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Temporal variation in riverine organic carbon concentrations and fluxes in two contrasting estuary systems: Geum and Seomjin, South Korea

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A R T I C L E I N F O

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A B S T R A C T

In this study, surface water samples were collected at sites located in the lowest reaches of closed (Geum) (i.e. with an estuary dam at the river mouth) and open (Seomjin) estuary systems between May 2016 and May 2018. We analyzed concentrations and stable isotopes of particulate organic carbon (POC) and dissolved organic carbon (DOC) to assess OC sources, to estimate fluxes of riverine OC, and to assess some of the factors driving OC exports in these two contrasting Korean estuary systems. Our geochemical results suggest that the contribution of the phytoplankton-derived POC to the total POC pool was larger in the Geum River than in the Seomjin River. Notably, a heavy riverine algae bloom occurred in the Geum River in August 2016, resulting in a high carbon isotopic composition (−19.4‰) together with low POC/PN ratio (< 10) and POC/Chl-*a* ratio (< 100). In contrast, potential DOC sources in both the Geum River and the Seomjin River were a mixture of C_3-derived forest soils and cropland organic matter. During the study period, the catchment area-normalized fluxes of POC and DOC were 0.40×10^{-3} tC/km^2/yr and 6.5×10^{-2} tC/km^2/yr in the Geum River and 5.2×10^{-4} tC/km^2/yr and 8.6×10^{-4} tC/km^2/yr in the Seomjin River, respectively. It appears that the POC flux was more weakly associated with the water discharge in the Geum River than in the Seomjin River, but the DOC fluxes were in general controlled by the water discharges in both rivers. Accordingly, the estuary dam of the Geum River might be one of the most strongly influencing factors on seasonal patterns in POC fluxes into the adjacent coastal seas, strongly modifying water residence times and thus biogeochemical processes.

1. Introduction

Estuary dams have been constructed in 228 estuaries in South Korea among the 463 estuary systems, including three (Nakdong, Yeongsan, and Geum) of the five major rivers (*plus* Han and Seomjin), for specific purposes such as land reclamation, flood prevention, freshwater supply, and recreation (Lee et al., 2011). The estuary dams hinder hydrological mixing between freshwater and seawater by blocking tidal flow; thus, the region upstream of an estuary dam is converted into a freshwater lake system (e.g. Jeong et al., 2014; Lee et al., 2009; Yoon et al., 2016). Such hydrological alterations cause physico-chemical changes in estuarine reservoirs such as thermal stratification and pollutant loadings, which result in changes to aquatic ecosystems (e.g. Jeong et al., 2014; Lee et al., 2009; Yang, 2014; Yoon et al., 2016). For instance, the phytoplankton size structure was changed in the Youngsan reservoir after the estuary dam construction in 1981, accompanied by a decline in fish diversity (Lee et al., 2009). Over the last 20 years, changes in fish assemblages also occurred in the Nakdong reservoir after the estuary dam construction in 1987 (Yoon et al., 2016).

Moreover, the construction of an estuary dam affects water quality due to slower water flow rates, increased water residence time and primary productivity, and heavy loading of anthropogenic constituents including nutrients and organic compounds in estuarine reservoirs (e.g. Jeong et al., 2014; Lee et al., 2009; Maavara et al., 2017; Tranvik et al., 2009). A number of efforts have been devoted to evaluating the effect of estuary dam construction on reservoir water quality in South Korea. For example, Seo et al. (2012) assessed water quality in the Nakdong estuary system using the Environmental Fluid Dynamics Code (EFDC) -

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Water Quality Analysis Simulation Program (WASP) modeling, which showed a significant change in water quality, with higher chlorophyll *a* (Chl-*a*) concentration, in the Nakdong reservoir. The concentrations of nutrients and organic matter were also higher in the reservoir than in the Nakdong estuary (Park et al., 2016). Similarly, the estuary dam construction in the Geum River in 1990 deteriorated water quality conditions with higher Chl-*a* and nutrients in the reservoir freshwater than in the estuarine seawater (Jeong et al., 2014). However, there is still a lack of studies characterizing organic matter in artificial lake environments, i.e. estuarine reservoirs created after blocking tidal flows in South Korea. Furthermore, most previous studies were based on a snapshot sampling strategy, and thus there is a lack of data on temporal variation.

In this study, we collected surface water samples from two contrasting Korean estuary systems, i.e. closed (Geum) and open (Seomjin) estuary systems from May 2016 to May 2018. We considered concentrations of particulate organic carbon (POC) and dissolved organic carbon (DOC) in combination with the stable carbon isotopic compositions. The aims of this study were 1) to assess the sources of OC that contribute to the POC and DOC pools, 2) to estimate the POC and DOC fluxes, and 3) to evaluate some of the factors driving riverine POC and DOC exports. Our results highlighted that the estuary dam of the Geum River influenced the sources and fluxes of riverine POC by increasing water residence time and thus facilitating phytoplankton production in the reservoir.

2. Material and methods

2.1. Study area

The Geum River and the Seomjin River are located in southwestern and southern Korea and discharge into the mid-eastern Yellow Sea and the South Sea of Korea (a northern extension of the East China Sea), respectively (Fig. 1). The southern part of Korea is located in the temperate climate region. The annual mean temperature is ~13 °C and the annual mean precipitation exceeds 1200 mm (http://www.weather.go.kr). Precipitation occurring from July to August accounts for over 50% of the total annual precipitation by the East Asian monsoon. The Geum River is impounded by an estuary dam, with a drainage area of 9914 km^2, a main stem length of 398 km, and a mean basin slope of 29.6%. Its basin was dominated by forest areas (62%) followed by agricultural (27%), city (6%), and wetland and water (5%) areas (Shin et al., 2016; Water Resources Management Information System (WAMIS); http://www.wamis.go.kr). The Geum estuary dam was built in 1990, blocking salinity diffusion to the upstream region and riverine freshwater release to the downstream region of the estuary. Riverine freshwater discharges into the estuary occur one to three times a week during the rainy season depending on the precipitation amount (Cho et al., 2016). The salinity maintains as 0‰ in the upper part of the estuary dam, but drastically increases up to 15.8 ± 7.1‰ after the estuary dam (Jeong et al., 2014). The concentration of NO_3^- also showed an abrupt change before and after the dam (2.05 ± 0.67 g/m^3 to 0.97 ± 0.6 g/m^3) as well as the phytoplankton concentration (36.7 ± 35.5 mg/m^3 to 7.6 ± 10.2 mg/m^3) (Jeong et al., 2014). In contrast, the Seomjin River does not have an estuary dam. Therefore, it shows a gradual change of salinity and other biogeochemical parameters such as pH, dissolved oxygen, nutrients, and Chl-*a*. The gradient of those biogeochemical parameters between the upper and lower parts of the estuary system is associated with the tidal cycles (Lee et al., 2018). The drainage area of the Seomjin River is 4914 km^2, and its main stem length and mean basin slope are 222 km and 33.7%, respectively. The basin is covered by 71% of forests, 22% of agricultural lands, 3% of city, and 4% of the wetland and water (Shin et al., 2016; WAMIS). Over 80% of the water discharge occurs during the wet season.

2.2. Sample collection

Surface water samples from the Geum River and the Seomjin River were collected every two to three months between May 2016 and May 2018 at sites near the last gauging station of the rivers, which are unaffected by seawater (Table 1). Surface water samples were taken directly into a high-density polyethylene carboy through Tygon tubing using an aspirator system. All the sampling tubes and bottles were cleaned with HCl and Milli-Q. About 0.1 to 2 L of water were filtered onto ashed (450 °C, 5 h) and pre-weighed 0.45-μm glass fiber filters (Macherey-Nagel, Dueren, Germany). Samples were collected replicate or triplicate. After filtration, the filters were brought to the lab, freeze-dried, and then weighed to calculate the concentration of total suspended matter (TSM). One part of each filter or filters collected separately were used for the elemental and stable isotope analysis. Filtrates were also sampled in 40-mL amber vials with $HgCl_2$ for the DOC concentration and stable isotope analysis.

2.3. Water hydrological and chemical parameters

Monthly precipitation data for the study areas were obtained from Korea Meteorological Administration (http://www.kma.go.kr). The river discharge and water quality of the sites were monitored by the

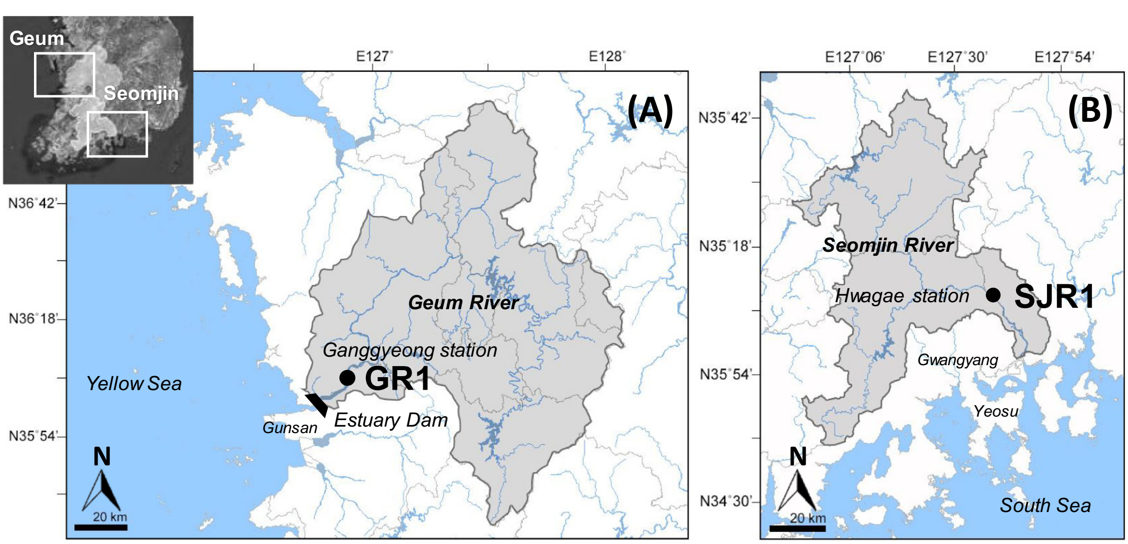

Fig. 1. Map showing the location of the sampling sites in (A) the Geum River and (B) the Seomjin River.

Table 1
Sample information and environmental parameters considered in this study.

Sampling site	Latitude	Longitude	Sampling date (YYYY-MM-DD)	Monthly precipitation (mm)	Water discharge (m^3/s)	Water temperature (°C)	pH	TN concentration (mg/L)	TP concentration (mg/L)	Chlorophyll *a* concentration (μg/L)	TSM concentration (mg/L)
GR1	N36° 5′56.00″	E126° 52′19.76″	2016-05-12	103	680	16.0	8.4	0.0	0.0	57.3	13.6 ± 4.7
			2016-08-17	10	257	31.6	9.9	1.5	0.2	178.2	30.3 ± 7.2
			2016-10-20	119	40	20.6	8.4	2.6	0.1	45.0	21.4
			2016-12-22	52	122	9.4	8.9	3.7	0.0	42.5	10.5 ± 3.9
			2017-03-06	8	49	11.5	9.3	4.3	0.1	72	14.6 ± 1.2
			2017-05-26	30	535	19.9	9.5	1.8	0.0	17.4	6.8 ± 1.7
			2017-08-01	179	117	31.6	8.7	3.1	0.1	22.1	18.6 ± 11.7
			2017-11-01	28	625	17.2	7.7	2.7	0.1	23.2	14.0 ± 1.8
			2017-12-13	47	204	3.4	8.2	4.1	0.1	90.4	13.4 ± 1.0
			2018-03-26	96	499	15.9	9.0	4.1	0.1	85.3	12.2
			2018-05-24	140	597	21.8	7.8	2.9	0.1	24.8	8.8 ± 0.7
SJR1	N35° 10′56.96″	E127° 37′28.56″	2016-05-19	126	37	23.4	6.9	1.8	0.1	2.4	6.0 ± 2.2
			2016-08-20	82	16	30.90	9.0	0.7	0.1	2.9	1.7 ± 0.7
			2016-10-18	147	352	16.39	7.5	1.7	0.1	2.7	7.9 ± 8.1
			2016-12-19	77	21	7.68	8.4	2.2	0.0	4	2.3 ± 0.1
			2017-03-09	16	26	4.83	7.4	2.3	0.0	4.7	1.9 ± 0.5
			2017-05-28	24	11	24.73	8.7	0.8	0.1	4.9	4.2 ± 1.4
			2017-08-04	301	26	26.2	7.2	1.1	0.1	2.8	1.9 ± 0.1
			2017-11-03	120	20	17.68	8.3	1.4	0.0	1.4	0.9 ± 0.1
			2017-12-11	21	16	5.36	7.9	2.3	0.0	6.4	2.0 ± 1.1
			2018-03-29	131.4	34	16.09	7.5	2.7	0.0	6.4	5.6
			2018-05-27	109.1	31	18.52	8.1	2.1	0.1	3.6	5.7 ± 3.3

Ministry of Environment Korea and the Ministry of Land, Infrastructure and Transport Korea. We obtained water discharge, total nitrogen (TN, mg/L), total phosphorus (TP, mg/L), and Chl-*a* (μg/L) data from the Water Environment Information System (http://water.nier.go.kr) and WAMIS. During the sampling campaigns, water parameters, including temperature (°C) and pH were also measured using a Hydrolab DS5 multi-parameter water quality sonde (OTT Hydromet, Kempten, Germany).

2.4. Carbon and nitrogen concentration and stable isotope analyses

The DOC concentrations were measured using a high-temperature combustion total organic carbon analyzer (TOC-V, Shimadzu, Kyoto, Japan) with an ASI-V auto-sampler. We checked the instrument blank using Milli-Q and used deep reference seawater (Dennis Hansell of Marine and Atmospheric Sciences, University of Miami) as a consensus reference material. Filtrate and filter samples were freeze-dried for determination of the concentration of POC and particulate nitrogen (PN) and the stable isotopes of DOC, POC, and PN. Inorganic carbon was removed using 1 M HCl for filtrate samples and 12 M HCl under the fume hood for filter samples. The POC and PN concentrations and the stable isotope ratios of DOC, POC, and PN were analyzed with an elemental analyzer combined with isotope ratio mass spectrometry at the Korea Polar Research Institute (Delta V, Thermo Fisher Scientific, Bremen, Germany) and Hanyang University (Isoprime, GV Instrument, Manchester, UK). The δ^{13}C and δ^{15}N were expressed by δ-notation relative to Vienna Pee-Dee Belemnite (VPDB) and Air, respectively. The concentrations of total organic carbon (TOC) were obtained as the sum of the POC and DOC concentrations.

2.5. Calculation of organic carbon fluxes

Fluxes of organic carbon in g C/s were calculated from the mean water discharge for each sampling day multiplied by the concentration of each sample using the following equation:

$$\text{Flux} = C \times Q \quad (1)$$

where C is the concentration of POC or DOC and Q is the mean water discharge (m^3/s). The TOC flux represents the sum of POC and DOC fluxes.

Annual mean POC and DOC fluxes in tC/yr for the study period were calculated according to Dolan et al. (1981). This method reduces the uncertainty of the sampling frequency when there is a large amount of water discharge data with relatively little concentration data (Dolan et al., 1981; Carey and Fulweiler, 2013; Ran et al., 2013). The calculation was conducted as follows:

$$\widetilde{\mu_y} = \mu_x \frac{m_y}{m_x}\left(\frac{1 + \frac{1}{n}\frac{S_{xy}}{m_x m_y}}{1 + \frac{1}{n}\frac{S_x^2}{m_x^2}}\right) \quad (2)$$

$$S_{xy} = \frac{1}{(n-1)}\sum_{i=1}^{n} x_i y_i - n m_x y_y \quad (3)$$

$$S_{x^2} = \frac{1}{(n-1)}\sum_{i=1}^{n} x_i^2 - n m_x^2 \quad (4)$$

where $\widetilde{\mu_y}$ is the estimated flux, μ_x is the mean water discharge over the entire study period, m_y is the mean flux for the days on which the concentrations were determined, m_x is the mean water discharge for the days on which the concentrations were determined, n is the number of samples, and x_i and y_i are the individual water discharge and flux measurements for each day when the concentration was measured. The POC and DOC fluxes in tC/km^2/yr were calculated by dividing the annual mean flux by the tributary area.

2.6. Statistical analysis

In order to determine the relationship among the different data sets, the Pearson test (R) was performed using IBM SPSS 21 (2011 SPSS Inc., IBM Corp., Armonk, New York, USA). Probabilities (*p*) were determined and a *p* value of < 0.05 was considered to be significant. In addition, the principal component analysis (PCA) was carried out in order to evaluate the relationships of the physicochemical variables with the variance of OC-related variables (concentration, flux, stable isotope value, and C/N ratio of POC and DOC) using R3.1.3 (R Core Team, 2015). The physicochemical variables used were as follows: water discharge (m^3/s), monthly precipitation (mm), water temperature (°C), pH, TN (mg/L), TP (mg/L), Chl-*a* (μg/L), and TSM (mg/L).

3. Results

3.1. Geum River

All data for the environmental parameters considered are presented in Table 1 and Supplementary Information Table A1. The water discharges varied between 39.8 m^3/s and 679.9 m^3/s during our survey period (Fig. 2A). The maximum monthly precipitation was 178.9 mm, in August 2017 (Fig. 2A). A seasonal trend of water temperatures (Fig. 2B) was observed, with the lowest temperature in December (6.4 ± 4.2 °C) and the highest one in August (31.6 ± 0.01 °C). The pH values were in the range of 7.7–9.9, with the highest value measured in August 2016 (Fig. 2B). The TN and TP concentrations varied between 0.003 mg/L and 4.3 mg/L and between 0.05 mg/L and 0.16 mg/L, respectively (Fig. 2C). The Chl-*a* concentrations widely varied, with the value of 17.4–178.2 μg/L. The TSM concentrations also showed a large variation with the range of 7.7–26.9 mg/L (Fig. 2D). The POC and DOC concentrations ranged from 0.64 mgC/L to 12.70 mgC/L and from 2.83 mgC/L to 5.25 mgC/L, respectively (Fig. 3A). The PN and DTN concentrations varied between 0.05 mgN/L and 0.18 mgN/L and between 0.03 mgN/L and 0.18 mgN/L, respectively. The average $\delta^{13}C_{POC}$ and $\delta^{13}C_{DOC}$ values were −27.2 ± 3.5‰ and –26.8 ± 0.8‰, respectively (Fig. 3B). The average $\delta^{15}N_{PN}$ was 9.0 ± 2.8‰. The POC and DOC fluxes were 772 gC/s and 1810 gC/s and 222 gC/s and 5747 gC/s, respectively (Fig. 3C).

3.2. Seomjin River

All data for the environmental parameters considered are presented in Table 1 and Supplementary Information Table A1. The water discharges during our survey period ranged from 13.7 m^3/s to 140.5 m^3/s, with peaks in October 2016 and August 2017 (Fig. 2A). Variation in the monthly precipitation data was similar to that of the water discharge data, with a range of 0–324 mm (Fig. 2A). The water temperatures were in the range of 4.8–30.9 °C, with the highest value in August 2016. A seasonal trend of water temperatures (Fig. 2B) was observed with the lowest temperature in December (6.5 ± 1.6 °C) and the highest one in August (28.6 ± 3.3 °C). The pH varied between 6.9 and 9.0 (Fig. 2B). The TN and TP concentrations ranged from 0.6 mg/L to 2.3 mg/L and from 0.03 mg/L to 0.1 mg/L, respectively (Fig. 2C). The Chl-*a* concentrations were 1.4–6.4 μg/L, while the TSM concentrations were 0.9–5.2 mg/L, with the maximum in May 2017 (Fig. 2D). The POC and DOC concentrations ranged from 0.1 mg C/L to 1.7 mg C/L and from 1.2 mgC/L to 2.4 mgC/L, respectively (Fig. 3A). The PN and DTN concentrations varied between 0.01 mgN/L and 0.23 mgN/L and between 0.58 mgN/L and 2.40 mgN/L. The average $\delta^{13}C_{POC}$ and $\delta^{13}C_{DOC}$ values were − 26.5 ± 1.4‰ and–25.3 ± 3.6‰, respectively (Fig. 3B). The average $\delta^{15}N_{PN}$ was 8.5 ± 1.6‰. The POC and DOC fluxes varied

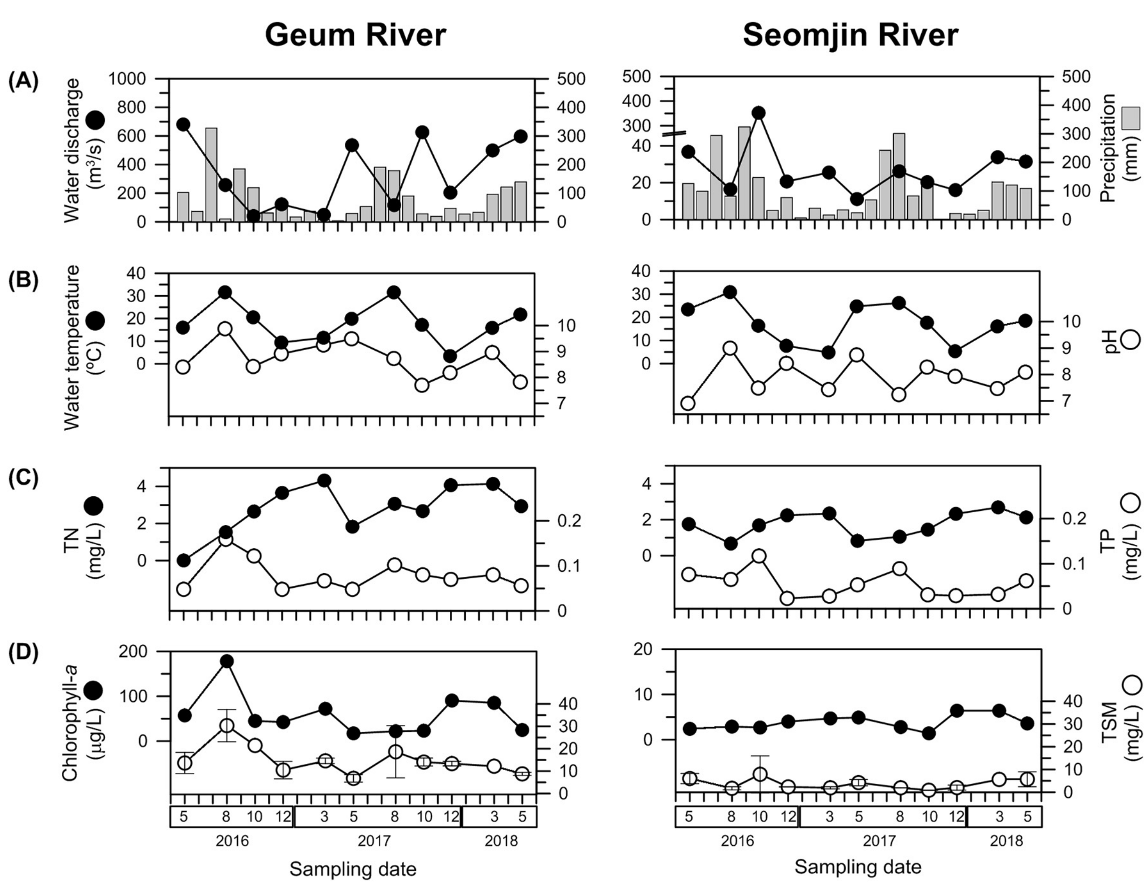

Fig. 2. Variation in hydrological and water parameters: (A) water discharges and monthly mean precipitations, (B) water temperature and pH, (C) TN and TP concentrations in mg/L, and (D) Chl-*a* and TSM concentrations in mg/L.

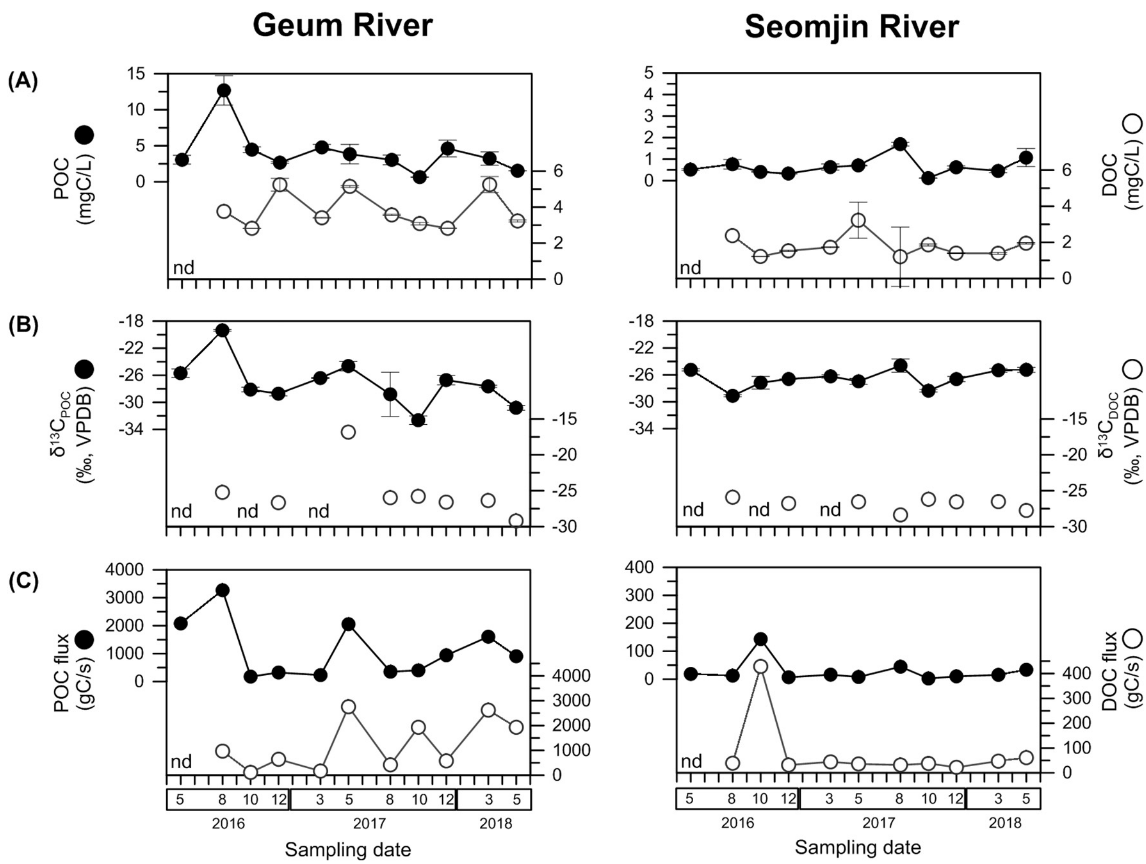

Fig. 3. Variation in (A) POC and DOC concentrations (mgC/L), (B) $\delta^{13}C_{POC}$ and $\delta^{13}C_{DOC}$ (‰), and (C) POC and DOC fluxes (gC/s) in the Geum River and the Seomjin River. "nd" denotes not determined.

between 11 gC/s and 139 gC/s and between 24 gC/s and 171 gC/s, respectively (Fig. 3C).

4. Discussion

4.1. Variation in POC and DOC sources

The POC concentrations in the Geum River showed a similar trend as the TSM concentrations (Figs. 2D and 3A), with a positive correlation ($R = 0.62$, $p = 0.04$, Fig. 4A) as has been observed in the world river datasets (e.g. Coynel et al., 2005; Ludwig and Probst, 1996; Meybeck, 1982; Meybeck and Ragu, 2012; Song et al., 2016). However, in the Seomjin River, this relationship was not apparent (R = –0.07, $p = 0.83$, Fig. 4A), which might be due to a very small range of TSM values. Notably, a relatively high concentration occurred in the Geum River in August 2016 (sample 1608), when a heavy riverine algae bloom was observed during the sampling campaign. The POC% calculated as POC/TSM × 100 was, however, similar in both rivers with average values of 26 ± 15% in the Geum River and 26 ± 24% in the Seomjin River (Fig. 4B). An exponentially decreasing POC% trend with increasing TSM concentrations has been observed in other world rivers (e.g. Balakrishna and Probst, 2005; Gao et al., 2000, 2002, 2007; Ludwig and Probst, 1996; Meybeck, 1982; Ran et al., 2013; Wu et al., 2013; Zhang et al., 2014). Low POC% with high TSM concentration has been observed in highly turbid rivers such as the Yellow River due to a dilution of riverine POC with mineral matter (e.g. Ludwig and Probst, 1996; Ran et al., 2013) (see Fig. 4B). On the other hand, high POC% with low TSM concentration has been considered to be mainly derived from phytoplankton production (Ludwig and Probst, 1996). In our study, relatively higher POC%, but low TSM concentrations, in the Geum River than in the Seomjin River thus hints higher contribution of phytoplankton-derived POC to the total POC pool in the Geum River. Supporting evidence can be found in a strong, positive relationship between POC and Chl-*a* concentrations in the Geum River ($R = 0.89$, $p < 0.0001$), although such a relationship was not observed in the Seomjin River (R = -0.01, $p = 0.98$). The average POC/Chl-*a* ratio, calculated based on concentrations, was lower in the Geum River (81 ± 55) than in the Seomjin River (195 ± 156, Fig. 5A). The POC/Chl-*a* ratios of 100 or less indicate a dominance of fresh phytoplankton in POC (e.g. Abril et al., 2002; Berg and Newell, 1986; Bianchi and Duan, 2006; Bouillon et al., 2010; Kang et al., 1999; Parsons, 1963; Tamooh et al., 2012; Yu et al., 2011; Zeitzschel, 1970). Accordingly, the POC/Chl-*a* ratio provides evidence that the contributions of the phytoplankton-derived POC to the total POC pool were higher in the Geum River than in the Seomjin River. The POC/PN ratios, calculated based on concentrations, were 5.6–15.7 in the Geum River and 7.4–17.1 in the Seomjin River (Table A1, Fig. 5B). The POC/PN of planktonic organic matter is < 10, while that of terrestrial organic matter is > 12 (e.g. Szczepańska et al., 2012; Wu et al., 2007). Thus, the POC/PN values in both rivers were less indicative of phytoplankton sources. Nonetheless, the POC/PN value of one of the Geum River samples (sample 1608) with the highest POC concentration (see Fig. 3A) and lower POC/Chl-*a* was < 10 (Fig. 5A), supporting that an in situ primary production was a principle source of POC for this sample. In contrast, positive correlations of the POC/PN ratio with the water discharge ($R = 0.69$, $p = 0.02$) and the POC/Chl-a ratio with the precipitation ($R = 0.75$, $p = 0.007$) in the Seomjin River indicated an increase in the proportion of allochthonous POC to the total POC pool. The $\delta^{13}C_{POC}$ values were similar in the Geum River (−27.2 ± 3.5‰) and the Seomjin River (−26.5 ± 1.4‰) (see Fig. 3B). These values are comparable with those reported in other Korean rivers such as the upper reaches of the Han River (−31.4 to −24.5‰; Kim et al., 2014), the Tamjin River (−26.1 to −24.9‰; Gal

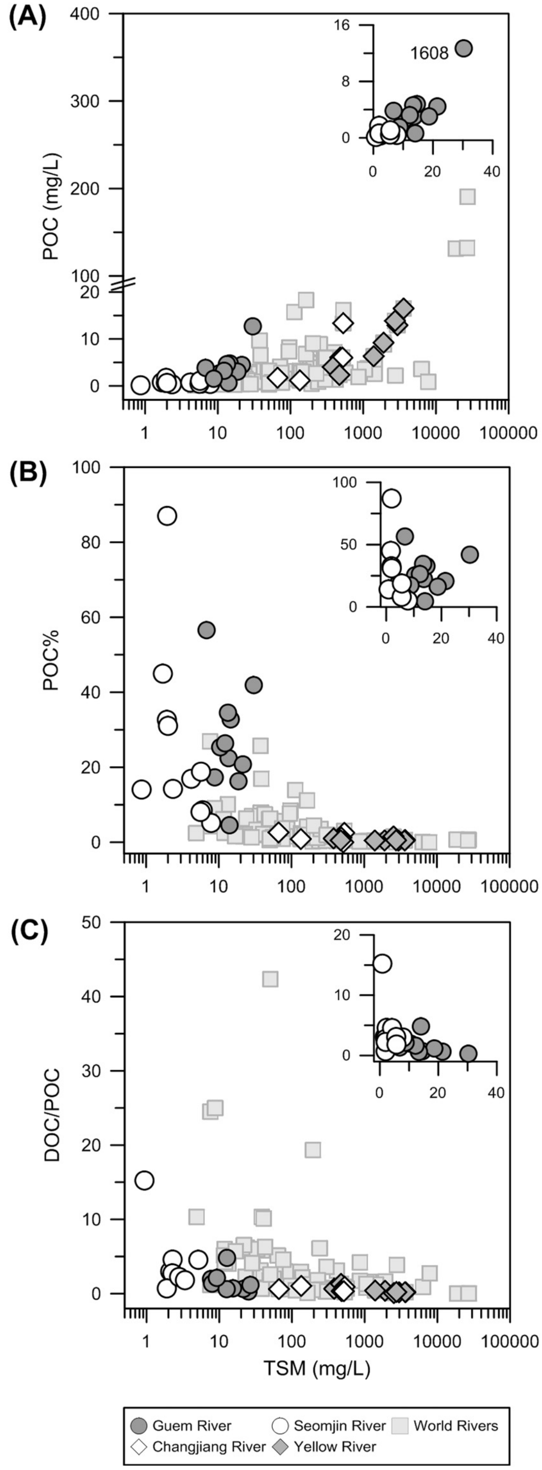

Fig. 4. Scatter plots of (A) POC in mg/L, (B) POC%, and (C) DOC/POC with TSM in mg/L from major rivers worldwide (data from Coynel et al., 2005; Liu et al., 2015; Ludwig and Probst, 1996; Meybeck and Ragu, 2012; Song et al., 2016 and references therein).

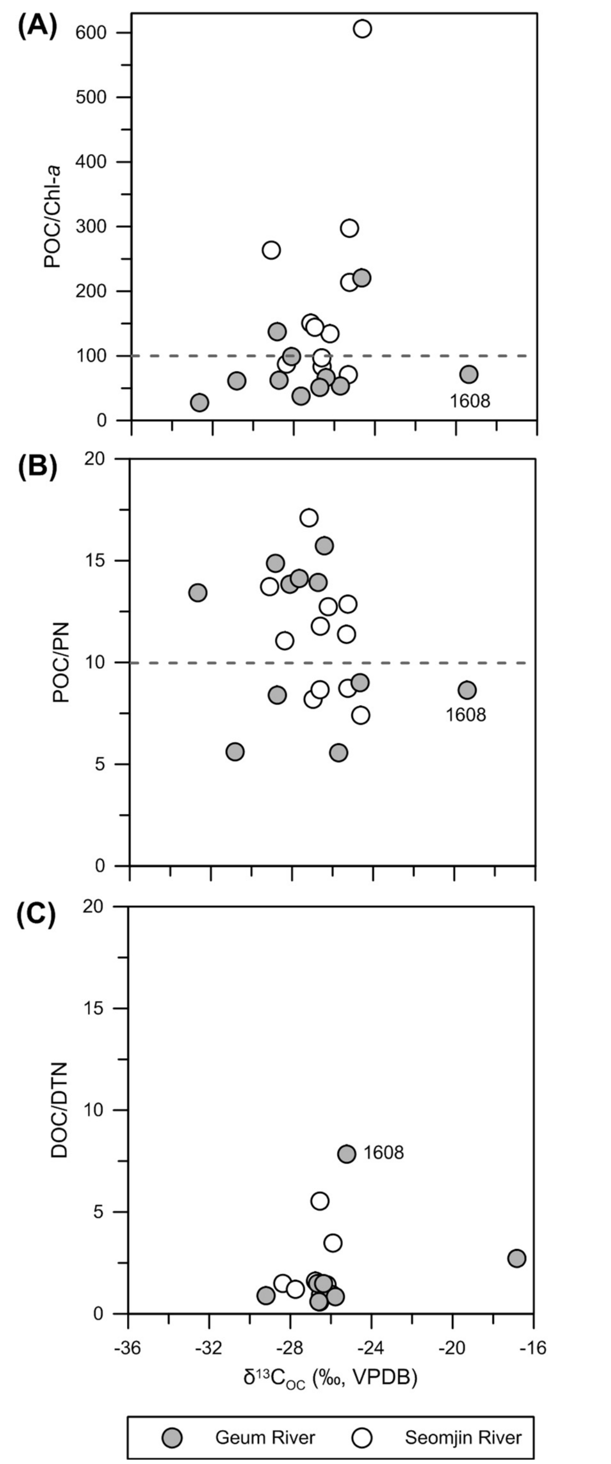

Fig. 5. Scatter plots of (A) POC/Chl-*a*, (B) POC/PN ratio, and (C) DOC/DTN ratio with $\delta^{13}C_{OC}$ of POC or DOC (‰).

et al., 2012; −31.1 to −21.9‰; Park et al., 2017), and the Yeongsan River (−31.1 to −13.3‰; Lee et al., 2013). In general, terrestrial C_3 plants, which use the Calvin pathway of carbon fixation, have $\delta^{13}C$ values of around −35 to −22‰, while terrestrial C_4 plants have high values between −16 and –9‰ (Marwick et al., 2015; Meyers, 1997; Peterson and Fry, 1987). The $\delta^{13}C$ values of riverine phytoplankton range widely, from −39 to −5.9‰, according to characteristics of the water environment such as CO_2 concentration and isotopic signature of DIC (Meyers, 1997; Vuorio et al., 2006; Wang et al., 2013; Zohary et al., 2010). Interestingly $\delta^{13}C_{POC}$ values showed significant and positive relationships with the POC concentration ($R = 0.90$, $p < 0.0001$) and the Chl-*a* concentration ($R = 0.77$, $p = 0.005$) in the Geum River. This indicates that the source of POC was mainly altered by the primary production in the Geum River. Moreover, the Geum River sample (sample 1608) collected during the algae bloom had a high $\delta^{13}C$ value of −19.4‰, distinctive from other samples from both rivers considered (Fig. 5). Freshwater algae in C_3-dominated environments tends to have

δ^{15}N values around 5‰ (Bănaru et al., 2007; Lamb et al., 2006 and references therein). Nitrogen fixing cyanobacteria such as *Anabaena* spp., *Aphanizomenon* spp. and G. *echinulate* have a relatively low δ^{15}N range which shows a similar value of atmospheric N_2 (i.e. 0‰) (Gu et al., 1996; Mino et al., 2002; Vuorio et al., 2006; Wada and Hattori, 1976). Hence, the $\delta^{15}N_{PN}$ value of the sample collected in the Geum River in August 2016 (11.2 ± 0.2‰, Table A1) suggests that nitrogen fixing cyanobacteria contributions seem to be insignificant to the total phytoplankton-derived POC. Supporting evidence can be found in a previous study (Han et al., 2016), which reported that the Chl-*a* concentration was the highest, when Bacillariophycea was more dominant than Cyanophyceae in the middle reaches of the Geum River during the summer (July to September) in 2014–2015. We speculate that distinctive processes altered temporal variations of POC sources in the Geum River and the Seomjin River. That is, the POC sources were more dependent on the primary production in the Geum River, while the hydrological dynamics was more important in the Seomjin River.

The DOC concentration trends were different from those of POC in both rivers (Fig. 3A), showing a weak relationship between the DOC and POC concentrations in the Geum River (R = –0.02, p = 0.95) and the Seomjin River (R = –0.05, p = 0.89). The main sources of DOC include decomposition of terrestrial organic matter (allochthonous), in situ production by aquatic plants and microbes (autochthonous), and anthropogenic activities such as fertilizer application, domestic sewage, and industrial wastewater disposal. Therefore, spatiotemporal variation of concentration and source composition is influenced by the basin land use and hydrology (e.g. Aitkenhead-Peterson and Mcdowell, 2000; Marwick et al., 2015; Sickman et al., 2007; Zhang et al., 2013). A high proportion of urban land uses exports high concentrations of DOC from point and non-point sources to the river system (e.g. Aitkenhead-Peterson et al., 2009; Aitkenhead-Peterson and McDowell, 2000). The proportion of the urban area in the Geum River (6%) is larger than in the Seomjin River (3%). Hence, the higher DOC concentration in the Geum River was possibly due to higher contribution of the urban anthropogenic-derived DOC than in the Seomjin River. In addition, the slope of the basin has a negative correlation with the DOC concentration because the short residence time of soil water can lower the DOC concentration in the river system (Shin et al., 2016). Therefore, the steeper basin slope in the Seomjin River (33.7%) than in the Geum River (29.6%) (Shin et al., 2016) might play a role in the lower DOC concentration in the Seomjin River than in the Geum River. The temporal variation of the DOC concentration in the Seomjin River also showed a possibility of the DOC source variation in this system. Relatively high DOC concentrations during the warm season than during the cold season in the Seomjin River (Fig. 2B) might be related to an increase in water discharge during the warm season, which increased inputs of DOC derived from terrestrial plants or soil into the river system. In general, the DOC/DTN ratios, calculated based on concentrations, in the Geum River (1.85 ± 2.1) and in the Seomjin River (1.86 ± 1.4) were lower than POC/PN ratios in both rivers (Figs. 5B, C). Furthermore, these DOC/DTN ratios were significantly lower than those reported for terrestrial refractory dissolved organic matter (29.6; Meybeck, 1982). The $\delta^{13}C_{DOC}$ is seasonally more variable in the Geum River than in the Seomjin River (Fig. 3C). The small variability of $\delta^{13}C_{DOC}$ values suggests relatively constant and homogeneous DOC sources. Previously, Kim et al. (2013) reported that $\delta^{13}C_{DOC}$ values differed according to the dominant land use in the North Han River in South Korea. The average $\delta^{13}C_{DOC}$ was −25.2 ± 0.5‰ in the agriculture-dominated watershed and − 27.3 ± 0.4‰ in the forest-dominated watershed. The average values of $\delta^{13}C_{DOC}$ in the Geum River (−26.82 ± 0.8‰) and the Seomjin River (−25.33 ± 3.6‰) thus lie between those of the agriculture- and forest-dominated watersheds, although basin-specific data are not available in the Geum River system. Typical woody terrestrial DOC has $\delta^{13}C_{DOC}$ signatures of −28‰ (Peterson and Fry, 1987). Thus, the $\delta^{13}C_{DOC}$ values from the Geum River and the Seomjin River were in the range of C_3 terrestrial plants. Therefore, potential DOC sources in the Geum River and the Seomjin River are possibly a mixture of C_3-derived forest soils and cropland organic matter.

4.2. Variation in POC and DOC concentrations and fluxes

The POC concentrations were on average 4.0 ± 3.1 mgC/L in the Geum River and 0.7 ± 0.4 mgC/L in the Seomjin River (see Table A1, Fig. 3A). These values were lower than those in the Yellow River (2–116 mgC/L, Hu et al., 2015) as well as in the Changjiang River (0.7–13.4 mgC/L, Liu et al., 2015; Ludwig and Probst, 1996), which are two of the largest rivers in the world, flowing into the Yellow Sea like the Geum River (Fig. 4A). They were also lower than the global mean value of 4.5 mgC/L reported by Perdue and Ritchie (2005). The DOC concentrations were on average 3.8 ± 1.0 mgC/L and 1.8 ± 0.6 mgC/L in the Geum River and the Seomjin River, respectively (see Table A1, Fig. 3A). The data from both Korean rivers are within the range of DOC concentrations in most non-contaminated rivers with relatively stable values of 1 to 10 mgC/L (Tao, 1998). They are also close to those of the Yellow River (1.6–3.3 mgC/L, Wang et al., 2012) and the Changjiang River (1.1–12.4 mgC/L, Ludwig and Probst, 1996; Song et al., 2016). However, the DOC concentrations in both rivers were lower than the mean concentration in other world rivers (5.7 ± 3.9 mgC/L; e.g. Ludwig and Probst, 1996; Meybeck and Ragu, 2012).

The POC and DOC fluxes during the study period (Table A1) were higher in the Geum River (on average 1122 ± 1007 gC/s and 1212 ± 1007 gC/s, respectively) than in the Seomjin River (on average 28 ± 40 gC/s and 78 ± 124 gC/s, respectively). The TOC (i.e. DOC + POC) fluxes were thus higher in the Geum River (289.7–4813.2 gC/s) than in the Seomjin River (32.3–571.8 gC/s). The estimated annual POC and DOC fluxes during the study period were 396.2 tC/yr and 645.4 tC/yr in the Geum River, and 0.25 tC/yr and 4.2 tC/yr in the Seomjin River, respectively. The resulting annual TOC fluxes were in the range of 1041.5 tC/yr in the Geum River and 4.5 tC/yr in the Seomjin River. The global annual mean POC and DOC fluxes are 0.06×10^6–18×10^6 tC/yr and 0.07×10^6 to 37.6×10^6 tC/yr (Coynel et al., 2005; Liu et al., 2015 and reference therein). Accordingly, the DOC and POC fluxes estimated from the Geum River and the Seomjin River lie in the lower limit of the global annual mean fluxes. The catchment area-normalized fluxes of POC and DOC were found to be 0.40×10^{-3} tC/km^2/yr and 6.5×10^{-2} tC/km^2/yr in the Geum River, respectively (Fig. 6). In the Seomjin River, the corresponding POC and DOC fluxes were 5.2×10^{-4} 0.00052 tC/km^2/yr and 8.6×10^{-4} tC/km^2/yr, respectively. The TOC fluxes were thus 1.1×10^{-1} tC/km^2/yr in the Geum River and 9.1×10^{-4} tC/km^2/yr in the Seomjin River. The ranges of POC and DOC fluxes in two Korean rivers are thus well within the range of POC (0.01–14.68 tC/km^2/yr) and DOC fluxes (0.04–7.95 tC/m^2/yr) reported for 99 catchments worldwide (Table A2, Coynel et al., 2005; Liu et al., 2015; Ludwig and Probst, 1996; Meybeck and Ragu, 2012; Song et al., 2016 and references therein). The POC and DOC fractions accounted for 38% and 62% of TOC exports, respectively, in the Geum River. In the Seomjin River, the POC fraction of TOC export (6%) was lower than that in the Geum River, but the DOC fraction of TOC export (94%) was higher.

4.3. Factors controlling riverine POC and DOC export

The TSM concentrations in rivers are mainly controlled by water discharge (e.g. Beusen et al., 2005; Bouchez et al., 2011; Håkanson et al., 2005; Rustomji et al., 2009; Wood, 1977). The nutrient levels including TN and TP would show similar trends to the TSM concentrations, since nutrients can be excessively supplied via riverine inputs (e.g. Beusen et al., 2005; Ittekkot and Laane, 1991; Ludwig and Probst, 1996). A stable environment with an enhanced supply of nutrients may then support excessive biological production (Li et al., 2014; Sin et al., 2015; Smith, 2003). Among nutrients, phosphorus

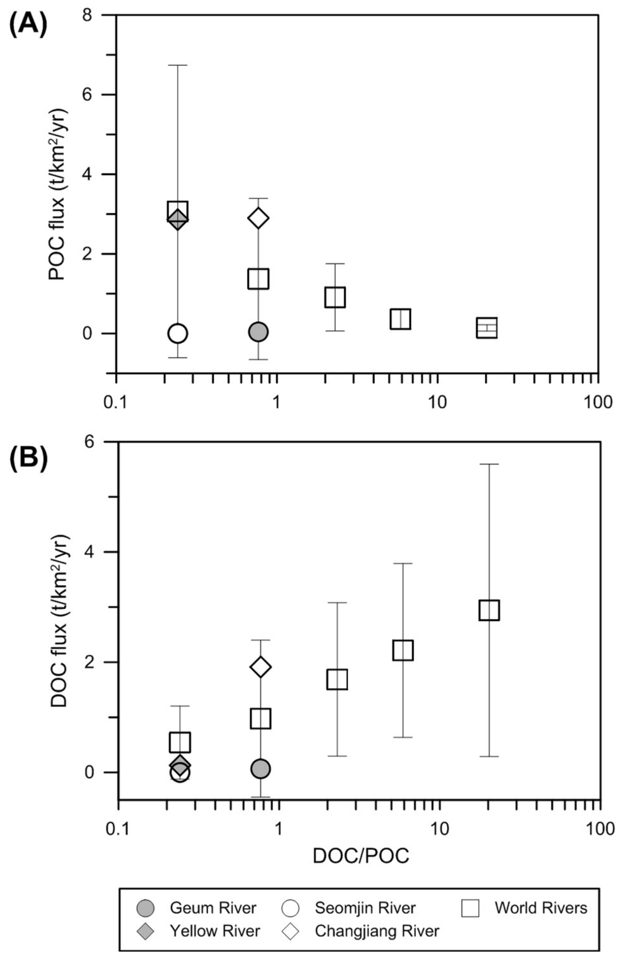

Fig. 6. Relationship between DOC/POC and (A) POC and (B) DOC fluxes (t/km^2/yr) for major world rivers (data from Coynel et al., 2005; Liu et al., 2015; Ludwig and Probst, 1996; Meybeck and Ragu, 2012; Song et al., 2016 and references therein). The bars indicate standard deviations at mean OC fluxes for samples with different DOC/POC ranges.

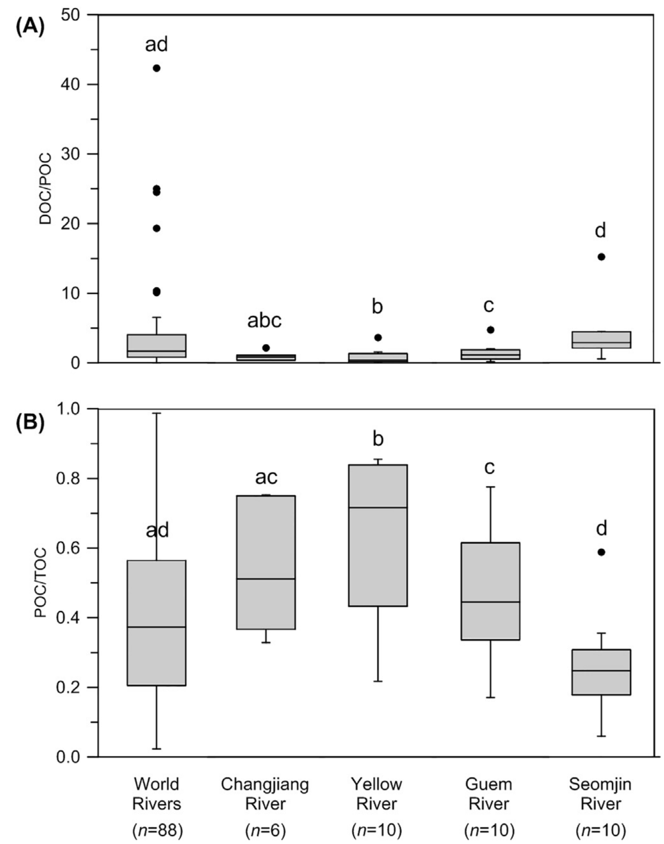

Fig. 7. Box plot of (A) DOC/POC and (B) POC/TOC from major rivers worldwide (data from Coynel et al., 2005; Liu et al., 2015; Ludwig and Probst, 1996; Meybeck and Ragu, 2012; Song et al., 2016 and references therein).

appears to be a major limiting factor for the phytoplankton growth in Korean rivers and reservoir systems (e.g. Hwang et al., 2003; Kim et al., 2003). In the Geum River, the TSM concentration showed a negative relationship with the water discharge (R = −0.43, p = 0.18). However, the TSM concentration showed a positive, significant correlation with the Chl-a concentration (R = 0.70, p = 0.02) and the TP concentration (R = 0.74, p < 0.01). In the Seomjin River, the TSM concentration had a positive relationship with the water discharge (R = 0.64, p < 0.05). In contrast to the Geum River, the TSM concentration did not have a strong, significant correlation with the Chl-a concentration (R = 0.03, p = 0.92) as well as other nutrients (R = 0.24 p = 0.49 for TN and R = 0.46, p = 0.16 for TP). Accordingly, our results suggest that the TSM concentrations in the Geum River were influenced by the in-situ phytoplankton production associated with an estuary dam construction while the water discharge was a more important factor in the Seomjin River.

Since the riverine OC is commonly derived from its drainage basin, OC concentrations generally co-vary with water discharge (Cai et al., 2016; Duan et al., 2007; Ni et al., 2008). During the study period, the POC concentrations did not, however, vary simultaneously with water discharge, showing weak, negative correlations in the Geum River (R = −0.35, p = 0.29) and in the Seomjin River (R = −0.19, p = 0.57). This differs from those observed in other river systems such as the Yellow River (Ran et al., 2013; Zhang et al., 2013) and the Changjiang River (Wu et al., 2007). The DOC concentrations also showed a weak relationship with water discharge in the Geum River (R = 0.22, p = 0.55) and in the Seomjin River (R = −0.36, p = 0.30). The general trend of decreasing DOC/POC ratios, calculated based on concentrations, with increasing TSM is typical for systems that are highly erosive and turbid (Fig. 4C; Bouillon et al., 2010; Ittekkot and Laane, 1991). The DOC/POC ratio thus reflects the environmental and hydrological characteristics of a river basin (Meybeck, 1982). The relationship between the DOC/POC ratios and the TSM concentrations in the Geum River and the Seomjin River were weak (Fig. 4C) and thus did not show a significant, negative relationship as shown in other world rivers (e.g. Le et al., 2017). The DOC/POC ratios of 1.5 ± 1.3 (n = 10) in the Geum River and 4.1 ± 4.1 (n = 10) in the Seomjin River (Fig. 7A) were close to the global mean value of 1.5 (Meybeck, 1982). However, these values were slightly higher than those of the Changjiang River (1.0; Wang et al., 2012) and the Yellow River (0.08–0.16; Hu et al., 2015; Ran et al., 2013). The low DOC/POC ratios were due to the high POC contribution from the erosion (Zhang et al., 2013). In contrast, the high concentration of DOC relative to POC (DOC/POC > 20) occurred in polluted rivers (Malcolm et al., 1976; Sickman et al., 2007). The watershed area of the Geum River is twice as large as that of the Seomjin River, and the urban area of the Geum River basin (6%) is also larger than that of the Seomjin River basin (3%) (WAMIS). The agricultural area occupies 27% in the Geum River basin while it is 22% in the Seomjin River basin (WAMIS). Therefore, DOC derived from anthropogenic activities should be potentially higher in the Geum River than in the Seomjin River, but the DOC/POC ratios were slightly lower in the Geum River than in the Seomjin River.

Interestingly, the ratio of POC to TOC (i.e. POC/TOC) was on average 0.52 ± 0.18 in the Geum River (Fig. 7B), with a maximum value of 0.77 in August 2016, when a phytoplankton bloom was observed. Lower POC/TOC values were reported in other large rivers, for example, the Amazon River (0.3; Coynel et al., 2005; Meybeck and Ragu, 2012; Wang et al., 2012; Xue et al., 2017) and the Mississippi River (0.3; Coynel et al., 2005; Liu et al., 2015; Ludwig and Probst, 1996; Wang et al., 2012; Xue et al., 2017). The mean POC/TOC value is around 0.2 in the world rivers (Zhang and Blomquist, 2018 and references therein). Thus, the POC/TOC value obtained from the Seomjin River (on average 0.27 ± 0.14) is closer to the world mean value than the Geum River. The mean POC/TOC value of the Geum River, however, was comparable to those of the Yellow River (0.8; Le et al., 2017; Liu et al., 2015; Song et al., 2016 and references therein) and the Changjiang River (0.5; Liu et al., 2015; Ludwig and Probst, 1996; Song et al., 2016 and references therein). High POC/TOC values also occurred in mountainous rivers in Taiwan (Kao and Liu, 1997). The higher POC concentrations during the rainy season can be attributed to the higher rainfall amounts and intensities that accelerate erosion and the leaching of organic carbon from soils in the basin (e.g. Ran et al., 2013; Zhang and Blomquist, 2018). Nonetheless, it should be noted that the nutrient loading in the Geum estuary reservoir increased after the estuary dam construction (Jeong et al., 2014). Therefore, during the warm season, the estuary reservoir has ideal conditions for primary production. Accordingly, higher POC/TOC values in the Geum River appear to be, at least partly, due to a phytoplankton bloom, leading to higher POC concentrations than in the Seomjin River, which has no estuary dam.

To further evaluate the relationships of the physicochemical variables with the variance of POC- and DOC-related variables, principal component analysis (PCA) was performed. In the Geum River, the first two principal components explained a cumulative variance of 60.1% (Fig. 8A). For the first principal component (PC1, explaining 34.6% of the variance), POC, Chl-*a*, $\delta^{13}C_{POC}$, DOC/DTN, water temperature, and pH were positively loaded with sample 1608, clearly distinguishing it from other samples. On the second principal component (PC2, explaining 23.7% of the variance), DOC, $\delta^{13}C_{DOC}$, DOC flux, and water discharge were positively loaded opposite to TSM, TP, TN POC/PN, and precipitation. Accordingly, water discharge was not the major driving factor for the POC flux but the DOC flux. Notably, sample 1608, which was collected during the warm season (August 2016), had the highest POC concentration (12.70 ± 2.0 mg/L) and $\delta^{13}C_{POC}$ value (−19.4 ± 0.1‰) among all the samples investigated. In line with these results, the highest Chl-*a* concentration of sample 1608 emphasized the fact that August of 2016 was dominated by POC originating from in-situ phytoplankton production. The impact of damming on river OC fluxes has been observed in several large Asian rivers, such as the Yellow River (e.g. Hu et al., 2015; Miao et al., 2010, 2011; Walling, 2006) and the Changjiang River (e.g. Wu et al., 2007). Damming rivers transforms aquatic ecosystems from a riverine type to a limnological type by altering hydrological conditions and material cycles (Baxter, 1977; Friedl and Wüest, 2002; Normile, 2010). Similarly, it has been reported that hydraulic residence times before the estuary dam construction was 2.00–2.14 days but increased up to 11.16–23.78 days afterwards in the Geum River (Yang, 2014). In addition, the Chl-*a* concentration increased > 1600% followed by an increase of the nutrient concentration and the TSM concentration decreased after the dam construction (Jeong et al., 2014; Yang, 2014). Accordingly, it appears that the estuary damming also mediates variations in the source and flux of POC in the Geum River. Nonetheless it should be also noted that PCA results without sample 1608 (data not shown) showed no relationship between the water discharge and the POC flux. It is thus probable that POC productions in two large dam reservoirs (Yongdam and Daecheong) and three weirs (Sejong, Gongju and Baekje weir) located in the upper and middle main stem of the Geum River (Ahn et al., 2002; Srivastava et al., 2015; Yu et al., 2015; Shim et al., 2018) would have influenced POC characteristics and fluxes in the downstream of the river, but further work is needed to test this connection. In the Seomjin River, the first two PCs explained most of the variance (28.4% for PC1 and 25.9% for PC2) of the PCA (Fig. 8B). The PCA results

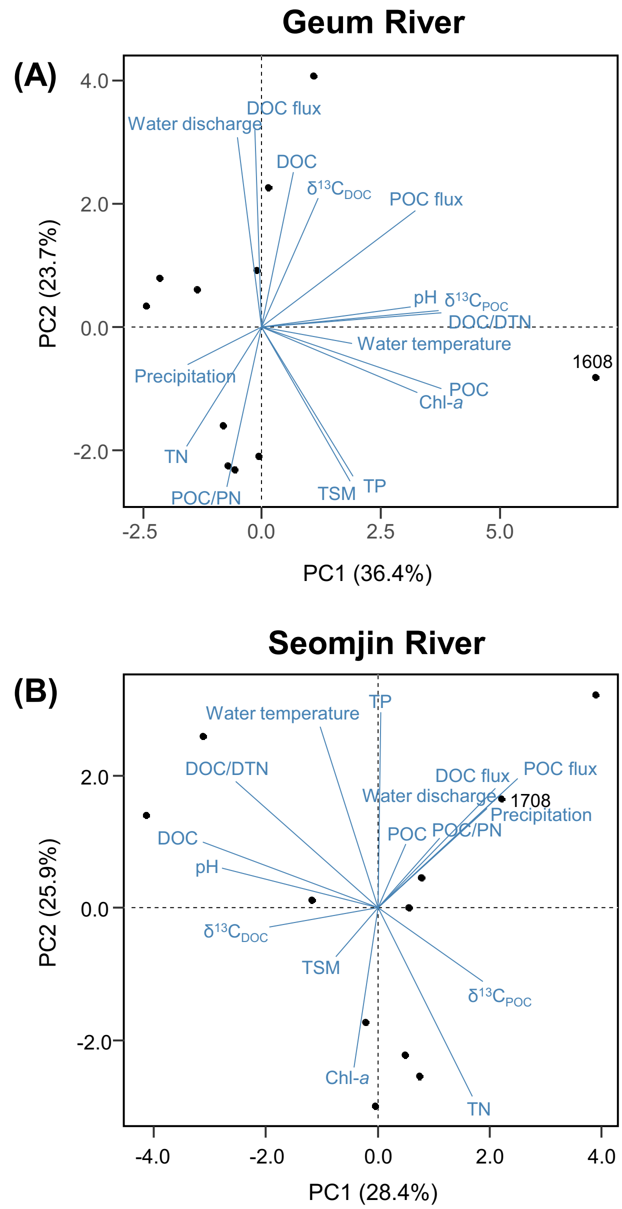

Fig. 8. PCA results based on physicochemical variables (water discharge (m^3/s), monthly precipitation (mm), water temperature (°C), pH, TN (mg/L), TP (mg/L), Chl-*a* (μg/L), and TSM (mg/L)) in each dataset from (A) Geum and (B) Seomjin River systems in comparison to OC parameters such as POC and DOC concentrations and fluxes, $\delta^{13}C_{POC}$, $\delta^{13}C_{DOC}$, POC/PN, and DOC/DTN.

showed that POC, POC flux, DOC flux, POC/PN, precipitation, and water discharge were closely loaded with sample 1708. In contrast to the Geum River, precipitation is positively related to water discharge and thus positively associated with POC and DOC fluxes. Hence, the water discharge was the major driving factor for the POC and DOC fluxes in the Seomjin River. Although other anthropogenic factors such as agricultural and urban land uses possibly impacted on POC and DOC fluxes in the Geum River and the Seomjin River, the TP concentration which was used as an index of eutrophication and as a major limiting factor for the phytoplankton growth showed an insignificant difference between both rivers during the study period (Mann-Whitney U value = 46.5, p = 0.37). Consequently, the estuary damming in the Geum River acts as a more influencing factor on seasonal patterns in POC flux into the adjacent coastal seas than in DOC flux, strongly modifying water residence times and thus biogeochemical processes.

5. Conclusion

We investigated surface water samples collected at sites located in the lowest reaches of the Geum River and the Seomjin River between May 2016 and May 2018. Our investigation of samples collected over a two-year period revealed insights into the sources of POC and DOC, POC and DOC fluxes, and some of the factors driving riverine POC and DOC exports in two contrasting Korean estuary systems. The freshwater phytoplankton production was the main contributor to POC during the hot summer in the Geum River, while its contribution to the total POC pool appears to be lower in the Seomjin River. However, a mixture of C_3-derived forest soils and cropland organic matter was the potential DOC source in both rivers. The catchment area-normalized fluxes of POC and DOC were 0.40×10^{-3} tC/km^2/yr and 6.5×10^{-2} tC/km^2/yr in the Geum River and 5.2×10^{-4} tC/km^2/yr and 8.6×10^{-4} tC/km^2/yr in the Seomjin River, respectively. The POC and DOC fluxes in both rivers were lower in comparison to the mean values of similar rivers worldwide. The POC fluxes in the Geum River were more weakly associated with the water discharges than in the Seomjin River. However, in general, the DOC fluxes were controlled by the water discharges in both rivers. The seasonal variation in POC concentration was greater in the Geum River than that in the Seomjin River because of the higher production of riverine algae in the Geum River. An extremely high POC concentration occurred in August 2016 in the Geum River due to a heavy algal bloom in the Geum reservoir, resulting in the highest POC flux during the study period. It also led to the proportion of POC to TOC being higher than those of most other rivers worldwide. Accordingly, our study showed that estuary damming affects the sources and fluxes of riverine POC by lowering the water flow rates, increasing residence time, and thus promoting primary productivity in the reservoirs. To the best of our knowledge, our study reports for the first time both POC and DOC fluxes and characteristics in two Korean major rivers. Hence, our study provides useful background information on coastal ecosystem managements and related studies.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envint.2019.105126.

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