FDOM_H$ is not the major portion of DOC in this bay.

Masan Bay has many potential land sources of DOM from different creeks. In addition, the treated sewage outflow from a STP is located near station M7-1 (Fig. 1). Many studies have been conducted to identify organic pollutants from

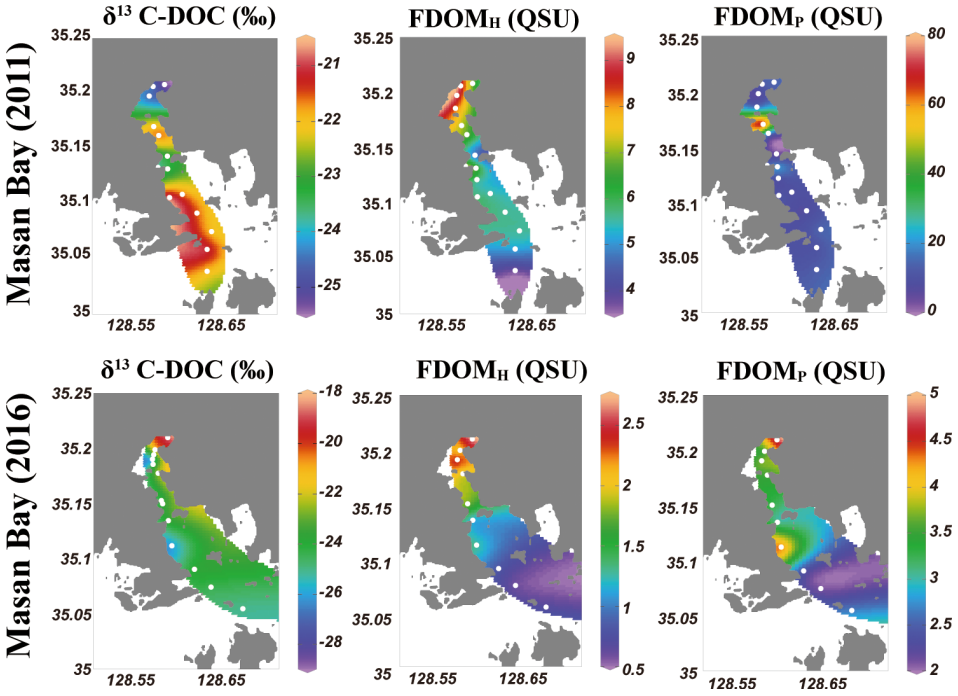


**Figure 3.** Surface distributions of $\delta^{13}$C-DOC, $FDOM_H$, and $FDOM_P$ in Masan Bay, Republic of Korea, in 2011 and 2016.

STPs (Kannan et al., 2010; Lee et al., 2011). In our study, however, station M7-1 samples did not have different DOM characteristics but rather had the following features:

1. The concentrations of DOC, $FDOM_H$, and $FDOM_P$ compared with salinity did not show anomalously higher or lower trends, relative to the other stations nearby.

2. The $\delta^{13}$C-DOC values at M7-1 (−20.6 ‰) were close to the marine values (Fry et al., 1998), similar to those from other stations nearby, although these values are known to be lighter in some US wastewater treatment plants (−26 ‰) (Griffith et al., 2009).

3. A fulvic-like peak was not observed, although a significantly higher fulvic-like peak (Ex/Em 320–340 nm/410–430 nm) was observed in treated sewage (Baker, 2001).

4. The increase in $FDOM_P$ intensities at stations M7-1 and M7-2 were insignificant relative to those at stations M6-1 and M8, although $FDOM_P$ is often used as a tracer of anthropogenic material including treated effluents (Hudson et al., 2007).

Thus, we conclude that the concentration of DOC at station M7-1 was not influenced by the STP. This STP appears to reduce TOC concentrations to a level that cannot influence DOC concentrations resulting from the other mixing sources, as shown in several other estuaries (Abril et al., 2002).

In general, anomalously high $FDOM_P$ was observed in anthropogenic sources (Coble, 1996; Baker and Inverarity, 2004). The $\delta^{13}$C values for sewage effluents generally ranged from −22 ‰ to −28.5 ‰ (Andrews et al., 1998; Barros et al., 2010), and those for STP effluents ranged from −24 ‰ to −28 ‰ (Griffith et al., 2009). The $\delta^{13}$C vs. $FDOM_P$ plot (Fig. 5b) shows that there was no increase in $FDOM_P$ concentrations in samples which had depleted $\delta^{13}$C values. Thus, we conclude that there was no significant DOC input from untreated sewage or STP sources in this bay.

## 4 Conclusions

We determined the sources of DOM in 2011 and 2016 using the $\delta^{13}$C-DOC, FDOM, and DOC/DON ratios. The main sources were separated into three groups based on DOC concentrations versus salinity plots. The DOM concentrations in the first group in 2011, which included the lowest salinity waters, were found to be mixtures of terrestrial DOM and open-ocean DOM sources based on the $\delta^{13}$C values of −25.4 ‰ to −23.3 ‰ and a good correlation between $FDOM_H$ and salinity. The excess DOC concentrations in the second group in high-salinity waters in 2011 were found to be produced by in situ biological production based on more enriched $\delta^{13}$C-DOC values (−22.0 ‰ to −20.6 ‰), high $FDOM_P$ concentrations, and low C/N ratios. The excess DOC concentrations in the third group in high-salinity waters in 2016 seemed to be produced by a direct interaction between land and seawater based on more depleted $\delta^{13}$C-DOC values (−28.8 ‰ and

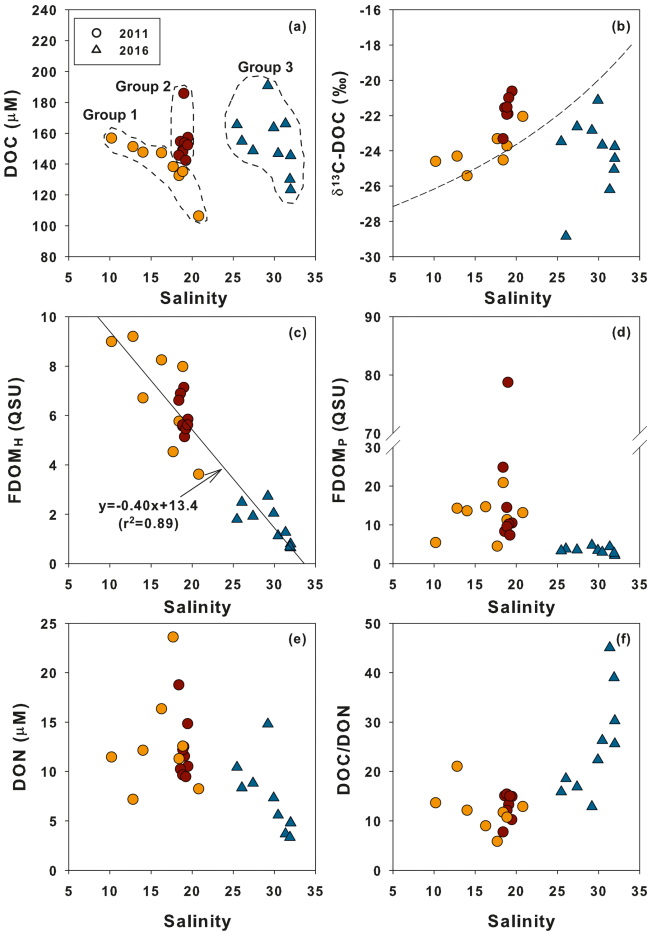


**Figure 4.** Relationships between salinity and **(a)** DOC, **(b)** $\delta^{13}$C-DOC, **(c)** $FDOM_H$, **(d)** $FDOM_P$, **(e)** DON, and **(f)** DOC/DON ratio values. The DOC concentrations are divided into three groups based on probable different sources (in the dashed circles). The dashed line **(b)** represents the binary conservative mixing line for $\delta^{13}$C-DOC between the terrestrial end-member and the marine end-member. The solid line **(c)** represents a linear regression fit of the data.

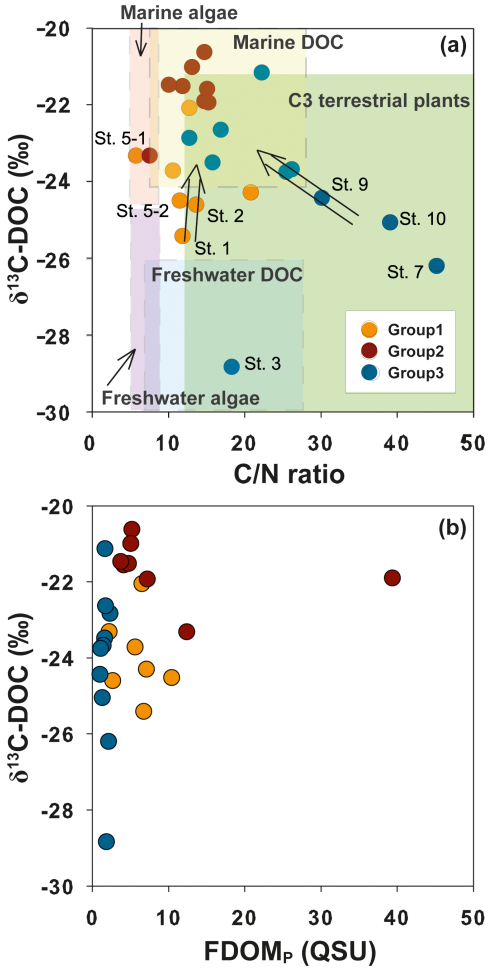


**Figure 5.** Relationships between $\delta^{13}$C-DOC values and **(a)** the DOC/DON (C/N) ratio and **(b)** $FDOM_P$ in Masan Bay, Republic of Korea. The ranges of the DOC/DON ratio and $\delta^{13}$C-DOC values for each group are based on the values reported by Lamb et al. (2006) and Beaupré (2015).

−21.1 ‰), low FDOM concentrations, and high C/N ratios. Our results show that using a combination of multiple DOM tracers including $\delta^{13}$C-DOC, FDOM, and C/N ratios is a powerful method for determining different sources of DOM occurring in coastal waters

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

*Supplement.* The supplement related to this article is available online at: https://doi.org/10.5194/bg-17-135-2020-supplement.

*Author contributions.* GK conceptualized the study. SAL and THK collected the samples. SAL performed the analyses. SAL and GK wrote the paper, and all authors contributed to the interpretation and discussion of the results.

*Competing interests.* The authors declare that they have no conflict of interest.

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