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Identification of sources and seasonal variability of organic matter in Lake Sihwa and surrounding inland creeks, South Korea

Yeonjung Lee [a], Seongjin Hong [b], Min-Seob Kim [c], Dahae Kim [d], Bo-Hyung Choi [d], Jin Hur [e], Jong Seong Khim [f], Kyung-Hoon Shin [d, *]

[a] Marine Ecosystem and Biological Research Center, Korea Institute of Ocean Science and Technology, Ansan 15627, Republic of Korea
[b] Department of Ocean Environmental Sciences, Chungnam National University, Daejeon 34134, Republic of Korea
[c] Department of Fundamental Environment Research, Environmental Measurement and Analysis Center, National Institute of Environmental Research, Incheon 22689, Republic of Korea
[d] Department of Marine Sciences and Convergent Technology, Hanyang University, Ansan 15588, Republic of Korea
[e] Department of Environment and Energy, Sejong University, Seoul 05006, Republic of Korea
[f] School of Earth and Environmental Sciences & Research Institute of Oceanography, Seoul National University, Seoul 08826, Republic of Korea

HIGHLIGHTS

- Sources of organic matter (OM) in Lake Sihwa were chemically characterized.
- Industrial OM showed great concentrations and active biodegradability.
- $\delta^{13}C$ and $\delta^{15}N$ values were clearly distinguished between sources of OM.
- Greater concentration of OM and smaller %PLF were found in upstream of lake.
- Allochthonous OM was largely contributed to Lake Sihwa in rainy season.

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ABSTRACT

Coastal areas are subjected to significant allochthonous organic matter deposits from surrounding areas; however, limited information is available on the source and delivery of this organic matter. In this study, to assess seasonal changes in the sources of organic matter in Lake Sihwa (Korea), biodegradability, fluorescence property, and stable isotopic compositions (carbon, nitrogen, and sulfur) of the organic matter were determined. Water samples were collected from the inner lake ($n = 9$) and inland creeks ($n = 10$) in five separate events, from November 2012 to October 2013. Organic matter originating from rural, urban, and industrial areas was examined as the potential sources. The organic matter contents and biodegradability in the industrial area were the highest, whereas low concentrations and poor biodegradability of organic matter were found in the rural area, and moderate properties were observed in the urban area. In Lake Sihwa, a large concentration of total organic matter and enhanced biodegradability were observed during March and August. However, main source of organic matter differed between the sampling events. The largest contribution of organic matter, deriving from marine phytoplankton, was found in March. On the other hand, in August, the organic matter originating from the industrial area, which is characterized by high levels of heavy metals and persistent organic pollutants, was significantly increased. Our results could be useful to enhance the management of water bodies aimed at reducing the organic matter concentrations and improving the water quality of Lake Sihwa, and even that of the Yellow Sea.

Abbreviations: ANOVA, analysis of variance; COD, chemical oxygen demand; DOC, dissolved organic carbon; DOM, dissolved organic matter; DTN, dissolved total nitrogen; $\delta^{13}C$, stable carbon isotopic composition; $\delta^{15}N$, stable nitrogen isotopic composition; $\delta^{34}S$, stable sulfur isotopic composition; FLF, fulvic-like fluorescence; HIX, humification index; HLF, humic-like fluorescence; $NBTOC_{28}$, non-biodegradable total organic carbon within 28 days; PCA, principal component analysis; PLF, protein-like fluorescence; PN, particulate nitrogen; POC, particulate organic carbon; SIAR, Stable Isotope Analysis in R; THLF, terrestrial humic-like fluorescence; TOC, total organic carbon; TPLMS, total pollution load management system.

* Corresponding author.
E-mail address: shinkh@hanyang.ac.kr (K.-H. Shin).

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1. Introduction

Globally, rapid and intense development of coastal areas has occurred over the past 50 years. In particular, significant increases in population and in land use for residential, commercial, agricultural, and industrial purposes have been concentrated mostly in coastal areas (McGinn, 1999; Crossland et al., 2005). Even though economic development has improved the quality of life, the consequence has been severe environmental pollution in the coastal areas and even further toward the ocean environment (Martínez et al., 2007; MOF, 2015). Organic matter originatedfrom different land uses has different chemical properties, such as concentration, biodegradability, toxic substance contamination, and isotopic compositions (Goericke et al., 1994; France, 1995; Moon et al., 2012; Lee et al., 2014b; Hong et al., 2016). Furthermore, these factors could have different influences on the water quality and ecosystem health. For example, a substantial input of organic matter accelerates microbial degradation and, subsequently, promotes oxygen depletion and regeneration of inorganic nutrients (Wei et al., 2007; Zhu et al., 2011). However, the decomposition potential of organic matter depends on the properties of the organic sources (Owen and Lee, 2004).

The amount of allochthonous organic matter deposited to coastal areas could be influenced by hydrology, with the most substantial inflows being linked to high-flow episodes (Meybeck, 1982; Schiff et al., 1998; Ågren et al., 2007; Lee et al., 2014b). In addition, hydrology in Korea is strongly influenced by the Asian summer monsoon. Precipitation during the monsoon period accounts for 50–70% of the annual rainfall in Korea (An and Park, 2002; Fig. S1). This leads to an increase in the allochthonous organic matter deposits after heavy rain and in the distinct difference of the organic matter sources between the seasons. In addition to Korea, similar trends have been noted worldwide (Oh et al., 2013; Lee et al., 2014b; Xu et al., 2016). Thus, further efforts are needed to characterize the chemical properties of the possible sources of organic matter.

Lake Sihwa is an artificial saltwater lake, located on the west coast of Republic of Korea (Fig. 1). This lake was created by the construction of a sea dike in 1994 to provide freshwater for irrigation and industrial use. However, massive anthropogenic impacts from various sources (i.e., surrounding large cities and industrial and rural areas) and insufficient water circulation resulted in the considerable deterioration of the water quality. For example, in 1997, the chemical oxygen demand (COD) value was 17.4 ppm (Lee et al., 2014a) and Lake Sihwa was listed as one of the most polluted coastal areas in Korea. To improve the water quality, various acts and other measures have been implemented by the Korean government. For example, a total pollution load management system (TPLMS) was introduced in 2013 to control the release of land-derived pollutants. In addition, the Sihwa tidal power plant was built in 2011 to increase tidal mixing, and approximately half of the volume of water in Lake Sihwa (160×10^6 m^3) circulates between the lake and the Yellow Sea every day (Lee et al., 2014a). A decreasing trend of COD in the lake has been observed during the last ~20 years, and management measures are being implemented continuously to achieve the target water quality (3.3 ppm COD until 2017). Although an improvement has been observed in the water quality of the lake, the enhanced seawater circulation could cause an increase in the transport of anthropogenic deposits from Lake Sihwa into the Yellow Sea. However, the sources and delivery of organic matter to Lake Sihwa are still poorly understood. Furthermore, observations of seasonal changes of these sources during the year are limited. In view of the increase in the anthropogenic effects from the land to the coastal areas, improved knowledge is required to identify the organic matter sources and properties. The present study was therefore conducted to (1) determine and define the property of organic matter originating from possible sources, as well as their seasonality, (2) assess the seasonal variability in the

Fig. 1. Sampling stations of surface water samples in Lake Sihwa and surrounding creeks.

delivery of the organic matter into Lake Sihwa, and (3) determine the contribution relevant to the seasons between autochthonous and allochthonous organic matter in the lake over the course of a year.

2. Materials and methods

2.1. Sample collection and preparation

Five seasonal sampling campaigns were carried out from November 2012 to October 2013. The amount of precipitation 15 days before sampling was similar between June and August 2013; however, 48% of the annual rainfall occurred between the two sampling events (Fig. S1). Surface water was collected from Lake Sihwa (S1–S9) and the surrounding creeks that flow across the potential sources, i.e., the industrial area (I1–I5), urban area (U), and rural area (W and R1–R3) (Fig. 1). We could not collect any samples from the southern basin area, as access had been restricted because of the construction of new cities. The water samples were separated into particulate and dissolved fractions by filtration through a pre-combusted (450 °C for 4 h) Whatman GF/F filter. The filters were freeze-dried and then stored at −80 °C until further analysis. The filtrate was analyzed immediately for dissolved organic carbon (DOC), dissolved total nitrogen (DTN), and fluorescence.

2.2. Concentrations of organic matter

Concentration of particulate organic carbon (POC) and particulate nitrogen (PN) was determined by using an elemental analyzer (Euro EA3028, EuroVector, Milan, Italy). The details of the procedures are provided elsewhere (Lee et al., 2016b). The concentrations of DOC and DTN were measured by using a total organic carbon (TOC) analyzer (TOC-V_{CPH}, Shimadzu, Kyoto, Japan). Certified reference material for DOC (Hansell Laboratory, University of Miami) was used for quality control during the sample analysis. The concentration of the remaining total organic carbon after four weeks in dark incubation was defined as non-biodegradable total organic carbon ($NBTOC_{28}$). The relative abundance of NBTOC (%$NBTOC_{28}$) was determined by following previously reported methodology (Nguyen and Hur, 2011; Lee et al., 2014b, 2016a).

2.3. Fluorescence characteristics of dissolved organic matter

The synchronous fluorescence spectra of dissolved organic matter (DOM) were determined with a luminescence spectrometer (LS-55, Perkin-Elmer, Liantrisant, UK), with constant offsets ($\Delta\lambda = 30$ nm), based on the analysis of Hur et al. (2008, 2011). Four integrated areas of fluorescence intensity in wavelength ranges at 250–300, 300–380, 380–420, and 420–600 nm were assigned to protein-like fluorescence (PLF), fulvic-like fluorescence (FLF), humic-like fluorescence (HLF), and terrestrial humic-like fluorescence (THLF), respectively. The relative distribution of four fluorescence regions was expressed by percentages (i.e., %PLF, %FLF, %HLF, and %THLF). The humification index (HIX) was estimated by the ratio of the area under the emission fluorescence spectra at 435–480 nm, divided by that at 300–345 nm, using the fluorescence emission spectra of the samples recorded under 254 nm excitation (Zsolnay et al., 1999).

2.4. Stable isotopic compositions of particulate organic matter

After inorganic carbon removal by HCl fumes, the stable carbon isotopic composition ($\delta^{13}C$) of suspended particles was determined by using an isotope ratio mass spectrometer (Isoprime, GV Instruments, Manchester, UK) with an elemental analyzer (Euro EA3028, EuroVector, Milan, Italy). The nitrogen and sulfur isotopic compositions ($\delta^{15}N$ and $\delta^{34}S$) of suspended particles were analyzed without inorganic removal (Connolly and Schlacher, 2013; Lee et al., 2016b). These isotopic compositions were expressed in the δ notation, following the formula: $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ (‰) = $((R_{sample}/R_{reference})\text{-}1) \times 1000$, where R is the corresponding ratios $^{13}C/^{12}C$, $^{15}N/^{14}N$, and $^{34}S/^{32}S$, respectively. Vienna Peedee Belemnite (VPDB), atmospheric N_2, and Vienna Canyon Diablo Troilite (VCDT) were used for the isotopic reference for carbon, nitrogen, and sulfur, respectively. The analytical errors were 0.06, 0.1, and 0.5‰ for carbon, nitrogen, and sulfur, respectively, estimated by IAEA standards (CH-6 for carbon, N-1 for nitrogen, and S-1 and NBS-127 for sulfur).

2.5. Statistical analysis and mixing model

The differences in TOC, %$NBTOC_{28}$, %PLF, and the stable isotopic compositions (i.e., $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$) between the inflow sources were compared by one-way analysis of variance (ANOVA) and Tukey's post-hoc test ($p < 0.05$). Principal component analysis (PCA) was carried out by using the standardized (z-scale transformation) 13 parameters, including POC, PN, DOC, DTN, HIX, %PLF, %FLF, %HLF, %THLF, %$NBTOC_{28}$, $\delta^{13}C_{POM}$, $\delta^{15}N_{POM}$, and $\delta^{34}S_{POM}$. The statistical analyses were performed by using IBM SPSS Statistics 21 software (IBM, USA).

The contribution of three potential sources, namely, industrial, rural, and marine phytoplankton to the organic matter in Lake Sihwa was estimated by using Stable Isotope Analysis in R (SIAR; Parnell et al., 2010). The urban area sources were not included in the SIAR mixing model, as they were not clearly categorized into distinct groups with intermediate values for all the measured stable isotopic compositions. Moreover, a smaller discharge rate was reported for the urban area sources compared with the other source areas (Choi et al., 2011). The mean of the $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ values in I1-I5 were used as the end-member of the industrial area source in the five sampling events, whereas those in the reed wetland (W) were used as the end-member of the rural area source during the spring and fall (i.e., November 2012, and March and October 2013), but the mean of R1–R3 were used in the summer (i.e., June and August 2013) in accordance with wetland operating conditions. The rural area sources flow into Lake Sihwa through a reed wetland during the dry season; however, during the rainy season, these sources are transported directly to the lake. The mean $\delta^{13}C$ and $\delta^{15}N$ values in the phytoplankton collected from the west coast of Korea with nets (i.e., 20–100 μm range; three times) according to a previously described procedure (Kang et al., 2003), were used as the end-member of marine phytoplankton (−18.5 ± 1.4‰ for $\delta^{13}C$ and 8.5 ± 1.3‰ for $\delta^{15}N$; unpublished data). The $\delta^{34}S$ value of the suspended particles collected from the outer regions of Lake Sihwa was used as the end-member of marine phytoplankton (20.7 ± 0.5‰; unpublished data). All the obtained isotopic compositions for marine phytoplankton were within the data ranges indicated by the literature (Kaplan et al., 1963; Kaplan and Rittenberg, 1964; Hartmann and Nielsen, 1968; Goericke et al., 1994; France, 1995; Fry, 2002; Kang et al., 2003).

3. Results and discussion

3.1. Characteristics of organic matter in various sources

Although the inflow sources showed a wide range of concentrations of TOC, %$NBTOC_{28}$, and %PLF during the entire sampling period, there were significant differences in the TOC and %PLF between the sources from the industrial and the rural areas (Fig. 2). In general, the concentrations of organic matter were higher in the

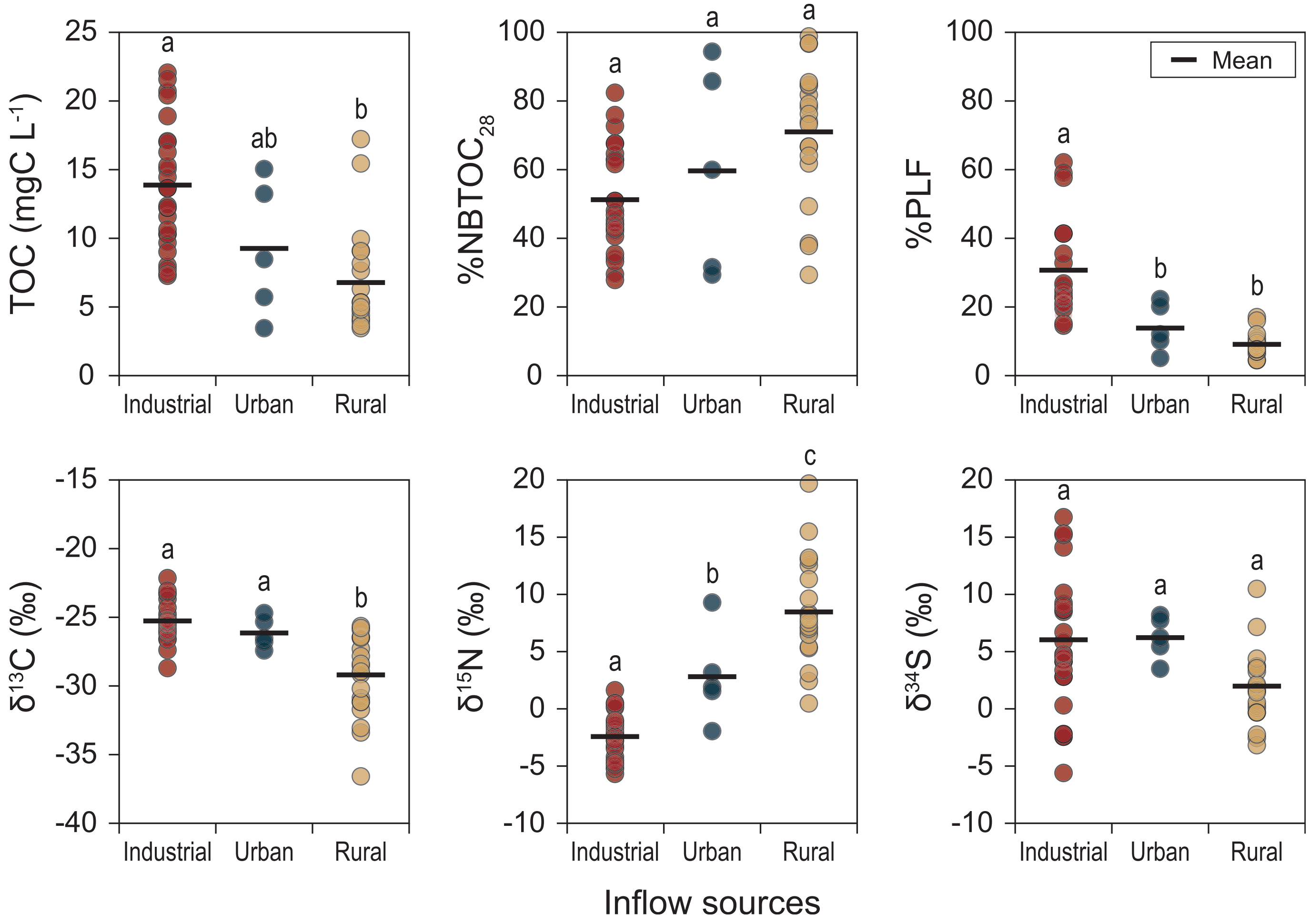

Fig. 2. Concentrations of total organic carbon (TOC), relative contribution of non-biodegradable TOC (%NBTOC$_{28}$), and protein-like fluorescence in dissolved organic matter (%PLF), and stable isotopic compositions of carbon (δ^{13}C), nitrogen (δ^{15}N), and sulfur (δ^{34}S) in particulate matter among three inflow sources (November 2012 to October 2013). Different letters indicate statistically significant differences among inflow sources (Tukey's post-hoc test; $p < 0.05$).

inflow sources than in the lake itself (Table 1). Among the possible sources, the largest values of the TOC concentration and %PLF (i.e., an index associated with labile organic matter [Keil et al., 2000; Hur et al., 2008]), and the smallest mean of %NBTOC$_{28}$ and HIX were found in the industrial area. The HIX has been reported to negatively correlate with bioavailable DOM and recently produced fluorophore groups (Williams et al., 2010; Hosen et al., 2014), and has been used to distinguish between fresh and mature organic matter (Zsolnay et al., 1999; Huguet et al., 2009). Although heavy rain could influence the properties of organic matter (Oh et al., 2013; Lee et al., 2014b; Xu et al., 2016), our evidence indicates that all-year round high concentrations and active biodegradability characterize the organic matter originating from the industrial area. On the other hand, low concentration of TOC and passive biodegradability (i.e., largest %NBTOC$_{28}$ and smallest %PLF) were found in the rural sources. Previous studies have reported that organic matter in rural areas mainly consisted of refractory materials, such as dead plant tissue, compost, paddy water, and soil-leached organic matter forms (Imai et al., 2001; Hur et al., 2009; Park et al., 2009; Nguyen and Hur, 2011). In this context, organic matter with passive biodegradability appears to be the major contributor to this source, although a relatively high concentration of chlorophyll *a* among the inflow sources was observed in the rural area (Fig. S2a). Intermediate levels of both organic matter concentration and biodegradability were observed in the urban source.

During the sampling periods, the stable carbon, nitrogen, and sulfur isotopic compositions showed wide ranges within a single source (Fig. 2), with significant differences in the δ^{13}C and δ^{15}N values being observed between the industrial and rural sources. The organic matter originating from the industrial area had larger δ^{13}C and smaller δ^{15}N values compared with the organic matter from rural sources. In particular, extremely small δ^{15}N values (mean = −2.3‰) were recorded throughout the year in the industrial sources. During the sampling periods, the smallest concentration of chlorophyll *a* (mean = 0.87 μg L^{-1}) was found in the industrial area (Fig. S2), and relatively positive δ^{15}N values were observed for nitrate (12.1‰) and ammonium (7.71‰) in the industrial source, collected from June 2013 (Table S1). Moreover, it has been reported that nitrogen isotopic fractionation factors are less than 1.1‰ during organic nitrogen formation through various pathways (i.e., N_2 fixation and assimilations of nitrate, nitrite, ammonia, or urea) by aquatic organisms, including algae, cyanobacteria, and bacteria (Ohkouchi and Takano, 2013). In this context, the organic nitrogen source with a highly small δ^{15}N value appeared to have been transported directly from the industrial regions. The sewage sludge, reported to show small δ^{15}N values (Van Dover et al., 1992; DeBruyn and Rasmussen, 2002; Gaston and Suthers, 2004; Liu et al., 2007; Hong and Shin, 2009), could presumably have an important role as a source from the industrial area. The samples from the rural area were distinguished from the

Table 1
Selected water quality parameters in surrounding inland creeks and Lake Sihwa for the five different sampling periods.

Parameters			Industrial area	Urban area	Rural area	Lake Sihwa	
Sampling			(I1–I5, n = 5)	(U, n = 1)	(W & R1–R3, n = 4)	(S1 & S2, n = 2)	(S3–S9, n = 7)
Year	Month	Season	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
Temperature (°C)							
2012	Nov.	Fall	9.9 ± 1.8	7.9	6.8 ± 1.4	7.6 ± 2.5	10 ± 1.3
2013	Mar.	Spring	8.7 ± 1.4	8.8	9.7 ± 1.7	8.3 ± 0.64	6.8 ± 0.58
	Jun.	Summer	22 ± 0.49	25	24 ± 1.5	23 ± 1.1	18 ± 0.69
	Aug.	Summer	29 ± 0.63	29	29 ± 1.4	29 ± 0.98	27 ± 0.43
	Oct.	Fall	20 ± 0.39	19	21 ± 1.5	21 ± 0.21	21 ± 0.24
Salinity (psu)							
2012	Nov.	Fall	0.69 ± 0.23	0.34	0.27 ± 0.059	1.3 ± 1.4	29 ± 0.95
2013	Mar.	Spring	0.91 ± 0.28	0.64	0.31 ± 0.091	12 ± 16	29 ± 0.69
	Jun.	Summer	5.2 ± 7.2	0.86	0.38 ± 0.11	7.5 ± 7.1	31 ± 0.17
	Aug.	Summer	4.6 ± 4.7	0.56	0.24 ± 0.048	12 ± 14	29 ± 0.63
	Oct.	Fall	0.48 ± 0.24	0.15	0.29 ± 0.10	12 ± 12	30 ± 0.41
TOC (mg C L^{-1})							
2012	Nov.	Fall	12 ± 6.3	6.0	4.4 ± 0.43	6.1 ± 1.2	3.0 ± 0.27
2013	Mar.	Spring	16 ± 5.1	3.5	4.5 ± 1.3	4.9 ± 1.1	3.7 ± 0.51
	Jun.	Summer	13 ± 5.7	15	10 ± 3.6	5.9 ± 3.0	2.4 ± 0.22
	Aug.	Summer	14 ± 4.2	13	10 ± 5.1	7.7 ± 3.1	4.7 ± 0.83
	Oct.	Fall	14 ± 2.3	8.5	5.0 ± 0.22	5.8 ± 0.27	2.2 ± 0.27
		Mean	**14 ± 4.7**	**9.3 ± 4.9**	**6.9 ± 3.8**	**6.1 ± 1.8**	**3.2 ± 1.0**
POC (mg C L^{-1})							
2012	Nov.	Fall	2.5 ± 0.87	2.1	0.74 ± 0.24	1.5 ± 0.69	0.38 ± 0.14
2013	Mar.	Spring	2.9 ± 1.2	1.1	1.4 ± 0.56	1.8 ± 0.39	1.5 ± 0.26
	Jun.	Summer	3.9 ± 2.7	4.2	2.2 ± 0.80	1.7 ± 0.94	0.72 ± 0.16
	Aug.	Summer	4.6 ± 1.1	6.3	5.3 ± 4.5	3.3 ± 1.5	1.1 ± 0.19
	Oct.	Fall	4.5 ± 2.2	3.4	1.5 ± 0.45	1.9 ± 0.61	0.36 ± 0.037
		Mean	**3.7 ± 1.8**	**3.4 ± 2.0**	**2.2 ± 2.5**	**2.1 ± 0.95**	**0.82 ± 0.48**
PN (mg N L^{-1})							
2012	Nov.	Fall	0.26 ± 0.14	0.26	0.088 ± 0.029	0.16 ± 0.040	0.045 ± 0.012
2013	Mar.	Spring	0.43 ± 0.12	0.18	0.26 ± 0.094	0.33 ± 0.016	0.16 ± 0.023
	Jun.	Summer	0.71 ± 0.63	0.81	0.37 ± 0.15	0.27 ± 0.14	0.14 ± 0.036
	Aug.	Summer	0.74 ± 0.35	1.1	0.71 ± 0.67	0.33 ± 0.14	0.14 ± 0.036
	Oct.	Fall	0.58 ± 0.48	0.47	0.22 ± 0.052	0.23 ± 0.084	0.047 ± 0.0062
		Mean	**0.54 ± 0.40**	**0.57 ± 0.40**	**0.33 ± 0.35**	**0.27 ± 0.10**	**0.11 ± 0.056**
DOC (mg C L^{-1})							
2012	Nov.	Fall	9.8 ± 5.8	3.8	3.6 ± 0.21	4.6 ± 0.46	2.6 ± 0.23
2013	Mar.	Spring	13 ± 4.4	2.4	3.1 ± 0.83	3.2 ± 0.72	2.2 ± 0.43
	Jun.	Summer	9.0 ± 4.1	11	7.8 ± 4.4	4.2 ± 2.1	1.7 ± 0.075
	Aug.	Summer	9.5 ± 3.8	7.0	5.1 ± 0.73	4.4 ± 1.6	3.6 ± 0.71
	Oct.	Fall	9.3 ± 1.9	5.2	3.5 ± 0.50	3.9 ± 0.33	1.8 ± 0.26
		Mean	**10 ± 4.1**	**5.9 ± 3.3**	**4.6 ± 2.5**	**4.0 ± 1.1**	**2.4 ± 0.78**
DTN (mg N L^{-1})							
2012	Nov.	Fall	3.6 ± 0.42	3.2	3.1 ± 0.66	3.5 ± 0.087	0.53 ± 0.13
2013	Mar.	Spring	5.6 ± 2.1	2.5	3.9 ± 1.5	2.1 ± 1.7	0.45 ± 0.044
	Jun.	Summer	4.4 ± 2.7	2.0	2.6 ± 0.76	1.5 ± 1.0	0.33 ± 0.049
	Aug.	Summer	2.8 ± 0.47	3.1	2.5 ± 1.1	1.4 ± 0.72	0.79 ± 0.26
	Oct.	Fall	4.8 ± 0.94	4.0	3.3 ± 2.1	4.6 ± 2.8	0.65 ± 0.062
		Mean	**4.3 ± 1.8**	**2.9 ± 0.76**	**3.1 ± 1.3**	**2.6 ± 1.7**	**0.55 ± 0.21**

Abbreviations TOC: total organic carbon; POC: particulate organic carbon; PN: particulate nitrogen; DOC: dissolved organic carbon; DTN: dissolved total nitrogen.

other sampling stations because of their highly small δ^{13}C values (mean = −29.2‰). Low carbon isotopic compositions (approximately −27‰) have been reported in the soil organic matter in areas dominated by C3 plants (Boutton, 1996; Lebreton et al., 2016). In particular, a highly small δ^{13}C value (−28.3‰) has been reported in the dominant reed species in station W (*Phragmites australis*) (Choi et al., 2005). In this context, organic matter derived from terrestrial plants and reeds, and soil-leached organic matter that show a refractory nature and small δ^{13}C values, could contribute to the organic sources of the rural area. The δ^{13}C and δ^{15}N values found in industrial and rural sources were clearly distinct from end-member of marine phytoplankton. There was no significant difference between the δ^{34}S values of the possible inflow sources (Fig. 2). Krouse et al. (1991) stated that atmospheric inputs, local mineral sources, and reduction processes in anaerobic environments could lead to a wide range of δ^{34}S values for soils and terrestrial plants. This is probably why no significant differences in the δ^{34}S values were found between the possible sources. However, smaller values were observed in the potential sources in comparison with those in Lake Sihwa (Table 2). These results are consistent with previously reported patterns; for example, Peterson and Howarth (1987) reported distinctive end-members of the δ^{34}S values for upland C3 plants (+1.8‰) and marine plankton (+20‰). These results indicate that the δ^{34}S values could be a good indicator to separate marine and allochthonous sources; however, the ability to distinguish between the allochthonous sources was inferior.

3.2. Chemical property of organic matter

The concentration of organic matter was smaller in the upstream stations (S1 and S2) and inner stations (S3–S9) of Lake Sihwa than in the inflow sources (Table 1). A larger concentration of organic matter and smaller %PLF were recorded in the upstream stations than in the inner stations (Fig. 3). The largest %PLF value among all the stations over a year was observed in the inner stations of Lake Sihwa, where a higher concentration of TOC and superior biodegradability were observed in March and August 2013. In general, a large phytoplankton peak in the spring and a smaller peak in fall have been reported in temperate regions (Cushing, 1959; Smayda, 1973), and similar seasonal patterns were observed in the S6 station in this study (Fig. S2b). In Korea, more than 50% of the annual rainfall is concentrated in the summer rainy season and large amounts of allochthonous organic matter can therefore be flushed into the coastal areas. Accordingly, the concentration and characteristics of organic matter in the coastal areas can be influenced by both seasonal changes in marine phytoplankton production and allochthonous organic matter contribution. Considering the difference in the temperature and/or amount of precipitation between March and August, the chemical properties of organic matter could differ, even though similar concentrations of TOC were recorded.

Larger δ^{13}C and δ^{34}S values were recorded in the inner stations of Lake Sihwa in comparison with those in the possible source areas (Table 2 and Fig. 3). A comparison between the upstream and inner stations revealed larger isotopic compositions in the inner stations. These results suggest that upstream stations are under continuous pressure from anthropogenic influences. The results for March and August indicate similar concentrations and biodegradability in

Table 2
Fluorescence properties of dissolved organic matter and stable isotopic compositions of suspended particles in surrounding inland creeks and Lake Sihwa for the five different sampling periods.

Parameters				Industrial area	Urban area	Rural area	Lake Sihwa	
	Sampling			(I1–I5, n = 5)	(U, n = 1)	(W & R1–R3, n = 4)	(S1 & S2, n = 2)	(S3–S9, n = 7)
	Year	Month	Season	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
Fluorescence properties of dissolved organic matter								
HIX	2012	Nov.	Fall	2.3 ± 1.2	4.4	5.2 ± 0.27	4.5 ± 1.1	2.1 ± 0.29
	2013	Mar.	Spring	1.9 ± 1.0	4.5	5.5 ± 0.91	4.3 ± 1.2	1.9 ± 0.27
		Jun.	Summer	2.3 ± 1.2	5.3	5.4 ± 0.40	5.9 ± 2.6	2.4 ± 0.18
		Aug.	Summer	2.9 ± 1.8	6.2	8.5 ± 0.71	7.7 ± 3.7	3.1 ± 0.39
		Oct.	Fall	3.8 ± 2.1	7.1	7.8 ± 0.30	8.0 ± 1.6	3.8 ± 0.37
			Mean	**2.6 ± 1.5**	**5.5 ± 1.2**	**6.2 ± 1.4**	**6.1 ± 2.3**	**2.7 ± 0.76**
%PLF[a]	2012	Nov.	Fall	29 ± 17	10	5.6 ± 2.2	10 ± 6.4	36 ± 3.0
	2013	Mar.	Spring	36 ± 17	20	9.3 ± 2.1	17 ± 11	42 ± 3.6
		Jun.	Summer	26 ± 12	5.3	9.3 ± 1.1	10 ± 12	29 ± 1.6
		Aug.	Summer	34 ± 17	23	17 ± 0.66	20 ± 1.9	33 ± 7.6
		Oct.	Fall	28 ± 17	12	8.7 ± 2.5	21 ± 7.1	36 ± 2.1
			Mean	**30 ± 15**	**14 ± 7.2**	**9.3 ± 3.7**	**16 ± 8.0**	**35 ± 5.7**
%FLF[a]	2012	Nov.	Fall	59 ± 11	71	73 ± 1.3	70 ± 4.2	50 ± 2.3
	2013	Mar.	Spring	53 ± 11	64	68 ± 4.6	61 ± 6.9	45 ± 2.7
		Jun.	Summer	59 ± 7.5	73	70 ± 0.53	67 ± 10	52 ± 2.4
		Aug.	Summer	56 ± 10	58	60 ± 0.87	62 ± 1.5	52 ± 4.3
		Oct.	Fall	60 ± 11	70	72 ± 1.6	63 ± 6.6	52 ± 1.6
			Mean	**58 ± 9.7**	**67 ± 6.1**	**70 ± 4.5**	**64 ± 6.0**	**51 ± 3.7**
%HLF[a]	2012	Nov.	Fall	6.7 ± 3.4	11	12 ± 0.43	11 ± 1.4	6.7 ± 0.55
	2013	Mar.	Spring	5.7 ± 3.1	8.3	11 ± 1.6	9.8 ± 1.1	6.1 ± 0.96
		Jun.	Summer	7.3 ± 2.9	11	12 ± 0.53	12 ± 1.5	8.8 ± 1.2
		Aug.	Summer	6.1 ± 3.8	8.6	9.7 ± 0.081	9.6 ± 0.22	7.1 ± 1.3
		Oct.	Fall	7.2 ± 3.4	11	12 ± 1.1	10 ± 0.087	6.3 ± 0.47
			Mean	**6.7 ± 3.1**	**10 ± 1.5**	**11 ± 1.2**	**11 ± 1.2**	**6.9 ± 1.3**
%THLF[a]	2012	Nov.	Fall	5.7 ± 3.0	8.4	9.7 ± 0.66	9.1 ± 0.83	7.3 ± 0.67
	2013	Mar.	Spring	5.0 ± 2.7	7.5	12 ± 4.9	11 ± 2.6	6.8 ± 1.3
		Jun.	Summer	7.1 ± 1.7	9.9	9.6 ± 0.33	12 ± 0.19	10 ± 0.55
		Aug.	Summer	4.6 ± 3.1	9.3	10 ± 0.49	9.1 ± 0.55	7.7 ± 1.8
		Oct.	Fall	4.7 ± 2.2	6.9	7.3 ± 1.0	5.9 ± 0.54	5.8 ± 0.41
			Mean	**5.5 ± 2.5**	**8.4 ± 1.3**	**9.7 ± 2.7**	**9.4 ± 2.4**	**7.4 ± 1.8**
Stable isotopic compositions of suspended particles								
δ^{13}C (‰)	2012	Nov.	Fall	−26.0 ± 0.77	−26.5	−27.9 ± 2.2	−26.5 ± 0.58	−24.3 ± 0.96
	2013	Mar.	Spring	−24.5 ± 1.1	−25.3	−28.7 ± 3.4	−27.3 ± 3.1	−19.5 ± 0.63
		Jun.	Summer	−24.4 ± 1.7	−27.4	−30.2 ± 2.0	−25.6 ± 4.3	−22.0 ± 0.34
		Aug.	Summer	−26.0 ± 2.0	−26.7	−28.6 ± 3.6	−26.4 ± 2.8	−21.7 ± 1.2
		Oct.	Fall	−25.2 ± 0.61	−24.6	−30.6 ± 4.0	−26.3 ± 2.7	−23.3 ± 0.70
			Mean	**−25.2 ± 1.4**	**−26.1 ± 1.1**	**−29.2 ± 3.0**	**−26.4 ± 2.3**	**−22.2 ± 1.8**
δ^{15}N (‰)	2012	Nov.	Fall	−1.0 ± 1.3	1.5	7.9 ± 3.4	5.7 ± 0.43	7.0 ± 0.97
	2013	Mar.	Spring	−1.4 ± 1.5	1.9	7.8 ± 5.6	5.7 ± 1.0	9.0 ± 0.62
		Jun.	Summer	−1.8 ± 2.2	3.1	6.9 ± 5.0	6.4 ± 1.6	6.7 ± 0.69
		Aug.	Summer	−2.9 ± 2.5	9.2	12 ± 5.4	5.9 ± 3.5	5.8 ± 2.4
		Oct.	Fall	−4.6 ± 1.0	−2.0	7.8 ± 4.1	3.9 ± 1.9	8.9 ± 1.0
			Mean	**−2.3 ± 2.1**	**2.8 ± 4.1**	**8.5 ± 4.6**	**5.5 ± 1.7**	**7.5 ± 1.8**
δ^{34}S (‰)	2012	Nov.	Fall	1.6 ± 5.2	6.2	1.0 ± 1.2	3.3 ± 2.5	15 ± 2.8
	2013	Mar.	Spring	5.2 ± 3.7	5.4	1.8 ± 1.9	9.9 ± 9.4	17 ± 0.9
		Jun.	Summer	6.8 ± 8.9	8.1	1.5 ± 3.2	12 ± 6.1	17 ± 1.3
		Aug.	Summer	9.0 ± 5.7	7.7	0.1 ± 2.9	10 ± 7.5	17 ± 0.84
		Oct.	Fall	6.7 ± 2.9	3.4	4.7 ± 5.4	6.1 ± 1.0	16 ± 1.9
			Mean	**6.0 ± 5.7**	**6.2 ± 1.9**	**1.9 ± 3.4**	**8.2 ± 5.6**	**16 ± 1.8**

Abbreviations HIX: humification index; PLF: protein-like fluorescence; FLF: fulvic-like fluorescence; HLF: humic-like fluorescence; THLF: terrestrial humic-like fluorescence.

[a] Synchronous fluorescence spectra of dissolved organic matter. The relative distribution of four fluorescence regions (i.e., PLF, FLF, HLF, and THLF) represented by percentage.

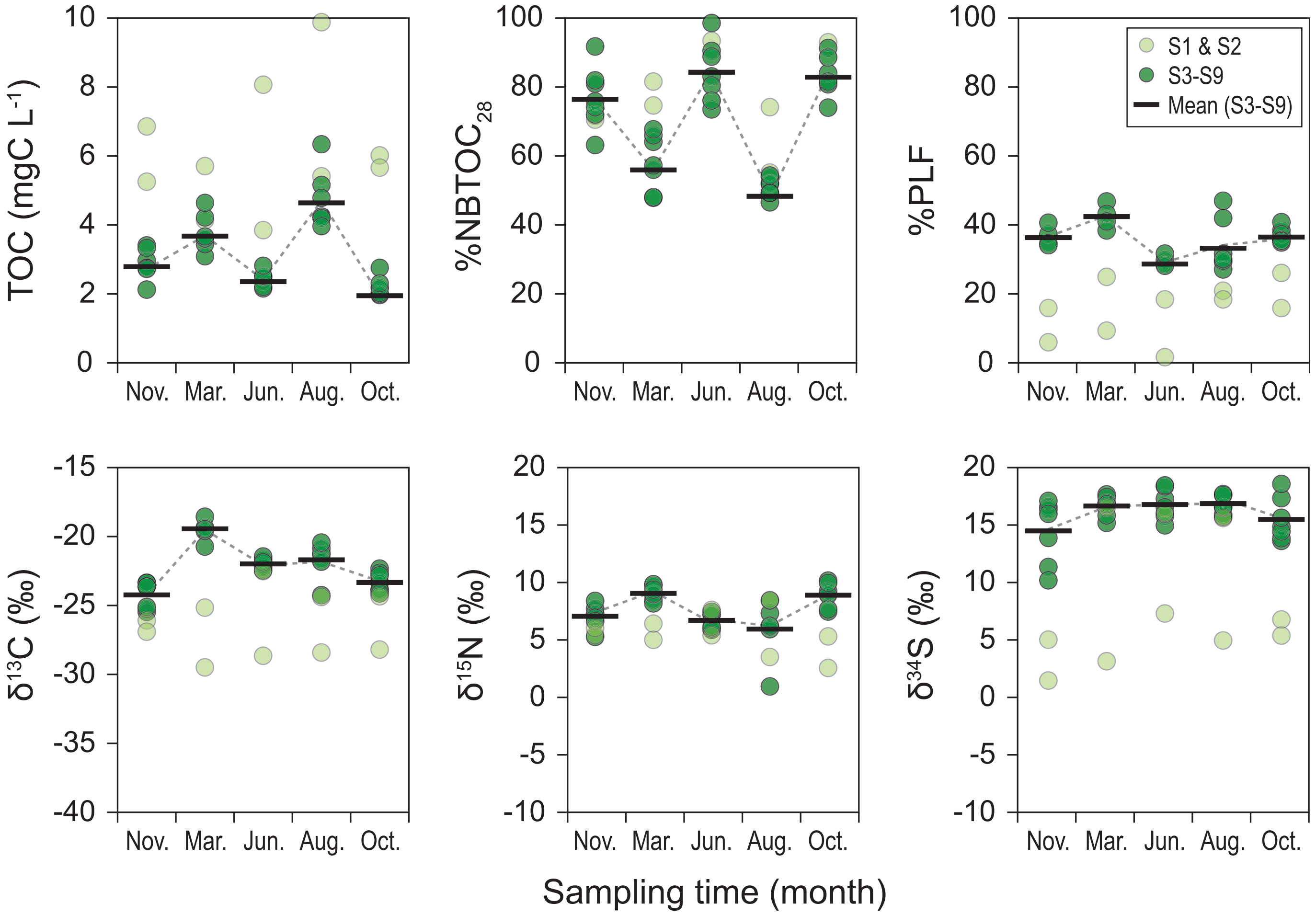

Fig. 3. Temporal variation in the concentration of total organic carbon (TOC), relative contributions of non-biodegradable TOC (%NBTOC$_{28}$) and protein-like fluorescence in dissolved organic matter (%PLF), and stable isotopic compositions of carbon ($\delta^{13}C$), nitrogen ($\delta^{15}N$), and sulfur ($\delta^{34}S$) in particulate matter at Lake Sihwa from November 2012 to October 2013.

organic matter; however, larger $\delta^{13}C$ values were observed in March and smaller $\delta^{15}N$ values in August among the other sampling periods. These differences in the carbon and nitrogen isotopic compositions imply that the organic matter source between the seasons could be different. Overall, a seasonal change in the chemical properties of organic matter was observed in Lake Sihwa. In addition, we found that similar concentrations and biodegradability of organic matter could not be attributed always to the same source. Chemical properties including stable isotopic compositions have been used to assess the sources and delivery of organic matter from land to coastal areas (Wada et al., 1987; Hedges et al., 1998a, b; Osburn and Stedmon, 2011). In particular, the distinctive differences observed in stable isotopic compositions between possible sources (i.e., industrial area, rural area, and marine phytoplankton) could be used to identify the source of organic matter in Lake Sihwa (Fig. S3).

3.3. Estimation of organic matter sources by using stable isotopic compositions

The contribution among the possible sources to the organic matter in Lake Sihwa varied according to the sampling location and sampling period (Fig. 4). Larger contributions of allochthonous organic matter (i.e., industrial and rural sources) were observed in the upstream stations of Lake Sihwa (S1 and S2) compared with those of the inner stations (S3–S9) over the year. In the inner stations, the overall organic matter derived from marine phytoplankton was a major contribution; however, the proportions of the samples showed seasonal fluctuations. The contribution of marine phytoplankton tended to increase from November 2012 to March 2013, with the largest mean being found in March. These contributions gradually decreased from June to August, with the smallest values being found in August. On the other hand, the largest contribution of allochthonous sources was observed in November 2012, with the smallest contribution being observed in March 2013. The contribution from the industrial sources tended to increase in August. Although a large concentration of TOC and enhanced biodegradability were found both in March and in August, the main sources differed between the sampling events. Marine phytoplankton largely contributed to the organic matter in the inner stations of Lake Sihwa in March; however, marine phytoplankton and organic matter originating from the industrial area were important sources in August. As mentioned earlier, in order to achieve the target water quality (i.e., 3.3 ppm COD and 0.063 ppm TP until 2017), the Korean government has implemented various measures (Lee et al., 2014a). The evaluation of pollution reduction in coastal ecosystems could be obscured by the environmental spatiotemporal variability (Boesch, 2002). Accordingly, it is necessary to understand the seasonality of the major environmental parameters; for instance, over the last 10 years, the mean concentration of COD exceeded 3.3 ppm in spring and summer (Fig. S4). Based on the present

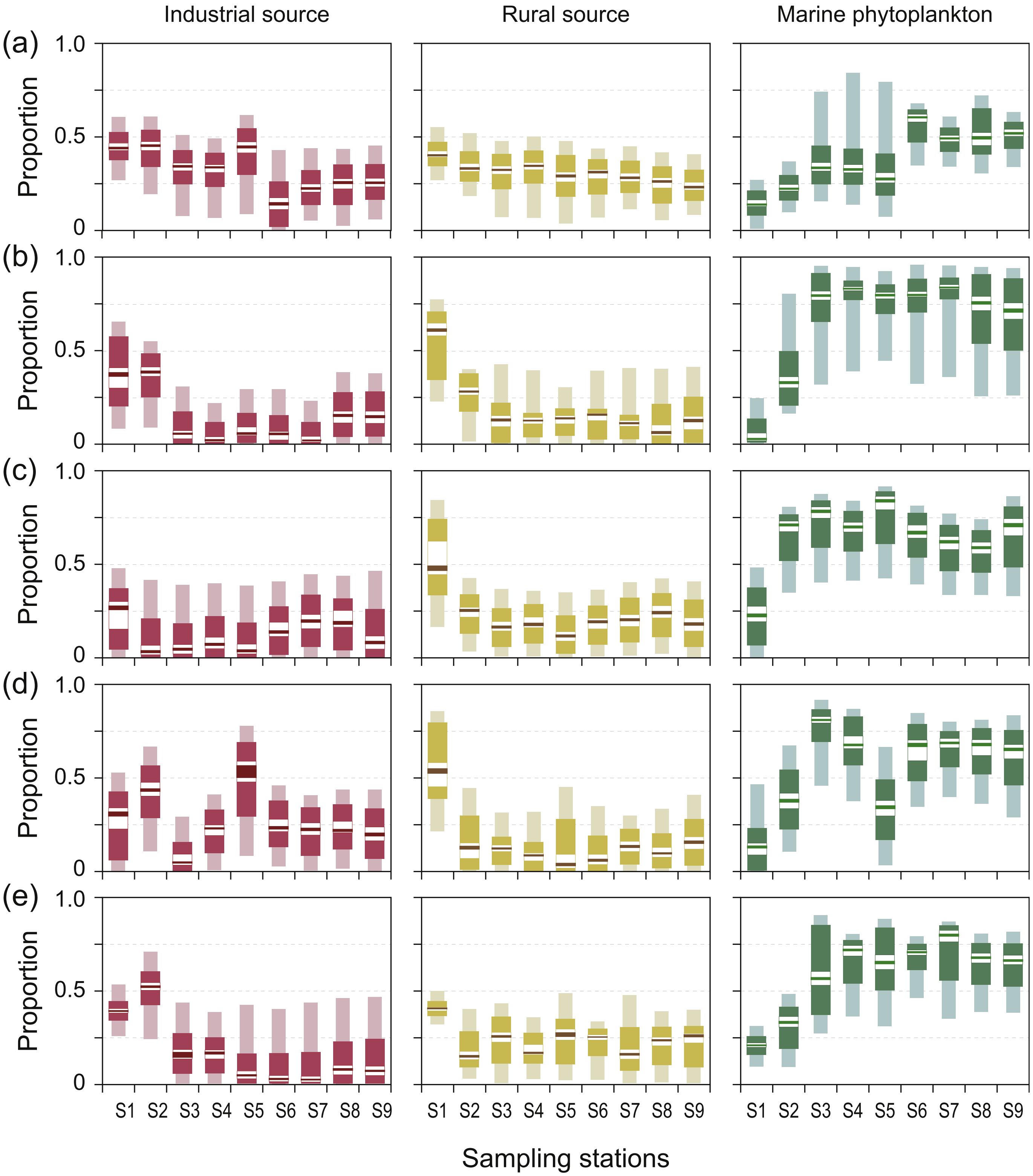

Fig. 4. Proportional contribution of three possible sources of organic matter to each station of Lake Sihwa determined by the SIAR mixing model in (a) November 2012, (b) March 2013, (c) June 2013, (d) August 2013, and (e) October 2013. The respective credibility intervals are indicated as follows 95% (light color), 75% (intermediate color), 25% (white), and 5% (dark color). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

study, autochthonous organic matter appears to play an important role in increasing the COD level in spring. On the other hand, both autochthonous and allochthonous (mainly industrial source) could contribute to the large COD in summer. Meanwhile, the rural source appears to play a different role in the organic matter properties of Lake Sihwa, as a low concentration and passive biodegradability were observed. Several studies have reported the origin and accumulation of non-biodegradable organic matter in

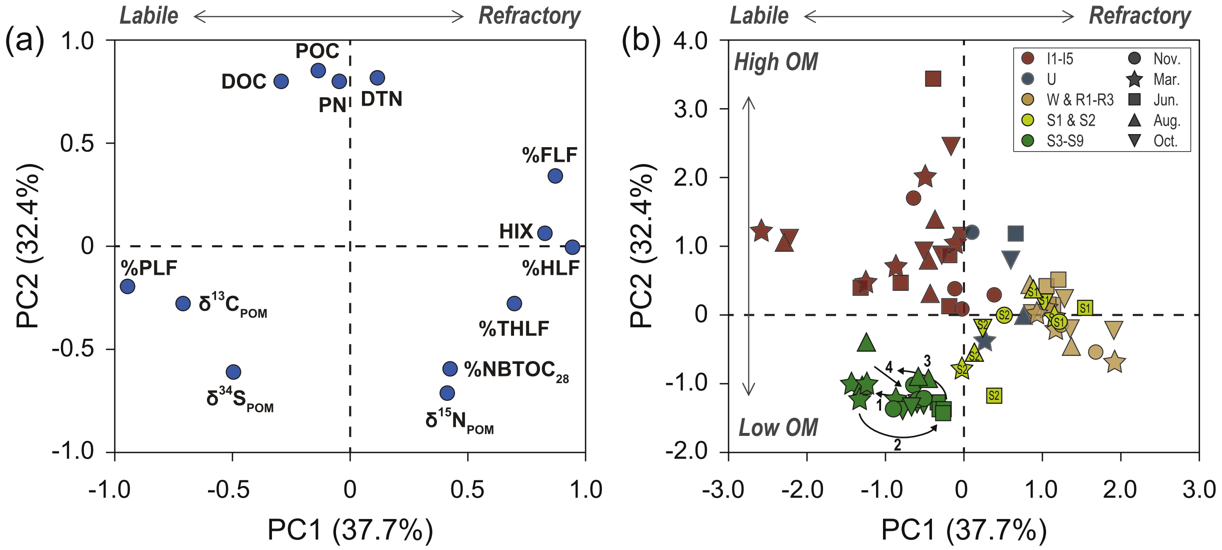

Fig. 5. (a) Factor loading plot for normalized parameters, and (b) factor score plot for each sampling station during five different sampling periods.

freshwater resources (Vollertsen and Hvitved-Jacobsen, 2002; Badawy and Ali, 2006); however, little is known about the coastal ecosystem (Watanabe and Kuwae, 2015). Hedges et al. (1998a) reported that land-derived organic matter was approximately five times more non-reactive than the marine-derived matter at the water-sediment interface in a coastal marine bay (Dabob Bay, Washington). In particular, vascular land plant debris could remain in the water column throughout the year and could be preserved in the underlying sediments for 100 years (Hedges et al., 1998b). In this respect, organic matter originating from the rural area could be a source of refractory organic matter in various pools (i.e., DOM, POM, or sediment) of Lake Sihwa and/or the Yellow Sea over the long period. In order to improve water quality of Lake Sihwa, various management measures and pollution controls have been implemented already (Lee et al., 2014a). However, the results of this study, carried out to identify sources and improve understanding of the chemical properties of organic matter, could assist in the development of further management strategies to improve the water quality of the coastal areas.

3.4. Seasonal change in source and delivery of organic matter

In the present study, PCA was employed to understand the seasonal change in the source and delivery of organic matter into the water of Lake Sihwa. The first and second principal components (PC1 and PC2) together explained over 70% of the total data variance (Fig. 5A). Among the chemical properties, PC1 was correlated positively with %HLF, %FLF, HIX, and %THLF, and negatively with % PLF and the $\delta^{13}C_{POM}$ value. Based on these loadings, PC1 could be considered the biodegradability of organic matter. On the other hand, the concentration of POC, DTN, PN, and DOC loaded positively on PC2, whereas the $\delta^{15}N_{POM}$ and $\delta^{34}S_{POM}$ values were negatively related to PC2, implying that PC2 could be attributable mainly to the concentration of organic matter. From the factor score plot (Fig. 5B), the organic matter originating from the industrial area showed good biodegradability and a high concentration, the organic matter from the rural area showed passive biodegradability and a low concentration, and that from the urban region had intermediate properties. The properties of organic matter in the upstream stations of Lake Sihwa (S1 and S2) were similar to those of the inflow sources. These results indicate that continuous transportation of allochthonous organic matter from various sources to Lake Sihwa occurs throughout the year. In particular, S1, which is located closest to the rural area showed properties close to those of the rural area, implying that refractory organic matters were consistently released into the lake. In the inner stations of Lake Sihwa, highly active biodegradability was observed compared with that in the upstream stations, and seasonal change was found in the properties of the organic matter. The factor scores of PC1 tended to decrease (viz. good biodegradability) through November 2012 to March 2013 (pathway 1 in Fig. 5B), changing repeatedly between the sampling periods, i.e., to a positive direction (viz. poor biodegradability) from March to June (pathway 2); a relatively negative direction from June to August (pathway 3); and to a positive direction from August to October (pathway 4). Similar factor scores were recorded between November 2012 and October 2013 (viz. fall). Active biodegradability, with a large contribution of the marine phytoplankton organic matter was reported in May 2012 (viz. spring), whereas passive biodegradability, with an increasing allochthonous organic matter contribution, was reported after heavy rain in early September 2012 (viz. summer) in the same region (Lee et al., 2014b). These results indicate that the source and delivery of organic matter in Lake Sihwa changed regularly according to the season.

The results obtained provide useful information on regular seasonal patterns in the characteristics and sources of organic matter in Lake Sihwa. In addition, consistent distinctive characteristics of various potential sources were observed on a year-round basis. Thus, our results could be useful to improve management measures aimed at reducing the concentrations of organic matter and improving the water quality of Lake Sihwa and, ultimately, those of the Yellow Sea.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.chemosphere.2017.02.148.

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<Supporting Information>

Identification of sources and seasonal variability of organic matter in Lake Sihwa and surrounding inland creeks, South Korea

Yeonjung Lee, Seongjin Hong, Min-Seob Kim, Dahae Kim, Bo-Hyung Choi, Jin Hur, Jong Seong Khim, Kyung-Hoon Shin*

*Corresponding author: shinkh@hanyang.ac.kr

Supporting Information: Table

Table S1. Nitrogen isotopic compositions of nitrate and ammonium in the potential sources. Water samples were collected from 10 stations in June 2013.

Potential sources	$\delta^{15}N_{NO3}$ (‰) (Mean ± SD)	$\delta^{15}N_{NH4}$ (‰) (Mean ± SD)
Industrial area (I1-I5)	12.1 ± 3.0	7.71 ± 1.6
Urban area (U)	12.6	10.1
Rural area (W & R1-R3)	17.6 ± 2.2	9.40 ± 4.4

The details of the procedures are provided elsewhere (Feast and Dinnis, 1996; ME, 2014). All analyses were conducted at the National Instrumentation Center for Environmental Management (NICEM), Seoul National University.

Supporting Information: Figures

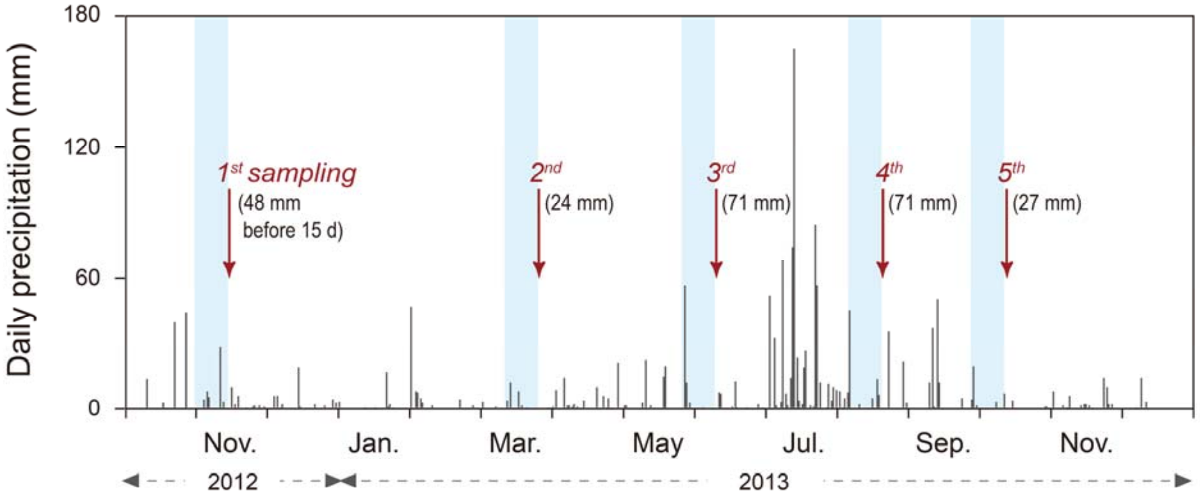

Fig. S1. Daily precipitation recorded at Ansan City station, the nearest meteorological observation station, from October 2012 to December 2013. Data were obtained from Korea Meteorological Administration (KMA, 2013).

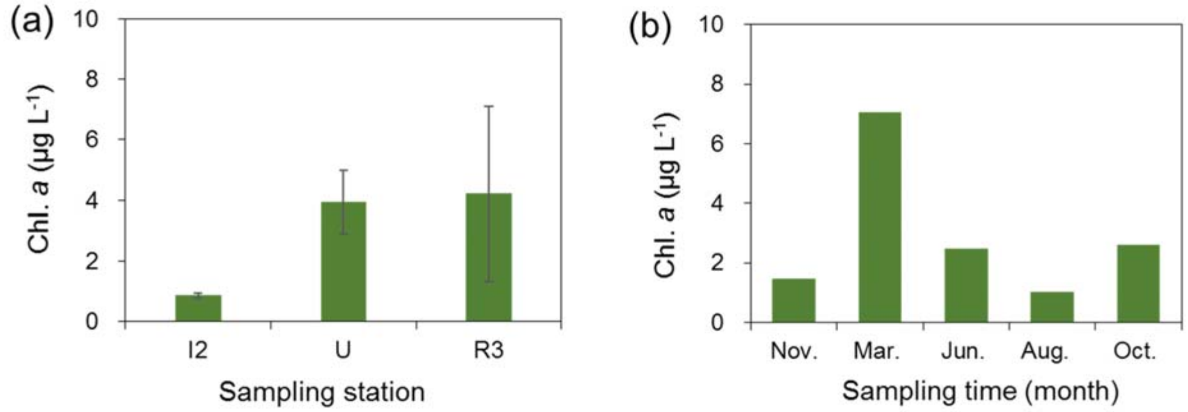

Fig. S2. Chlorophyll *a* concentrations in (a) inflow sources (I2: industrial area; U: urban area; R3: rural area) and (b) Lake Sihwa (S6) from November 2012 to October 2013. The details of the analytical method are provided elsewhere (Ha et al., 2014).

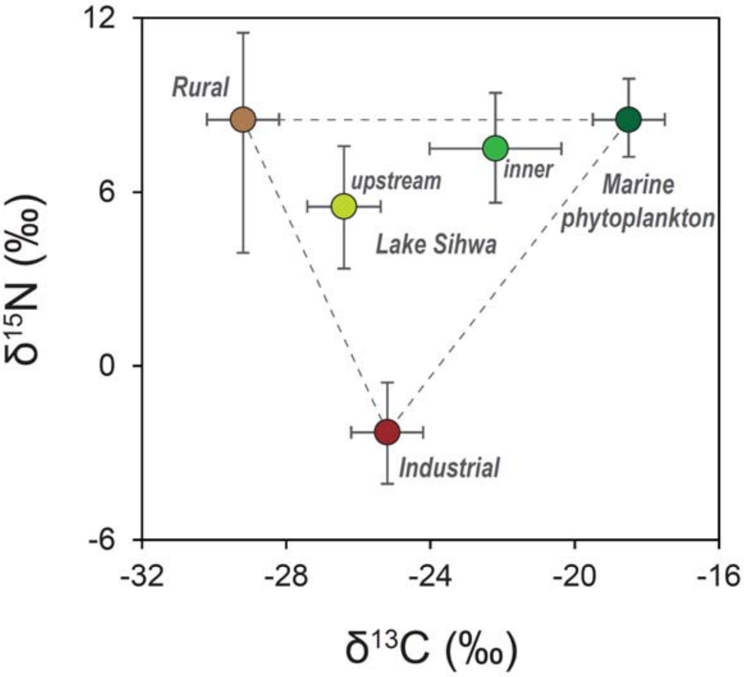

Fig. S3. The mean $\delta^{13}C$ and $\delta^{15}N$ values in the possible sources (i.e., industrial, rural, and marine phytoplankton) and Lake Sihwa.

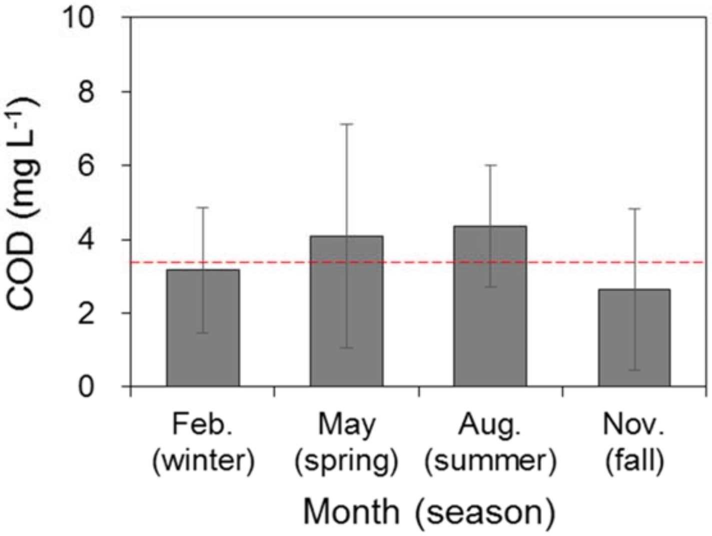

Fig. S4. Seasonal mean concentrations of chemical oxygen demand (COD) in the Lake Sihwa during 10 years (2004-2013). The red dotted line indicates the target water quality level (3.3 ppm COD) of Total Pollution Load Management System (TPLMS). Data were collected from Marine Environment Information System (MEIS, 2013).

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