Biogeosciences Discuss., https://doi.org/10.5194/bg-2017-339
Manuscript under review for journal Biogeosciences
Discussion started: 22 August 2017

Biogeosciences Discussions

Sources, fluxes, and behaviors of fluorescent dissolved organic matter (FDOM) in an estuarine mixing zone: Results from the Nakdong-River Estuary, Korea

Shin-Ah Lee[1] and Guebuem Kim[1]*

[1]School of Earth and Environmental Sciences/Research Institute of Oceanography, Seoul National University, Seoul 08826, Republic of Korea

*Corresponding author. Tel : +82-2-880-7508; Fax : +82-2-876-6508

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

Submitted to *Biogeosciences*

Biogeosciences Discuss., https://doi.org/10.5194/bg-2017-339
Manuscript under review for journal Biogeosciences
Discussion started: 22 August 2017

Abstract

We monitored seasonal variations of dissolved organic carbon (DOC), stable carbon isotope of DOC (δ^{13}C-DOC), and fluorescent DOM (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 September 2014 to August 2015. The concentrations of DOC and FDOM showed significant negative correlations against salinity (r=0.55-0.99), 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 (-25.3‰) 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, potentially due to higher fluvial production of humic-like FDOM. The slopes of protein-like FDOM against salinity, however, were 70-80% higher in spring, which could be 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 estuarine 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 (Coble, 2007). As FDOM accounts for 20 - 70% of DOC in coastal waters 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. Additionally, FDOM is known to be a powerful indicator of humic and protein-like substances (Coble, 2007). 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, the main sources of protein-like FDOM are biological production or 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 a 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 known to be 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 either 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 of DOC export from rivers to the ocean as high as 40% (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 as we can collect water samples of a wide range of salinity throughout tidal fluctuations. Using the data obtained from this unique station, we were able to determine (1) the behavior of DOM in the estuarine mixing zone, (2) the fluxes of DOM from rivers based on the slopes between salinity and DOM components, and (3) the changes of DOM sources using δ^{13}C-DOC in estuarine samples. The slope measurement in the mixing zone represents the endmember of DOM components in rivers better than site specific measurements in the river.

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 drinking, agricultural, and industrial supply water. The main channel of Nakdong River is approximately 510 km in length with an 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, with a depth 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, and stored in pre-combusted glass ampoules. 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.

2.3 Analytical methods

DOC concentration was 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 seawater reference samples for DOC (44-46 μmol L^{-1}) produced by the University of Miami, USA. They were consistent within 5%.

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 were 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 entirely 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 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 by low carbon water 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. Standard sample was analyzed at every sample queue (once before or after ten samples) to identify a drifting effect during 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 Deep-Sea Water Reference (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. Daily fresh distilled water backgrounds were subtracted 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. EEMs-PARAFAC analysis was performed using a MATLAB R2013a program with a DOMFluor toolbox. The analyses identified two main components in all the samples collected in this study (humic-like component: $FDOM_H$, protein-like component: $FDOM_P$).

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 primarily dependent on the volume of river water discharge from the dam. The volumes of river discharge were larger in October, April, July, and August. The mean annual surface water temperature was 16℃, with the lowest temperature (avg. 8℃) in December and the highest temperature in August (avg. 26℃).

3.1 Behavior 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 in February (avg. 115 μM), consistent with the typical DOC concentration ranges (Wang et al., 2004; Raymond and Bauer, 2001). The concentrations of DOC correlated significantly with salinity ($r = 0.78$-0.96, $p < 0.0001$), 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, the slope of DOC versus salinity was higher in July and lower in May, which could be due to higher terrestrial DOC loading in the summer monsoon period, as observed in Horsens Fjord, Denmark (Markager et al., 2011) (Fig. 2). To determine the source of DOC in fresh water, we plotted δ^{13}C-DOC values against salinity (Fig.

Biogeosciences Discuss., https://doi.org/10.5194/bg-2017-339
Manuscript under review for journal Biogeosciences
Discussion started: 22 August 2017

2B). Generally, δ^{13}C-DOC values range from −18 to −22‰ for marine phytoplankton, from −23‰ to −34‰ for terrestrial C3 plants, and from −16‰ to −10‰ for terrestrial C4 plants (Gearing 1988; Clark and Fritz, 1997). The carbon isotope values in our plot are well fitted with the conservative mixing curve of δ^{13}C value for the two end-member 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, and marine endmember salinity, respectively; F_r is the riverine freshwater fraction calculated from salinity; $[DOC]_s$, $[DOC]_r$, and $[DOC]_m$ are the DOC concentrations at a given salinity, the river, and marine end-members, respectively.

The curve fit shows that the end-member value of DOC and δ^{13}C-DOC approaches 270 µM and -26‰, respectively, for the riverine freshwater end-member (S=0‰) and 100 µM and -19‰, respectively for the marine end-member (S=29‰). These carbon isotope values confirm that the main source of DOC in the estuarine mixing zone is consistently from terrestrial C3 plants during all seasons.

3.2 Behavior and sources of FDOM in the estuarine mixing zone

The concentrations of $FDOM_H$ ranged from 2.4 to 19.7 quinine sulphate unit (QSU), with the highest concentrations in July (avg. 17.6 µM) and the lowest in June (avg. 3.4 µM)

(Fig. 2C). The concentrations of $FDOM_P$ ranged from 0.6 to 22.4, with the highest concentrations in March (avg. 15.1 QSU) followed by October (avg. 13.6 QSU) (Fig. 2D).

The concentrations of both FDOM were significantly correlated with salinity ($r = 0.73$-0.99, $p<0.0001$ for $FDOM_H$ and $r = 0.55$-0.98, $p<0.0001$ for $FDOM_P$), indicating that they are conservative in the mixing zone (Fig. 2). The monthly slopes of $FDOM_H$ and $FDOM_P$ ranged from -0.15 to -0.59 and -0.15 to -0.71, respectively. The higher $FDOM_H$ slopes in July and October are similar to the trend of DOC (Fig. 2C), however, the seasons (March, February 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).

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 sources of $FDOM_H$ and DOC are mainly from terrestrially-driven DOM based on $\delta^{13}C$-DOC values. As 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) demonstrate that stronger correlations are observed between DOC and FDOM, as humus substances derived from terrestrial DOM are more colored than *in situ* produced DOM. Generally, terrestrial DOM occurring in rivers mainly originates from plant decomposition and leaf litter in the form of humic substances (Huang and Chen, 2009). Thus, higher $FDOM_H$ slopes in October and November 2014, relative to the other periods, could be associated with higher terrestrial inputs of organic weathering products in the fall (Dowell, 1985; Qualls et al., 1991).

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

3.3 Fluxes of DOC and FDOM in the estuarine mixing zone

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

River discharge was highest in April and July following heavy precipitation, and the largest discharge volume was about five-fold higher than that of winter discharges (Fig. 4A). However, the monthly variations of DOC endmember (y-intercept) values were quite constant, ranging from 174 - 284 μM. This indicates that the concentrations of DOC in the river are independent of river discharge volumes (Fig. 4B). The DOC endmember values were the highest in December, followed by July and June (Fig. 4B). The monthly variation trend of $FDOM_H$ endmember values was similar to that of DOC, except December value, which has a large uncertainty owing to the narrow, high salinity range of the samples collected. Excluding December value, the $FDOM_P$ endmember values were highest in March, February, and October. These endmember trends are consistent with the slope variations explained in the previous section. Although these endmember values have large uncertainties for high salinity ranges in the winter, their contributions to the flux trend would be relatively small as discharge volumes were relatively small during these periods.

The riverine DOC flux ranged from 1.6×10^6 mol day^{-1} in February to 12.3×10^6 mol day^{-1} in July. The flux of DOC in July was about 8-fold larger than that in February, indicating that there are large variations of DOC fluxes to the ocean. 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 flux of $FDOM_H$ in July was about 12-fold larger than that in February. The fluxes of $FDOM_P$ in March and April were about 5-fold higher than those in February.

Biogeosciences Discuss., https://doi.org/10.5194/bg-2017-339
Manuscript under review for journal Biogeosciences
Discussion started: 22 August 2017

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 are largely biased, depending on sampling resolution. For example, summer data are extrapolated to annual river water discharge, the DOC and $FDOM_H$ fluxes can be overestimated up to 3 times.

4. Conclusions

Large seasonal variations in the slopes of DOC, $FDOM_H$, and $FDOM_P$ versus salinity were observed. The concentrations of $FDOM_H$ and DOC showed significant positive correlations with 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 salinity were higher in July, due to larger terrestrial DOC loading during the summer monsoon period. The carbon isotope values showed that the main source of DOC in the estuarine mixing zone is from terrestrial C3 plants over all seasons. The slopes of $FDOM_P$ versus salinity were relatively higher in March and April in association with spring phytoplankton blooms in this river. 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 these components 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).

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.

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

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

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

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

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

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

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

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

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

Biogeosciences Discuss., https://doi.org/10.5194/bg-2017-339
Manuscript under review for journal Biogeosciences
Discussion started: 22 August 2017

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

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

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

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

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

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

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

Markager, S., Stedmon, C. A., and Søndergaard, M.: Seasonal dynamics and conservative mixing of dissolved organic matter in the temperate eutrophic estuary Horsens Fjord, Estuarine

Coastal Shelf Sci., 92, 376-388, 2011.

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

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

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

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

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

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

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

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

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

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

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

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

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

Zepp, R. G., Sheldon, W. M., and Moran, M. A.: Dissolved organic fluorophores in southeastern US coastal waters: correction method for eliminating Rayleigh and Raman scattering peaks in excitation–emission matrices, Mar. Chem., 89, 15-36, 2004.

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

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

Biogeosciences Discuss., https://doi.org/10.5194/bg-2017-339
Manuscript under review for journal Biogeosciences
Discussion started: 22 August 2017

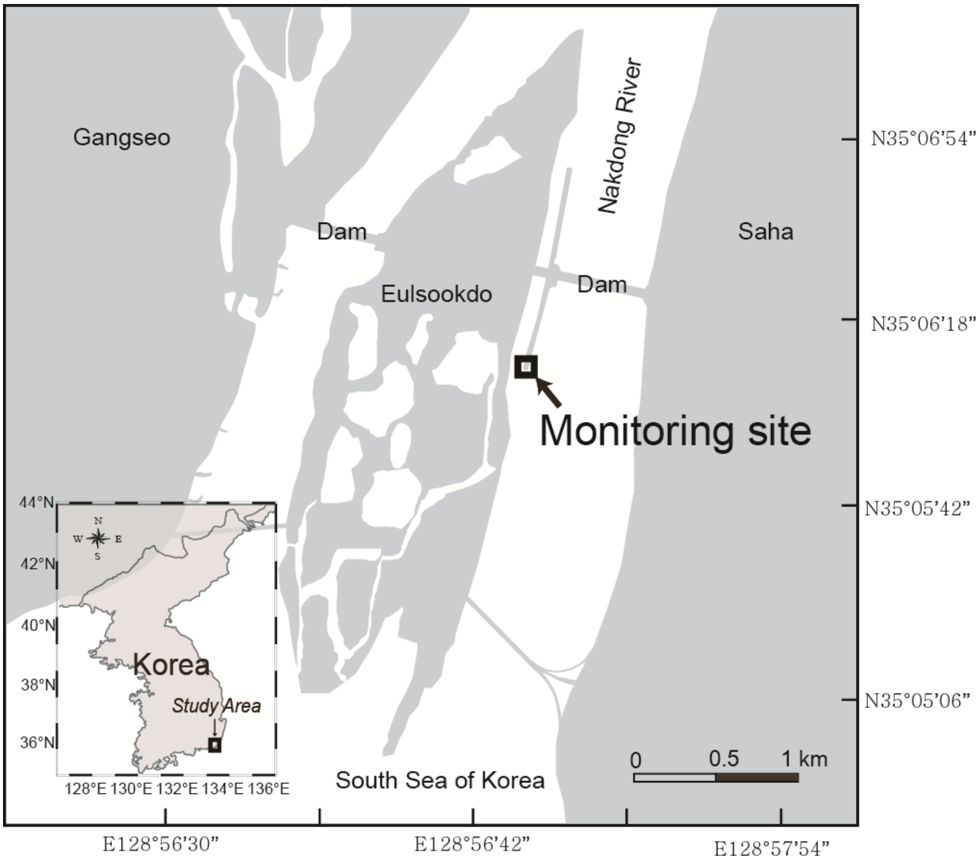


Figure 1 Map of Nakdong-River estuary. The square indicates a fixed monitoring site, located 560 m downstream from the dam.

Biogeosciences Discuss., https://doi.org/10.5194/bg-2017-339
Manuscript under review for journal Biogeosciences
Discussion started: 22 August 2017

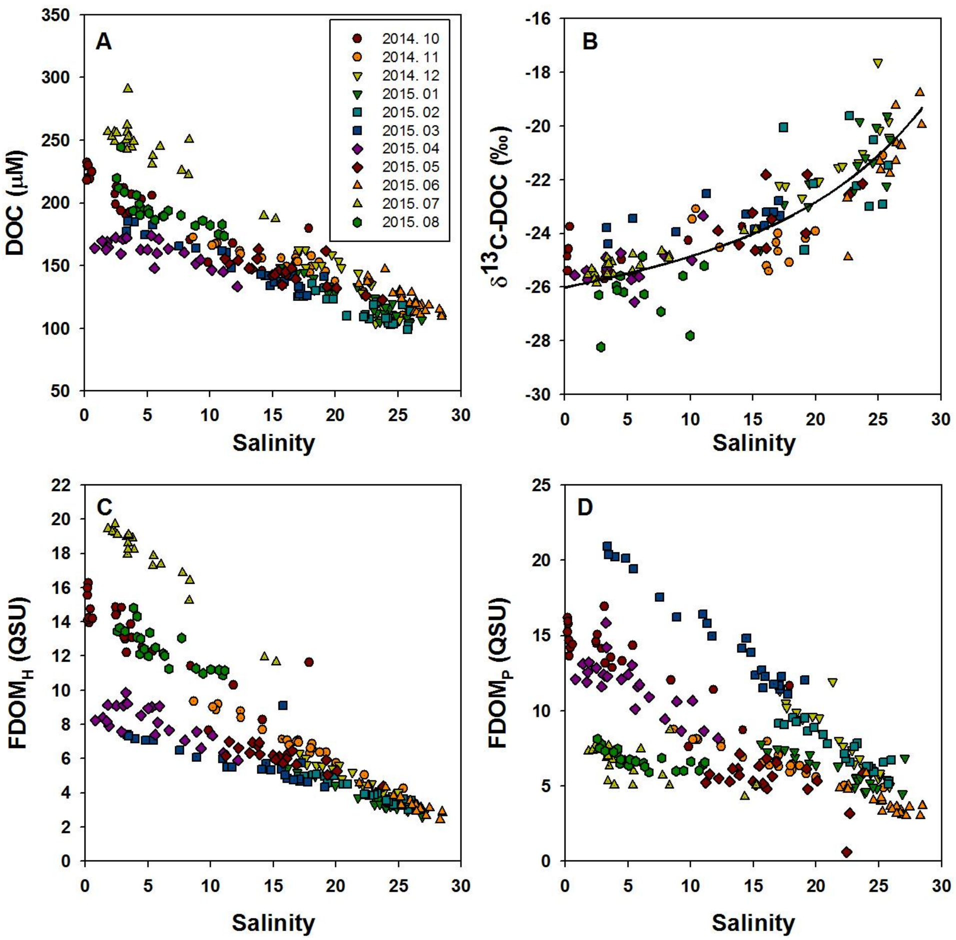
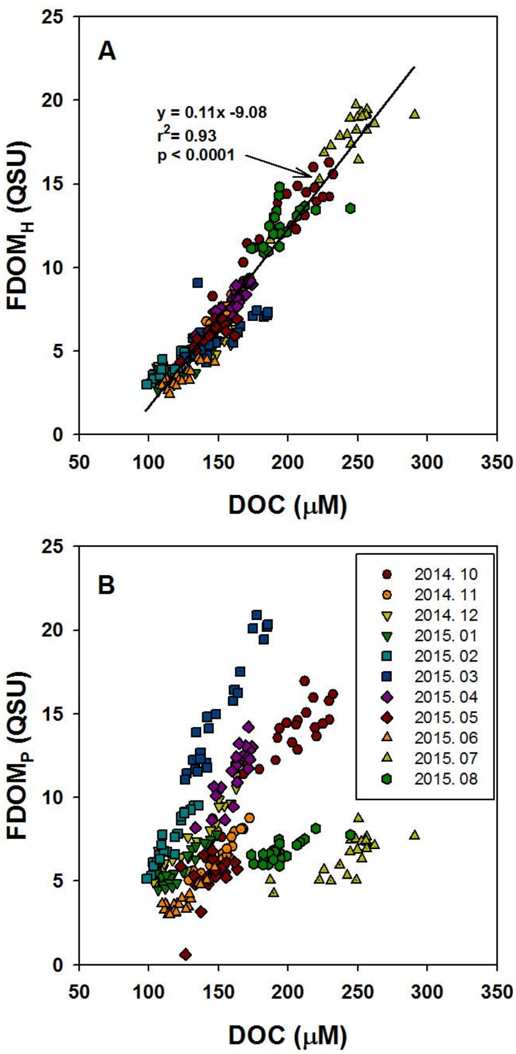


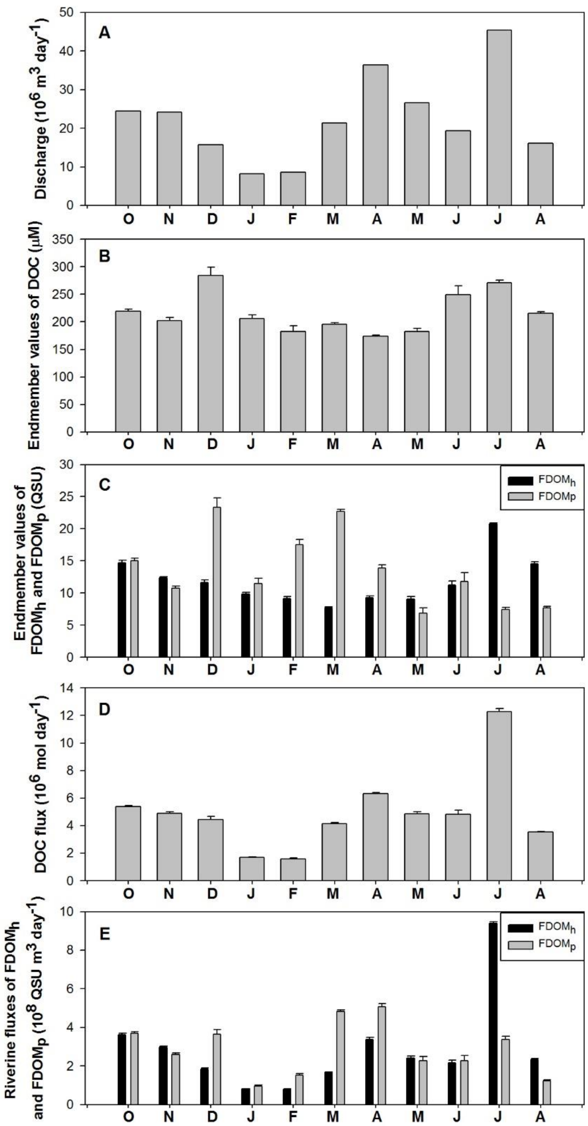
Figure 2 Salinity vs. (A) DOC, (B) δ^{13}C-DOC, (C) $FDOM_H$, and (D) $FDOM_P$. The solid curve (B) is conservative mixing line for two end-member mixing equation.



409

410 Figure 3 DOC vs. (A) $FDOM_H$, and (B) $FDOM_P$. Solid line (A) is regression line and the slope
411 and r^2 is shown.

412

413 

414 Figure 4 Temporal variations of discharge, endmember values of DOC, FDOM$_H$, and FDOM$_P$,

415 and riverine fluxes of DOC, FDOM$_H$, and FDOM$_P$ from October 2014 to August 2015.

416