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), δ^{13}C-DOC, and fluorescent dissolved organic matter (FDOM) in coastal bay waters surrounded by large 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 high-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, excess DOC observed in high-salinity waters in 2016 was 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 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 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.

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; Lee and Kim, 2018). 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). DOC/DON ratios 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 isotopic ratio of bulk sample alone in complex coastal environments is somewhat complicated by the overlap of the isotopic ranges. Thus, several studies have used δ^{13}C-DOC combined with FDOM (Osburn and Stedmon, 2011; Osburn et al., 2011; Ya et al., 2015; Lu et al., 2015) or carbon isotope ratios combined with C/N ratio (Thornton and McManus, 1994; Andrews et al., 1998; Wang et al., 2004; McCallister et al., 2006; Pradhan et al., 2014) to discriminate different sources of DOM in estuarine and coastal waters. As far as we know, these three tracers together have not yet been used together to determine DOM sources in coastal waters.

Our study aimed at discriminating DOM sources in coastal waters, where various sources are present, using δ^{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. 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). Red tides and 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 of sewage treatment plants (STPs) which manage domestic and industrial wastewater from Masan and Changwon cities. 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 the creeks, inner bay, and 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 to differentiate complicated DOM sources in other areas of the world's coastal regions.

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. 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 temperatures 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 6M 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 two min to remove dissolved inorganic carbon. Samples were carried into a combustion tube heated to 720 ℃ where the DOC was converted quantitatively to CO_2. CO_2 gas was detected by a non-dispersive infrared detector (NDIR). Our DOC and TDN methods were verified using the seawater reference samples for DOC of 44–46 μ mol L^{-1} and for TDN of 32–34 μ mol L^{-1}, which were produced by the University of Miami (Hansell's lab, USA). Inorganic nutrients were measured using nutrient auto-analyzers (Alliance Instruments, FUTURA+ for 2011 samples and 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 δ^{13}C-DOC were determined using a TOC-IR-MS instrument (Isoprime, 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's 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-CH6 sucrose (International Atomic Energy Agency, −10.45 ± 0.03‰) was used for standardization. The standard solution was measured for every ten samples to monitor the drifting effect. Our measured values of δ^{13}C-DOC of the Deep-Sea Water 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 two days from 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 for the signal of Milli-Q water produced daily to remove Raman scattering peaks. All data were converted to ppb quinine sulfate equivalent (QSE) using a quinine sulfate standard solution dissolved in 0.1N 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 on MATLAB (R2013a) using a DOMFluor toolbox, and the three components (C1-C3) were validated by split-half analysis (Figs. S1 and S2).

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 μM to 200 μM (Fig. 2), which fall within the DOC ranges commonly observed in coastal waters (Gao et al., 2010; Osburn and Stedmon, 2011; 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 M5-1 in 2011 and at M1 in 2016 (Fig. 2).

EEM-PARAFAC dataset analyses identified three components in the surface water samples. EEMs contour plots and split-half validation results of three components are shown in the supplementary (Figs. S1 and S2). Based on the comparison with the 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; 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; 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 ppb QSE and 4–79 ppb QSE, respectively (Fig. 3). The intensities of $FDOM_H$ and $FDOM_P$ in 2016 were in the range of 2.7–0.6 ppb QSE and 4.8–2.1 ppb QSE, respectively (Fig. 3). An exceptionally higher concentration of $FDOM_P$ was observed at station M4-1 (78 ppb QSE) relative to that of other stations (2–25 ppb QSE) in 2011 (Fig. 4d).

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 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 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 potential sources of excess DOC occurring in this bay water may include terrestrial freshwater in 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 δ^{13}C-DOC, FDOM, and DOC/DON ratios, the excess DOC stations 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). 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‰ (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 δ^{13}C values of Group 1 fall into the mixing line or are slightly heavier than the mixing line within 1.5 ‰, indicating the conservative mixing between the terrestrial C3 land plant (−23‰ to −32‰; Deines, 1980) in freshwater and the open ocean seawater. The slightly heavier values could be produced by *in situ* biological production during the mixing processes. As such, the plot of δ^{13}C-DOC values versus C/N ratios also indicates that the excess DOC of 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 δ^{13}C-DOC values of 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 δ^{13}C-DOC values (−22 to −18‰) (Fry et al., 1998), except for one station (M6), in this group (−23.3‰). The δ^{13}C-DOC values of Group 2 suggest that excess DOM was added *in situ* by biological production in seawater. As such, the plot of δ^{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 of both campaigns were different from those in 2011, with a narrow high salinity range in 2016. The δ^{13}C-DOC values for Group 3 also showed significantly different values relative to those sampled in 2011 (Group 1 and Group 2). The δ^{13}C-DOC values for Group 3 were depleted (−28.8‰ and −21.1‰) relative to the conservative mixing curve (Fig. 4b). The plot of δ^{13}C-DOC values versus C/N ratios indicates that the excess DOC of Group 3 is from C3 terrestrial plants through direct land (including the possible sources from a newly-built artificial island)-seawater interactions, based on the fact that the excess DOC occurred in high-salinity (26–32) waters (Fig. 5a).

$FDOM_H$ showed 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 $FDOM_P$ showed no correlation with salinity. In general, $FDOM_P$ shows non-conservative 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 DOC concentration was highest. This trend also supports the argument, based on the δ^{13}C-DOC results, that the main source of DOC at this station is from *in situ* biological production. We observed the decoupling between DOC and $FDOM_H$ because $FDOM_H$ is not the major portion of DOC in this bay, except M4-1 station.

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 STP (Kannan et al., 2010; Lee et al., 2011). In our study, however, station M7-1 did not show different DOM characteristics: (1) the concentrations of DOC, $FDOM_H$, and $FDOM_P$ against salinity did not show anomalously higher or lower trends, relative to the other stations nearby. (2) The δ^{13}C-DOC values at M7-1 (−20.6‰) were close to the marine values (Fry et al., 1998), similar to those in other stations nearby, although they 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 and Inverarity, 2004). (4) The increase of $FDOM_P$ intensities at stations M7-1 and M7-2 was 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 STP. This STP appears to reduce TOC concentrations to a level that cannot influence the 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 for anthropogenic sources (Coble, 1996; Baker et al., 2003). The δ^{13}C values of sewage effluents generally ranged from –22‰ to –28.5‰ (Andrews et al., 1998; Barros et al., 2010), and those of STP effluents ranged from –24‰ to –28‰ (Griffith et al., 2009). The δ^{13}C vs $FDOM_P$ plot (Fig. 5b) shows that there was no increase in FDOM_P concentrations for samples which had depleted δ^{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 δ^{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 δ^{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 higher salinity waters in 2011 were found to be produced *in situ* by biological production based on more enriched δ^{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 direct interaction between land and seawater based on more depleted δ^{13}C-DOC values (−28.8‰ and −21.1‰), low FDOM concentrations, and high C/N ratios. Our results show that the combination of multiple DOM tracers, including δ^{13}C-DOC, FDOM, and DOC/DON ratios, is powerful for discriminating the complicated 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.

Author contribution

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.

Competing interests

The authors declare that they have no conflict of interest.

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Table 1. Salinity, DOC, FDOM$_H$, FDOM$_P$, and δ^{13}C-DOC in surface water of Masan Bay in August 2011 and August 2016.

Sampling	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

n/a = not available.

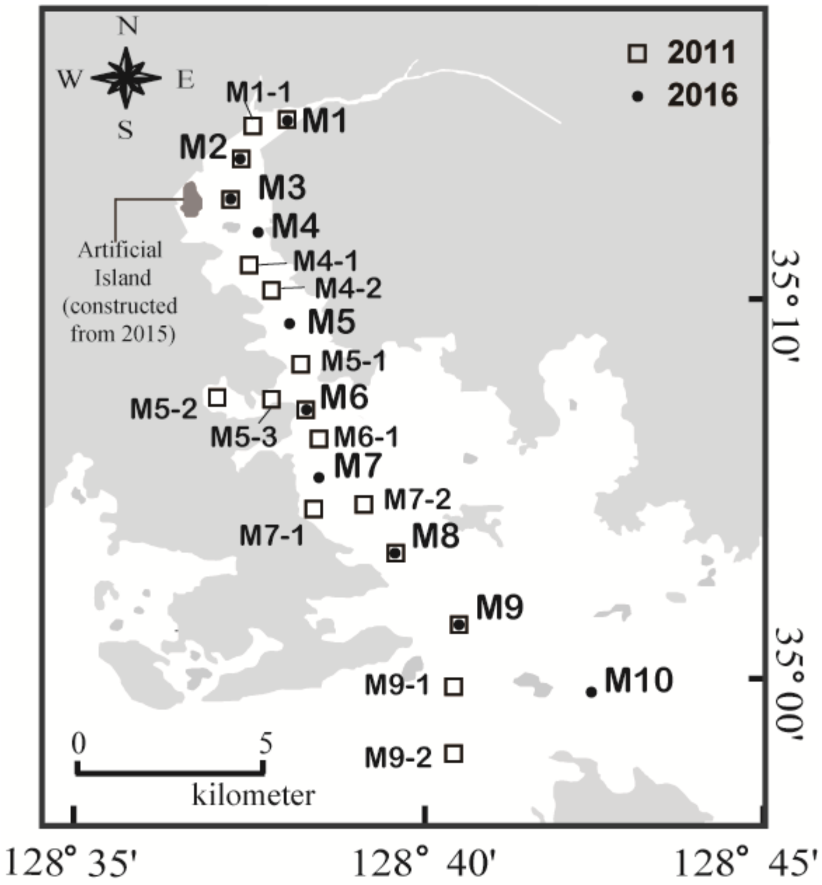

Figure 1. A map showing the sampling stations for DOC, δ^{13}C-DOC, FDOM, and DOC/DON ratio in Masan Bay, Korea, in 2011 and 2016.

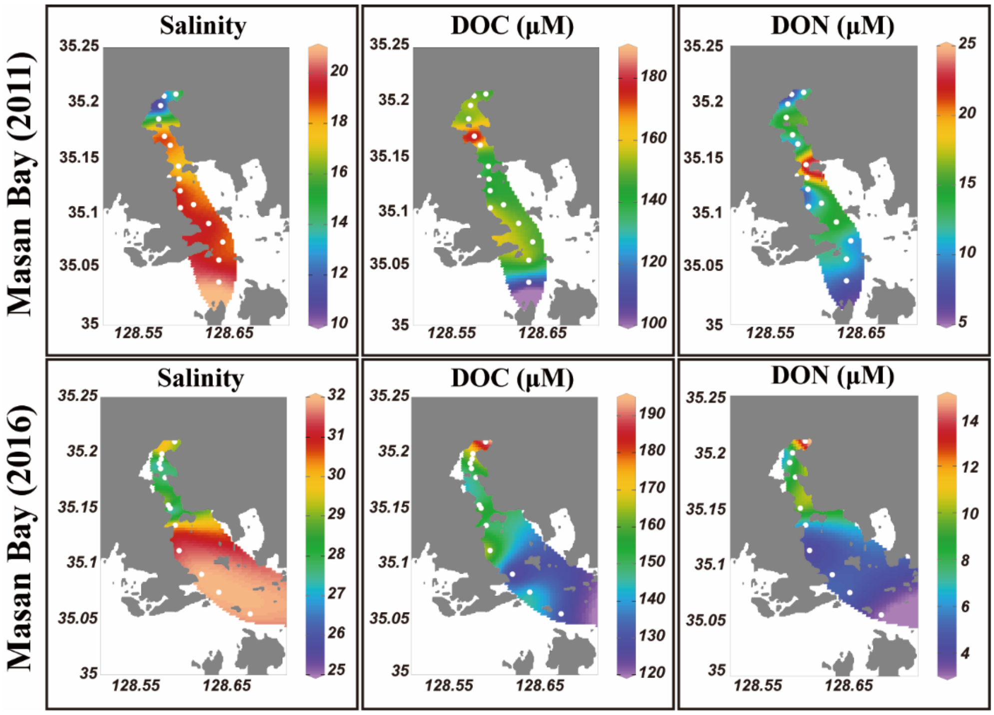

Figure 2. Surface distributions of salinity, DOC, and DON in Masan Bay, Korea, in 2011 and 2016.

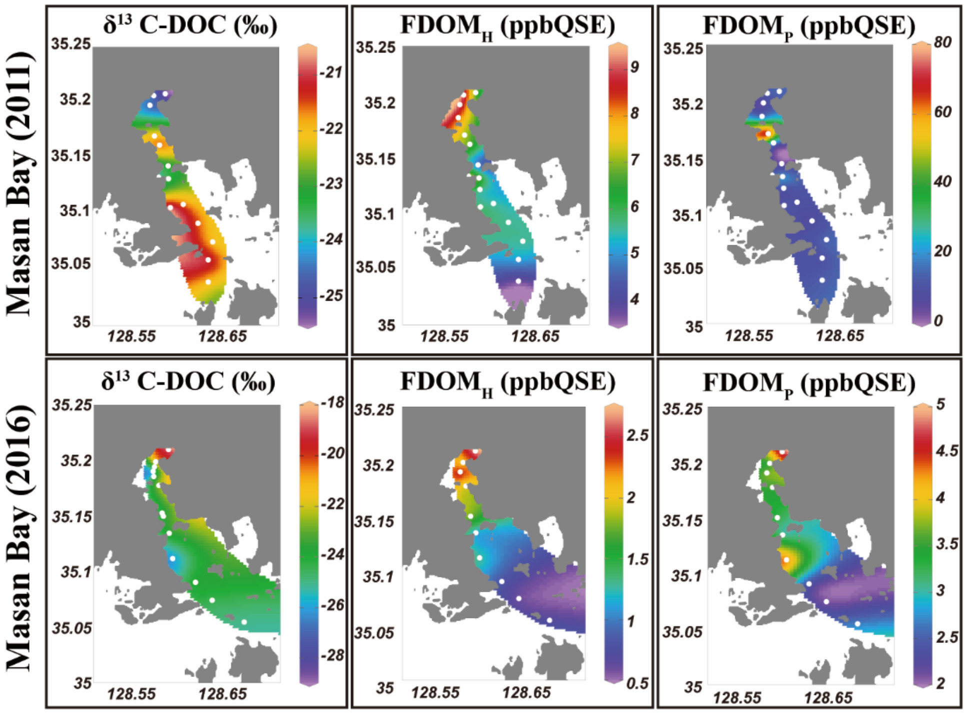

Figure 3. Surface distributions of δ^{13}C-DOC, FDOM$_H$, and FDOM$_P$ in Masan Bay, Korea, in 2011 and 2016.

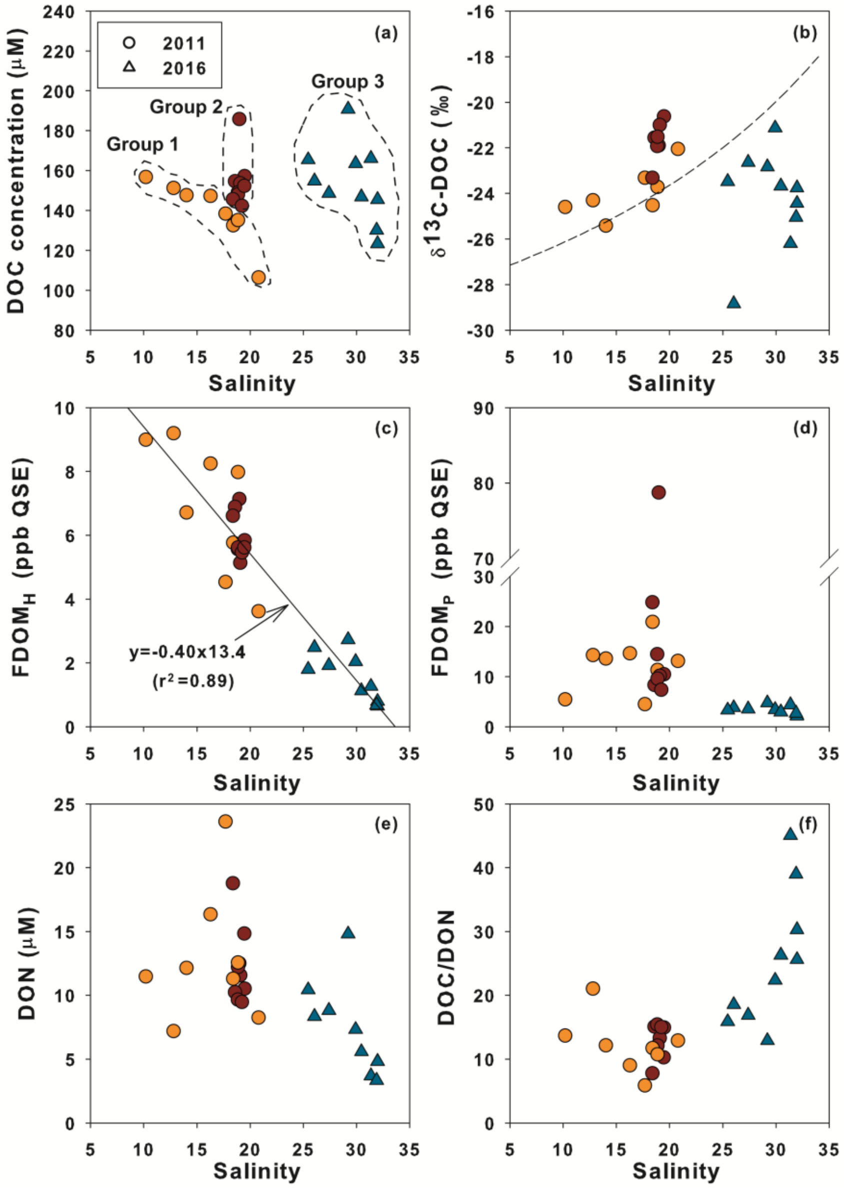

Figure 4. Relationships between salinity versus (a) DOC, (b) δ^{13}C-DOC, (c) FDOM$_H$, (d) FDOM$_T$, (e) DON, and (f) DOC/DON values. The DOC concentrations are divided into three groups based on probable different sources (in the dashed circles). The dashed line (b) represents the binary conservative mixing line for δ^{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.

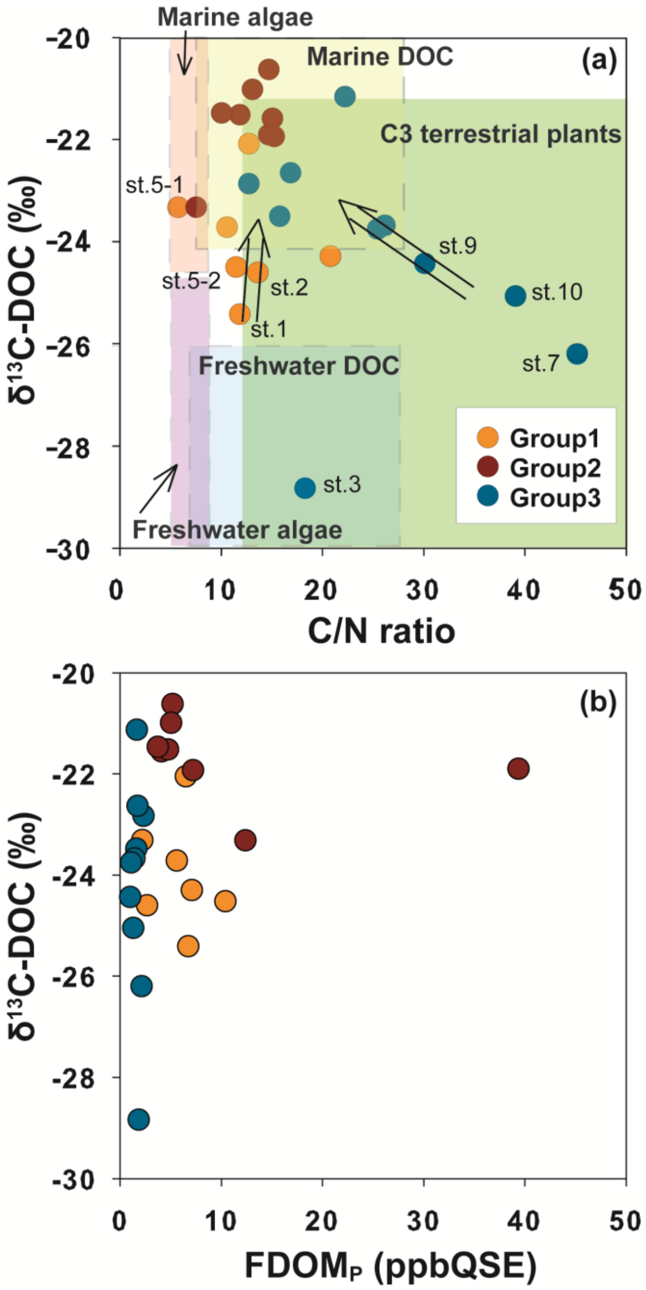

Figure 5. Relationships between δ^{13}C-DOC values versus (a) DOC/DON ratio and (b) FDOM$_{\mathrm{P}}$ in Masan Bay, Korea. The ranges of DOC/DON ratio and δ^{13}C-DOC values for each group are based on the values reported by Lamb et al. (2006) and Beaupré (2015).