Interactive comment on "Sources, fluxes, and behaviors of fluorescent dissolved organic matter(FDOM) in an estuarine mixing zone: Results from the Nakdong-River Estuary, Korea" by Shin-Ah

Lee and Guebuem Kim
Anonymous Referee #1

Major comments

In this manuscript, the authors determined variations of dissolved organic carbon (DOC), stable carbon isotope of DOC (δ13C-DOC), and fluorescent DOM (FDOM) with tide from monthly observation at a 24 hours monitoring station in the Nakdong-River Estuary, Korea. The authors found significant relationships between salinity and DOC as well as FDOM (both of humic-like and protein-like) throughout a year, implying that riverine DOM were conservatively distributed with estuarine mixing but contribution of autochthonous DOM were minor in the estuarine mixing zone. The conservative behavior of terrestrial DOM was also supported by the spatial variation of δ13C-DOC at the estuary. The authors also found that the relationships (slopes and intercepts of linear regressions) between salinity and DOC as well as FDOM differed among months, due to different levels of their riverine end-members. From the findings, the authors pointed out that the estimation of annual riverine flux of DOC (and also FDOM) requires careful considerations of seasonal changes. I think the methods in the manuscript are technically sound, and manuscript is logically well written. Even that said, I have two major comments on the manuscript.

(1) I thought that data analyses and discussion were insufficient. In the Introduction section, the authors described that the behavior of DOM in the estuarine mixing zone and fluxes of DOM from the river can be determined in the manuscript. However, the authors basically focused differences in fluxes of DOM from the river among months but did not discuss about different behavior of DOM in the estuarine mixing zone. It seemed that correlation coefficients (or coefficients of determination) between salinity and DOM parameters were largely different among months. Such different correlation coefficients imply that the behavior of DOM in the estuarine mixing zone, e.g., photo-degradation, sedimental inputs, autochthonous production, were different among months. I think it's better to add some discussions about different behavior of DOC and FDOM in the estuarine mixing zone among months based on different correlation coefficients.

=> Thank you for the valuable comments. In the revised version, we added more detailed demonstrations about these mixing trends. The differences in slopes and y-intercepts are discussed in the results and discussion section (lines 164-167 and 212-219). It is very difficult to compare scatterings for different seasons in order to discuss the different behaviors of DOM since the scattering is generally larger for the narrow salinity ranges. This seems to be the limitation of our study. However, we added more discussion about the behavior of DOM based on correlation coefficients for the other seasons in the revised version (lines 221-230): "In March, during the highest biological production period in the river, the correlation coefficient against salinities was the highest for $FDOM_P$ and lowest for $FDOM_H$. In contrast, in June, during the highest fluvial DOM discharge period, the correlation coefficient against salinities was the highest for $FDOM_H$ and lowest for $FDOM_P$. This suggests that the biological production and removal, together with other generally known factors such as photo-degradation and sedimentary inputs, may affect the scattering of these FDOM components in the estuarine mixing zone".

(2) The authors evaluated monthly "variable" concentrations (i.e., 174-284 μM) of riverine end-member of DOC from relationships between DOC concentration and salinity. On the other hand, the authors also obtained one "fixed" riverine end-member with 270 μM from the conservative mixing curve of δ13C-DOC with the two end-members. These interpretations derived from different analyses seemed to be contradicted. I think the authors should also analyze conservative mixing curve of δ13C-DOC for each month.
=> Thank you for your valuable suggestion. We analyzed the mixing curves of δ^{13}C-DOC for each month for the different end-member values and showed them in Figure 2B as a dotted line. Except for the winter period (the narrow salinity range period), the trend of δ^{13}C-DOC for each month fitted well into the overall trend. The extrapolated endmember value of δ^{13}C-DOC for each month ranged from -27.5 to -24.5, indicating that the main source of DOC is C3 plants. However, the value was heavier in March samples, perhaps in association with the higher biological production in the river. This is mentioned in the revised version (lines 192-194).

Specific comments
Line 32, line 153 and lines 185-186: I think correlation coefficients of relationships between salinity and DOM parameters should be minus value. For example, in line 32, "r=0.55-0.99" should be minus 0.55 to minus 0.99? Otherwise, these values were r2?
=> In the revised version, r^2 values were used.

Line 44-45: Please add reference(s) to a description "As FDOM accounts for 20 – 70
=> added as suggested.

Line 80: Is 23,380 km2 area of watershed? Please clarify it.
=> added the wording "watershed".

Lines 89-91: The system of auto-sampler is not clear from the description. Please add some information for the auto-sampler (structure, model number, manufacture etc) or cite previous work(s).
=> added the information on the auto-sampler (RoboChem^{TM}Autosampler, Model S3-1224N, Centennial Technology, Korea)

Lines 94-96: How did the authors preserve DOC and δ^{13}C-DOC samples? Freezing? Please make it clearer.
=> The DOC and δ^{13}C-DOC samples were acidified to pH ~2 with 6M HCl to avoid biological activities and stored in pre-combusted glass ampoules. Ampoules were fire-sealed for preventing the samples from any contaminations. The samples were analyzed within a week for DOC and CDOM. This is mentioned in the revised version.

Lines 101-129: The authors determined DOC concentrations using two different instruments, i.e., TOC-VCPH and TOC-IR-MS with NDIR. Which DOC concentration was used for the manuscript? Please make it clearer. In addition, for some readers who are interested in use of TOC-IR-MS, it would be great if the authors can add some information regarding with comparison of DOC concentrations determined by two different instruments.
=> We used TOC-V_{CPH} for DOC concentration measurements and TOC-IR-MS only for δ^{13}C-DOC measurements. DOC concentrations using TOC-V_{CPH} (Shimadzu, Japan) were calibrated with acetanilide and verified with Deep Seawater Reference (DSR) samples (University of Miami). We did not quantitatively measure DOC concentrations for TOC-IR-MS (Elementar,

Germany) although they were measured routinely to check any drifting effects. $DO^{13}C$ values were verified with IAEA-CH_6 sucrose and Deep Seawater Reference (DSR) samples (University of Miami).

Lines 131-147: Since DOC concentrations were relatively high, in particular in the low salinity waters, inner filter correction may be necessary to obtain precise EEMs. Did the authors apply an inner filter correction to EEMs? For the inner filter correction, please see Miller et al. (2010) AquatSci 72, 269-275 and references in therein.
=> We did not correct EEM data for the inner filter effects or dilute the samples before measurements since the inner filter effects were found to be negligible using this instrument for these estuarine water samples. The correlation between the uncorrected and corrected values for inner filter effect was very significant (r^2=1, n=5). This is mentioned in the revised version.

Lines 137-140: Please add validation method(s) of PARAFAC. I think that the authors should show spectra or describe peak positions of two PARAFAC components. In addition, previous EEMs-PARAFAC studies with DOMFluoro toolbox generally identified more than 2 fluorescence components. Did the authors have any idea why only two component model was validated with dataset of this manuscript?
=> More details on PARAFAC analysis were added as suggested. "Four components were identified in the water samples from the EEMs dataset. Based on the excitation-emission peak location, Component 1 ($FDOM_H$, Ex/Em = 320/418 nm) is found to be a terrestrial humic-like component (C peak) shown by Coble (2007). Component 2 ($FDOM_P$, Ex/Em = 280/328 nm) is found to be a tryptophan-like component (T peak), which is produced by microbial processes. Component 3 (Ex/Em = 300,325/364 nm) is found to be a marine humic-like component (M peak). Since Component 3 values were significantly correlated with Component 1 (r^2=0.95) values, we simply focused on Component 1 ($FDOM_H$) and Component 2 ($FDOM_P$) for data interpretations"

Lines 145-147: How did the authors measure water temperature? Please add the method in the Materials and Methods section.
=> We added this information in the Materials and Methods section. "The monitoring program at this station is maintained by Korea Environment Management Corporation (KOEM). The water temperature data are recorded automatically at the site. The data are available at https://www.koem.or.kr."

Lines 158-160: I could not understand how did the authors exclude high salinity periods. In other words, what was the definition of the high salinity periods? Please explain it in detail.
=> We excluded the high-salinity periods (>20), including December, January, February, and June, in this comparison since they showed narrow and low DOC concentration ranges (103-163 μM), resulting in large uncertainties by extrapolating them to the fresh water. We excluded these periods in the comparison to avoid misinterpretations. This is mentioned in the revised version (lines 167-170).

Lines 202-205: The authors only discussed the case of October and November here, even though $FDOM_H$ slopes were higher for July, August, October, and November compared with other months. How about July and August? Please discuss it.
=> Thank you for the important comment. We revised the text to include July, August, October, and November and to explain higher $FDOM_H$ loading in the revised version (lines 216-217 and

237-245). “The higher $FDOM_H$ slopes in July and October are similar to the trend of DOC (Fig. 2C), which could be due to higher terrestrial FDOM production”. And “Stedmon et al., (2006) demonstrated that stronger correlations were observed between DOC and FDOM as humus substances derived from terrestrial DOM are more colored than DOM produced in situ. In general, terrestrial DOM occurring in rivers originates mainly from plant decomposition and leaf litter in the form of humic substances (Huang and Chen, 2009). As such, Gueguen et al., (2006) showed that humic materials are more effectively extracted from soils during August-September under high temperatures. Thus, higher $FDOM_H$ slopes in August, October, and November, relative to the other periods, could be associated with higher terrestrial inputs of degradation products of soil organic matter (Dowell, 1985; Qualls et al., 1991).”

Line 204: The term of “organic weathering” is usually used for the breakdown of rocks by plant or animal action, e.g., extension of roots. Thus, I think “degradation products of soil organic matter” (for example) is much better than “organic weathering products”.
=> Yes, corrected as suggested.

Lines 212-214: Mayer et al. (1999) and Zhang et al. (2009) did not determine the spring and fall phytoplankton blooms in the Nakdong-River. Please cite more proper studies here.
=> We rephrased this sentence to be read as “higher $FDOM_P$ concentrations, relative to DOC concentrations, in the spring and fall seems to be associated with the spring and fall phytoplankton blooms in river waters (Mayer et al., 1999; Zhang et al., 2009).”

Line 257: “positive” should be “negative”? Please check it!
=> corrected.

Interactive comment on “Sources, fluxes, and behaviors of fluorescent dissolved organic matter (FDOM) in an estuarine mixing zone: Results from the Nakdong-River Estuary, Korea” by Shin-Ah
Lee and Guebuem Kim
Anonymous Referee #2
Received and published: 14 September 2017

Major comments
This manuscript by Lee and Kim set out to examine sources, fluxes, and mixing behavior of fluorescent dissolved organic matter in the Nakdong-River estuary in Korea. Time series samples were collected once a month during Sept 2014 – Aug 2015. In addition to humic-like and protein-like fluorescent DOM, the authors also measured bulk DOC concentration as well as its stable C isotopic composition to track DOM sources. They found both DOC and FDOM behaved conservatively, with concentration decreased with increasing salinity, showing the river as a major source for DOM. Values of DOC-d13C, on the other hand, increased with increasing salinity, demonstrating changes in DOM source along the estuary.
In general, this is an interesting manuscript, presenting time series DOM data, including bulk DOC, fluorescent DOM and stable isotopic data, along the river-estuary transect in the Nakdong River Estuary. The authors show a strong seasonality in DOM export fluxes. In addition, different FDOM components seemed to contribute disproportionally to the bulk DOM pool between different seasons. These are new findings which provide insights into better understanding of DOM dynamics in estuarine environments. Therefore this manuscript is a welcome addition. I support publication after minor revision.

Having said that some of the data need more discussion. For example, while both DOC and FDOM concentrations decreased linearly with increasing salinity showing an apparent conservative mixing behavior, stable carbon isotope signatures did not show a linear mixing between riverine and marine DOC, as also shown in other estuaries (e.g., Guo et al., 2009, Mar. Chem). The concave mixing curve indicated preferential removal of fluvial/terrestrial DOM during estuarine mixing (Zhou et al., 2016, GCA) and source of DOC had been changed to more marine or autochthonous to maintain the somewhat linear mixing of DOC and FDOM, as shown in Figure 2 in the manuscript. These are very interesting results and the authors could add a few sentences in their discussion. In addition, if DOM sources had shifted in the higher salinity regions, is the FDOM in the estuary terrestrial or marine? Or what portion is from terrestrial DOM? Also, if portions of DOC and FDOM in the estuary are from in situ produced DOM, then, terrestrial DOM is not conservative, at least in the middle and higher salinity regions?

=> Thank you for your valuable suggestions. The stable carbon isotope mixing curve was constructed based on the two end-member mixing equation (Spiker, 1980; Peterson et al., 1994; Raymond and Bauer, 2001). The curved mixing line for the conservative mixing was clearly explained previously by Spiker (1980) and Peterson et al. (1994). In general, the conservative mixing line for δ^{13}C-DOC is "not curved" for a constant DOC concentrations, however, it is "curved" when DOC concentrations decrease as salinities increase due to the weighting effect of the endmember isotopic compositions by the DOC concentrations (Spiker, 1980; Peterson et al., 1994). This is also shown in the equation. Since our DOC concentrations decrease as salinities increase, our data are generally fitted to the theoretical conservative mixing line. This suggests that DOC behaves conservatively in this system. The extrapolated endmember value of δ^{13}C-DOC for each month ranged from -27.5 to -24.5, indicating that the main source of DOC is C3 plants. However, the value was heavier at lower salinity ranges (S<10) in March and April samples, perhaps in association with higher biological production in the river. This is mentioned in the revised version (lines 184-194).

As explained to Reviewer #1, it is very difficult to compare scatterings for different seasons in order to discuss the different behaviors of DOM since the scattering is generally larger for the narrow salinity ranges. This seems to be the limitation of our study. However, we added more discussion about the behavior of DOM based on correlation coefficients for the other seasons in the revised version (lines 221-230): "In March, during the highest biological production period in the river, the correlation coefficient was the highest for $FDOM_P$ and lowest for $FDOM_H$ against salinities. In contrast, in June, during the highest fluvial DOM discharge period, the correlation coefficient was the highest for $FDOM_H$ and lowest for $FDOM_P$ against salinities. This suggests that the biological production and removal, together with other generally known factors such as photo-degradation and sedimentary inputs, may affect the scattering of these FDOM components in the estuarine mixing zone".

Minor comments for the authors:

1) Title: could be shortened to read: "Sources, fluxes, and behaviors of fluorescent dissolved organic matter in the Nakdong-River Estuary, Korea".

=> corrected as suggested.

2) Line-24: add p values if available;

=> In the revised version, p values were added.

3) Line-28/29: "…...due to higher fluvial production of humic-like FDOM"; This is not

necessarily the case here. Data in Figure 3 show a constant slope for humic-like FDOM among different seasons although there is not a constant slope value for the protein-like FDOM.
=> We rephrased this sentence to be read as "higher terrestrial input of humic-like FDOM".

4) Line-31/32: Are there any difference in export fluxes between the bulk DOC and different FDOM? This could be an interesting issue.
=> As shown in Figure 4, the fluxes of bulk DOC and $FDOM_H$ showed similar patterns over the seasons (the highest fluxes in July and lowest in January and February), while $FDOM_P$ showed the highest fluxes in April and lowest fluxes in January. This is mentioned in the revised version. "The fluxes of $FDOM_P$ in December and March were twofold higher than those of $FDOM_H$ whereas the flux of $FDOM_H$ in July was 2-3 folds higher than that of $FDOM_P$. This shows that the fluxes of both components of FDOM differ significantly by seasons owing to the different source inputs even though their magnitudes are controlled mainly by river discharges".

5) Line-89: Here the sampling date is October 2014-Aug 2015, which is different from the date shown in the abstract: Sept 2014 to Aug 2015. This should be fixed.
=> corrected.

6) Pg-7 on FDOM analysis: the extraction of FDOM-H and FDOM-P data from EEM-PARAFAC results should be mentioned briefly here.
=> More details on PARAFAC analysis were added as suggested. "Four components were identified in the water samples from the EEMs dataset. Based on the excitation-emission peak location, Component 1 ($FDOM_H$, Ex/Em = 320/418 nm) is found to be a terrestrial humic-like component (C peak) shown by Coble (2007). Component 2 ($FDOM_P$, Ex/Em = 280/328 nm) is found to be a tryptophan-like component (T peak), which is produced by microbial processes. Component 3 (Ex/Em = 300,325/364 nm) is found to be a marine humic-like component (M peak). Since Component 3 values were significantly correlated with Component 1 (r^2=0.95) values, we simply focused on Component 1 ($FDOM_H$) and Component 2 ($FDOM_P$) for data interpretations"

7) Line-180/181: Both QSU and _M are used here for FDOM. How to convert QSU to _M should be mentioned a bit here or in M&M.
=> corrected to QSU.

8) Pg-12: DOM fluxes are calculated from the integration of available time series data. Given the strong seasonality in DOC abundance and river discharge, how much difference will have in the fluxes if calculation is based on USGS LOADEST program although, in my opinion, showing the variability in DOM fluxes among sampling months, as provided in this manuscript, is very important. Maybe the authors can also plot data DOC vs discharge and show in Supplementary Materials.
=> We attempted to calculate the fluxes using USGS LOADEST program as suggested. However, we failed to obtain meaningful results since the river flow of this system was operated periodically by man and the concentrations were obtained from the slopes between DOC and salinity correlations at the downstream of the dam. Also, our sampling period (monthly average) does not meet the number of data needed for this program (i.e., 12 months are needed…but we have 11-month data). Although we see a quite significant correlation (r^2=0.52) between DOC concentrations and discharge volumes each month, this can be simply due to higher discharge volume in summer monsoon season and higher temperatures in

summer. In order to avoid this complication, we do not include this plot in supplementary.

9) Line- 251: add: “and specific river” after resolution.
=> “and hydrogeologic settings of a specific river” is added.

10) Line-254: add: “for the Nakdong River”, after 3 times.
=> added as suggested.

11) Line-257: “positive” should read “negative’
=> corrected as suggested.

12) Finally, are all the data, including DOC, FDOM, d13C, and discharge, documented in supplementary materials?
=> added all data in supplementary materials as suggested.

[END]

Sources, fluxes, and behaviors of fluorescent dissolved organic matter (FDOM) in the Nakdong-River Estuary, Korea

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Submitted to *Biogeosciences* (Revised version)

Abstract

We monitored seasonal variations of dissolved organic carbon (DOC), stable carbon isotope of DOC (δ^{13}C-DOC), and fluorescent dissolved organic matter (FDOM) in water samples from a fixed station in the Nakdong-River Estuary, Korea. Sampling was performed every hour during spring tide once a month from October 2014 to August 2015. The concentrations of DOC and humic-like FDOM showed significant negative correlations against salinity (r^2=0.42-0.98, $p < 0.0001$), indicating that the river-originated DOM components are the major source and behave conservatively in the estuarine mixing zone. The extrapolated δ^{13}C-DOC values (-27.5 – 24.5‰) in fresh water confirm that both components are mainly of terrestrial origin. The slopes of humic-like FDOM against salinity were 60-80% higher in the summer and fall, due to higher terrestrial production of humic-like FDOM. The slopes of protein-like FDOM against salinity, however, were 70-80% higher in spring, due to higher biological production in river water. Our results suggest that there are large seasonal changes in riverine fluxes of humic and protein-like FDOM to the ocean.

1. Introduction

The global annual flux of dissolved organic carbon (DOC) via rivers is approximately 0.17 - 0.36 × 10^{15} g (Meybeck, 1982; Ludwig et al., 1996; Dai et al., 2012). The DOC delivered from riverine discharges as well as *in situ* production through biological activities significantly affects carbon and biogeochemical cycles in coastal waters (Hedges, 1992; Bianchi et al., 2004; Bauer et al., 2013; Moyer et al., 2015).

Generally, DOC includes fluorescent dissolved organic matter (FDOM), which emits fluorescent light due to its chemical characteristics. As FDOM accounts for 20 - 70% of the DOC in coastal waters (Coble, 2007) and controls the penetration of harmful UV radiation in the euphotic zone, it plays a critical role in carbon cycles as well as biological production. In addition, FDOM is known as a powerful indicator of humic and protein-like substances (Coble, 2007) in coastal waters. River discharge is generally the main source of humic-like FDOM in coastal waters, although it is also produced through *in situ* microbial activity (Romera-Castillo et al., 2011). In contrast, protein-like FDOM is known to be from biological production as well as anthropogenic sources (Baker and Spencer, 2004). Terrestrial humic substances behave conservatively in coastal areas due to their refractory characteristics (Del Castillo et al., 2000), whereas protein substances behave non-conservatively in many estuaries due to their relatively rapid production and degradation (Vignudelli et al., 2004).

The magnitudes of DOC and FDOM fluxes from rivers are generally dependent on rainfall, discharge, and temperatures (Maie et al., 2006; Jaffé et al., 2004; Huang and Chen,

2009). In the estuarine mixing zone, intensive biogeochemical processes occur through photo-oxidation, microbial degradation, or physicochemical transformations (i.e., flocculation, sedimentation) (Bauer and Bianchi, 2011; Moran et al., 1991; Benner and Opsahl, 2001; Raymond and Bauer, 2001). Recent studies have demonstrated large seasonal variations as high as 40%, in DOC export from rivers to the ocean (Burns et al., 2008; Bianchi et al., 2004; Dai et al., 2012). However, the seasonal variations in sources, fluxes, and behaviors of DOC and FDOM in the estuarine mixing zone are still poorly understood.

In this study, we analyzed DOC, δ^{13}C-DOC, and FDOM in estuarine water samples collected monthly from the Nakdong-River estuary. Sampling was conducted at a fixed platform, which has been utilized for monitoring various environmental parameters. This sampling station is advantageous because we can collect water samples for a wide range of salinities throughout tidal fluctuations. Using the data obtained from this unique station, we were able to determine (1) the behaviors of DOM in the estuarine mixing zone, (2) the fluxes of DOM from rivers based on the slopes between salinities and DOM components, and (3) the changes in DOM sources using δ^{13}C-DOC in the estuarine samples. The slope measurement in the mixing zone may represent the endmember of DOM components in rivers better than site-specific measurements in the river, by integrating larger spaces and times.

2. Materials and methods

2.1 Study site

The Nakdong-River Estuary, which is the estuary of the longest river in Korea, is a

major source of water supplying the needs for drinking, agriculture, and industry. The main channel of Nakdong River is approximately 510 km in length with a watershed area of approximately 23,380 km^2. It faces the south-eastern coastal area of the Korean peninsula, passing through Busan which is the second largest city in Korea. The mean annual precipitation is 1150 mm, and most precipitation (60-70%) occurs during the summer monsoon and typhoon seasons (Jeong et al., 2007). To manage water supply and saltwater intrusion, estuary dams were constructed in the mouth of the river in 1987.

2.2 Sampling

Water samples were collected at the sampling site which is located 560 m downstream from the dam (Fig. 1). The sampling period was from October 2014 to August 2015. The 2-L water sampling was conducted every hour for 24 hours during spring tide using an auto-sampler (RoboChem™Autosampler, Model S3-1224N, Centennial Technology, Korea), with a depth of the water intake 1 m below the surface. After samples were collected in acid-cleaned polyethylene bottles, they were moved to the laboratory within 24 hours. All water samples were filtered using pre-combusted GF/F filters. The FDOM samples were stored in pre-combusted amber glass vials and kept below 4°C in a refrigerator before analysis. The DOC and δ^{13}C-DOC samples were acidified to pH ~2 using 6 M HCl to avoid bacterial activities and stored in pre-combusted glass ampoules. Ampoules were fire-sealed to prevent the samples from any contaminations. The samples were analyzed for DOC and CDOM within a week. Salinity was measured using a YSI Pro Series conductivity probe sensor in the laboratory. The real-time and compulsory discharge volume data from the dam are available at http://www.water.or.kr, provided by K-Water. The monitoring program at this station is

maintained by Korea Environment Management Corporation (KOEM). The water temperature data are recorded automatically at the site. The data are available at https://www.koem.or.kr.

2.3 Analytical methods

The concentrations of DOC were determined by a high-temperature catalytic oxidation (HTCO) method using a TOC-VCPH analyzer (Shimadzu, Japan). Standardization was performed based on the calibration curve of acetanilide in ultra-pure water. The acidified samples were purged with carbon dioxide (CO_2) free carrier gas for 2 min to remove inorganic carbon. The samples were then injected into a combustion column packed with Pt-coated alumina beads and heated to 720°C. The CO_2 evolving from combusted organic carbon was detected by a non-dispersive infrared detector (NDIR). Our DOC method was verified with Deep Seawater Reference (DSR) samples for DOC (44-46 μmol L^{-1}) produced by the University of Miami, USA.

The values of δ^{13}C-DOC were measured using a TOC–IR–MS instrument consisting of an IR–MS instrument coupled with a Vario TOC cube (Isoprime, Elementar, Germany). The TOC instrument uses a common high-temperature catalytic combustion method (Kirkels et al., 2014). The analytical method is fully described in Kim et al. (2015). Briefly, 10 mL of filtered samples was purged with O_2 gas for 20–30 min to completely remove DIC after the samples were acidified to pH ~2. Then, 1 mL of the sample was injected into Pt-impregnated catalyst in a quartz tube. In this tube, the DOC was converted completely to CO_2 at 750°C, which was then fed through a water trap followed by a halogen trap. After DOC was detected by an NDIR

detector, the CO_2 gas was entered the TOC–IR–MS interface by the O_2 carrier gas. In the interface, the CO_2 was transferred to the IR–MS instrument following the removal of any interfering gasses. The δ^{13}C-DOC value of blank was measured using the Low Carbon Water (LCW) from Hansell lab (University of Miami), which contains less than 2 μM DOC. Certified IAEA-CH6 sucrose (International Atomic Energy Agency, −10.45 ± 0.03‰) prepared with the low carbon water was used as a standard solution. A standard sample was analyzed for every sample queue (once before or after ten samples) to check a drifting effect during the measurements. The blank correction was performed using a method previously described in De Troyer et al. (2010) and Panetta et al. (2008). Our measurement result of δ^{13}C-DOC for the DSR (University of Miami) was −21.5 ± 0.1‰, which is consistent with the results reported by Panetta et al. (2008) and Lang et al. (2007). The reproducibility of TOC–IR–MS was ~0.3‰.

FDOM fluorescence was determined in a scan mode using a spectrofluorometer (SCINCO FluoroMate FS-2) within two days after sampling. Emission (Em) spectra were collected from 250 to 600 nm at 2 nm intervals at excitation (Ex) wavelengths from 250 nm to 500 nm at 5 nm intervals. Backgrounds were subtracted for fresh distilled water prepared daily from the sample data to eliminate Raman Scatter peaks (Zepp et al., 2004). All data were obtained in counts per second (cps) and converted to a ppb quinine sulfate standard solution in 0.1 N sulfuric acid at Ex/Em of 350/450 nm. The inner filter effect was negligible for these estuarine water samples using this instrument since the correlation between the uncorrected and corrected values for the inner filter effect was very significant for some samples (r^2=1, n=5). EEMs-PARAFAC analysis was performed using a MATLAB R2013a program with a DOMFluor toolbox.

3. Results and Discussion

Salinities ranged from 0.1 to 28.5 over the sampling period of a year. Salinities in the sampling location were dependent primarily on the volume of river-water discharge from the dam. The volumes of river discharge were relatively larger in October, April, July, and May. The mean annual surface water temperature was 16°C, with the lowest temperature (avg. 8°C) in December and the highest temperature in August (avg. 26°C).

3.1 Behaviors and sources of DOC in the estuarine mixing zone

The concentrations of DOC ranged from 100 to 300 μM, with the highest concentrations in July (avg. 243 μM) and the lowest concentrations in February (avg. 115 μM), consistent with the typical DOC concentration ranges in coastal waters (Wang et al., 2004; Raymond and Bauer, 2001). The concentrations of DOC correlated significantly with salinities (r^2 = 0.59-0.92, $p < 0.0001$), indicating that DOC behaves conservatively in the mixing zone of this estuary (Fig. 2A), which is commonly observed in estuarine mixing zones (Laane, 1980; Mantoura and Woodward, 1983; Del Castillo et al., 2000; Clark et al., 2002; Jaffé et al., 2004).

If the high salinity periods are excluded, both the slope and y-intercept of DOC concentrations versus salinities were highest in July (Fig. 1), which could be due to a higher terrestrial DOC loading in the summer period, as observed in Horsens Fjord, Denmark (Markager et al., 2011). For this comparison, we excluded the high-salinity periods (>20), including December, January, February, and June, since they showed a narrow and low DOC

concentration range (103-163 μM), resulting in large uncertainties by extrapolating them to the fresh water.

The carbon isotope values in the Nakdong-River Estuary ranged from -28.2 ‰ to -17.6. In order to determine the source of DOC in fresh water, we plotted δ^{13}C-DOC values against salinities (Fig. 2B). The conservative mixing curve of δ^{13}C values can be obtained using the two endmember mixing equation (Spiker, 1980; Raymond and Bauer, 2001):

$$\delta^{13}C_s = \frac{F_r\delta^{13}C_r[DOC]_r+(1-F_r)\times\delta^{13}C_m[DOC]_m}{[DOC]_s} \quad (1)$$

where $\delta^{13}C_s$, $\delta^{13}C_r$ and $\delta^{13}C_m$ are the δ^{13}C-DOC values at a given sample salinity, river endmember salinity, and marine endmember salinity, respectively; F_r is the riverine freshwater fraction calculated from the measured salinities; $[DOC]_s$ and $[DOC]_m$ are the DOC concentrations at a given salinity and marine endmember salinity, respectively; $[DOC]_r$ is the endmember DOC value for the river water (Fig. 1).

The riverine DOC endmember values (S=0‰) ranged from 174 to 284 μM. The marine endmember value (S=29‰) of DOC is 100 μM with the δ^{13}C-DOC value of -19‰. If these values from each month are applied, the δ^{13}C-DOC endmember values for the river water extrapolated to be from -27.5 to -24.5‰ (average: -26.2‰). Overall, the carbon isotope values of our samples are fitted well into the conservative mixing curve of the overall trend, with a slight change using different endmember values for different months (Fig. 2B). In general, δ^{13}C-DOC values range from −22 to −18‰ for marine phytoplankton, from −34‰ to −23‰ for terrestrial C3 plants, and from −16‰ to −10‰ for terrestrial C4 plants (Gearing 1988; Clark

and Fritz, 1997). Carbon isotope values in our study confirm that the main source of DOC in the estuarine mixing zone is dominantly from terrestrial C3 plants over all seasons. However, the value was heavier at lower salinity ranges (S<10) in March and April samples, perhaps in association with the higher biological production in the river.

3.2 Behaviors and sources of FDOM in the estuarine mixing zone

Four components were identified in the water samples from the EEMs dataset. Based on the excitation-emission peak location, Component 1 ($FDOM_H$, Ex/Em = 320/418 nm) is found to be a terrestrial humic-like component (C peak) shown by Coble (2007). Component 2 ($FDOM_P$, Ex/Em = 280/328 nm) is found to be a tryptophan-like component (T peak), which is produced by microbial processes. Component 3 (Ex/Em = 300,325/364 nm) is found to be a marine humic-like component (M peak). Since Component 3 values were significantly correlated with Component 1 (r^2=0.95) values, we simply focused on Component 1 ($FDOM_H$) and Component 2 ($FDOM_P$) for data interpretations.

The concentrations of $FDOM_H$ ranged from 2.4 to 19.7 quinine sulfate unit (QSU), with the highest concentration in July (avg. 17.6 QSU) and the lowest concentration in June (avg. 3.4 QSU) (Fig. 2C). The concentrations of $FDOM_P$ ranged from 0.6 to 22.4 QSU, with the highest concentration in March (avg. 15.1 QSU) followed by October (avg. 13.6 QSU) (Fig. 2D).

The concentrations of both FDOM components were significantly correlated with salinities (r^2 = 0.42-0.98, $p<0.0001$ for $FDOM_H$ and r^2 = 0.27-0.96, $p<0.0001$ for $FDOM_P$), indicating that they are conservative in the mixing zone (Fig. 2). The slopes of $FDOM_H$ and $FDOM_P$ for each month ranged from -0.15 to -0.59 and -0.15 to -0.71, respectively. The higher $FDOM_H$ slopes in July and October were similar to the trend of DOC (Fig. 2C), which could be due to higher terrestrial FDOM production. However, the seasons (March and April) in which higher $FDOM_P$ slopes occurred differ from those of DOC and $FDOM_H$, indicating that both FDOM components have different source inputs (Fig. 2D).

Although there are large differences in scattering of FDOM components against salinities, it is very difficult to compare scatterings for different seasons in order to discuss the different behaviors of DOM since the scattering is generally larger for the narrow salinity ranges. If the winter data are excluded, in March, during the highest biological production period in the river, the correlation coefficient against salinities was the highest for $FDOM_P$ and lowest for $FDOM_H$. In contrast, in June, during the highest fluvial DOM discharge period, the correlation coefficient against salinities was the highest for $FDOM_H$ and lowest for $FDOM_P$. This suggests that the biological production and removal, together with other generally known factors such as photo-degradation and sedimentary inputs, may affect the scattering of these FDOM components in the estuarine mixing zone.

As such, there was a significant positive correlation between $FDOM_H$ and DOC concentrations throughout all sampling periods ($r^2 = 0.93$, $p<0.0001$) (Fig. 3A), suggesting that the main source of $FDOM_H$ and DOC is terrestrial based on δ^{13}C-DOC values. Since FDOM

does not usually contribute to a major portion of DOC, a positive correlation between FDOM and DOC has only been observed in specific areas, such as river-estuarine systems (Del Vecchio and Blough, 2004; Coble, 2007). Stedmon et al., (2006) demonstrated that stronger correlations were observed between DOC and FDOM as humic substances derived from terrestrial DOM are more colored than DOM produced *in situ*. In general, terrestrial DOM occurring in rivers originates mainly from plant decomposition and leaf litter in the form of humic substances (Huang and Chen, 2009). As such, Gueguen et al., (2006) showed that humic materials are more effectively extracted from soils during August and September under high temperatures. Thus, higher $FDOM_H$ slopes in August, October, and November, relative to the other periods, could be associated with higher terrestrial inputs of degradation products of soil organic matter (Dowell, 1985; Qualls et al., 1991).

In the study region, $FDOM_P$ concentrations were poorly correlated with DOC concentrations (r^2=0.11) (Fig. 3B). The slopes of $FDOM_P$ concentrations against DOC concentrations varied significantly over different seasons, with steeper gradients in the spring (March and April) and fall (October). In general, $FDOM_P$ is known to be produced efficiently by biological production in water (Coble, 1996; Belzile et al., 2002; Steinberg et al., 2004; Zhao et al., 2017). Thus, higher $FDOM_P$ concentrations, relative to DOC concentrations, in the spring and fall seems to be associated with the spring and fall phytoplankton blooms in river waters (Mayer et al., 1999; Zhang et al., 2009).

3.3 Fluxes of DOC and FDOM in the estuarine mixing zone

257 The fluxes of DOC and FDOM from rivers to the ocean are calculated using the
258 endmember values (C) of these components in rivers multiplied by the river discharge volumes
259 (Q) for each month (Fig. 4). For this estimation, we assumed that (1) the endmember values
260 are the same as the intercepts of the DOC, $FDOM_H$, and $FDOM_P$ versus salinity plots, and (2)
261 the endmember values measured in the spring tides represent the concentrations of these
262 components for each month.

263

264 River discharge was highest in April and July following heavy precipitation, and the
265 largest discharge volume was about five-fold higher than that of winter discharges (Fig. 4A).
266 However, the monthly variations of DOC endmember (y-intercept) values were quite constant,
267 ranging from 174 - 284 μM. This indicates that the concentrations of DOC in the river are
268 independent of river discharge volumes (Fig. 4B). The DOC endmember values were highest
269 in December, followed by July and June (Fig. 4B). The monthly variation trend of $FDOM_H$
270 endmember values was similar to that of DOC, except for the December value. Excluding the
271 December values, the $FDOM_P$ endmember values were highest in March, February, and
272 October. These endmember trends are consistent with the slope variations explained in the
273 previous section. Although there are large uncertainties in fresh water endmember values of
274 DOC and FDOM in winter owing to narrow, high salinity ranges, we used the endmember
275 values for the flux comparisons since the contribution of the uncertainties may be relatively
276 small due to smaller river discharge volumes in winter.

277

278 The riverine DOC flux ranged from 1.6×10^6 mol day^{-1} (February) to 12.3×10^6 mol
279 day^{-1} (July), indicating that there are large variations of DOC fluxes to the ocean. The riverine

flux of $FDOM_H$ and $FDOM_P$ ranged from 1.4×10^9 QSU m^3 day^{-1} (December) to 23.1×10^9 QSU m^3 day^{-1} (July) and from 1.6×10^9 QSU m^3 day^{-1} (June) to 16.4×10^9 QSU m^3 day^{-1} (March), respectively. The seasonal variation trend of $FDOM_H$ was similar to that of DOC. The fluxes of $FDOM_P$ in December and March were twofold higher than those of $FDOM_H$ whereas the flux of $FDOM_H$ in July was 2-3 folds higher than that of $FDOM_P$. This shows that the fluxes of both components of FDOM differ significantly by seasons owing to the different source inputs even though their magnitudes are controlled mainly by river discharges

It is well known that the single sampling event is not enough to capture the full range of natural variability in DOM abundance over all seasons (Stedmon et al., 2006; Huang and Chen, 2009; Markager et al., 2011; Dai et al., 2012; Moyer et al., 2015). Overall, our results show that monthly variations are significant. This implies that our understanding of DOC fluxes from large rivers is largely biased, depending on sampling resolution, methods, and hydrogeological settings of a specific river. For example, if summer data are extrapolated to annual river water discharge, the DOC and $FDOM_H$ fluxes can be overestimated up to three times for the Nakdong River.

4. Conclusions

The concentrations of $FDOM_H$ and DOC showed significant negative correlations against salinities throughout all sampling periods, indicating that they behave conservatively in this estuarine mixing zone. The slopes of both DOC and $FDOM_H$ concentrations versus salinities were highest in July, due to the largest terrestrial DOC loadings. The carbon isotope values showed that the main source of DOC in the estuarine mixing zone is terrestrial C3 plants

over all seasons. The slopes of $FDOM_P$ versus salinity were relatively higher in March and April in association with the spring phytoplankton blooms in river and estuarine waters. The monthly fluxes of DOC, $FDOM_H$, and $FDOM_P$ showed large seasonal variations (5-10 folds), suggesting that the estimation of annual riverine fluxes of DOC, $FDOM_H$, and $FDOM_P$ requires careful considerations of seasonal changes in rivers.

Competing interests

The authors declare that they have no conflict of interest.

Acknowledgements

We thank the Environmental and Marine Biogeochemistry Laboratory (EMBL) members for their assistance with sampling and laboratory analyses. This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MEST) (NRF-2015R1A2A1A10054309) and by the project titled "Deep Water Circulation and Material Cycling in the EAST Sea (2016)", funded by the Ministry of Oceans and Fisheries, Korea.

References

Baker, A., and Spencer, R. G.: Characterization of dissolved organic matter from source to sea using fluorescence and absorbance spectroscopy, Sci. Total Environ., 333, 217-232, 2004.

Bauer, J., and Bianchi, T.: 5.02—dissolved organic carbon cycling and transformation, Treatise on estuarine and coastal science. Academic Press, Waltham, 7-67, 2011.

Bauer, J. E., Cai, W.-J., Raymond, P. A., Bianchi, T. S., Hopkinson, C. S., and Regnier, P. A.: The changing carbon cycle of the coastal ocean, Nature, 504, 61, 2013.

Belzile, C., Gibson, J. A., and Vincent, W. F.: Colored dissolved organic matter and dissolved organic carbon exclusion from lake ice: Implications for irradiance transmission and carbon cycling, Limnol. Oceanogr., 47, 1283-1293, 2002.

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

Bianchi, T. S., Filley, T., Dria, K., and Hatcher, P. G.: Temporal variability in sources of dissolved organic carbon in the lower Mississippi River, Geochim. Cosmochim. Acta, 68, 959-967, 2004.

Burns, K. A., Brunskill, G., Brinkman, D., and Zagorskis, I.: Organic carbon and nutrient fluxes to the coastal zone from the Sepik River outflow, Cont. Shelf Res., 28, 283-301, 2008.

Clark, I.J., and Fritz, P.: Environmental Isotopes in Hydrogeology, CRC Press/Lewis Publishers, Boca Raton, 1997.

Clark, C. D., Jimenez-Morais, J., Jones, G., Zanardi-Lamardo, E., Moore, C. A., and Zika, R. G.: A time-resolved fluorescence study of dissolved organic matter in a riverine to marine transition zone, Mar. Chem., 78, 121-135, 2002.

Coble, P. G.: Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy, Mar. Chem., 51, 325-346, 1996.

Coble, P. G.: Marine optical biogeochemistry: the chemistry of ocean color, Chemical reviews, 107, 402-418, 2007.

346 Dai, M., Yin, Z., Meng, F., Liu, Q., and Cai, W.-J.: Spatial distribution of riverine DOC inputs
347 to the ocean: an updated global synthesis, Current Opinion in Environmental Sustainability, 4,
348 170-178, https://doi.org/10.1016/j.cosust.2012.03.003, 2012.

349 De Troyer, I., Bouillon, S., Barker, S., Perry, C., Coorevits, K., and Merckx, R.: Stable isotope
350 analysis of dissolved organic carbon in soil solutions using a catalytic combustion total organic
351 carbon analyzer-isotope ratio mass spectrometer with a cryofocusing interface, Rapid Commun.
352 Mass Spectrom., 24, 365-374, 2010.

353 Del Castillo, C. E., Gilbes, F., Coble, P. G., and Müller-Karger, F. E.: On the dispersal of
354 riverine colored dissolved organic matter over the West Florida Shelf, Limnol. Oceanogr., 45,
355 1425-1432, 2000.

356 Del Vecchio, R., and Blough, N. V.: Spatial and seasonal distribution of chromophoric
357 dissolved organic matter and dissolved organic carbon in the Middle Atlantic Bight, Mar.
358 Chem., 89, 169-187, 2004.

359 Dowell, W. H.: Kinetics and mechanisms of dissolved organic carbon retention in a headwater
360 stream, Biogeochemistry, 1, 329-352, 1985.

361 Gearing, J.N., The use of stable isotope ratios for tracing the nearshore–offshore exchange of
362 organic matter. In: Jansson, B.-O. (Ed.), Coastal-Offshore Ecosystem Interactions, Springer-
363 Verlag, Berlin, 69–101, 1988.

364 Gueguen, C., Guo, L., Wang, D., Tanaka, N., Hung, C.-C.: Chemical characteristics and origin
365 of dissolved organic matter in the Yukon River, Biogeochemistry, 77, 139-155, 2006.

366 Hedges, J. I.: Global biogeochemical cycles: progress and problems, Mar. Chem., 39, 67-93,
367 1992.

368 Huang, W., and Chen, R. F.: Sources and transformations of chromophoric dissolved organic
369 matter in the Neponset River Watershed, Journal of Geophysical Research: Biogeosciences,
370 114, 2009.

371 Jaffé, R., Boyer, J., Lu, X., Maie, N., Yang, C., Scully, N., and Mock, S.: Source
372 characterization of dissolved organic matter in a subtropical mangrove-dominated estuary by
373 fluorescence analysis, Mar. Chem., 84, 195-210, 2004.

374 Jeong, K.-S., Kim, D.-K., and Joo, G.-J.: Delayed influence of dam storage and discharge on
375 the determination of seasonal proliferations of Microcystis aeruginosa and Stephanodiscus
376 hantzschii in a regulated river system of the lower Nakdong River (South Korea), Water Res.,
377 41(6), 1269-1279.

378 Kim, T.-H., Kim, G., Lee, S.-A., and Dittmar, T.: Extraordinary slow degradation of dissolved
379 organic carbon (DOC) in a cold marginal sea, Sci. Rep., 5, 2015.

380 Laane, R.: Conservative behaviour of dissolved organic carbon in the Ems-Dollart estuary and
381 the western Wadden Sea, Neth. J. Sea Res., 14, 192-199, 1980.

382 Lang, S. Q., Lilley, M. D., and Hedges, J. I.: A method to measure the isotopic (13 C)
383 composition of dissolved organic carbon using a high temperature combustion instrument, Mar.
384 Chem., 103, 318-326, 2007.

385 Ludwig, W., Probst, J. L., and Kempe, S.: Predicting the oceanic input of organic carbon by
386 continental erosion, Global Biogeochem. Cycles, 10, 23-41, 1996.

387 Maie, N., Boyer, J. N., Yang, C., and Jaffé, R.: Spatial, geomorphological, and seasonal
388 variability of CDOM in estuaries of the Florida Coastal Everglades, Hydrobiologia, 569, 135-
389 150, 2006.

390 Mantoura, R., and Woodward, E.: Conservative behaviour of riverine dissolved organic carbon
391 in the Severn Estuary: chemical and geochemical implications, Geochim. Cosmochim. Acta,
392 47, 1293-1309, 1983.

393 Markager, S., Stedmon, C. A., and Søndergaard, M.: Seasonal dynamics and conservative
394 mixing of dissolved organic matter in the temperate eutrophic estuary Horsens Fjord, Estuarine
395 Coastal Shelf Sci., 92, 376-388, 2011.

396 Mayer, L. M., Schick, L. L., and Loder, T. C.: Dissolved protein fluorescence in two Maine
397 estuaries, Mar. Chem., 64, 171-179, 1999.

398 Meybeck, M.: Carbon, nitrogen, and phosphorus transport by world rivers, Am. J. Sci, 282,
399 401-450, 1982.

400 Moran, M. A., Pomeroy, L. R., Sheppard, E. S., Atkinson, L. P., and Hodson, R. E.: Distribution
401 of terrestrially derived dissolved organic matter on the southeastern US continental shelf,
402 Limnol. Oceanogr., 36, 1134-1149, 1991.

403 Moyer, R. P., Powell, C. E., Gordon, D. J., Long, J. S., and Bliss, C. M.: Abundance, distribution,
404 and fluxes of dissolved organic carbon (DOC) in four small sub-tropical rivers of the Tampa
405 Bay Estuary (Florida, USA), Applied Geochemistry, 63, 550-562, 2015.

406 Panetta, R. J., Ibrahim, M., and Gélinas, Y.: Coupling a High-Temperature Catalytic Oxidation
407 Total Organic Carbon Analyzer to an Isotope Ratio Mass Spectrometer To Measure Natural-
408 Abundance δ13C-Dissolved Organic Carbon in Marine and Freshwater Samples, Anal. Chem.,
409 80, 5232-5239, 2008.

410 Qualls, R. G., Haines, B. L., and Swank, W. T.: Fluxes of dissolved organic nutrients and humic
411 substances in a deciduous forest, Ecology, 72, 254-266, 1991.

412 Raymond, P. A., and Bauer, J. E.: DOC cycling in a temperate estuary: a mass balance approach
413 using natural 14C and 13C isotopes, Limnol. Oceanogr., 46, 655-667, 2001.

414 Romera-Castillo, C., Sarmento, H., Álvarez-Salgado, X. A., Gasol, J. M., and Marrasé, C.: Net
415 production and consumption of fluorescent colored dissolved organic matter by natural
416 bacterial assemblages growing on marine phytoplankton exudates, Applied and environmental
417 microbiology, 77, 7490-7498, 2011.

418 Spiker, E.: The Behavior of C-14 and C-13 in Estuarine Water-Effects of Insitu Co2 Production
419 and Atmospheric Exchange, Radiocarbon, 22, 647-654, 1980.

420 Stedmon, C. A., Markager, S., Søndergaard, M., Vang, T., Laubel, A., Borch, N. H., and
421 Windelin, A.: Dissolved organic matter (DOM) export to a temperate estuary: seasonal
422 variations and implications of land use, Estuaries and Coasts, 29, 388-400, 2006.

423 Steinberg, D. K., Nelson, N. B., Carlson, C. A., and Prusak, A. C.: Production of chromophoric
424 dissolved organic matter (CDOM) in the open ocean by zooplankton and the colonial
425 cyanobacterium Trichodesmium spp, Mar. Ecol. Prog. Ser., 267, 45-56, 2004.

426 Vignudelli, S., Santinelli, C., Murru, E., Nannicini, L., and Seritti, A.: Distributions of
427 dissolved organic carbon (DOC) and chromophoric dissolved organic matter (CDOM) in
428 coastal waters of the northern Tyrrhenian Sea (Italy), Estuarine Coastal Shelf Sci., 60, 133-149,
429 2004.

430 Wang, X.-C., Chen, R. F., and Gardner, G. B.: Sources and transport of dissolved and
431 particulate organic carbon in the Mississippi River estuary and adjacent coastal waters of the
432 northern Gulf of Mexico, Mar. Chem., 89, 241-256, 2004.

433 Zepp, R. G., Sheldon, W. M., and Moran, M. A.: Dissolved organic fluorophores in

434 southeastern US coastal waters: correction method for eliminating Rayleigh and Raman
435 scattering peaks in excitation–emission matrices, Mar. Chem., 89, 15-36, 2004.

436 Zhang, Y., van Dijk, M. A., Liu, M., Zhu, G., and Qin, B.: The contribution of phytoplankton
437 degradation to chromophoric dissolved organic matter (CDOM) in eutrophic shallow lakes:
438 field and experimental evidence, water research, 43, 4685-4697, 2009.

439 Zhao, Z., Gonsior, M., Luek, J., Timko, S., Ianiri, H., Hertkorn, N., Schmitt-Kopplin, P., Fang,
440 X., Zeng, Q., and Jiao, N.: Picocyanobacteria and deep-ocean fluorescent dissolved organic
441 matter share similar optical properties, Nature Communications, 8, 2017.

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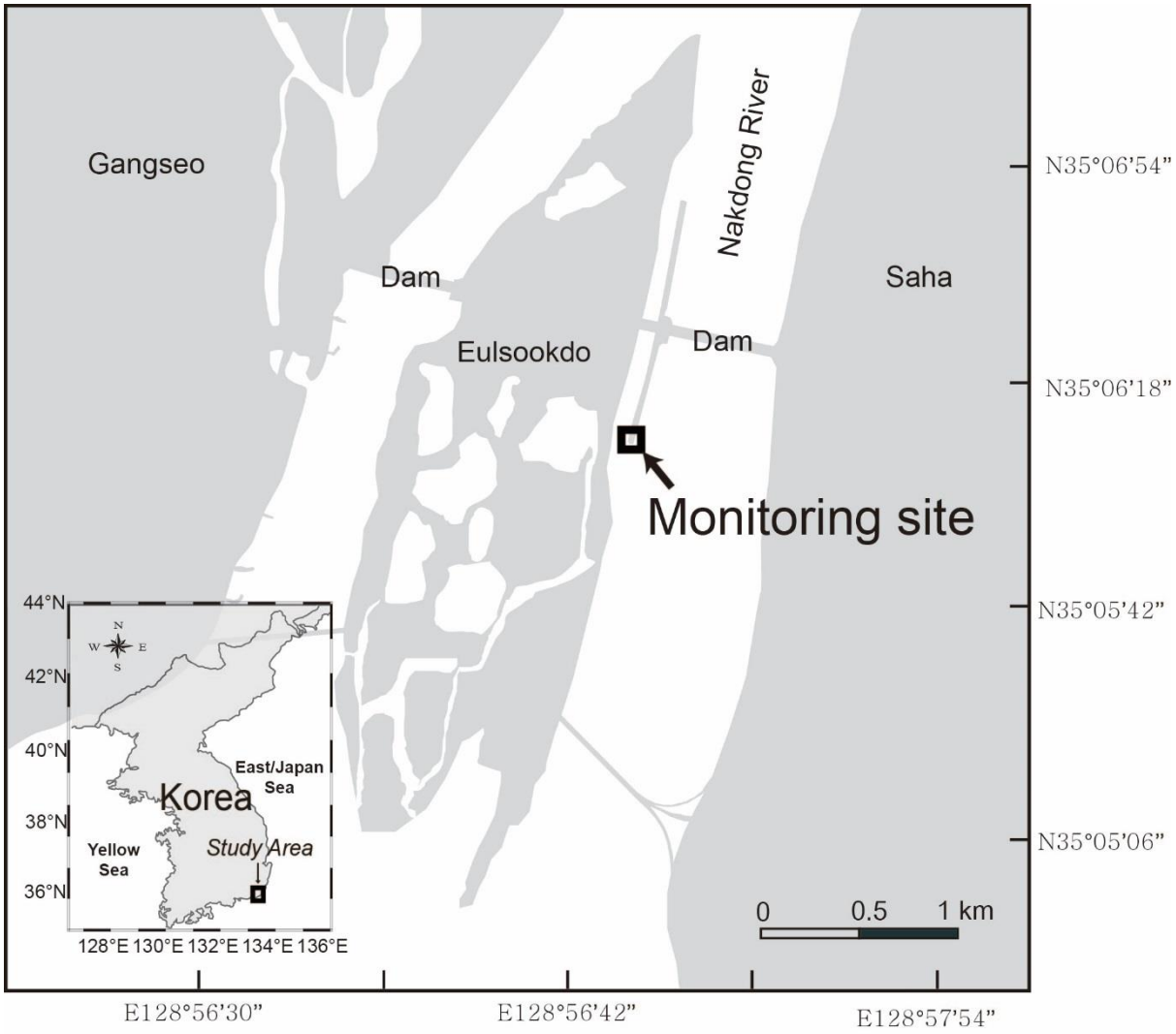


443

444 Figure 1. Map of the Nakdong-River Estuary. The square indicates a fixed monitoring site,

445 located 560 m downstream from the dam.

446

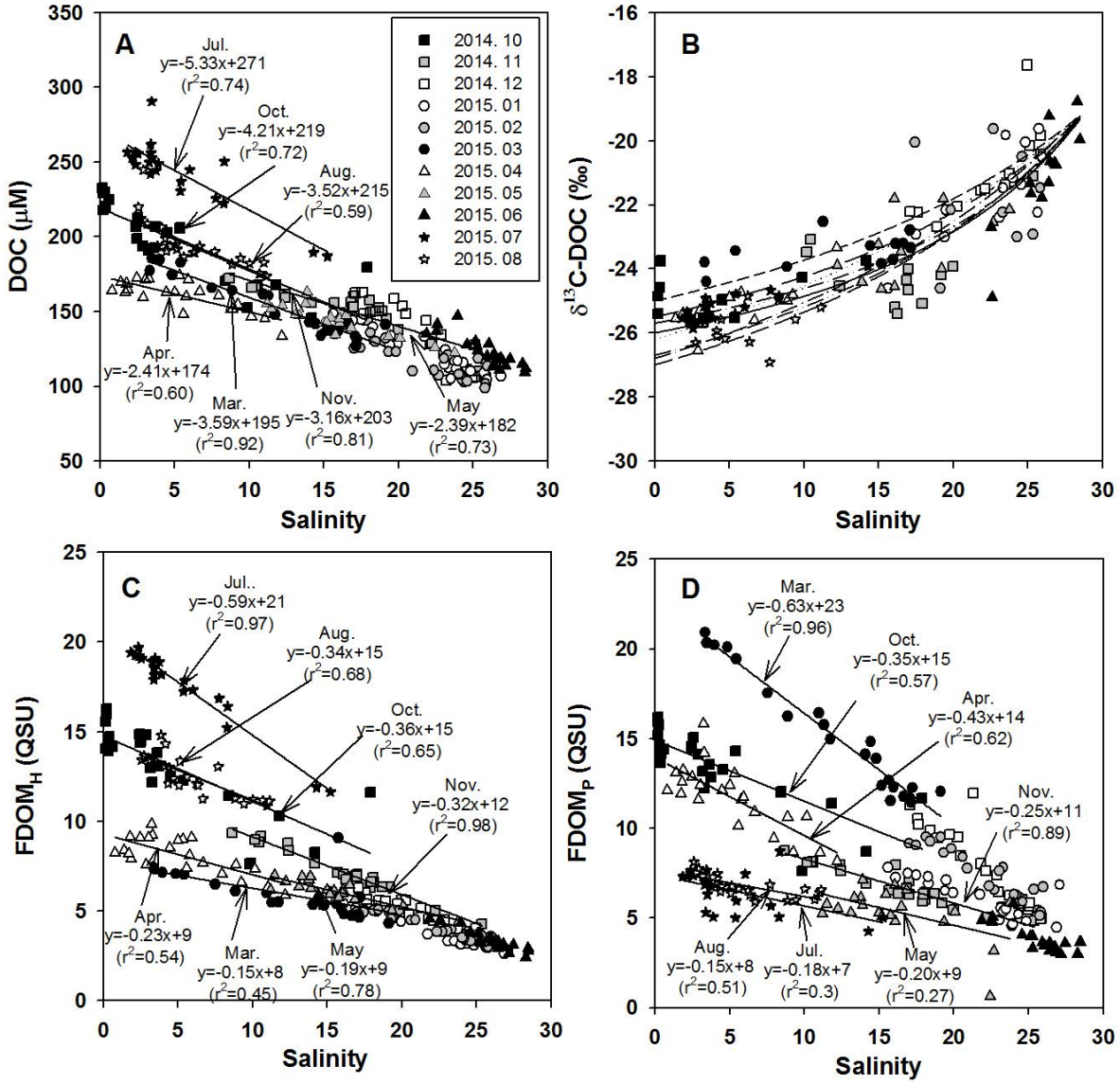
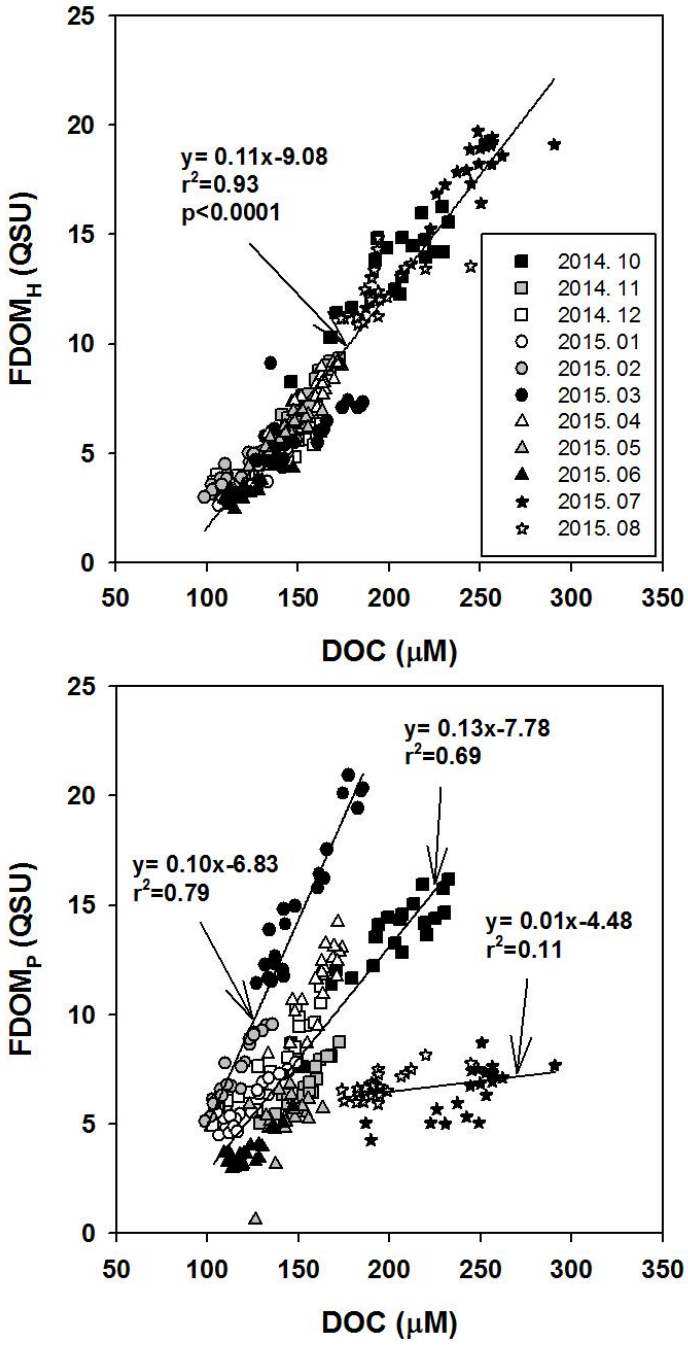


Figure 2. Salinities versus the concentrations of (A) DOC, (B) δ^{13}C-DOC, (C) $FDOM_H$, and (D) $FDOM_P$. The values for the regression lines are excluded for high-salinity periods (>20), including December, January, February, and June, which have large uncertainties in extrapolation. The solid curve (B) is the average conservative mixing line for the two endmember mixing equation. The dotted lines represent the monthly changes in mixing lines for the different monthly endmember values.



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455 Figure 3. The plots of the concentrations of DOC versus the concentrations of (A) $FDOM_H$ and

456 (B) $FDOM_P$.

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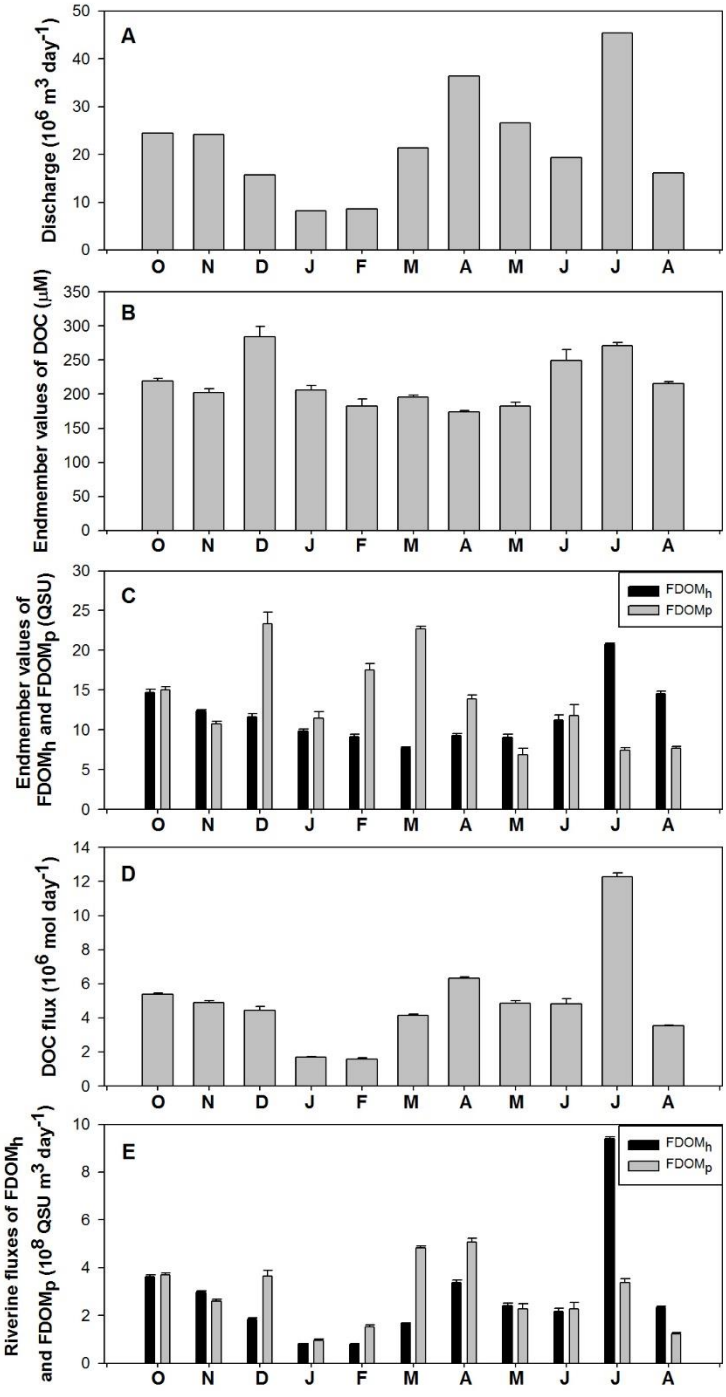

458

459 Figure 4. Temporal variations in discharge volumes, the endmember values of DOC, $FDOM_H$,

460 and $FDOM_P$, and riverine fluxes of DOC, $FDOM_H$, and $FDOM_P$ in the Nakdong-River Estuary

461 from October 2014 to August 2015.