Original article



Assessment of Organic Matter Sources in the Singil Stream Flowing into Lake Shihwa, South Korea

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Abstract The Singil Stream, flowing into an artificial lake, Lake Shihwa (South Korea), experiences a strong anthropogenic pressure with continuous organic matter (OM) inputs from rural, urban, and industrial areas. In this study, we investigated suspended particulate matter (SPM) and streambed sediments collected along the Singil Stream in 2014 and 2016, by applying a dual element approach (δ^{13} C and δ^{15} N) to identify OM sources. The SPM and streambed sediment samples from the industrial area showed higher organic carbon and nitrogen concentrations (or contents) than those from the other areas, with distinctively lower δ^{15} N values. Accordingly, our dual element approach indicates that the industrial area was the predominant OM source influencing OM quality and thus water quality of the Singil Stream flowing into Lake Shihwa during the study periods. However, further studies are necessary to better constrain OM sources in the Singil Stream since OM sources from the industrial area appear to be complex.

Key words: Lake Shihwa, Singil Stream, stable carbon isotope, stable nitrogen isotope

INTRODUCTION

Diverse human activities such as agricultural, residential, and industrial land uses near coastal areas can potentially modify the transfer of organic matter (OM) from terrestrial environments to aquatic ecosystems (McGinn, 1999; Crossland *et al.*, 2005; Park *et al.*, 2009; Lu *et al.*, 2014). Such anthropogenic pressures may thus influence the water quality of streams or rivers (Hudson *et al.*, 2007; Vidon *et al.*, 2008). Lake Shihwa is an artificial lake (surface area of 56.5 km², drainage basin of 476.5 km², total reservoir volume of 332 million tons) created by sea dike construction (12.7 km long) in January 1994. The initial purpose of Lake Shihwa was to serve as a fresh water resource for agricultural and industrial uses. However, the dike construction deteriorated the lake water quality since anthropogenic OM are continuously flowing into the lake through the Singil Stream (e.g. Khim *et al.*, 1999). The Singil Stream passes three different land-use types such as rural, urban, and industrial areas (Lee *et al.*, 2014; Hong *et al.*, 2019). Along the Singil Stream, the rural areas account for 57.6% of the watershed with 13.0%

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of the agriculturual areas (Ansan Green Environment Center, 2018). The urban and industrial areas account for 13.3% and 30.0% of the watershed, respectively. The industrial areas are mostly occupided by electric (36%) and mechanical (37.6%) industries. Hence, it is essential to disentangle relative contributions of OM from three different land-use types along the Singil Stream, and thus assess the effects of anthropogenic OM input on the ecosystem of Lake Shihwa.

Previous studies conducted in the Singil Stream focused on the quantification of chemical pollutants, such as nonylphenolic compounds, trace metals, etc. (Hong et al., 2010; Jeong et al., 2016, 2017). They showed that the continuous inflow of anthropogenic pollutants from surrounding large cities to streams, especially those located in industrial areas (such as the Singil Stream), aggravated the poor water quality of Lake Shihwa (Moon et al., 2012; Lee et al., 2014). However, there is still lack of data characterizing OM sources along the Singil Stream. The stable isotope analysis might be useful for characterizing the OM, and thus distinguishing its sources (e.g. Grey et al., 2001; Derrien et al., 2018). For instance, δ^{13} C and δ^{15} N compositions have been widely used to elucidate the source of OM in various environments (e.g. Fry and Sherr. 1984: Maksymowska et al., 2000: Cloern et al., 2002: Goni et al., 2003). Furthermore, C/N ratios have been used as a tracer to separate the source of OM in aquatic environments (e.g. Thornton et al., 1994).

In this study, we aim to disentangle relative contributions of OM from rural, urban, and industrial areas along the Singil Stream from upstream to downstream. For this purpose, we analyzed concentrations (or contents) and stable isotopes of carbon and nitrogen for suspended particulate matter (SPM), as well as for streambed sediments collected along the Singil Stream. Relative contributions of OM to the total OM pool were estimated at the sampling site located closest to Lake Shihwa by applying the IsoSource mixing model with three end-members.

MATERIALS AND METHODS

1. Study area

Lake Shihwa is known as one of the most polluted coastal areas in South Korea. Several streams from surrounding industrial areas are flowing into Lake Shihwa. Among them, the Singil Stream with a length of 6.09 km and a drainage area of 8.75 km^2 is the major channel for supplying OM into Lake Shihwa. Notably, the Singil Stream passes both rural and urban areas in upstream and the crucial industrial complex in downstream (Lee *et al.*, 2014; Hong *et al.*, 2019). In general, more than 50% of the annual rainfall is concentrated for the summer season. Thus, heavy rainfalls in summer are important events delivering a large amount of various substances from lands to the streams, and further into the coastal areas (e.g. Lee *et al.*, 2017; Hong *et al.*, 2019).

2. Sample collection

We collected SPM and streambed sediments from rural (SG1), urban (SG2 and SG3), and industrial areas (SG4~SG9) in May 2014 and in August 2016 (Table 1, Fig. 1). Notably, the samples in 2016 were taken just after a heavy rainfall. It should also be noted that the SPM samples would well capture a feature occurring at the sampling point, while the sediments would be more representative of longer-term integrated characteristics. All the streambed sediments were collected at the depth of $0 \sim 0.5$ cm. We additionally collected SPM samples from two sewer outlets (SG7' and SG8') located in the lower part of the industrial area in August 2016. The surface sediments were taken into pre-combusted (4 h at 450°C) glass jars using a stainless spatula. The SPM samples were obtained by filtering surface water ($10 \sim 300 \text{ mL}$) using a pre-combusted (4 h at 450°C) Whatman GF/F filter. All samples were immediately frozen using dry ice. Upon delivery to the laboratory, all samples were freeze-dried at - 80°C. Sediment samples (ca. 1 g) were homogenized prior to bulk elemental analyses.

3. Bulk elemental analysis

Analyses for SPM and surface sediments were performed at the University of Hanyang (South Korea). For the analyses of particulate organic carbon (POC) and total organic carbon (TOC), inorganic carbon was removed using 12 M HCl and 1 M HCl solutions, respectively, while particulate nitrogen (PN) and total nitrogen (TN) were analyzed using the bulk material (Kim *et al.*, 2016). The analyses were performed using an elemental analyzer (EuroEA3028, EuroVector, Milan, Italy) interfaced with an isotope ratio mass spectrometer (Isoprime 100, GV Instruments, UK). All the samples were calibrated to the internal standards CH6 (C = 42.1 wt.%, δ^{13} C = -10.44%) and N1 (N = 21.4 wt.%, δ^{15} N = 0.4‰), which are

Table 1. S	ample informa	tion and results ol	btained from this	s study.							
Sample name	Sample type	Sampling area	Latitude	Longitude	Sampling year	Sampling month	POC or TOC (mg L^{-1} or wt.%)	PN or TN (mg L^{-1} or wt.%)	C/N ratios	δ ¹³ C (%o VPDB)	δ ¹⁵ N (% Air)
SG 1	SPM	Rural	37°20.345′	126°47.305'	2014	May	0.8	0.1	7.8	- 25.1	5.1
SG 2	SPM	Urban	37°20.207′	126°47.172′	2014	May	0.8	0.1	5.2	- 24.9	7.3
SG 3	SPM	Urban	37°19.502'	126°47.710′	2014	May	0.6	0.1	8.0	- 28.9	10.4
SG 6	SPM	Industrial	37°19.334'	126°45.242'	2014	May	12.1	2.5	4.9	-23.9	-2.2
SG 7	SPM	Industrial	37°19.290'	126°45.460′	2014	May	3.0	0.6	4.8	- 24.9	-3.5
SG 8	SPM	Industrial	37°19.111′	126°44.571'	2014	May	4.0	1.1	3.7	- 23.8	-3.4
6 DS	SPM	Industrial	37°18.189′	126°44.536′	2014	May	1.9	0.2	9.8	- 26.6	-3.1
SG 1	SPM	Rural	37°20.345′	126°47.305′	2016	Aug.	2.4	0.4	6.0	- 24.9	3.5
SG 2	SPM	Urban	37°20.207′	126°47.172′	2016	Aug.	1.9	0.1	19.0	- 29.5	2.3
SG 3	SPM	Urban	37°19.502'	126°47.719′	2016	Aug.	1.0	0.1	10.0	- 29.3	10.2
SG 4	SPM	Industrial	37°19.369′	126°47.664′	2016	Aug.	10.9	2.8	3.9	- 25.3	-1.2
SG 5	SPM	Industrial	37°19.357′	126°46.413′	2016	Aug.	11.2	3.0	3.7	-25.1	- 2.3
SG 6	SPM	Industrial	37°19.334′	126°45.242'	2016	Aug.	8.1	1.7	4.8	- 24.5	- 3.5
SG 7	SPM	Industrial	37°19.280'	126°45.460′	2016	Aug.	5.8	0.8	7.3	-26.5	- 3.4
SG 8	SPM	Industrial	37°19.111′	126°44.571′	2016	Aug.	6.2	1.0	6.2	- 27.5	- 3.6
8G 9	SPM	Industrial	37°18.189′	126°44.536′	2016	Aug.	4.8	0.8	6.0	- 29.9	- 8.1
SG 7'	SPM	Sewer Outlet	37°19.280'	126°45.460′	2016	Aug.	4.3	0.7	6.0	- 24.8	- 2.1
SG 8′	SPM	Sewer Outlet	37°19.111′	126°44.571′	2016	Aug.	6.0	1.0	5.8	- 21.6	- 4.3
SG 1	Sediment	Rural	37°20.345′	126°47.305'	2014	May	5.2	0.4	13.3	- 26.5	6.9
SG 2	Sediment	Urban	37°20.207′	126°47.172′	2014	May	3.8	0.6	6.1	- 24.9	9.2
SG 3	Sediment	Urban	37°19.502'	126°47.710'	2014	May	10.1	0.6	16.4	-25.8	7.9
9 DS	Sediment	Industrial	37°19.334′	126°45.242'	2014	May	3.3	1.2	2.8	-24.1	0.3
2G 7	Sediment	Industrial	37°19.280'	126°45.460′	2014	May	42.4	3.7	11.4	-25.2	- 1.7
SG 8	Sediment	Industrial	37°19.111′	126°44.571'	2014	May	18.1	1.3	14.4	-25.8	1.7
6 DS	Sediment	Industrial	37°18.189′	126°44.536′	2014	May	28.5	4.7	6.1	- 26.3	- 2.5
SG 1	Sediment	Rural	37°20.345′	126°47.305'	2016	Aug.	14.0	1.4	9.7	- 25.8	1.7
SG 2	Sediment	Urban	37°20.207′	126°47.172′	2016	Aug.	3.0	0.2	15.6	- 27.8	4.9
SG 3	Sediment	Urban	37°19.502′	126°47.719′	2016	Aug.	7.9	0.6	12.5	- 28.9	9.9
SG 4	Sediment	Industrial	37°19.369′	126°47.664′	2016	Aug.	32.1	3.0	10.6	-26.4	- 1.9
SG 5	Sediment	Industrial	37°19.357′	126°46.413′	2016	Aug.	33.3	3.2	10.4	-26.3	- 1.2
SG 6	Sediment	Industrial	37°19.334′	126°45.242'	2016	Aug.	21.4	2.6	8.2	-26.5	- 2.2
SG 7	Sediment	Industrial	37°19.280'	126°45.460′	2016	Aug.	1.1	0.1	11.1	- 25.6	- 1.5
SG 8	Sediment	Industrial	37°19.111′	126°44.571′	2016	Aug.	8.4	0.6	13.9	- 25.5	-0.7
6 DS	Sediment	Industrial	37°18.189′	126°44.536′	2016	Aug.	4.4	0.9	4.8	- 25.7	- 1.4

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Fig. 1. Map showing the sampling sites, and corresponding photographs along the Singil Stream. The photographs were taken in 2016.

certified by the International Atomic Energy Agency (IAEA). All carbon and nitrogen isotope ratios (δ^{13} C and δ^{15} N) were reported using the δ -notation (per mill) with respect to the Vienna Pee Dee Belemnite (VPDB) and to N₂ atmosphere (Air), respectively. The analyses were performed at least twice with the analytical errors narrower than 0.03 wt.% and 0.05% for carbon and 0.01 wt.% and 0.1% for nitrogen.

4. IsoSource model

To determine the relative OM contributions of various sources to SPM and streambed sediments in the Singil Stream, we used the IsoSource model, version 1.3.1 (http:// www.epa.gov/wed/pages/models/stableisotopes/iso-source/ isosource.htm). The IsoSource mixing model is designed to quantify the contributions of a set of sources in situations where these exhibit variabilities in the isotopic signatures. The optimal mixture of the sources is found using a mass balance tolerance and source increments (Fry, 2013). The mass balance tolerance and source increment values were set at 0.1‰ and 1%, respectively.

RESULTS

1. Suspended particulate matter

POC and PN concentrations showed similar values in the rural and urban areas, with the ranges of $0.6 \sim 2.4 \text{ mg L}^{-1}$ and $0.1 \sim 0.4 \text{ mg L}^{-1}$, respectively, although higher in 2016 than in 2014 (Table 1, Fig. 2A, B). POC and PN concentrations in the industrial area varied between 1.9 and 12.1 mg L⁻¹, and between 0.2 and 3.0 mg L^{-1} , respectively, showing much higher values than those in the rural and urban areas for both 2014 and 2016. C/N ratios were 3.7~9.8 in 2014 and 3.7~19.0 in 2016, and showed higher values in the urban areas than in other areas (Table 1). The values of $\delta^{13}C_{POC}$ ranged from -28.9% to -23.8% in 2014, and from -29.9% to -21.6% in 2016, with the lowest value of -29.9% in the industrial area (site SG9) in 2016 (Fig. 2C). $\delta^{15}N_{PN}$ varied in a wide range, from -8.1% to 10.4%, showing the most depleted value of -8.1% in the industrial area (site SG9) in 2016, and the most enriched value of 10.4% in the urban area (site SG3) in 2014 (Fig. 2D).



Fig. 2. POC and PN concentrations (mg L⁻¹) and stable isotope ($\delta^{13}C_{POC}$ in % VPDB and $\delta^{15}N_{PN}$ in % Air) values for SPM samples collected (A, B) in 2014 and (C, D) in 2016. The data refer to three areas (rural area, urban area, and industrial area).



Fig. 3. TOC and TN contents (wt.%) and stable isotope ($\delta^{13}C_{TOC}$ in % VPDB and $\delta^{15}N_{TN}$ in % Air) values for streambed sediment samples collected (A, B) in 2014 and (C, D) in 2016. The data refer to three areas (rural area, urban area, and industrial area).

The SPM samples collected at two sewer outlets (SG7' and SG8') located in the industrial area showed relatively higher POC, PN, and C/N ratio values with $4.3 \sim 6.0 \text{ mg L}^{-1}$,

 $0.7 \sim 1.0 \text{ mg L}^{-1}$, and $5.8 \sim 6.0$, respectively (Table 1). The values of $\delta^{13}C_{POC}$ were -24.8% and -21.6% for SG7' and SG8', respectively, while the $\delta^{15}N_{PN}$ values were -2.1% and



Fig. 4. Scatter plots for (A) POC (mg L⁻¹) vs. $\delta^{13}C_{POC}$ (% VPDB), (B) PN (mg L⁻¹) vs. $\delta^{15}N_{PN}$ (% Air), (C) TOC (wt.%) vs. $\delta^{13}C_{TOC}$ (% VPDB), and (D) TN (wt.%) vs. $\delta^{15}N_{TN}$ (% Air) for SPM and streambed sediment samples collected in 2014 and 2016.



Fig. 5. Scatter plots for (A) δ^{13} C (% VPDB) vs. δ^{15} N (% Air), (B) δ^{13} C (% VPDB) vs. C/N ratio, and (C) δ^{15} N (% Air) vs. C/N ratio for SPM and streambed sediment samples collected in 2014 and 2016. Note that the mixing triangle of three end-member values were shown as green.

-4.3% for SG7' and SG8', respectively.

2. Streambed sediments

TOC contents ranged from 3.3 wt.% to 42.4 wt.% in 2014, and from 1.1 wt.% to 33.3 wt.% in 2016 (Table 1, Fig. 3A). TN contents varied between 1.2 wt.% and 4.7 wt.% in 2014, and between 0.1 wt.% and 3.2 wt.% in 2016 (Fig. 3B). C/N ratios were in the range of 2.8~16.4 in 2014, and of 4.8~15.6 in 2016 (Table 1). $\delta^{13}C_{TOC}$ varied between -28.9% and -24.1%, showing the lowest value of -28.9% in the urban area (site SG3) in 2016, and the highest value of -24.1% in the industrial area (site SG6) in 2014 (Fig. 3C). $\delta^{15}N_{TN}$ ranged from -2.5% to 9.9%, with the most depleted value of -2.5% in the industrial area (site SG9) in 2014, and the most enriched value of 9.9% in the urban area (site SG3) in 2016 (Fig. 3D).

DISCUSSION

The runoff and transport of terrestrial OM through stream networks play a critical role as a linkage between terrestrial and aquatic systems (e.g. Vannote *et al.*, 1980; Tank *et al.*, 2010; Johnson et al., 2018). Especially in the stream systems such as the Singil Stream located in the industrial complex, particulate and sedimentary OM are considered to be a mixture of OM originated from diverse allochthonous sources from surrounding areas, including domestic and industrial wastewaters (e.g. Requejo et al., 1986; Tam et al., 1998). In general, the POC and PN concentrations in the industrial area were much higher than those in the rural and urban areas in both 2014 and 2016. This is especially evident by the highest value of 12.1 mg L^{-1} for POC in 2014, and by the value of 3.0 mg L^{-1} for PN in 2016. Notably, the upper industrial sites (SG4~SG6) had much higher POC and PN concentrations than the rural and urban sites as well as the lower industrial sites (SG7~SG9) for both 2014 and 2016 (Table 1, Fig. 4). Hence, we hypothesize that a large amount of OM was supplied from the upper part of the industrial areas to the Singil Stream.

According to a previous study (Lee et al., 2014), particulate OM supplied from the industrial areas into Lake Shihwa had mostly protein-like fluorescence properties associated with a relatively labile OM, showing a strong correlation with the biochemical oxygen demand. This means that the OM derived from industrial areas was degraded rapidly, consuming oxygen in the water column and thus deteriorating the water quality of the stream. Previous studies in the upper brackish region of Lake Shihwa showed that the POC concentration had on average the value of 1.7 mg L^{-1} (MMAF, 2005, 2006; Choi et al., 2013). Accordingly, the POC concentrations (on average $6.5 \sim 3.3 \text{ mg L}^{-1}$) in the downstream area, i.e. the industrial area, of the Singil Stream were much higher than those in the adjacent Lake Shihwa. This suggests that OC inputs from the Singil Stream to Lake Shihwa would affect the OM compositions in Lake Shihwa.

Similar to the SPM samples, TOC and TN contents of the streambed sediments were higher in the industrial area (on average $19.3 \sim 14.6$ wt.% and $2.1 \sim 1.5$ wt.%, respectively) than in the rural area (on average $9.6 \sim 6.2$ wt.% and $0.9 \sim 0.7$ wt.%, respectively) and in the urban area (on average $6.2 \sim 3.3$ wt.% and $0.5 \sim 0.2$ wt.%, respectively) for both 2014 and 2016 (Table 1, Fig. 3). Interestingly, the lower industrial sites (SG7~SG9) had much higher TOC contents in 2014 than in 2016 (see Table 1). This might be due to higher lithogenic inputs from upstream areas to the lower industrial sites in 2016 than in 2014 increasing the dilution effect, considering that the samples were taken before a rainfall in 2014 but just

after a heavy rainfall in 2016. Furthermore, it is worthwhile to note that the TOC and TN contents were higher in the rural area than in the urban area, especially in 2016 (Fig. 3). The rural area around the Singil stream is a typical agricultural land which comprises of mostly C_3 plants such as beans (Kim *et al.*, 2018). In addition, fertilizers with high N contents have been widely used in the rural area affecting TN contents in the samples investigated. Thus, it appears that the contribution of terrestrial-derived OM was more elevated in the rural area than in the urban area.

The δ^{13} C values of the rural and urban areas (-29.5%) to -24.9%) largely overlapped with those of the industrial area (-29.9% to -23.8%, Fig. 4). Similarly, the C/N ratios of the rural and urban areas (5.2 to 19.0) showed a similar range with the values of 2.8 to 14.4 in the industrial area (Fig. 5). In contrast to δ^{13} C, the δ^{15} N values were distinctively lower in the industrial area (on average $-2.3 \pm 1.9\%$) than those in the rural and urban areas (on average $6.6 \pm 3.1\%$, Fig. 4). Consistently, the scatter plot of δ^{13} C and δ^{15} N showed that both SPM and streambed sediments collected in the industrial area grouped separately from those collected in the rural and urban areas, largely due to the difference of $\delta^{15}N$ (Fig. 5). Notably, the sewer outlet samples (SG7' and SG8') showed similar δ^{15} N values to those of the industrial samples, but different from those of the rural and urban areas (Fig. 5). This suggests that OM in the Singil Stream was supplied from the industrial area via sewer outlets.

Interestingly, the sample collected at the mouth of the Singil Stream (SG9) in 2016 showed more depleted values of δ^{13} C (-29.9%) as well as δ^{15} N (-8.1%) in comparison to those of other samples from the industrial area as well as the sewer outlet samples (Table 1, Fig. 5). The $\delta^{13}C_{POC}$ and $\delta^{15}N_{PN}$ values of SPM were previously reported in the industrial areas at the mouth of five streams flowing into Lake Shihwa in May 2012, exhibiting, on average, the values of $-24.1 \pm 1.1\%$ and $-4.1 \pm 1.0\%$, respectively (Lee *et* al., 2014). More recently, Hong et al. (2019) also reported $\delta^{13}C_{POC}$ and $\delta^{15}N_{PN}$ values of SPM samples collected along the Singil Stream and in sewer outlets of the industrial areas in 2013, indicating that stormwater originating from the industrial areas was the main source of low $\delta^{15}N_{PN}$. Hence, the δ^{13} C and δ^{15} N values at SG9 in 2016 were distinctively different from other published data thus far. Moreover, the $\delta^{13}C_{POC}$ and $\delta^{15}N_{PN}$ values at SG9 in 2016 were different from those of the sewer outlet samples collected in the middle part of the industrial area. This implies that OM was delivered from a different source to the SG9 site in 2016, which had different characteristics even compared to those of the lower part of the industrial area. Accordingly, it appears that OM sources within the industrial area are diverse, with different δ^{13} C and δ^{15} N values.

To calculate the relative contributions of OM from different sources at SG9 closest to Lake Shihwa, we applied a dual-isotopic (δ^{13} C and δ^{15} N) mass balance using the Iso-Source model (cf. Fry, 2013). We assigned three end-member regions based on the observation discussed above: S1 for the upstream area (i.e. rural and urban areas, SG1~SG3), S2 for the upper part of the industrial area (SG4~SG5), and S3 for the lower part of the industrial area (SG7'~SG8'). The three end-member values were constrained using the data obtained from the SPM samples collected in 2014 and 2016. For better containing comprehensive end-member values, we also combined the published data from the SPM samples collected at the same sites in 2015 (Hong *et al.*, 2019). The δ^{13} C and δ^{15} N end-member values constrained were as follows: for S1 $-27.1 \pm 1.6\%$ and $6.5 \pm 2.7\%$, respectively, for S2 -25.0 $\pm 0.2\%$ and $-1.2 \pm 1.1\%$, respectively, and for S3 $-24.5 \pm$ 0.8% and $-3.5\pm0.8\%$, respectively. The IsoSource source apportionment at the site SG9 showed that 17.8% of the OM was derived from S1, 34.3% from S2, and 47.9% from S3 for the sediment sample collected in 2016. However, the calculations for other SPM and sediment samples collected in 2014 and 2016 were not successful, because the mixing triangle of three end members could not surround the most target samples (Fig. 5A). Our IsoSource model approach thus indicates that the OM sources are much more diverse in the Singil Stream. Accordingly, the end-member appointment needs to be refined by obtaining more data from the various industrial area and by applying a multi-element approach.

CONCLUSIONS

In this study, we assessed OM sources along the Singil Stream flowing into Lake Shihwa, by applying a dual element (carbon and nitrogen) approach. Our results revealed that the POC concentrations and the TOC contents were much higher in the industrial area than in the rural and urban areas. Furthermore, the δ^{15} N values of both SPM and streambed sediments were distinctively lower in the industrial area than in the rural and urban areas. Our dual isotope approach

implies that a large proportion of OM was supplied from the industrial area to the Singil Stream during the study periods. Our study further highlights that OM sources from the industrial area appear to be complex. Therefore, further studies are necessary to better constrain OM sources within the industrial area, which would affect the aquatic ecosystems in the Singil Stream and, by association, in Lake Shihwa.

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Author contribution statement DHK and J-HK coordinated the study and led the writing. SJK, M-SK, and K-HS designed the field survey and contributed to data acquisition. All authors commented on the manuscript and contributed to the writing.

Conflict of interest The authors declare no conflict of interest and the sponsors had no role in the design, execution, interpretation, or writing of the study.

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REFERENCES

- Ansan Green Environment Center. 2018. Development of water quality model for the water quality management of Singil stream. AGEC report, Ansan, Korea, pp. 5-14.
- Choi, K., S.-W. Kim, D.-S. Kim and W. Heo. 2013. Effect of algal fraction to particulate organic matter in the upper regions of a brackish Lake Shihwa. *Korea Journal of Environment* and Ecology 46: 499-506.
- Cloern, J.E., E.A. Canuel and R.P. Harris. 2002. Stable carbon and nitrogen isotope composition of aquatic and terrestrial plants of San Francisco Bay estuarine system. *Limnology and Oceanography* 47: 713-729.

- Crossland, C.J., H.H. Kremer, H. Lindeboom, J.I.M. Crossland and M.D. Le Tissier. 2005. Coastal fluxes in the Anthropocene: the land-ocean interaction in the coastal zone project of the international geosphere-biosphere programme. Springer Science and Business Media, Berlin and Heidelberg, Germany, p. 253.
- Derrien, M., M.-S. Kim, G. Ock, S. Hong, J. Cho, K.-H. Shin and J. Hur. 2018. Estimation of different source contributions to sediment organic matter in an agricultural-forested watershed using end member mixing analyses based on stable isotope ratios and fluorescence spectroscopy. *Science of the Total Environment* **618**: 569-578.
- Dunn, J.J.K., D.T. Welsh, P.R. Teasdate, S.Y. Lee, D.J. Lemckert and T. Meziane. 2008. Investigating the distribution and sources of organic matter in surface sediment of Coombabah lake (Australia) using elemental, isotopic and fatty acid biomarkers. *Continental Shelf Research* 28: 2535-2549.
- Fry, B. 2013. Alternative approaches for solving underdetermined isotope mixing problems. *Marine Ecology Progress Series* 472: 1-13.
- Fry, B. and E.B. Sherr. 1984. δ¹³C measurements as indicators of carbon flow in marine and freshwater ecosystems. *Contributions in Marine Science* 27: 13-47.
- Goni, M.A., M.J. Teixeira and D.W. Perkey. 2003. Sources and distribution of organic matter in a river-dominated estuary (Winyah Bay, SC, USA). *Estuarine, Coastal and Shelf Science* 57: 1023-1048.
- Grey, J., R.I. Jones and D. Sleep. 2001. Seasonal changes in the importance of the source of organic matter to the diet of zooplankton in Loch Ness, as indicated by stable isotope analysis. *Limnology and Oceanography* 46: 505-513.
- Hong, S., E.-J. Won, H.-J. Ju, M.-S. Kim and K.-H. Shin. 2010. Current nonylphenol pollution and the past 30 years record in an artificial Lake Shihwa, Korea. *Marine Pollution Bulletin* 60: 303-313.
- Hong, S., Y. Lee, S. Yoon, J. Lee, S. Kang, E.-J. Won, J. Hur, J. Khim and K.-H. Shin. 2019. Carbon and nitrogen stable isotope signature linked to anthropogenic toxic substances pollution in a highly industrialized area of South Korea. *Marine Pollution Bulletin* 144: 152-159.
- Hudson, N., A. Baker and D. Reynolds. 2007. Fluorescence analysis of dissolved organic matter in natural, waste and polluted waters - A review. *River Research and Applications* 23: 631-649.
- Jeong, H., K.-T. Kim, E.-S. Kim, K. Ra and S.-Y. Lee. 2016. Sediment quality assessment for heavy metals in streams around the Shihwa Lake. *Journal of the Korean Society for Marine Environment and Energy* 19: 25-36.
- Jeong, H., K.-T. Kim, E.-S. Kim, S.-Y. Lee and K. Ra. 2017. Regional variation and discharge characteristics of stream water quality and heavy metals around the Shihwa Lake basin. *Journal of the Korean Society for Marine Environment and Energy* 20: 76-83.

- Johnson, E.R., S. Inamdar, J. Kan and R. Vargas. 2018. Particulate organic matter composition in stream runoff following large storms: Role of POM sources, particle size, and event characteristics. *Journal of Geophysical Research: Biogeosciences* 123: 660-675.
- Khim, J.S., D.L. Villeneuve, K. Kannan, K.T. Lee, S.A. Snyder, C.H. Koh and J.P. Giesy. 1999. Alkylphenols, polycylic aromatic hydrocarbons and organochlorines in sediment from Lake Shihwa, Korea: instrumental and bioanalytical characterization. *Environmental Toxicology and Chemistry* 18: 2424-2432.
- Kim, D., J.-H. Kim, M.-S. Kim, K. Ra and K.-H. Shin. 2018. Assessing environmental changes in Lake Shihwa, South Korea, based on distributions and stable carbon isotopic compositions of *n*-alkanes. *Environmental Pollution* 240: 105-115.
- Kim, M.-S., W.-S. Lee, K.S. Kumar, K.-H. Shin, W. Robarge, M. Kim and S.R. Lee. 2016. Effect of HCl pretreatment, drying, and storage on the stable isotope ratios of soil and sediment samples. *Rapid Communications in Mass Spectrometry* **30**: 1567-1575.
- Lee, C.-H., B.-Y. Lee, W. Chang, S. Hong, S. Song, J. Park, B.-O. Kwon and J. Khim. 2014. Environmental and ecological effects of Lake Shihwa reclamation project in South Korea: A review. Ocean and Coastal Management 102: 545-558.
- Lee, Y., J. Khim and K.-H. Shin. 2017. Identification of sources and seasonal variability of organic matter in Lake Shihwa and surrounding inland creeks, South Korea. *Chemosphere* 17: 109-119.
- Lu, Y., J.E. Bauer, E.A. Canuel, Y. Yamashita, R.M. Chambers and R. Jaffe. 2013. Photochemical and microbial alteration of dissolved organic matter in temperate headwater streams associated with different land use. *Journal of Geophysical Research: Biogeosciences* 118: 1-15.
- Maksymowska, D., P. Richard, H. Piekarek-Jankowska and P. Riera. 2000. Chemical and isotopic composition of the organic matter sources in the Gulf of Gdansk (Southern Baltic Sea). *Estuarine, Coastal and Shelf Sciences* 51: 585-598.
- McGinn, A.P. 1999. Safeguarding the Health of Oceans. Worldwatch Paper, pp. 1-87.
- MMAF (Ministry of Maritime Affairs and Fisheries). 2005. The project for improvement of marine environment of Lake Shihwa. MMAF.
- MMAF (Ministry of Maritime Affairs and Fisheries). 2006. The project for improvement of marine environment of Lake Shihwa. MMAF.
- Moon, H.B., M. Choi, H.G. Choi and K. Kannan. 2012. Severe pollution of PCDD/Fs and dioxin-like PCBs in sediments from Lake Shihwa, Korea: Tracking the source. *Marine Pollution Bulletin* 64: 2357-2363.
- Park, H.-K., M.-S. Byeon, Y.-N. Shin and D.-I. Jung. 2009. Sources and spatial and temporal characteristics of organic

carbon in two large reservoirs with contrasting hydrologic characteristics. *Water Resources Research* **45**: W11418, doi:10.1029/2009WR008043.

- Phillips, D.L. and J.W. Gregg. 2003. Source partitioning using stable isotope: coping with too many sources. *Oecologia* 136: 261-269.
- Tank, J., E. Rosi-Marshall, N.A. Griffiths, S.A. Entrekin and M.-L. Stephen. 2010. A review of allochthonous organic matter dynamics and metabolism in streams. *Journal of the North American Benthological Society* 29: 118-146.
- Thornton, S.F. and J. McManus. 1994. Application of organic carbon and nitrogen stable isotope and C/N ratios as source indicators of organic matter provenance in estuarine system: Evidence from the Tay Estuary, Scotland. *Estuarine*,

Coastal and Shelf Science 38: 219-233.

- Vannote, R.L., G.W. Minshall, K.W. Cummins, J.R. Sedell and C.E. Cushing. 1980. The river continuum concept. *Canadian Journal of Fisheries and Aquatic Sciences* 37: 130-137.
- Vidon, P., L.E. Wagner and E. Soyeux. 2008. Changes in the character of DOC in streams during storms in two Midwestern watersheds with contrasting land uses. *Biogeochemistry* 88: 257-270.
- Wigington, P.J., J.P. Baker, D.R. DeWalle, W.A. Krester, P.S. Murdoch, H.A. Simonin, J. Van Sickle, M.K. McDowell, D.V. Peck and W.R. Barchet. 1996. Episodic acidification of small streams in the northeastern United States: ionic control of episodes. *Ecology Application* 6: 389-407.