



Baseline

Carbon and nitrogen stable isotope signatures linked to anthropogenic toxic substances pollution in a highly industrialized area of South Korea



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ABSTRACT

Sources of organic matter in a polluted coastal embayment (Lake Sihwa) indicated that $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of suspended particulate matter (SPM) and sediments could be distinguished by land-use type and surrounding activities. Specifically, low $\delta^{15}\text{N}$ occurred in inland creeks near industrial complex, where severe contamination by persistent toxic substances (PTSs) is evidenced. To identify the sources of ^{15}N -depleted organic matter and PTSs, the SPM and/or sediments were collected along ~8 km of the Singil Creek and in stormwater drainage pipes that carried pollutants to the creeks from upland areas. Results indicated that stormwater originating in industrial areas was the main source of low $\delta^{15}\text{N}$ and elevated PTSs, which appeared to flow into stormwater drains with rainwater and eventually into the creeks at stormwater outfalls. To improve the water quality of inland creeks, it will be necessary to reduce the amount of untreated stormwater entering stormwater drainage system from industrial complex.

Lake Sihwa is an artificially created body of water behind a sea dike constructed in 1994 (Lee et al., 2014a, 2016a) (Fig. 1). Lake Sihwa is one of the most polluted coastal areas in South Korea due to the large inputs of sewage and toxic substances from surrounding areas and very limited tidal exchange (Hong and Shin, 2011; Khim and Hong, 2014). Originally, the sea dike was built to supply freshwater for use in nearby agricultural lands and industrial complexes (Lee et al., 2014a). However, the environment of Lake Sihwa rapidly deteriorated after dike embankment, which trapped runoff of contaminants from surrounding industrial and urban areas (Lee et al., 2014a, 2016a). Since its creation, the Korean government has attempted to improve water quality in Lake Sihwa by constructing a water gate (1999), designating the lake as a Special Management Zone (2000), constructing and upgrading wastewater treatment plants (WWTP), and launching a of Total Pollution Load Management System (2013) (Lee et al., 2016a). As a result, water quality in Lake Sihwa has timely improved somewhat. However, inland creeks (i.e., tributary creeks) flowing through the industrial complexes are still extremely polluted and great concentrations of persistent toxic substances (PTSs) have been detected in both water column and bottom

sediments (Hong et al., 2010, 2016a; Khim et al., 1999; Lee et al., 2017a, 2018a; Moon et al., 2012a, 2012b). Thus, it is still crucial to identify the sources and fate of organic matter and PTSs flowing into the Lake Sihwa.

Methods for tracing the source(s) of water pollution and identifying organic matter in aquatic environments have been rapidly improving. These methods include using stable isotope ratios of carbon (C) and nitrogen (N) ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, respectively) in suspended particulate matter [SPM; particulate organic carbon (POC) or particulate nitrogen (PN)] and sediments (Kim et al., 2018; Lee et al., 2014b, 2017b). However, bulk $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values could not completely differentiate among potential local sources of organic matter; thus, it is only possible to apply the method within a localized area (Machiwa, 2010; Maksymowska et al., 2000). Recently, the stable isotope techniques have been applied to the Lake Sihwa ecosystem and surrounding inland creeks (Lee et al., 2014b, 2017b). Lee et al. (2014b) identified the various sources of organic matter in Lake Sihwa, using $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ to differentiate among rural, industrial, and marine phytoplankton sources. Particulate organic matter (POM) inputs from industrial areas

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Fig. 1. Map showing the sampling sites in (a) Lake Sihwa and (b) tributary creek (Singil Creek). Stormwater samples were collected from four outfall pipes in tributary creeks near Stations SG6, SG7, SG8, and SG10 (marked with arrows).

contain much lower $\delta^{15}\text{N}$ values (-2.3‰) compared to those from other sources (Lee et al., 2017b).

Industrial areas are major sources of organic matter and toxic chemicals into Lake Sihwa (Hong et al., 2016a; Moon et al., 2012a, 2012b). In addition, especially in rainy season, organic matter originating from industrial area largely contributed to Lake Sihwa (Lee et al., 2017b). However, such previous studies have not been able to identify where the low $\delta^{15}\text{N}$ in SPM originates in the industrial area or how POM might be related to the behavior and fate of organic toxic substances. Stormwater flows into creeks from the stormwater drainage system located within the industrial complexes (Loganathan et al., 1997). Stormwater is rainwater and/or groundwater that is derived from runoff from impervious surfaces in industrial complexes and city streets. Unlike wastewater, they flow directly into nearby inland creeks via stormwater drainage pipes (without being treated) and eventually into the Lake Sihwa.

Polycyclic aromatic hydrocarbons (PAHs), styrene oligomers (SOs), and alkylphenols (APs) are the typical PTSs identified in Lake Sihwa (Hong et al., 2016a; Lee et al., 2017a). These pollutants mainly originate from nearby industrial areas and are transported to Lake Sihwa from both point and non-point sources. These classes of chemicals have been reported to cause adverse (or toxic) effects on aquatic organisms; for example, PAHs are carcinogenic, SOs are genotoxic, and APs are estrogenic (Neff et al., 2005; Ohyama et al., 2001; Soares et al., 2008; Tatarazako et al., 2002). PTSs are generally adsorbed in POM and sediments and accumulate near the pollution source because they are hydrophobic and cannot be transported very far by flowing water (Hong et al., 2016a). However, bottom sediments can be resuspended during the rainy season, thus sedimentary PTSs can be reintroduced into the water column.

Many unknown toxic substances are also being discharged from the industrial areas. In vitro cell bioassays can be used to screen and identify these substances, because mechanism-based toxic responses can be induced by unknown toxic substances in mixture (Hong et al., 2012; Khim et al., 1999; Villeneuve et al., 2002). In a previous effect-directed analysis (EDA) study using H4IIE-*luc* in vitro bioassay, we successfully identified SOs (aryl hydrocarbon receptor (AhR) agonists) in sediments of the inland creeks of Lake Sihwa (Hong et al., 2016a). The bioassays are rapid, sensitive, and inexpensive and provide an information relating to both known and unknown toxicants in environmental samples, thus it is a useful assessment tool.

In the present study, we aimed to understand behavior and sources of organic matter by analyzing bulk $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in SPM and sediments of Lake Sihwa and nearby inland creeks. In particular, we monitored $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of SPM and sediments in Singil Creek and its

tributaries. To understand the contribution of pollution delivered by stormwater pipes in the industrial area, we also measured concentrations of selected PTSs (PAHs, SOs, and APs) in the study region and determined potential AhR- and estrogen receptor (ER)-mediated activities in sediments near the pipes outlets.

In March 2013, the first survey was conducted at 19 stations; Lake Sihwa ($n = 9$; Stations S1–S9) and inland creeks ($n = 10$) that flow through various land-use types such as rural (Stations W, R1–R3), urban (Station U), and industrial area (Stations I1–I5) (Fig. 1a). All sediment samples were collected in duplicate at each station. For each station, we analyzed $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in sediments. The corresponding data in SPM were selectively used from published data (Lee et al., 2017b) to compare isotopic compositions between media (SPM vs. sediment) and locality (lake vs. inland creek) (Fig. 2a). Further, to identify the sources of pollutant, we collected water and sediment samples in duplicate from upstream to downstream ($n = 10$) stations along the Singil Creek in June 2015. Because Singil Creek passes through urban, rural, and industrial areas, we established sampling locations within reaches of these land-use types: Stations SG1–SG3 were established in an urban area, Station SG4 in a rural area, and Stations SG5–SG10 in industrial locations (Fig. 1b). Stations SG6–SG8 and SG10 were situated near stormwater outfall pipes along a reach of Singil Creek flowing through an industrial area. We also collected duplicate water samples from the four stormwater pipes at those stations. Three indicator parameters in water and stormwater samples, such as conductivity, pH, and turbidity, were measured in situ using a calibrated multi-probe (YSI-650 MDS, YSI Inc., Yellow Springs, OH), which aids to identify industrial discharges (Brown et al., 2004). The SPM samples obtained from the water and stormwater pipes were filtered through a Whatman GF/F glass micro-fiber filter (Dassel, Germany) with a $0.7\ \mu\text{m}$ nominal pore-size. Filters were freeze-dried and then stored at $-80\ ^\circ\text{C}$. Sediment samples were freeze-dried and sieved (2-mm mesh) and stored at $-20\ ^\circ\text{C}$ until further analyses.

After we removed inorganic carbon by the HCl treatment, a Euro EA3028 elemental analyzer (EuroVector, Milan, Italy) combined with an Isoprime isotope ratio mass spectrometer (GV Instruments, Manchester, UK) was used to determine carbon stable isotope ratios of SPM ($\delta^{13}\text{C}_{\text{POC}}$) and sediments ($\delta^{13}\text{C}_{\text{TOC}}$). We analyzed nitrogen stable isotope ratio of SPM ($\delta^{15}\text{N}_{\text{PN}}$) and sediments ($\delta^{15}\text{N}_{\text{TN}}$) without removing inorganics (*sensu* Lee et al., 2016b). All isotopic compositions were expressed in δ notation, based on the following formula:

$$\delta^{13}\text{C} \text{ or } \delta^{15}\text{N} (\text{‰}) = [(R_{\text{sample}}/R_{\text{reference}}) - 1] \times 1000$$

wherein R is the ratios of either $^{13}\text{C}/^{12}\text{C}$ or $^{15}\text{N}/^{14}\text{N}$. Vienna Peedee Belemnite and atmospheric N_2 were used as reference materials for

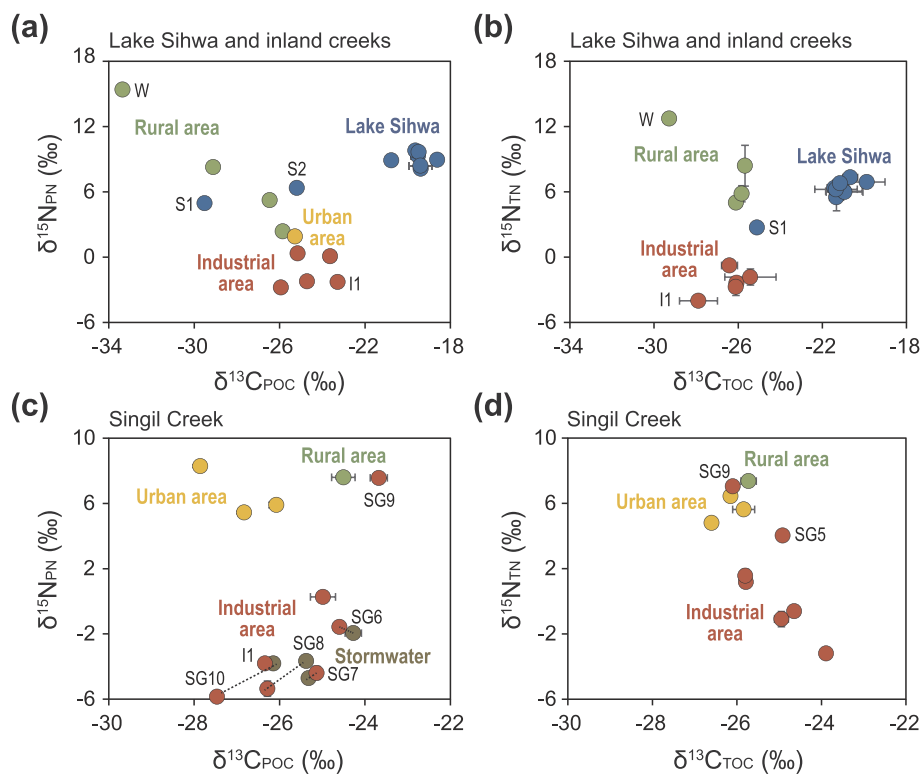


Fig. 2. Scatter plots for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values for (a) suspended particulate matter [SPM; particulate organic carbon (POC) or particulate nitrogen (PN)]* and (b) sediments samples collected from Lake Sihwa and inland creeks and in (c) SPM and (d) sediments of the Singil Creek (*Data from Lee et al., 2017b).

carbon and nitrogen, respectively. The analytical errors were 0.06‰ for C and 0.1‰ for N estimated by IAEA working standards (CH-6 for carbon and N-1 for nitrogen, International Atomic Energy Agency (IAEA), Vienna, Austria). Concentrations of total organic carbon and total nitrogen in SPM and sediments were determined using an elemental analyzer (Euro EA3028, EuroVector, Milan, Italy). The acidified filter and sediment samples were used to determine organic carbon concentrations.

We quantified concentrations of PTSs (e.g., PAHs, SOs, and APs) in sediments of Singil Creek with an Agilent 7890 gas chromatograph (GC) equipped with a 5975C mass-selective detector (Agilent Technologies, Santa Clara, CA). Detailed information on instrumental conditions, target analytes, method detection limits, and surrogate recoveries are provided in Tables S1 and S2 of the Supplementary Materials (S). We analyzed 22 PAHs, 10 SOs, and 6 APs (Table S1) using methods previously reported by Hong et al. (2016a) and Lee et al. (2018b). Unfortunately, SOs of samples from Station SG10 could not be analyzed due to the limit of sample volume. The detection limits for PAHs, SOs, and APs in sediments, defined as 3.707 times the standard deviation of mean of sample standards, were 0.24–0.90 ng g⁻¹ dry weight (dw) for PAHs, 0.30–0.94 ng g⁻¹ dw for SOs, and 0.09–0.97 ng g⁻¹ dw for APs, respectively (Table S2). Five surrogate standards were used to assess the recovery rates of PAHs, SOs, and APs, which were generally within the acceptable ranges (Table S2). APs concentrations are expressed as toxic equivalent concentrations (TEQ-APs), wherein TEQ values were based on the concentrations of individual compounds multiplied by their toxic equivalency factors (TEFs) and normalized to 1% total organic carbon (TOC), an approach suggested by CCME (CCME, 2002).

We performed H4IIE-*luc* and MVLN bioassays, using methods of Hong et al. (2012), Khim et al. (1999), and Villeneuve et al. (2002), to detect AhR- and ER-mediated potencies in sediment organic extracts. These bioassay results, expressed as mean relative luminescence units, were converted to percentages of standard materials, such as 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (i.e., 300 pM TCDD = 100% TCDD) and

17 β -estradiol (i.e., 1235 nM E2 = 100% E2). The luciferase activity was determined after 72 h of exposure (*sensu* Villeneuve et al., 2002). Significant responses were defined as those that were at least three times the standard deviation of the mean of solvent controls. All samples were tested in triplicate. Unfortunately, the bioassays for samples from Station SG10 could not be conducted due to the limit of sample volume.

Linear regression analysis was used to understand the effects of toxic substances (PTSs concentrations and potential toxicities) on carbon and nitrogen isotopic compositions in sediments. The cluster analysis was performed using Ward's method, then the statistical differences between two groups were assessed using the Student's *t*-test. Statistical significance was defined as $p < 0.05$. Statistical analyses were conducted in SPSS 23.0 software (SPSS Inc., Chicago, IL).

$\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values between SPM and sediments of Lake Sihwa and adjacent inland creeks did not greatly vary, however, stable isotope ratios could differentiate the various land uses surrounding Lake Sihwa (i.e., industrial, rural, and urban areas) (Fig. 2a–b). For example, except for the two uppermost stations of Lake Sihwa (Stations S1 and S2), the particulate matter of Lake Sihwa represented a typical marine phytoplankton signature (*sensu* Lee et al., 2014b), with $\delta^{13}\text{C}_{\text{POC}}$ values ranging between -20.76‰ and -18.61‰ and the $\delta^{15}\text{N}_{\text{PN}}$ values ranging between 8.12‰ and 9.78‰ (Table S3 and Fig. S1). In contrast, the particulate matter of rural area (Station W, R1-R3) indicated a typical terrestrial land-use [i.e., C3 plants signatures (*sensu* Maksymowska et al., 2000), with stable isotopic ratios of light carbon (-28.69‰) and heavy nitrogen (7.82‰)]. In particular, Station W showed most low $\delta^{13}\text{C}_{\text{POC}}$ value (-33.36‰) and most high $\delta^{15}\text{N}_{\text{PN}}$ value (15.41‰). This station is reed wetland dominated by *Phragmites australis* which have been reported to show low carbon isotopic composition (-28.3‰) (Choi et al., 2005). The terrestrial and aquatic plants-derived organic matter could influence on the low $\delta^{13}\text{C}$ of POM in rural area. Despite rural areas which seem to use fertilizer, high $\delta^{15}\text{N}$ values were observed. Dillon and Chanton (2005) noted that although fertilizer has low $\delta^{15}\text{N}$ value (~0‰), the excess N by fertilizer application could

stimulate nitrification/denitrification processes, resulting in ^{15}N enrichment in residual NH_4^+ and NO_3^- . At the industrial stations, $\delta^{13}\text{C}_{\text{POC}}$ values indicated a moderate derivation (-25.94% to -23.28%) of marine phytoplankton and terrestrial plants, whereas $\delta^{15}\text{N}_{\text{PN}}$ values indicated considerably lower values (-2.79% to 0.34%). High $\delta^{15}\text{N}$ values have been reported in dissolved inorganic nitrogen and/or primary producer near WWTP outfall (Gaston and Suthers, 2004; Wayland and Hobson, 2001). On the other hand, low $\delta^{15}\text{N}$ values have been observed in the sewage-derived particulate matter (DeBruyn and Rasmussen, 2002; Spies et al., 1989; Tucker et al., 1999). Considering low concentrations of chlorophyll-*a* (Chl-*a*) in the industrial area (Lee et al., 2014b), low $\delta^{15}\text{N}_{\text{PN}}$ values could be largely influenced by sewage-derived organic matter. In summary, the origin of organic matter in the Lake Sihwa could be distinguished using bulk $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values in SPM and sediments (i.e., rural area was lower in $\delta^{13}\text{C}$, whereas industrial was lower $\delta^{15}\text{N}$ values).

Data on $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in SPM and sediments collected from upstream to downstream reaches in Singil Creek are provided in Fig. 2c–d. Influent samples, collected from the stormwater drainage pipes flowing into Singil Creek (near Stations SG6–SG8 and SG10), showed that stable isotopic signatures ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) in SPM and sediments varied station by station (Table 1 and Fig. 2c–d). This suggests that influent water quality from stormwater pipes fluctuated temporally. The $\delta^{13}\text{C}_{\text{POC}}$ and $\delta^{15}\text{N}_{\text{PN}}$ in stormwater were similar to those for Singil Creek water samples. In addition, the stable isotopic compositions of Station SG9 exhibited the characteristic signature of a rural area even though it was near an industrial area (Fig. 2c–d; There was no stormwater discharge pipe near Station SG9). These results indicate that ^{15}N -depleted SPM would be mainly attributable to stormwater pipes in the industrial areas. Considering high POC and low Chl-*a* concentrations in the SPM (POC: $2920 \mu\text{g C L}^{-1}$; Chl-*a*: $3.8 \mu\text{g L}^{-1}$) from stormwater pipes of the industrial area in Singil Creek (K-water, 2009), low $\delta^{15}\text{N}_{\text{PN}}$ seemed to be directly introduced into the creek through stormwater pipes, even while low $\delta^{15}\text{N}$ values of inorganic nitrogen being discharged from the rainwater (Dillon and Chanton, 2005; Yue et al., 2015). The rainwater that flows from impervious surfaces (non-point pollution sources) accumulates in gutters and flows through stormwater drains into tributary creeks (at a stormwater outfalls). Thus, water from stormwater drainage pipes reflects the degree and type of contamination washed from impervious surfaces in the watershed (Loganathan et al., 1997).

TOC content was significantly and positively correlated with $\delta^{13}\text{C}_{\text{TOC}}$ values in sediments of Singil Creek; likewise, TN content was significantly and negatively correlated with $\delta^{15}\text{N}_{\text{TN}}$ in sediments along the Singil Creek (Fig. S2). We not only found great TOC content and heavy $\delta^{13}\text{C}_{\text{TOC}}$ values in the sediments of the industrial stations, but also found the great TN content and low $\delta^{15}\text{N}_{\text{TN}}$ values. The $\delta^{13}\text{C}$ values in SPM and sediments near the industrial complexes were mainly from carbon emissions from vehicles and coal combustion; the $\delta^{15}\text{N}$ values indicated fuel oil as a pollution source (Maksymowska et al., 2000).

We found great concentrations of PAHs, SOs, and APs in sediments of Stations SG5–SG10, and I1, all of which (except for SG9) were located adjacent to industrial areas (Table 1 and Fig. 3). Concentrations of PTSs in sediments of urban and rural areas were not very high compared to those of industrial areas. Detected concentrations of PAHs (except for anthracene) and APs at the sampling stations of Singil Creek flowing through industrial areas exceeded interim sediment quality guidelines (ISQGs) recommended by CCME (CCME, 1999, 2002) (Table S4). Guidelines for SOs in sediments are not available and so we could not evaluate sediment quality relative to SOs; however, those concentrations were greater in Singil Creek than in other coastal areas of South Korea [e.g., Masan Bay (Lee et al., 2018b) and Geum River Estuary (Yoon et al., 2017)].

We found great concentrations of PTSs in sediments at sampling stations near stormwater outlets, such as at Stations SG6–SG8 and SG10 (Fig. 3a–c). Stormwater flowing into Singil Creek from industrial areas (Fig. 3d) were difficult to link to any particular type of industry due to

our lack of data on concentrations and incoming flow rates of stormwater. However, qualitatively, great concentrations of PAHs were associated with Station SG6 (located near printing industries), whereas great concentrations of SOs and APs were associated with Stations SG7 and SG8 (located near electronic, metal, and plating industries). Concentrations of PTSs at stormwater outlets near Station SG9 were lower than those at other stations associated with industrial area (i.e., Stations SG6–SG8 and SG10). Therefore, it seems that the inputs of PTSs into Singil Creek (via stormwater pipes) are mainly from surrounding industrial areas.

Among the target pollutants, some were mainly detected in sediments of the Singil Creek: PAHs, pyrene, benzo[*g,h,i*]perylene, and fluoranthene; SOs, 2,4-diphenyl-1-butene, 2,4,6-triphenyl-1-hexene, and 1a-Phenyl-4e-(1-phenylethyl)-tetralin; and APs, nonylphenols, 4-*tert*-octylphenol, and nonylphenol-monoethoxylates (Fig. S3). We found higher ratios of NPs/(NP1EOs + NP2EOs) and SDs/STs at sampling stations near stormwater outfalls, such as at Stations SG6–SG8 and SG10 (Fig. S4). Such stations (near outfalls) could be used to identify nearby sources of PTSs pollution (Hong et al., 2016a; Yoon et al., 2017). Based on PAHs diagnostic ratios, we determined that the PAHs identified in this study were mainly derived from petroleum products and petroleum and coal combustion by-products (Fig. S5). This conclusion concurs with results of recent studies identifying sources of PAHs in Lake Sihwa and its tributary creeks (Hong et al., 2016a; Lee et al., 2017a).

Results for potential AhR- and ER-mediated activities in sediments of the Singil Creek are summarized in Table 1 and Fig. 3e–f. We found greater AhR- and ER-mediated potencies in sediments collected from Singil Creek near industrial sites, similar to what we found for PTSs. Significant bioassay responses were observed even when tested cells were exposed to small concentrations of sediment extracts to prevent cytotoxicity ($2 \text{ mg sediment mL}^{-1}$). When cells were exposed to five times greater concentrations ($10 \text{ mg sediment mL}^{-1}$), cytotoxicity was suspected in organic extracts of sediments from Stations SG5, SG8, and I1 in the H4IIE-*luc* bioassay and of sediments from Station I1 for the MVLN bioassay (Fig. S6). Thus, AhR- and ER-mediated potencies in sediments could be explained based on results of a 2-mg mL^{-1} sediment exposure (Table 1 and Fig. 3). The greatest AhR-mediated potency was found in the sediments of Station SG8, followed by potencies in sediments of Stations I1 and SG6, whereas the greatest ER-mediated potency was observed in Station SG5 sample, followed by Stations SG7 and SG8 samples. In contrast, sediment from Station SG9, where there was no stormwater outfall pipe, showed small AhR- and ER-mediated potencies. Overall, the responses of in vitro cell bioassays were generally greater in sediments of industrial areas (with greater PTS concentrations) than in those of rural and urban areas.

PAHs and SOs are known to be AhR agonists and APs are well known as ER agonists (Hong et al., 2016a; Khim et al., 1999). Responses of bioassays reflect the sample potency of known AhR and ER agonists, but the bioassays also respond to the effects of unknown toxic chemicals in mixture samples. In this study, we could not quantitatively compare results of our chemical analyses and bioassays with other studies because we only conducted screening tests. Because the contributions of known AhR agonists in previous studies performed in Lake Sihwa and its tributary creeks accounted for only about 10% of the induced toxicity (Hong et al., 2016a; Lee et al., 2017a), it will be necessary to conduct effect-directed analysis (EDA) studies to quantitatively identify both known and unknown toxic substances in sediments and sewage samples (Hong et al., 2016b).

When the $\delta^{13}\text{C}_{\text{TOC}}$ and $\delta^{15}\text{N}_{\text{TN}}$ values in sediments of Singil Creek were compared with PTSs concentrations and bioassay results (Fig. 4), we found a significant, positive relationship between for $\delta^{13}\text{C}_{\text{TOC}}$ and APs concentrations and a significant, negative correlation between $\delta^{15}\text{N}_{\text{TN}}$ and PTSs concentrations. We also found significant relationships between AhR- and ER-mediated potencies relative to $\delta^{13}\text{C}_{\text{TOC}}$ and a significant relationship between AhR-mediated potency and $\delta^{15}\text{N}_{\text{TN}}$. In

Table 1
 Chemical characteristics of suspended particulate matter [SPM; particulate organic carbon (POC) or particulate nitrogen (PN)] and sediments in tributaries flowing to Lake Sihwa. Characteristics include stable isotope ratios of carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$) in SPM, TOC and TN contents, and concentrations of persistent toxic substances (PAHs, SOs, and APs), and Ahr- and ER-mediated potencies in sediments collected from Singil Creek (June 2015).

| Surrounding activity | Sampling sites | Sediments | | | | | | | | | | |
|----------------------|-----------------|---|--|------------|--------------|---|--|--|---------------------------------------|--|------------------------|------------------------|
| | | SPM | | | | | Sediments | | | | | |
| | | $\delta^{13}\text{C}_{\text{POC}}$ (‰) | $\delta^{15}\text{N}_{\text{PN}}$ (‰) | TOC (%) | TN (%) | $\delta^{13}\text{C}_{\text{TOC}}$ (‰) | $\delta^{15}\text{N}_{\text{TN}}$ (‰) | Σ PAHs (ng g ⁻¹) | Σ SOs (ng g ⁻¹) | APs-TEQs ^a (ng g ⁻¹) | Ahr potency (%TCDD) | ER potency (%E2) |
| Urban area | SG1 | -26.9 ± 0.04 ^b | 5.4 ± 0.07 | 4.4 ± 1.0 | 0.65 ± 0.02 | -26.6 ± 0.05 | 4.8 ± 0.21 | 481 | 261 | 130 | 4.34 ± 0.89 | 5.00 ± 0.95 |
| | SG2 | -26.2 ± 0.03 | 5.9 ± 0.17 | 5.3 ± 0.1 | 0.53 ± 0.03 | -26.2 ± 0.03 | 6.4 ± 0.09 | 502 | 245 | 127 | 6.65 ± 1.84 | 4.11 ± 1.66 |
| Rural area | SG3 | -28.0 ± 0.13 | 8.3 ± 0.09 | 1.7 ± 0.2 | 0.040 ± 0.01 | -25.8 ± 0.26 | 5.6 ± 0.28 | 195 | 150 | 48.5 | 3.55 ± 0.48 | 6.25 ± 0.28 |
| | SG4 | -24.6 ± 0.27 | 7.6 ± 0.10 | 3.2 ± 0.1 | 0.42 ± 0.02 | -25.7 ± 0.18 | 7.4 ± 0.13 | 238 | 148 | 119 | 3.70 ± 1.37 | 6.78 ± 2.40 |
| Industrial area | SG5 | -25.0 ± 0.29 | 0.3 ± 0.10 | 21 ± 0.1 | 2.1 ± 0.2 | -24.9 ± 0.03 | 4.0 ± 0.28 | 1430 | 632 | 3960 | 8.16 ± 1.12 | 29.4 ± 2.01 |
| | SG6 | -24.6 ± 0.14 | -1.6 ± 0.02 | 18 ± 0.1 | 1.8 ± 0.1 | -25.8 ± 0.05 | 1.2 ± 0.32 | 2420 | 895 | 4820 | 10.0 ± 2.32 | 16.2 ± 1.73 |
| | SG7 | (-24.3 ± 0.19) ^c | (-1.9 ± 0.02) | 16 ± 0.3 | 1.5 ± 0.06 | -25.8 ± 0.01 | 1.6 ± 0.32 | 1700 | 1730 | 7450 | 5.37 ± 1.01 | 21.5 ± 4.92 |
| | SG8 | (-25.3 ± 0.06) | (-4.7 ± 0.11) | 24 ± 0.1 | 2.4 ± 0.07 | -25.0 ± 0.16 | -1.1 ± 0.41 | 1410 | 1240 | 3890 | 17.0 ± 1.91 | 19.3 ± 2.03 |
| | SG9 | (-25.4 ± 0.12) | (-3.7 ± 0.05) | 3.0 ± 0.4 | 0.38 ± 0.03 | -26.1 ± 0.01 | 7.0 ± 0.74 | 236 | 164 | 192 | 5.06 ± 1.44 | 8.64 ± 0.69 |
| | SG10 | -23.7 ± 0.20 | 7.6 ± 0.04 | 41 ± 0.1 | 2.4 ± 0.07 | -23.9 ± 0.01 | -3.2 ± 0.24 | 1600 | na ^d | 1480 | na | na |
| | II ^e | -27.5 ± 0.10 | -5.8 ± 0.12 | 37 ± 1.1 | 3.7 ± 0.3 | -24.6 ± 0.05 | -0.61 ± 0.52 | 1040 | 1430 | 2270 | 15.1 ± 5.72 | 15.0 ± 2.81 |
| | | (-26.2 ± 0.07) | (-3.8 ± 0.06) | | | | | | | | | |
| | | -26.3 ± 0.11 | -3.8 ± 0.37 | | | | | | | | | |

^a Toxic equivalent concentration of alkylphenols using the toxic equivalency factors (TEFs) (CCME, 2002) and normalized to 1% TOC.

^b Mean ± SD.

^c C and N stable isotope ratios for SPM of stormwater samples.

^d na: not analyzed.

^e Station II was monitored both two sampling campaigns performed in March 2013 and June 2015.

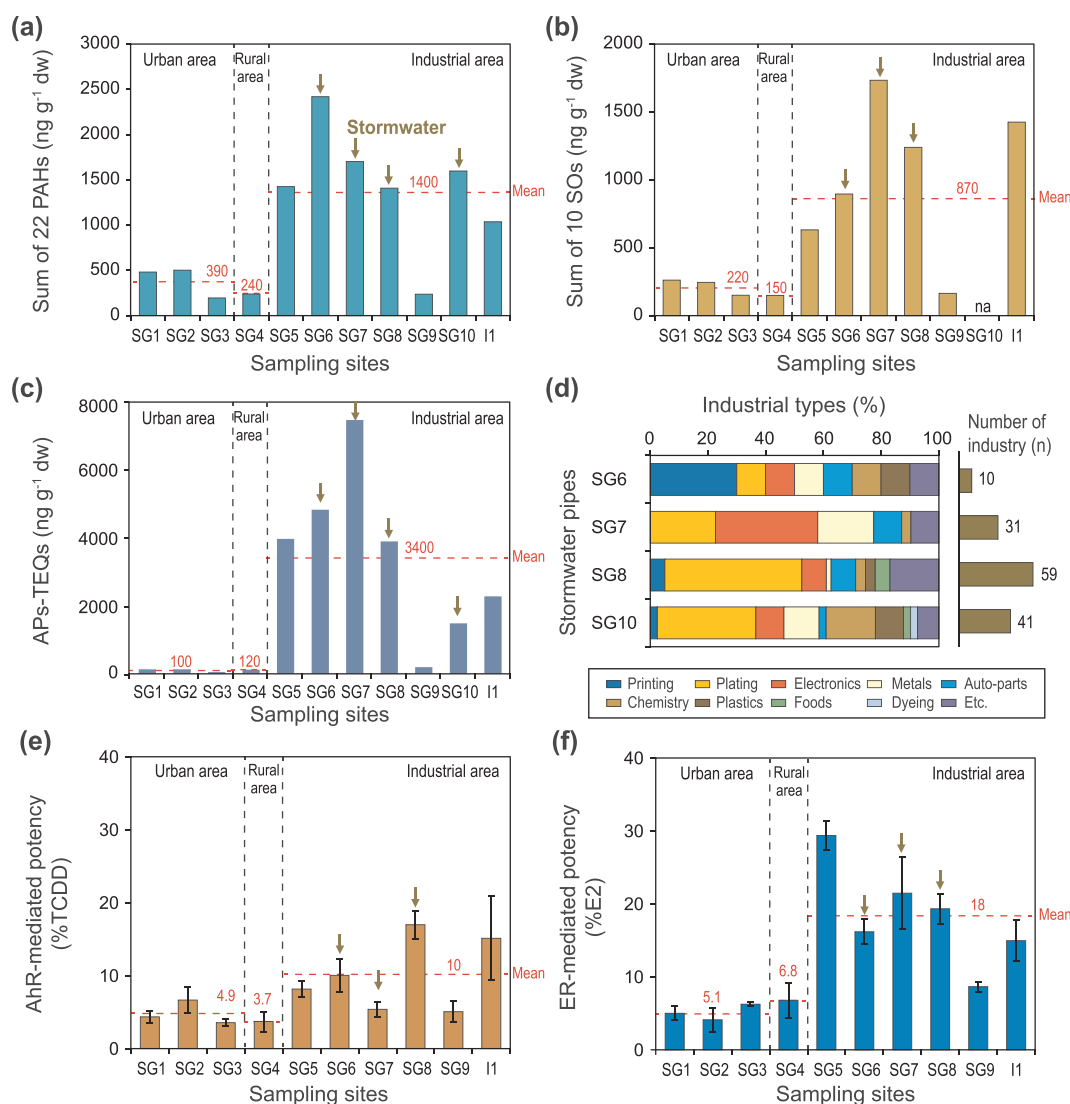


Fig. 3. Concentrations of persistent toxic substances in sediments of Singil Creek: (a) PAHs, (b) SOs, and (c) APs. (d) Relative compositions of industrial types and number of industries associated with outfall pipes near Stations SG6, SG7, SG8, and SG10. (e) Potential AhR- and (f) ER-mediated potencies in sediments of Singil Creek.

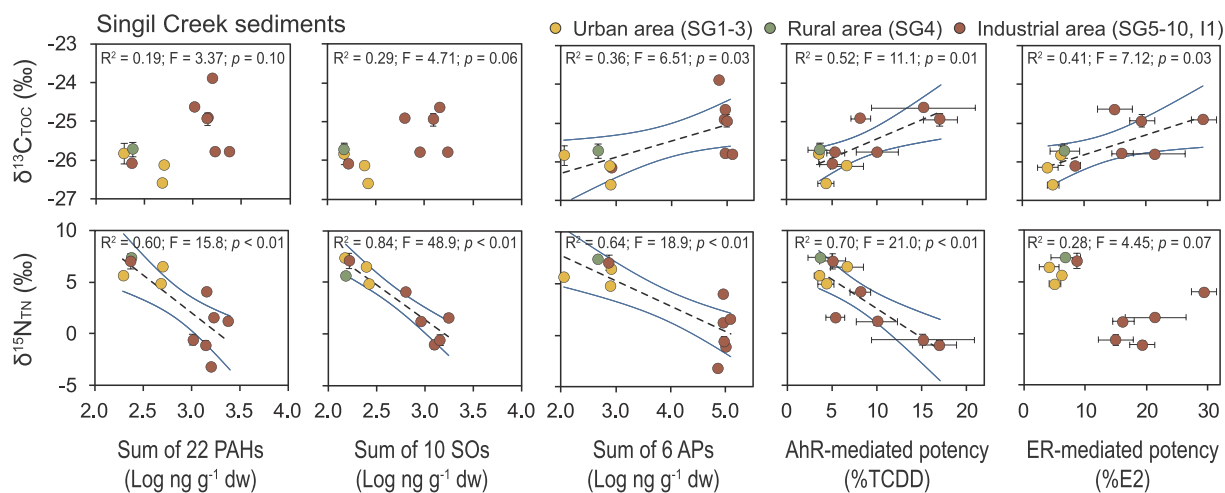


Fig. 4. Scatter plots for $\delta^{13}\text{C}_{\text{TOC}}$ and $\delta^{15}\text{N}_{\text{TN}}$ values and correlations for concentrations of persistent toxic substances and potential AhR- and ER-mediated potencies of sediments in Singil Creek. Blue lines represent 95% confidence intervals. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

general, $\delta^{15}\text{N}_{\text{TN}}$ values showed more significant correlations with PTSs and bioassay responses than did $\delta^{13}\text{C}_{\text{TOC}}$ values. That is, $\delta^{15}\text{N}_{\text{TN}}$ appeared to relate better to the inflow of anthropogenic organic matter and toxic substances at outfall pipes. Collectively, the stormwater had low $\delta^{15}\text{N}$ values, great concentrations of PTSs, and great toxic potencies. We attribute the water quality in these outfall pipes to the industrial complexes from which they flowed and pollutants in the pipes seem to have behaved similarly before reaching outfalls at the creek. Our results indicate that bulk $\delta^{15}\text{N}$ values in this region are useful for identifying the sources of organic matter and anthropogenic toxic chemicals that flow into coastal areas from a variety of land-uses. Meanwhile, conductivity has been used as an indicator ($\geq 2000 \mu\text{S cm}^{-1}$) to identify industrial discharges (Brown et al., 2004). Greater conductivities were observed in two stormwater pipe outfalls (near SG6 and SG8) than corresponding reference value (Table S5). Considering great conductivity, PTSs concentration, and bioassay responses at outfall pipes, the illicit wastewater connections and/or contamination of stormwater by leakage from old sewage pipes might be suspected in the Singil Creek.

Lake Sihwa and its tributary creeks are one of the most polluted bodies of water in South Korea. It appears that organic and inorganic toxic substances, originating mainly in adjacent industrial areas, flow through stormwater drains and then into creeks that eventually flow into Lake Sihwa. Although much effort has been focused on reducing the contamination of land-driven pollutants in Lake Sihwa, the pollution of inland creeks remains ongoing problem. Through this study, it was confirmed for the first time that low $\delta^{15}\text{N}$, great concentrations of PTSs, and great AhR and ER agonists were introduced together to inland creeks through stormwater pipes. Despite the close distances between the sampling stations, the presence of stormwater pipe outfalls significantly affected the contaminations of the creek sediments (Fig. S7). Toxic substances distributed throughout industrial areas adjacent to Lake Sihwa (non-point pollution) appeared to get washed into stormwater drains during rainfall events and then might be shunted to stormwater outfalls at inland creeks. At present, inland creeks of Lake Sihwa act as sedimentation basins and thus store highly polluted sediments of anthropogenically produced organic matter and other toxic substances. These polluted sediments likely get re-suspended during rain events and flow into the Lake Sihwa and its coastal environments. Therefore, more effort is needed to prevent this continuing input of pollutants from surrounding uplands. To clean inland creeks, we suggest that the water quality of stormwater draining industrial areas should be improved. In particular, in areas receiving a large input of non-point pollutants, such as in industrial complexes, it is important to prevent untreated stormwater from flowing directly into creeks, but more efficiently to treat the contaminated water in WWTP. Overall, the present study provides useful information on sources and fate of toxic organic matter in the highly industrialized area as baseline data for the future study of tracking the source of pollutants. In the future, more advanced analytical techniques such as compound-specific isotope analysis (e.g., $\delta^{13}\text{C}$ in fatty acids or n-alkanes) can be applied to track the sources of organic matter and/or trace organic chemicals.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.marpolbul.2019.05.006>.

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Carbon and nitrogen stable isotope signatures linked to anthropogenic toxic substances pollution in a highly industrialized area of South Korea

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Supplementary Tables

Table S1. Instrumental conditions for analyses (GC/MSD) of persistent toxic substances, such as PAHs, SOs, and APs.

| GC/MSD system | Agilent 7890A GC and 5975C MSD |
|------------------------------------|--|
| Column | DB-5MS (30 m long, 0.25 mm i.d., 0.25 µm film thickness) |
| Gas flow | 1 mL/min He |
| Injection mode | Splitless |
| Injection volume | 2 µL |
| MS temperature | 180 °C |
| Detector temperature | 230 °C |
| Oven temperature (PAHs and SOs) | 60 °C hold 2 min Increase 6 °C/min to 300 °C 300 °C hold 13 min |
| Oven temperature (APs) | 60 °C hold 5 min Increase 10 °C/min to 100 °C Increase 20 °C/min to 300 °C |
| Target PAHs (22) | Naphthalene (Na), 2-Methylnaphthalene (2-Na), 1-Methylnaphthalene (1-Na), 1,3-Dimethylnaphthalene (1,3-Na), Acenaphthylene (Acl), Acenaphthene (Ace), Fluorene (Flu), Phenanthrene (Phe), 3-Methylphenanthrene (3-Phe), Anthracene (Ant), Fluoranthene (Fl), Pyrene (Py), Benzo[a]anthracene (BaA), Chrysene (Chr), 3-Methylchrysene (3-Chr), Benzo[b]fluoranthene (BbF), Benzo[k]fluoranthene (BkF), Benzo[a]pyrene (BaP), Perylene (Pery), Indeno[1,2,3-cd]pyrene (IcdP), Dibenz[a,h]anthracene (DbahA), and Benzo[g,h,i]perylene (BghiP), |
| Target SOs (10) | 1,3-Diphenylpropane (SD1), <i>cis</i> -1,2Diphenylcyclobutane (SD2), 2,4-Diphenyl-1-butene (SD3), 2,4,6-Triphenyl-1-hexene (SD4), 2,4,6-Triphenyl-1-hexene (ST1), 1e-Phenyl-4e-(1-phenylethyl)-tetralin (ST2), 1a-Phenyl-4e-(1-phenylethyl)-tetralin (ST3), 1a-Phenyl-4a-(1-phenylethyl)-tetralin (ST4), 1e-Phenyl-4a-(1-phenylethyl)-tetralin (ST5), and 1,3,5-Triphenylcyclohexane (isomer mix) (ST6) |
| Target APs (6) | 4-tert-Octylphenol (OP), 4-tert-Octylphenol monoethoxylate (OP1EO), 4-tert-Octylphenol diethoxylate (OP2EO), Nonylphenols (NPs, isomer mix), Nonylphenol-monoethoxylates (NP1EOs, isomer mix), and Nonylphenol diethoxylates (NP2EOs, isomer mix) |

Table S2. Detection limit of analytical method and surrogate recoveries for analytes of persistent toxic substances, such as PAHs, SOs, and APs.

| Compounds | Method detection limit | Surrogate standard recovery |
|--|---------------------------------|-----------------------------|
| | (ng g dw ⁻¹ , n = 7) | (%, n = 11) |
| <i>Polycyclic aromatic hydrocarbons (PAHs)</i> | | |
| Naphtalene | 0.43 | |
| 2-Methylnaphthalene | 0.80 | |
| 1-Methylnaphthalene | 0.78 | |
| 1,3-Dimethylnaphthalene | 0.65 | |
| Acenaphthylene | 0.85 | |
| Acenaphthene | 0.84 | |
| Fluorene | 0.80 | |
| Phenanthrene | 0.79 | |
| Anthracene | 0.41 | |
| 3-Methylphenanthrene | 0.28 | |
| Fluoranthene | 0.78 | |
| Pyrene | 0.90 | |
| Benzo[a]anthracene | 0.60 | |
| Crysene | 0.72 | |
| 3-Methylchrysene | 0.24 | |
| Benzo[b]fluoranthene | 0.69 | |
| Benzo[k]fluoranthene | 0.71 | |
| Benzo[a]pyrene | 0.59 | |
| Perylene | 0.66 | |
| Indeno[1,2,3-cd]pyrene | 0.43 | |
| Dibenz[a,h]anthracene | 0.27 | |
| Benzo[g,h,i]perylene | 0.33 | |
| <i>Styrene oligomers (SOs)</i> | | |
| 1,3-Diphenylproane | 0.34 | |
| cis-1,2-Diphenylcyclobutane | 0.65 | |
| 2,4-Diphenyl-1-butene | 0.94 | |
| trans-1,2-Diphenylcyclobutane | 0.28 | |
| 2,4,6-Triphenyl-1-hexene | 0.57 | |
| 1e-Phenyl-4e-(1-phenylethyl)-tetralin | 0.53 | |
| 1a-Phenyl-4e-(1-phenylethyl)-tetralin | 0.30 | |
| 1a-Phenyl-4a-(1-phenylethyl)-tetralin | 0.49 | |
| 1e-Phenyl-4a-(1-phenylethyl)-tetralin | 0.32 | |
| 1,3,5-Triphenylcyclohexane(isomer mix) | 0.34 | |
| <i>Surrogate standards for PAHs and SOs analyses</i> | | |
| Acenaphthene-d10 | | 111 ± 17 ^a |
| Phenanthrene-d10 | | 117 ± 16 |
| Crysene-d12 | | 100 ± 9 |
| Perylene-d12 | | 117 ± 17 |
| <i>Alkylphenols (APs)</i> | | |
| 4-tert-Octylphenol | 0.09 | |
| Nonylphenols | 0.97 | |
| 4-tert-Octylphenol-monoethoxylate | 0.10 | |
| Nonylphenol-monoethoxylates | 0.49 | |
| 4-tert-Octylphenol-diethoxylate | 0.10 | |
| Nonylphenol-diethoxylates | 0.88 | |
| <i>Surrogate standards for APs analysis</i> | | |
| Bisphenol A-d16 | | 75 ± 19 |

^a Mean ± SD

Table S3. Characteristics of stable isotopes of carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$) in suspended particulate matter [SPM; particulate organic carbon (POC) or particulate nitrogen (PN)] and sediments collected from the Lake Sihwa and tributary creeks (March 2013).

| Sampling location | | SPM | | Sediments | | | | C/N ratio |
|-------------------|----|--|---------------------------------------|--------------|-----------|--|---------------------------------------|-----------|
| | | $\delta^{13}\text{C}_{\text{POC}}$ (‰) | $\delta^{15}\text{N}_{\text{PN}}$ (‰) | TOC (%) | TN (%) | $\delta^{13}\text{C}_{\text{TOC}}$ (‰) | $\delta^{15}\text{N}_{\text{TN}}$ (‰) | |
| Rural area | R1 | -25.85±0.03 | 2.36±0.13 | 1.81±0.39 | 0.19±0.03 | -26.10±0.26 | 5.01±0.20 | 93 |
| | R2 | -29.11±0.06 | 8.28±0.15 | 1.66±0.13 | 0.16±0.02 | -25.83±0.26 | 5.83±0.74 | 103 |
| | R3 | -26.46±0.09 | 5.24±0.19 | 0.75±0.15 | 0.07±0.02 | -25.68±0.10 | 8.41±1.88 | 106 |
| | W | -33.36±0.16 | 15.41±0.07 | 2.51±0.47 | 0.30±0.05 | -29.28±0.13 | 12.74±0.46 | 84 |
| Urban area | U | -25.27±0.01 | 1.89±0.10 | ^a | - | - | - | - |
| Industrial area | I1 | -23.63±0.30 | 0.08±0.17 | 13.47±2.0 | 1.27±0.20 | -27.89±0.90 | -4.02±0.09 | 106 |
| | I2 | -25.15±0.01 | 0.34±0.31 | 8.69±2.3 | 0.53±0.12 | -26.41±0.38 | -0.76±0.25 | 163 |
| | I3 | -23.28±0.02 | -2.29±0.02 | 10.34±2.8 | 0.84±0.23 | -26.07±0.20 | -2.36±0.10 | 123 |
| | I4 | -25.94±0.08 | -2.79±0.10 | 5.37±0.72 | 0.32±0.09 | -26.11±0.16 | -2.73±0.79 | 166 |
| | I5 | -24.71±0.14 | -2.23±0.06 | 2.68±0.10 | 0.26±0.02 | -25.42±1.21 | -1.83±0.74 | 105 |
| Lake Sihwa | S1 | -29.51±0.13 | 4.95±0.14 | 2.22±0.15 | 0.27±0.01 | -25.10±0.23 | 2.73±0.34 | 83 |
| | S2 | -25.19±0.14 | 6.36±0.07 | 1.39±0.34 | 0.15±0.05 | -19.88±2.86 | 6.91±0.52 | 92 |
| | S3 | -19.51±0.31 | 9.32±0.04 | 0.82±0.11 | 0.11±0.01 | -20.67±0.36 | 7.33±0.45 | 7.8 |
| | S4 | -19.64±0.05 | 9.78±0.04 | 1.04±0.12 | 0.13±0.01 | -21.33±0.34 | 5.51±1.25 | 8.0 |
| | S5 | -20.76±0.18 | 8.88±0.20 | 1.23±0.10 | 0.16±0.01 | -21.42±0.36 | 6.36±0.14 | 7.7 |
| | S6 | -18.61±0.20 | 8.95±0.06 | 0.98±0.32 | 0.12±0.04 | -20.98±0.86 | 6.07±0.30 | 7.9 |
| | S7 | -19.48±0.05 | 9.65±0.11 | 1.03±0.15 | 0.13±0.02 | -20.94±0.87 | 5.99±0.29 | 7.8 |
| | S8 | -19.39±0.06 | 8.12±0.12 | 0.55±0.10 | 0.06±0.01 | -21.35±1.01 | 6.24±0.34 | 8.8 |
| | S9 | -19.40±0.54 | 8.40±0.05 | 0.92±0.07 | 0.12±0.01 | -21.15±0.35 | 6.79±0.14 | 7.6 |

^a Mean ±SD.

^b -: not collected.

Table S4. Concentrations of PAHs and APs in sediments of Singil Creek relative to interim sediment quality guidelines (ISQGs) recommended by the Canadian Council of Ministers of the Environment (CCME, 1999, 2002).

| Compounds | ISQG | SG1 | SG2 | SG3 | SG4 | SG5 | SG6 | SG7 | SG8 | SG9 | SG10 | SG11 |
|-----------------------|------|-----------------|-------|------|------|--------------------|-------|-------|-------|------|-------|-------|
| Naphthalene | 34.6 | 29.8 | 24.0 | 33.0 | 28.4 | 104.7 ^a | 102.6 | 82.5 | 87.7 | 24.5 | 83.0 | 113.5 |
| 2-Methylnaphthalene | 20.2 | 15.9 | 13.5 | 18.0 | 13.2 | 58.0 | 74.3 | 76.5 | 66.7 | 8.7 | 49.2 | 71.6 |
| Acenaphthylene | 5.87 | nd ^c | nd | nd | nd | 7.2 | 7.2 | 7.3 | 7.9 | nd | 10.8 | 3.0 |
| Acenaphthene | 6.71 | nd | nd | 2.5 | nd | 13.0 | 24.0 | 13.5 | 12.4 | nd | 31.0 | 8.4 |
| Fluorene | 21.2 | 9.4 | 7.8 | 7.2 | 8.3 | 19.6 | 33.0 | 25.0 | 8.5 | 4.6 | 34.8 | 10.6 |
| Phenanthrene | 41.9 | 35.9 | 34.6 | 19.0 | 16.9 | 105.4 | 131.4 | 62.7 | 144.4 | 17.0 | 90.9 | 34.3 |
| Anthracene | 46.9 | 1.1 | 2.5 | 0.7 | 3.2 | 17.1 | 16.0 | 5.1 | 9.2 | 1.9 | 19.8 | 16.2 |
| Fluoranthene | 111 | 20.0 | 45.3 | 20.1 | 20.2 | 191.8 | 106.5 | 138.4 | 118.9 | 12.9 | 128.3 | 109.5 |
| Pyrene | 53 | 165.0 | 104.0 | 25.6 | 31.8 | 364.5 | 732.0 | 519.9 | 255.7 | 61.1 | 513.3 | 245.2 |
| Benzo[a]anthracene | 31.7 | 10.5 | 14.9 | 5.0 | 4.9 | 26.9 | 44.8 | 66.2 | 45.9 | 6.0 | 55.9 | 64.3 |
| Chrysene | 57.1 | 17.5 | 21.2 | 6.4 | 14.4 | 45.4 | 82.4 | 41.6 | 47.1 | 13.1 | 74.9 | 55.9 |
| Benzo[a]pyrene | 31.9 | 12.3 | 17.9 | 4.7 | 5.3 | 36.3 | 98.3 | 56.6 | 38.5 | 5.7 | 62.1 | 24.6 |
| Dibenz[a,h]anthracene | 6.22 | 3.1 | 4.8 | nd | 2.2 | 5.3 | 8.9 | 8.2 | 6.4 | 1.8 | 4.9 | 3.7 |
| APs-TEQs | 1000 | 130 | 127 | 48.5 | 119 | 3960 | 4820 | 7450 | 3890 | 192 | 1480 | 2270 |

^a Shade indicates parameters that exceed ISQG values.

^b Toxic equivalent concentrations of alkylphenols using the toxic equivalency factors (TEFs) (CCME, 2002) and normalized to 1% TOC.

^c nd: not detectible.

Canadian Council of Ministers of the Environment (CCME). 1999. Canadian sediment quality guidelines for the protection of aquatic life: Polycyclic aromatic hydrocarbons (PAHs). In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.

Canadian Council of Ministers of the Environment (CCME). 2002. Canadian sediment quality guidelines for the protection of aquatic life: Nonylphenol and its ethoxylates. In: Canadian environmental quality guidelines, 2002, Canadian Council of Ministers of the Environment, Winnipeg.

Table S5. Conductivity, pH, and turbidity in water and stormwater samples of Singil Creek and comparison to industrial flow benchmark values recommended by Brown et al. (2004).

| Surrounding activity | Sampling sites | Indicator parameter | | |
|----------------------|-----------------|--|-----------------|-----------------|
| | | Conductivity ($\mu\text{S cm}^{-1}$) | pH | Turbidity (NTU) |
| Urban area | SG1 | 410 | 7.28 | 17 |
| | SG2 | 456 | 7.49 | 22 |
| | SG3 | 571 | 7.32 | 45 |
| Rural area | SG4 | 520 | 7.90 | 51 |
| | SG5 | 707 | 7.03 | 68 |
| Industrial area | SG6 | 682 | 7.10 | 231 |
| | | (2,519) ^a | 7.08 | 101 |
| | SG7 | 774 | 7.54 | 198 |
| | | (842) | 7.05 | 14 |
| | SG8 | 3,891 | 7.40 | 57 |
| | | (2,516) | 7.27 | 23 |
| | SG9 | 804 | 8.22 | 23 |
| | SG10 | 1,490 | 7.23 | 13 |
| | | (1,817) | 6.08 | 33 |
| | I1 ^b | 1,486 \pm 667 | 7.56 \pm 0.23 | 43 \pm 31 |

^a Shade indicates that exceed benchmark values (Brown et al., 2004).

^b Station I1 was monitored both two sampling campaigns performed in March 2013 and June 2015.

Brown, E.D., Caraco, D., Pitt, R., 2004. Illicit Discharge Detection and Elimination: A Guidance Manual for Program Development and Technical Assessments. Report EPA X-82907801-0. Center for Watershed Protection, Ellicott City, Maryland, US.

Supplementary Figures

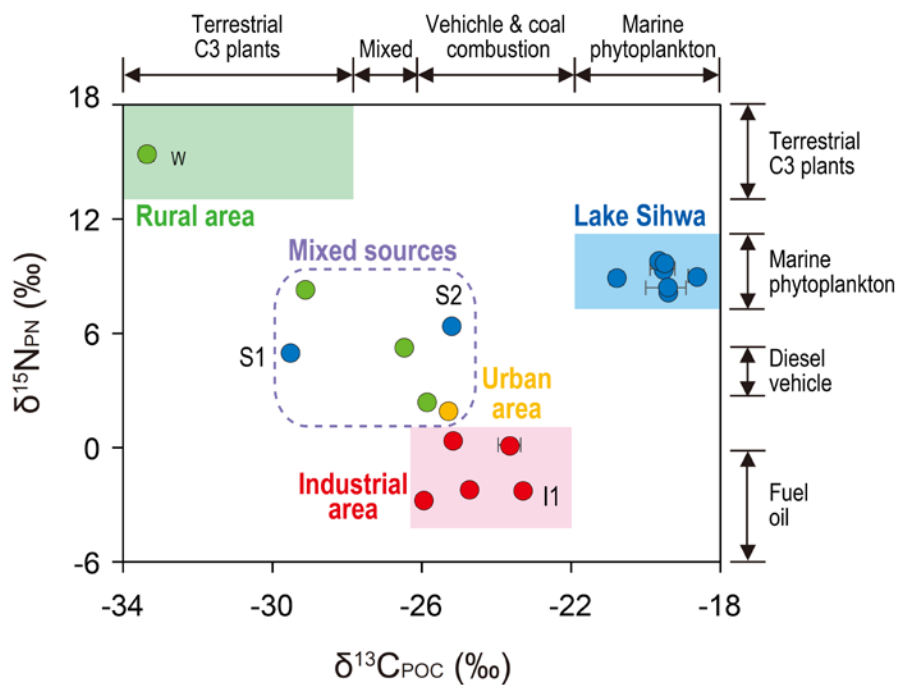


Fig. S1. Scatter plots for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values for suspended particulate matter [SPM; particulate organic carbon (POC) or particulate nitrogen (PN)] samples collected from the Lake Sihwa and tributary creeks relative to potential sources of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ reported by Maksymowska et al. (2000).

Maksymowska, D., Richard, P., Piekarek-Jankowska, H., Riera, P., 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.

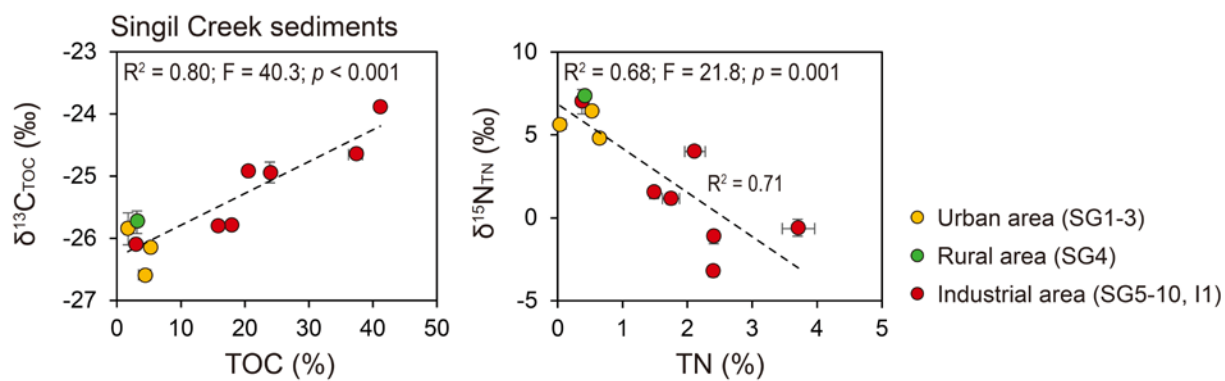


Fig. S2. Scatter plots for $\delta^{13}C$ relative to TOC content and $\delta^{15}N$ relative to TN content in sediments of Singil Creek.

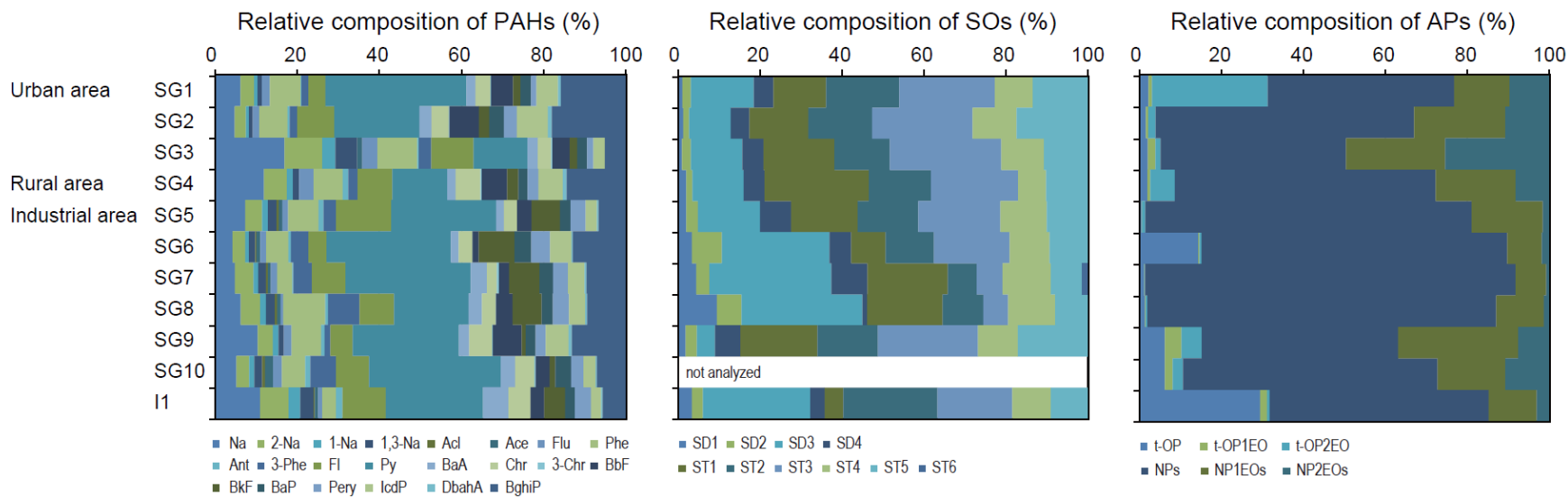


Fig. S3. Relative compositions of 22 PAHs, 10 SOs, and 6 APs in sediments of Singil Creek.

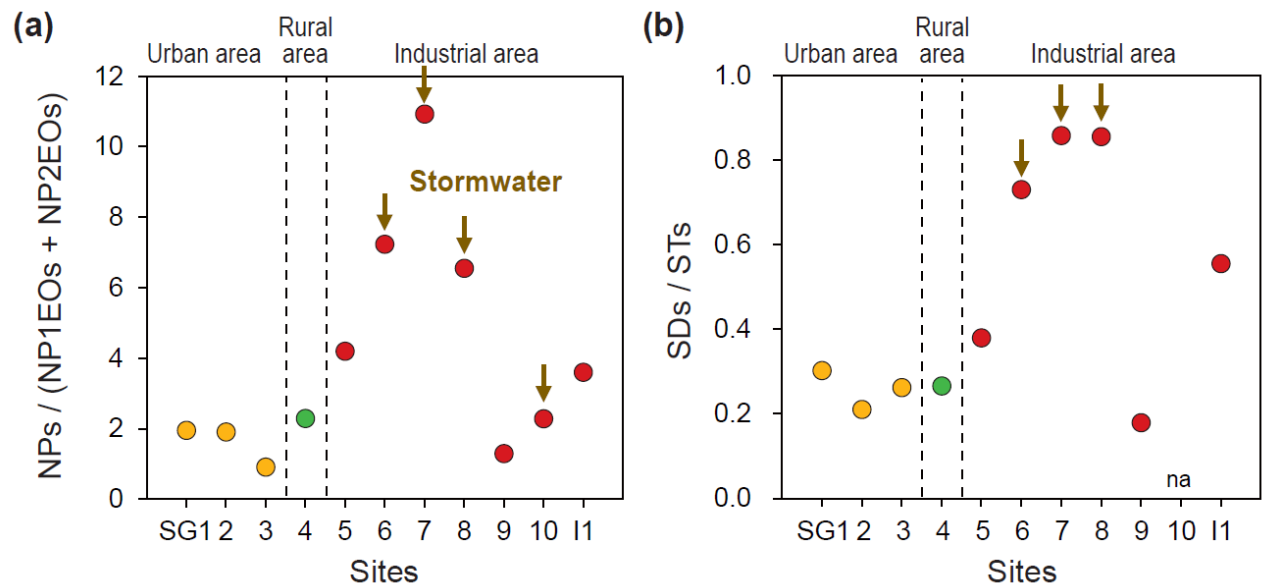


Fig. S4. Concentration ratios for (a) NPs and NPEOs and (b) SDs and STs in sediments of Singil Creek.

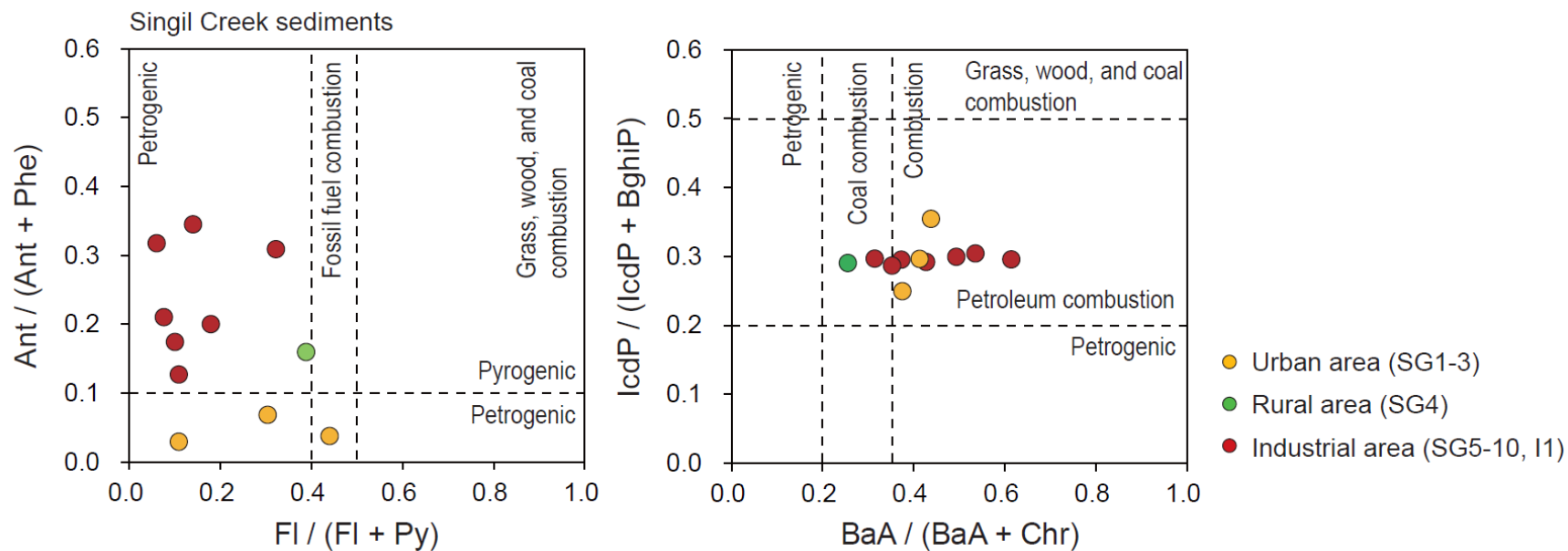


Fig. S5. Diagnostic ratio plots of individual PAHs compounds relative to sources of pollution in sediments of Singil Creek.

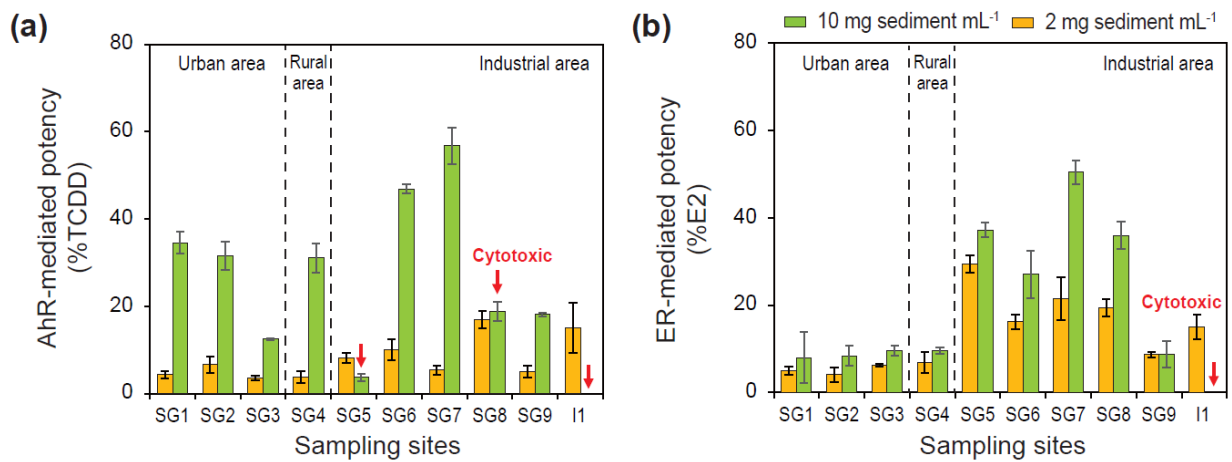


Fig. S6. AhR- and ER-mediated potencies of organic extracts (2 and 10 mg sediment mL⁻¹) in sediments in Singil Creek.

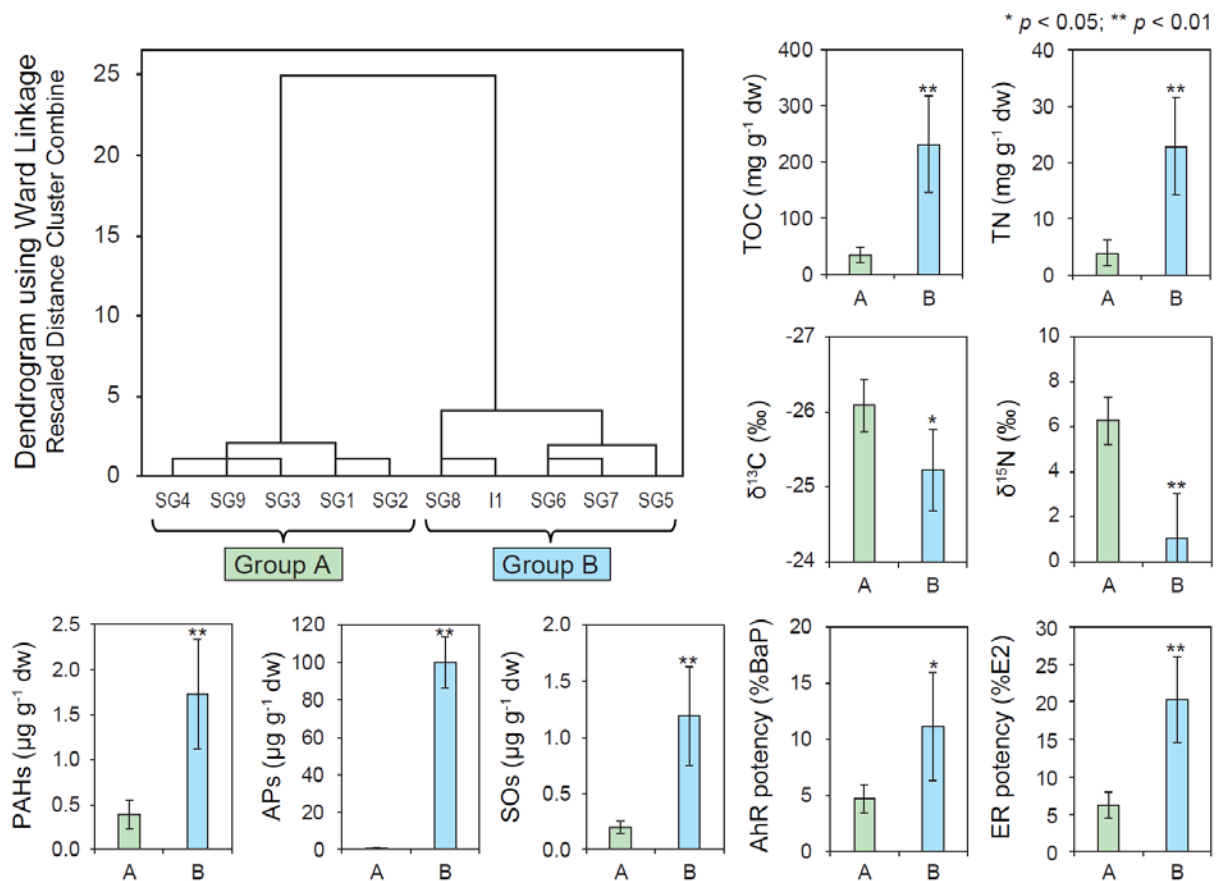


Fig. S7. Dendrogram of cluster analysis (Ward's method) of TOC, TN, stable isotope ratios, persistent toxic substances, and AhR- and ER-mediated potencies in sediments from urban, rural, and industrial areas of Singil Creek. All analyzed variables are significantly different between two groups (t -test, * $p < 0.05$; ** $p < 0.01$).