Baseline

Current contamination status of traditional and emerging persistent toxic substances in the sediments of Ulsan Bay, South Korea

Yoonyoung An[a], Seongjin Hong[a,*], Seo Joon Yoon[b], Jihyun Cha[a], Kyung-Hoon Shin[c], Jong Seong Khim[b]

[a] *Department of Ocean Environmental Sciences, Chungnam National University, Daejeon 34134, Republic of Korea*
[b] *School of Earth and Environmental Sciences & Research Institute of Oceanography, Seoul National University, Seoul 08826, Republic of Korea*
[c] *Department of Marine Science and Convergence Engineering, Hanyang University, Ansan 15588, Republic of Korea*

ABSTRACT

Contamination status of traditional and emerging persistent toxic substances (PTSs) in sediments and their major sources were investigated in Ulsan Bay, Korea. A total of 47 PTSs, including 15 traditional PAHs, ten styrene oligomers (SOs), six alkylphenols (APs), and 16 emerging PAHs (E-PAHs) were analyzed. Concentrations of traditional PAHs, SOs, and APs ranged from 35 to 1300 ng g^{-1} dry weight (dw), 30 to 3800 ng g^{-1} dw, and 30 to 430 ng g^{-1} dw, respectively. For the last 20 years, PTSs contamination in the bay area has been improved. However, 12 E-PAHs were widely detected in sediments, with a maximum of 240 ng g^{-1} dw (for benzo[e] pyrene) at the creek site. These E-PAHs seemed to originate from surrounding activities, such as biomass combustion, mobile sources, and diesel combustion. Due to environmental concerns for E-PAHs, further research on the potential toxicity, distribution, and behavior of these compounds should be implemented.

Persistent toxic substances (PTSs) originating from human activities generally enter the marine environment through river runoff and atmospheric deposition, ultimately being buried in marine sediments. Thus, contamination of land-driven PTSs in marine sediments indicates their long-term influx followed by coastal accumulation, and negatively impacts diverse benthic organisms (Christophoridis et al., 2009; Dassenakis et al., 2003). Although the degree of contamination would decrease in aquatic lotic system naturally, potential biological impacts might increase (Kim et al., 2020). This is because of contributions by unknown chemicals, mixture effects, and site(species)-specific toxicity variations. Meantime, worldwide efforts to reduce marine pollution by PTSs, during the past decades, seemed to bring environmental improvement in sediments and water qualities (Khim and Hong, 2014; Kim et al., 2020; Lorgeoux et al., 2016). However, contaminations of emerging PTSs and the potential increase of chemical toxicities still warrant continuing monitoring efforts on assessment of sedimentary PTSs, particularly in the contaminated sites worldwide.

Polycyclic aromatic hydrocarbons (PAHs), mainly originating from the combustion of fossil fuels and the use of petroleum products, are reported to be one major PTSs in coastal environments globally. PAHs are readily adsorbed on suspended particulate matter in the water column, due to their inherent properties (i.e., hydrophobic nature),

after which they settle on sediment (Witt, 1995). Some PAHs have mutagenic and carcinogenic effects on organisms by activating the aryl hydrocarbon receptor (AhR) (Van den Berg et al., 2006). While, environmental occurrence of styrene oligomers (SOs), breakdown products of polystyrene plastics, was recently documented (Amamiya et al., 2019; Hong et al., 2016; Kwon et al., 2014). Studies on the SOs in marine environments are very few compared to other PTSs (Amamiya et al., 2019; Kwon et al., 2014). The SOs exhibit AhR- and estrogen receptor (ER)-mediated activities (Hong et al., 2016; Ohyama et al., 2001), and thus monitoring of SOs in marine sediments is timely important. Alkylphenol ethoxylates (APEOs) are compounds that are included in commercial surfactants, which are increasingly recognized priority PTSs of environmental concern. Alkylphenols (APs), degradation products of APEOs, include nonylphenols (NPs) and octylphenols (OPs), which derive from nonylphenol ethoxylates (NPEOs) and octylphenol ethoxylates (OPEOs), respectively. NPs and OPs normally accumulate in aquatic sediments and exhibit estrogenic activity (Routledge and Sumpter, 1997). Altogether, PTSs (such as PAHs, SOs, and APs) finally accumulate in the sediments of marine environments, with these compounds being reported in a wide range of coastal areas in South Korea (Hong et al., 2014; Khim et al., 1999; Kim et al., 1999, 2020; Koh et al., 2002, 2006; Lee et al., 2018; Yoon et al., 2017, 2020).

In addition to known PTSs, many organic pollutants have not yet been investigated in coastal environments. In particular, substituted PAHs (such as amino-, cyano-, and alkyl-PAHs) and PAHs not included in the 16 EPA PAHs have often been ignored in environmental monitoring programs, despite their potential risks (Andersson and Achten, 2015). For example, the environmental distribution of polycyclic aromatic compounds (PACs), such as 1,6-dinitropyrene, 6-nitrochrysene, and dibenzo[*c,g*]carbazole has not been extensively investigated, despite their similar or greater potential toxicities relative to benzo[*a*]pyrene (BaP) (Andersson and Achten, 2015). Over the last 10-years, the effect-directed analysis (EDA) approach has been increasingly utilized to identify the major toxicants in environmental samples, such as sediments. Grung et al. (2011) identified nitrogen and oxygen-containing PACs as AhR-active compounds in marine sediments. Another study suggested that 11H-indeno[2,1,7,*cde*]pyrene, methylbenzo[*e*]pyrene, and methylperylene exhibit AhR activity (Brack et al., 2005). In addition, Kim et al. (2019) newly reported seven AhR agonists [1-methyl-chrysene (1MC), benzo[*j*]fluoranthene (BJF), 3-methylchrysene (3MC), 5-methylbenz[*a*]anthracene (5MBA), 11H-benzo[*b*]fluorene (11BF), benzo[*b*]-naphtho[2,3-*d*]furan (BBNF), and benzo[*b*]naphtho[2,1-*d*] thiophene (BBNT)] in the sediments of the inland creeks of Ulsan Bay, Korea. These compounds, which could potentially cause adverse effects on the marine organisms, must be included in the monitoring study and/or program.

Ulsan City, which is where Ulsan Bay is located, is one of the most industrialized cities in South Korea. Ulsan Bay has an industrial complex nearby, which includes various types of factories, such as petrochemical plants, smelters, and shipyards. There is an industrial port (Ulsan Port), where large vessels enter and exit every day (Fig. 1). In addition, Taehwa River passes through Ulsan City and flows into the bay, along with various small rivers and streams, such as Woehwang River, Yeocheon Creek, and Daejeong Creek. Thus, various land-driven pollutants associated with industrial activities and wastewater inflow likely enter and contaminate Ulsan Bay. Previous studies showed that the concentrations of PTSs in sediments had exceeded the environmental quality guidelines in some areas of Ulsan Bay (Khim et al., 2001; Moon et al., 2001). The Korean Government has designated Ulsan Bay as a special management area, implementing various policies to reduce pollutants, such as constructing and upgrading of sewage treatment facilities, burying sewage pipes, etc.

The present study investigated the current contamination status of PTSs in the surface sediments of Ulsan Bay. We investigated the major rivers [Taehwa River (R1) and Woehwang River (R2)] and inland creeks (C1 and C2) as major sources of PTSs and investigated bay sites (U1–U5) from inner to outer regions (see Fig. 1). Contents of organic carbon (OC) and total nitrogen (TN) and their stable isotope ratios in sediments were measured to determine the sources of sedimentary organic matter. In addition, various diagnostic ratios of individual PTSs were used to predict the sources of contaminants and their recent influx into the bay. Finally, the distributions and potential toxicities of emerging PAHs (E-PAHs) identified in a previous study conducted in Ulsan Bay (Kim et al., 2019) were determined. This study is the first to investigate the distributions and concentrations of E-PAHs in riverine and coastal sediments.

Sampling was conducted during June 2017. Sediments from nine sites were collected, including four in rivers (R1 and R2) and inland creeks (C1 and C2) and five in Ulsan Bay (U1–U5) (Fig. 1). Surface sediments (< 1.5 cm) were collected using a Van Veen grab sampler. All sediment samples were placed on dry ice and transported to the laboratory and stored at −20 °C until analysis. For chemical analyses, all sediment samples were freeze-dried and sieved, and then homogenized using a mortar and pestle.

To analyze the OC content and carbon stable isotope ratio (δ^{13}C), 1 M HCl was added to each sample to remove inorganic carbon. Then, each sample was rinsed with distilled water and freeze-dried. In the case of TN content and nitrogen stable isotope ratio (δ^{15}N), non-acidified samples were used for the analysis, because acid treatment could affect the δ^{15}N in sediments. All analyses followed the same method as described in Kim et al. (2018), using an elemental analyzer (EA; Euro EA3028, EuroVector, Milan, Italy) coupled with an isotope ratio mass spectrometer (IRMS; GV Instruments, Manchester, UK). Stable isotope ratios were expressed in delta notation (‰) as equation (Eq. (1)):

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

where R is the ratio of ^{13}C/^{12}C or ^{15}N/^{14}N. Vienna Peedee Belemnite and atmospheric N$_2$ were used as reference values for carbon and nitrogen, respectively. Analytical errors were 0.05‰ for δ^{13}C and 0.1‰ for δ^{15}N, estimated by the International Atomic Energy Agency (IAEA) working standards (CH-6 for carbon and N-1 for nitrogen, IAEA, Vienna, Austria).
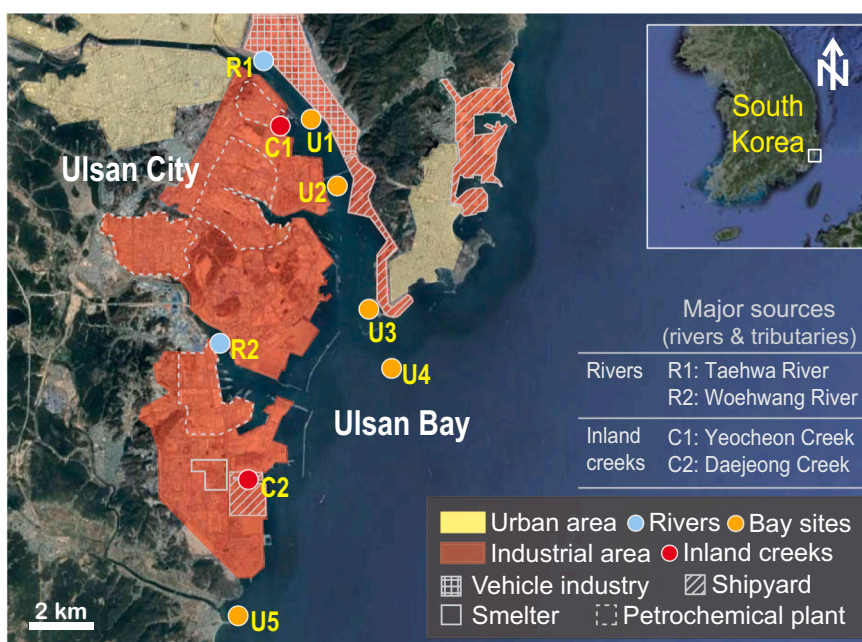

Fig. 1. Map showing the sampling sites of surface sediments in Ulsan Bay, Korea, and major sources, including rivers and creeks (June 2017).

Target compounds of PTSs in the present study included: 15 PAHs [acenaphthylene (Acl), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fl), pyrene (Py), benzo[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (IcdP), dibenz[*a,h*]anthracene (DbahA), and benzo[*g,h,i*]perylene (BghiP)], 10 SOs [1,3-diphenylpropane (SD1), *cis*-1,2-diphenylcyclobutane (SD2), 2,4-diphenyl-1-butene (SD3), *trans*-1,2-diphenylcyclobutane (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 (ST6)], and six APs [4-*tert*-octylphenol (OP), 4-*tert*-octylphenol monoethoxylate (OP1EO), 4-*tert*-octylphenol diethoxylate (OP2EO), NPs, nonylphenol monoethoxylates (NP1EOs), and nonylphenol diethoxylates (NP2EOs)]. As for the E-PAHs, 16 compounds were targeted; namely, 3-methylphenanthrene (3MP), 2-methylphenanthrene (2MP), 2-methylanthracene (2MA), 9-ethylphenanthrene (9EP), 1,6-dimethylphenanthrene (16DMP), 1,2-dimethylphenanthrene (12DMP), BBNF, 11BF, BBNT, triphenylene (Trl), 3MC, 5MBA, 1,12-dimethylbenzo[*c*]phenanthrene (BCP), 1MC, BJF, and benzo[*e*]pyrene (BEP). Standard materials for target PTSs were obtained from ChemService (West Chester, PA) for PAHs, from Wako Pure Chemical Industries, Ltd. (Osaka, Japan) and Hayashi Pure Chemical Industries, Ltd. (Osaka, Japan) for SOs, from Sigma-Aldrich (Saint Louis, MO) for APEOs, and from Sigma-Aldrich, Santa Cruz Biotechnology, Inc. (Dallas, TX), and AHH Chemical Co., Ltd. (Changzhou, China) for E-PAHs.

For the analyses of PTSs, 10 g homogenized sample was extracted with 350 mL dichloromethane (DCM, Burdick & Jackson, Muskegon, MI) using a Soxhlet extractor for 16 h. Before extraction, surrogate standards [Ace-d10, Phe-d10, Chr-d12, and Pery-d12 for PAHs and SOs (ChemService) and bisphenol A-d16 for APs (Sigma-Aldrich)] were added to the sample for quality control. The organic extract was concentrated using a rotary evaporator, exchanged to hexane, and reacted with activated copper powder (Merck, Darmstadt, Germany) to remove elemental sulfur for 1 h. The extract was cleaned through an open column chromatography packed with 8 g activated silica gel (70–230 mesh, Merck). The first fraction (F1), containing PAHs and SOs, was eluted with 60 mL hexane:DCM (8:2, v/v). The second fraction (F2), for analyzing APs, was collected by elution with 50 mL DCM:acetone (6:4, v/v) (Hong et al., 2016). Each fraction was concentrated on a rotary evaporator, transferred to a 12 mL glass tube, and concentrated to 1 mL under nitrogen gas flow. The concentrate was transferred to a GC vial for instrumental analysis after adding 100 μL internal standard (2-fluorobiphenyl, ChemService). PTSs were quantified using an Agilent 7890B GC coupled with a 5977B mass spectrometer detector (MSD, Agilent Technologies, Santa Clara, CA). Detailed instrumental conditions for analyzing PTSs are presented in Table S1 of the Supplementary Materials. Concentrations of PAHs (including E-PAHs) and SOs in sediments from rivers and inland creeks were partially reported in a previous study (Kim et al., 2019).

The recovery rates of surrogate standards were measured to assess the loss of any compound that occurs during the pretreatment process. The average recovery of surrogate standards for PAHs was 72%, 76%, 88%, and 90% for Ace-d10, Phe-d10, Chr-d12, and Pery-d12, respectively. Bisphenol A-d16 (for APs) showed a recovery rate of 75%, on average (Table S2). The method detection limit (MDL) was calculated as the standard deviation $\times$ 3.707 of the calibration standard. The MDLs of PAHs, SOs, and APs ranged from 0.03 to 0.81 ng g^{-1}, 0.11 to 0.89 ng g^{-1}, and 0.08 to 3.7 ng g^{-1}, respectively. More information on QA/QC is provided in Table S2.

The EPA positive matrix factorization (PMF) model (version 5.0) was used to identify the major source of PAHs. The model was implemented using the individual concentrations of traditional 15 PAHs. Out of 16 E-PAHs, 12 compounds were detected in the sediment samples of Ulsan Bay. The toxic potencies of these compounds were

evaluated (including mutagenicity, carcinogenicity, developmental toxicity, and estrogen receptor activity) using the VEGA-QSAR platform (http://www.vega-qsar.eu/) (Benfenati et al., 2013; Cha et al., 2019; Marzo et al., 2016; Pizzo et al., 2013).

The OC contents of sediment samples ranged from 1.6 to 6.2%, with a mean value of 2.9% (Table S3). TN contents ranged from 0.18 to 0.38% (mean = 0.23%) in the sediments of Ulsan Bay. The average OC and TN in the sediments of river and creek sites (OC = 4.2 ± 1.4%; TN = 0.25 ± 0.08%) were generally greater than those of bay sites (OC = 1.9 ± 0.3%; TN = 0.22 ± 0.04%). The greatest OC and TN contents were recorded at site C2, where wastewater was discharged from the surrounding industrial area. The lowest organic content was recorded at site U2, which was located in the Taehwa River Estuary. OC and TN ratios ranged from 14 to 20 in river and creek sediments and from 6.4 to 13 in bay sediments. These results show that the sediments of river and creek sites were strongly affected by terrestrial organic matters (Fig. S1). In comparison, the sedimentary organic matters of bay sites were mainly of marine origin. Some bay sites near land showed mixed sources of terrestrial and marine origins.

The δ^{13}C values in sediments ranged from -26.1 to $-21.6‰$ (mean = $-24.2‰$), while δ^{15}N values ranged from -1.91 to $5.44‰$ (mean = $3.19‰$) (Table S3). The previous study reported that δ^{13}C values of sedimentary OC ranged between -27 and $-25‰$ in terrestrial organic matter, and between -22 and $-20‰$ in marine organic matter (Peters et al., 1978). The depleted δ^{13}C values were found in the sediments of river and creek sites and inner parts of the bay (U1 and U2) compared to those in the outer parts of the bay (U3–U5) (Fig. S1). Similarly, the depleted δ^{15}N values were characteristic for river and creek sediments, and generally enriched δ^{15}N values were found for bay sediments. In particular, the relatively lower δ^{15}N values were recorded at sites C1 (0.95‰) and C2 ($-1.91‰$), potentially due to excessive inputs of sewage-derived organic matters (Tucker et al., 1999), fertilizer, and/or industrial activities (Hong et al., 2019; Lee et al., 2019). Overall, the OC and TN contents, and their stable isotope ratios, indicate that there was an influx of terrestrial and anthropogenic organic matter in the sediments of the study area, particularly in rivers and inland creeks.

All of 15 traditional PAHs were detected in the sediments of the study area, and ΣPAHs ranged from 35 to 4000 ng g^{-1} dw (Fig. 2a and Table S4). In general, inland river and creek sediments showed much higher ΣPAHs with great spatial variations (mean = 1200 ng g^{-1} dw) compared to those in bay sediments. The greatest ΣPAHs were found at site C1, of which concentration was more than ten times greater than those in other inland sites (except for C2). Site C1 seemed to be affected by industrial wastewater from nearby petrochemical plants. The next greatest concentration of ΣPAHs was found at site C2, which was located adjacent to a petrochemical plant and smelter. In comparison, relatively low concentrations of ΣPAHs were detected at the river sites (R1 and R2), probably because of the lower direct inputs of wastewater (i.e., point and nonpoint sources) compared to creek sites (C1 and C2).

At the sites in Ulsan Bay, the average concentration of ΣPAHs in sediments was 53 ng g^{-1} dw, and greater concentrations of ΣPAHs were found in the inner region of the bay compared to those in the outer region. The lowest PAH concentration was detected at site U4, which was farthest situated from the coastline; thus, the impacts by land-driven pollutants would be minimal at the site. Four- to six-ring PAHs were the predominant PAHs at river and creek sites, accounting for more than 70% of ΣPAHs. The relative compositions of individual PAHs in sediments were similar across all sites in Ulsan Bay (Fig. 2d). PAHs with high molecular mass tend to be more hydrophobic, accumulating in sediments near the land (Moon et al., 2001). Thus, PAHs in the sediments of Ulsan Bay likely mainly originate from surrounding industrial complexes, and could not be transported far, instead of an immediate sink nearby the corresponding sources.

The concentrations of PAHs in the sediments of Ulsan Bay did not exceed the existing sediment quality guidelines suggested by the
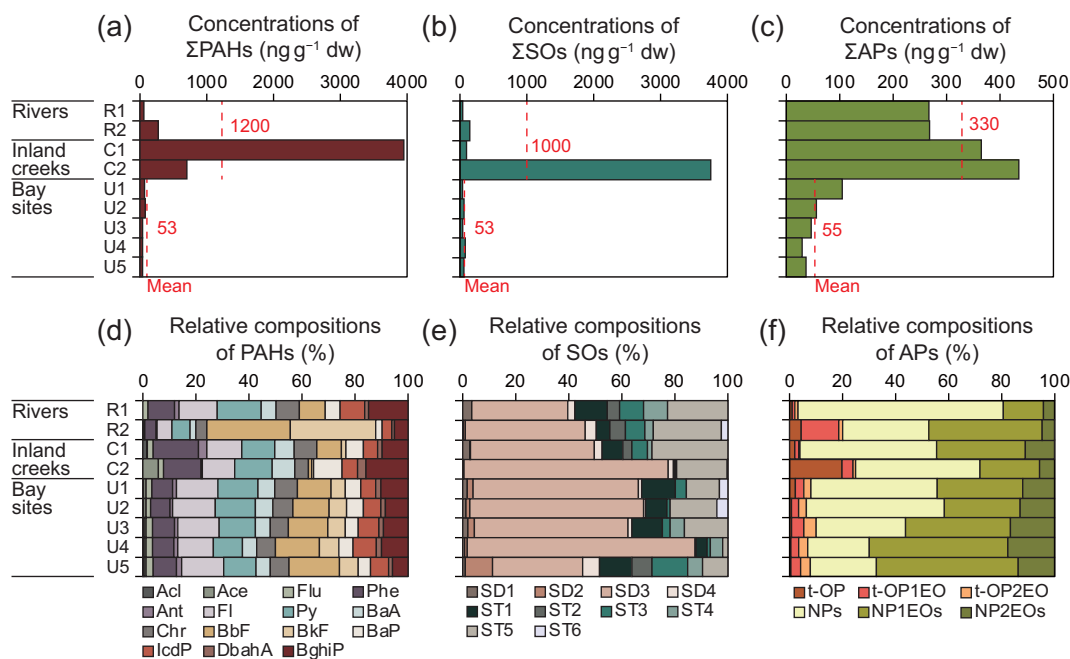
Fig. 2. Distributions and relative compositions of 31 PTSs, including (a & d) PAHs, (b & e) SOs, and (c & f) APs in the sediments from Ulsan Bay, Korea.

Canadian Council of Ministers of the Environment (CCME) (CCME, 1999). Thus, the level of sedimentary PAHs in Ulsan Bay might not necessarily impact the coastal benthic ecosystem at the moment. The current status of PAHs pollution in sediments was generally lower than those reported by previous studies conducted in similar areas (Choi et al., 2011; Khim et al., 2001; Moon et al., 2001). In particular, the concentrations of ΣPAHs in sediments in Ulsan Bay were about 2 to 20 times lower than those reported in 2000 (Moon et al., 2001), implying some improvements to the benthic environment. In addition, this study recorded relatively lower concentrations of ΣPAHs compared to previous studies conducted in other coastal areas of South Korea, including Busan coast (Han et al., 2016), Lake Sihwa (Hong et al., 2019), Gwangyang Bay (Yim et al., 2007), and Masan Bay (Hong et al., 2014; Yim et al., 2005) (Table S5).

The concentrations of 10 SOs (ΣSOs) ranged from 34 to 3800 ng g^{-1} dw in the sediments of the study area (Fig. 2b and Table S4). The average concentration of ΣSOs was 1000 ng g^{-1} dw at river and creek sites, with C2 having the greatest ΣSOs (3800 ng g^{-1} dw). This site (C2) is situated adjacent to a petrochemical plant and plastic products manufacturing plants are also located nearby. Thus, the great concentration of ΣSOs detected at C2, which is not surprising, seemed to be influenced by surrounding industrial activities, because SOs predominantly originate from polystyrene plastic materials (Amamiya et al., 2019). At the sites of Ulsan Bay, the average concentration of ΣSOs was 53 ng g^{-1} dw, with no clear trends in spatial distribution. Unlike PAHs, which showed similar relative compositions between sites, the relative composition of 10 SOs greatly varied between sites (Fig. 2e). The most prevalent and widely distribution SO detected in all sediment samples was SD3, but the relative proportions of SD3 differed among sites. The relative compositions of styrene dimers and styrene trimers in sediments also differed among sites. Such spatial heterogeneity in distributions of SOs in the study area might influence site-specific effects due to variations in mobility and/or volatility cross the varying SOs detected (Kwon and Moon, 2019). However, it should be noted that SOs were relatively low at all sites (except for site C2) when compared to their reported concentrations at Lake Sihwa (Hong et al., 2019), Masan Bay (Lee et al., 2018), and Saemangeum coast (Yoon et al., 2017) (Table S5). Overall, the current level of contamination of SOs was not high in the study area, except for a few hotspot sites which

are situated very close to the corresponding sources (such as site C2).

The concentrations of six APs (ΣAPs) in sediments ranged from 30 to 430 ng g^{-1} dw (Fig. 2c and Table S4). The mean concentrations of ΣAPs in the sediments of river and creek sites were 330 ng g^{-1} dw, which were greater than those of bay sites (55 ng g^{-1} dw). The concentrations of APs in sediments tended to decrease from the inner to outer regions of the bay (Fig. 2c). This result is similar to previous studies showing a seaward decrease of APs in the sediments in the coastal area (Isobe et al., 2001). At river and creek sites, the greatest concentration of ΣAPs was detected at the C2 and C1 sites. APs pollution levels were lower in the current study compared to previous studies conducted in the coastal waters of Korea, including Busan coast (Han et al., 2016) and Jinhae Bay (Hong et al., 2014). The concentrations of APs in the sediments of the study area did not exceed the interim sediment quality guidelines of the CCME (CCME, 2002). At all sites, NPs were more predominant than OPs, accounting for approximately 75 to 97% of the total (Fig. 2f). The compositions of APs found in the present study were comparable to those reported for the sediment collected in 1999 from the Ulsan Bay study (Khim et al., 2001). Meanwhile, the OC contents in the sediments can affect the distributions of hydrophobic pollutants (Yang et al., 2009). However, the distribution patterns of PTSs in the sediments of Ulsan Bay did not differ between dry weight-based concentrations and OC normalized concentrations (except for APs) in the present study (Fig. S2). Overall, the distribution and concentrations of PTSs for Ulsan Bay sediments showed that the three groups of chemicals had slightly different characteristics depending on the sources of pollutants. Specifically, PTSs originated from the surrounding area and appeared to accumulate in the nearby sediments of river and inland creeks.

To better understand the sources (for PAHs) and recent inputs of pollutants (for SOs and APs) in the sediments of Ulsan Bay, in site- and compound-specific manners, diagnostic analyses have been performed (Hong et al., 2016; Katsoyiannis et al., 2011; Tobiszewski and Namiesnik, 2012; Yoon et al., 2020). The sources of PAHs in sediments were estimated using Ant, Phe, Fl, Py, IcdP, and BghiP (see Fig. 3a and b for results). The values of Ant/(Ant + Phe), Fl/(Fl + Py), and IcdP/(IcdP + BghiP) were 0.11 to 0.19, 0.37 to 0.56, and 0.23 to 0.55, respectively. Thus, the sedimentary PAHs in Ulsan Bay appeared to be of combustion origin. The prevalence of combustion origin at all sites in the current study differed to those of previous studies, in which
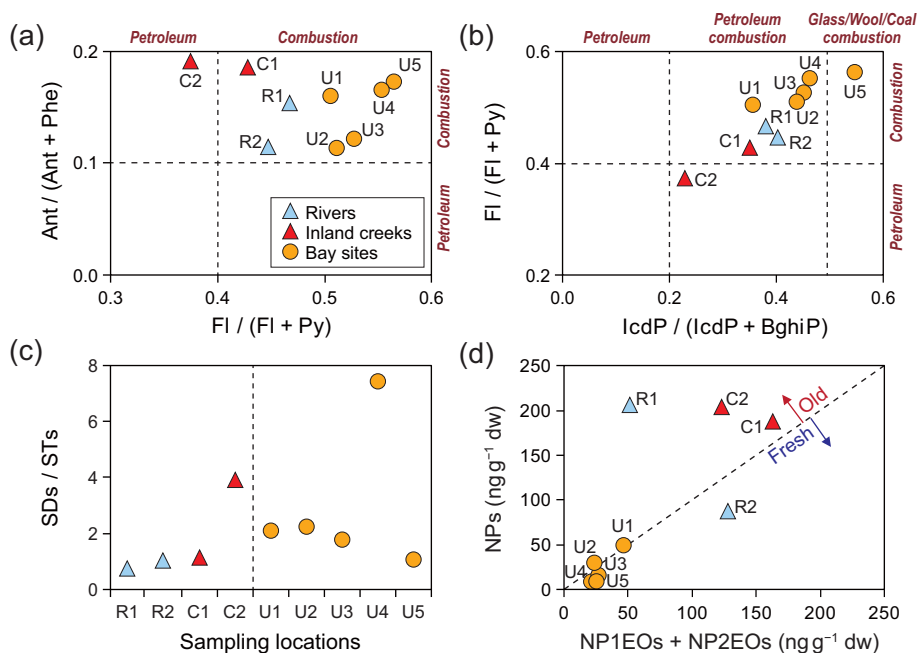
Fig. 3. Source identification of PTSs, including (a & b) PAHs, (c) SOs, and (d) APs in sediments from Ulsan Bay, Korea.
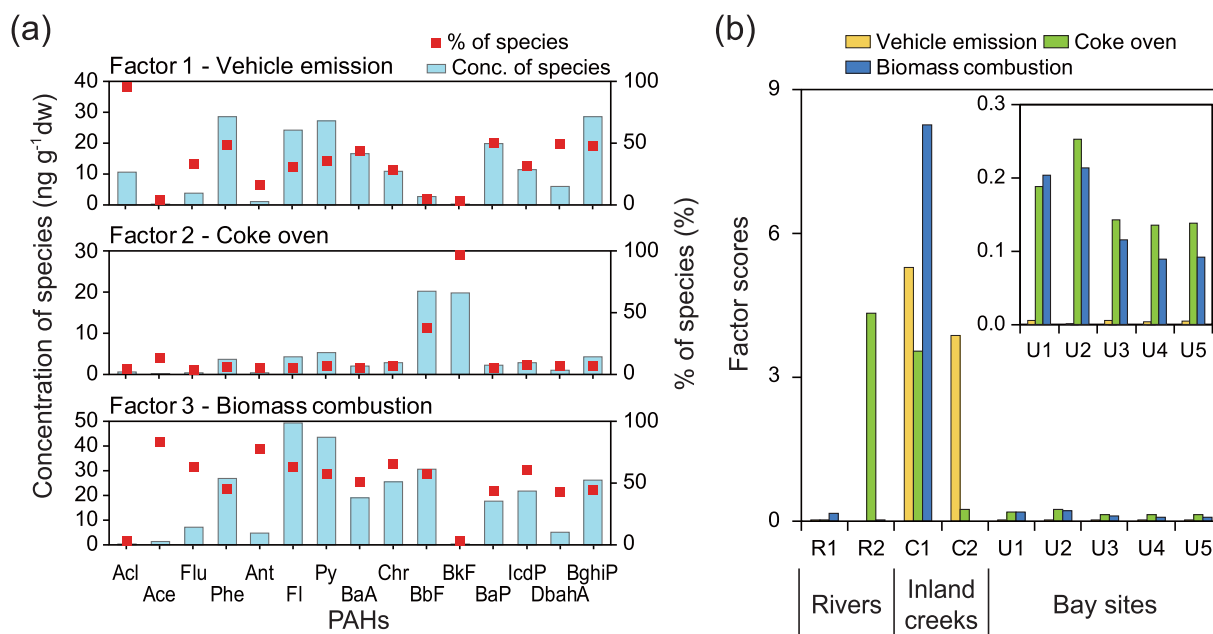

Fig. 4. (a) Factor profiles and (b) factor scores resulting from the PMF model for predicting potential sources of PAHs in the sediments from Ulsan Bay, Korea.

petroleum sources dominated some sites along the Ulsan coast (Moon et al., 2001). Thus, the major source of PAHs seemed to change from petroleum sources to combustion sources in Ulsan Bay.

The concentration ratios of styrene dimers (sum of SDs) and styrene trimers (sum of STs) ranged between 0.74 and 7.4 (Fig. 3c). At sites C2 and U4, SDs/STs were 3.9 and 7.4, respectively, and were distinct to the other sites. Thus, sources of polystyrene plastic pollution in the study area might vary depending on the site and surrounding local activities (Hong et al., 2016). In addition, a recent study suggested that the sources of SOs in the environments can be estimated using the ratio of ST1 to SD3 (Tian et al., 2020). In this study, the ratio of ST1/SD3 in the sediments of Ulsan Bay showed similar results to those of SDs/STs, indicating that there were fresh inputs of SOs at the sites C2 and U4 (Fig. S3). Finally, assuming that APs are produced through the

degradation of APEOs after being introduced to the coastal environment, we evaluated whether there was a fresh influx of APs based on the ratios of APs and APEOs (Isobe et al., 2001). In brief, if the APEOs/ APs ratio exceeds 1, it would indicate a fresh influx of pollutants in the given site. The (NP1EOs + NP2EOs)/NPs ratios were calculated (Fig. 3d). Sites U3, U4, U5, and R2 had (NP1EOs + NP2EOs)/NPs ratios exceeding 1, while these ratios were less than 1 at sites with relatively greater concentrations of APs (e.g., R1, C1, and C2). The Korean government has officially banned the use of NPs in all domestic applications since 2007, in some industrial applications (including paint and ink) since 2010, and in all industrial applications since 2016 (Choi et al., 2011; Kim et al., 2020). A diagnostic result with the fact of widespread distribution of APs cross offshore sites in the Ulsan Bay indicated either the fresh input of local sources and/or long-term

sedimentary sink due to their long persistence.

In this study, datasets with 15 PAHs × 9 sites were used as input data for the PMF model. The Q values with 2–5 factors were calculated, and Q_{True}/Q_{Exp} values were 22.9, 4.04, 5.17, and 4.40, respectively. The 3-factor solution was shown the most reliable result with the smallest Q_{True}/Q_{Exp} value; thus, the 3-factor solution was selected in the present study (Crilley et al., 2017). The Q_{Robust} and Q_{True} values were the same as 108.946. The modeled PAH concentrations were compared with the measured concentrations to assess the accuracy of the fitted results. The slope in the linear regression formula ranged from 0.37 to 1.30, with R^2 value of 0.99, which suggests that the PMF model result is satisfactory. Factor 1 showed high loadings of Phe, Fl, Py, and BghiP. This result indicates a mixture of PAHs originating from gasoline and diesel engines and was indicative of vehicle emission origin (Bzdusek et al., 2004) (Fig. 4). Relatively high scores of Factor 1 observed for sites C1 and C2 indicated that the PAHs of combustion origin from nearby industrial complexes could be introduced via inland creeks. Factor 2 exhibited high loadings of BbF and BkF, implying with previous studies considering it to be of coke oven origin (Li et al., 2003). PAHs of coke oven origin were documented in all regions (except site R1), especially site R2. Site C1 had high scores for all factors, possibly due to recent and long-term contamination associated with PAHs. Indeed, this area had relatively great potential toxicity, with AhR-mediated potencies being reported in a previous study (Kim et al., 2019). Finally, Factor 3 showed relatively high loadings of Fl and Py and moderate loadings of BbF and Chr, collectively indicating biomass combustion (Lin et al., 2011). Relatively high scores of Factor 3 were obtained at site R1 and bay sites, with higher factor scores in the inner parts compared to the outer parts of the bay. Thus, the influx of PAHs through the Taehwa River might affect the entire bay.

A total of 16 E-PAHs in the sediments of Ulsan Bay were analyzed. Out of these compounds, Trl and BjF were excluded from the analysis, because they could not be separated from Chr and BkF in the GC-MSD, respectively. In addition, 12DMP and BCP were not detected in any of the sediment samples. The total concentration of 12 E-PAHs (ΣE-PAHs) ranged from 26 to 1200 ng g^{-1} dw. The average ΣE-PAHs at the river and creek sites and bay sites were 440 and 70 ng g^{-1} dw, respectively. Greater concentrations of ΣE-PAHs were detected at sites C1 and C2 (Table S6). Greater concentrations of ΣE-PAHs were detected in the inner part of the bay compared to the outer regions. This result was similar to that of traditional PAHs (Fig. 5). These spatial distribution patterns indicate that traditional and emerging PAHs might originate from similar sources. Previous studies reported that 3MP, 2MP, 9EP, and 11BF were derived from biomass combustion (Benner et al., 1995; bin Abas et al., 1995; Wu et al., 2002). 16DMP and BEP were attributed to mobile sources (Benner et al., 1995; Khalili et al., 1995), and 3MC

and BBNT were considered to originate from diesel combustion (Olson and McDow, 2009; Smith and Harrison, 1996). The results of previous studies on the origin of E-PAHs were consistent with the PMF results for traditional PAHs obtained in the present study, with PAHs originating from various combustion sources. In particular, site C2 contained a large portion of vehicle emissions, with 16DMP, BEP, and BBNT being the most dominant compounds in the sediments of Ulsan Bay.

E-PAHs (including 11BF, BBNF, BBNT, 1MC, 3MC, and 5MBA) were identified as AhR-active compounds in a previous study using EDA with full-scan screening analysis (Kim et al., 2019). In addition, E-PAHs that are not AhR-active compounds (such as 3MP, 2MP, 9EP, 16DMP, BEP, and BCP) also have other potential toxicities. Previous studies showed that 2MP, 2MA, and 9EP have mutagenicity (Gibson et al., 1978; LaVoie et al., 1983; Onodera et al., 1994), while another study suggested that BEP has carcinogenicity (Villemin et al., 1994). Furthermore, VEGA-QSAR was used in this study to predict the unknown potential toxicities of these E-PAHs (Table 1). The results showed that some E-PAHs (including 11BF, BBNT, 1MC, 3MC, BCP, and 5MBA) have estrogen activity, mutagenicity, carcinogenicity, and developmental toxicity. For 2MP, 2MA, and 9EP, carcinogenicity and developmental toxicity were predicted, in addition to the known mutagenicity. The potential mutagenicity, carcinogenicity, and developmental toxicity of 3MP, 16DMP, and BBNF were also determined. The potential toxicity of E-PAHs predicted using VEGA-QSAR shows that these compounds might negatively impact marine ecosystems, with continued monitoring and research being vital. Consistent with this suggestion, research is needed for emerging PAHs (e.g., alkylated-, amino-, cyano-PAHs, etc.), in addition to the well-studied EPA 16 PAHs, as highlighted in a previous study (Andersson and Achten, 2015). Due to environmental concerns for E-PAHs, further research on the potential toxicity, distribution, and behavior of these compounds is required.

This study delineated the current contamination status of traditional PTSs (PAHs, SOs, and APs) and E-PAHs in the surface sediments of the rivers, inland creeks, and Ulsan Bay, Korea. Current contamination levels of PTSs in sediments were much lower compared to ~10–20 years ago and were below sediment quality guidelines. The PTS groups showed different distribution characteristics according to the sources. E-PAHs were widely distributed in the sediments of Ulsan Bay, with sources being estimated to be similar to those of traditional PAHs. Previously, studies on the distribution and potential risk of PAHs focused on 16 traditional PAHs (or 15, except for naphthalene). However, the results obtained from this study suggested that a number of emerging PAHs exist in the coastal environment, of which occurrence, distribution, and sources are similar to traditional PAHs. In terms of risk, these E-PAHs are just as important as traditional PAHs. Therefore, immediate attention and monitoring to further investigate E-PAHs in
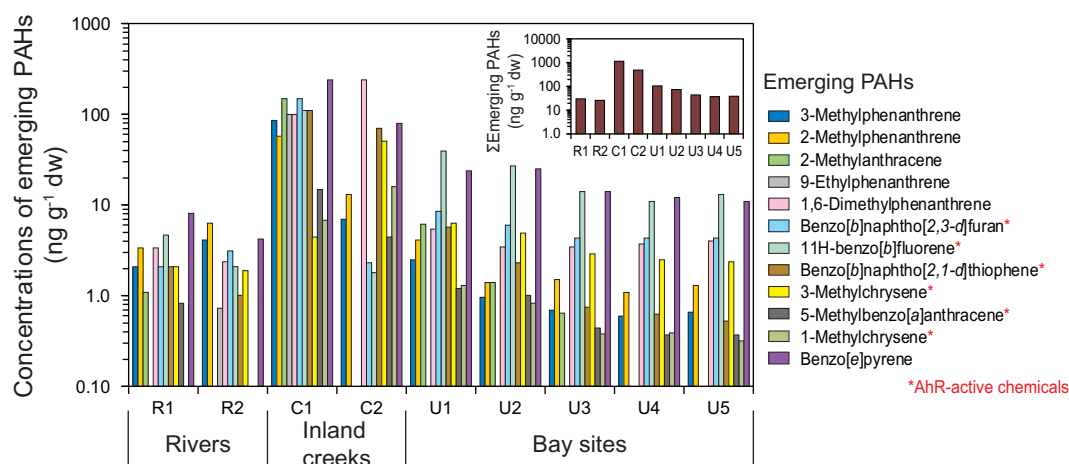

Fig. 5. Distributions of emerging PAHs in the surface sediments from Ulsan Bay, Korea.

Table 1

Predicted potential toxic effects of emerging PAHs using VEGA QSARs. Total 12 emerging PAHs were detected in the sediments of Ulsan Bay, Korea (Concentrations in sediments and potential sources were presented in Fig. 5 and Table S6).

Compounds	Reported toxicity (references)	Predicted potential toxicity using VEGA QSARs			
		Estrogenic activity[a]	Mutagenicity[b]	Carcinogenicity[c]	Developmental toxicity[d]
3-Methylphenanthrene	na[e]	− [f]	+ + + + +[g]	+ + − +	+ −
2-Methylphenanthrene	Mutagenicity (Gibson et al., 1978)	−	+ + + + +	+ + − +	+ −
2-Methylanthracene	Mutagenicity (Onodera et al., 1994)	−	+ + + + +	+ + − +	+ −
9-Ethylphenanthrene	Mutagenicity (LaVoie et al., 1983)	−	+ + + + +	+ + + +	+ −
1,6-Dimethylphenanthrene	na	−	+ + + + +	+ + + +	+ −
Benzo[*b*]naphtho[2,3-*d*]furan	na	−	+ + + + −	− + + +	+ −
11H-benzo[*b*]fluorene	Developmental toxicity (Hawliczek et al., 2012)	+	+ + + + −	+ + − +	+ −
Benzo[*b*]naphtho[2,1-*d*]thiophene	na	+	+ + + + +	− + + +	+ −
3-Methylchrysene	na	+	+ + + + +	+ + − +	+ −
5-Methylbenzo[*a*]anthracene	Carcinogenicity (Villemin et al., 1994)	+	+ + + + +	+ + + +	+ −
1-Methylchrysene	Carcinogenicity (Villemin et al., 1994)	+	+ + + + +	+ + + +	+ −
Benzo[*e*]pyrene	Carcinogenicity (Villemin et al., 1994)	−	+ + + + +	+ + − +	+ −

[a] Predicted estrogenic activity of compounds using VEGA QSAR with one model (IRFMN).
[b] Predicted mutagenicity of compounds using VEGA QSAR with five models (CAESAR, ISS, CONSENSUS, KNN/Read-Across, and SarPY/IRFMN).
[c] Predicted carcinogenicity of compounds using VEGA QSAR with four models (CAESAR, ISS, IRFMN/Antares, and IRFMN/ISSCAN-CGX).
[d] Predicted developmental toxicity of compounds using VEGA QSAR with two models (CAESAR and PG).
[e] na: not available.
[f] −: non-active.
[g] +: active.

the coastal environments are needed in the future. Overall, the present study would provide useful information on distributions and sources of important classes of some traditional PTSs together with emerging coastal pollutants in Korean coastal waters and elsewhere to the polluted marine environment.

CRediT authorship contribution statement

Yoonyoung An: Conceptualization, Investigation, Formal analysis, Data curation, Visualization, Writing - original draft.**Seongjin Hong:**Conceptualization, Writing - original draft, Writing - review & editing, Project administration, Funding acquisition, Supervision.**Seo Joon Yoon:**Investigation, Formal analysis, Data curation.**Jihyun Cha:**Investigation, Formal analysis, Data curation.**Kyung-Hoon Shin:**Conceptualization, Writing - review & editing, Supervision.**Jong Seong Khim:**Conceptualization, Writing - review & editing, Supervision.

Declaration of competing interest

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

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2020.111560.

References

Amamiya, K., Saido, K., Chung, S.Y., Hiaki, T., Lee, D.S., Kwon, B.G., 2019. Evidence of transport of styrene oligomers originated from polystyrene plastic to oceans by runoff. Sci. Total Environ. 667, 57–63.

Andersson, J.T., Achten, C., 2015. Time to say goodbye to the 16 EPA PAHs? Toward an up-to-date sse of PACs for environmental purposes. Polycycl. Aromat. Compd. 35, 330–354.

Benfenati, E., Manganaro, A., Gini, G., 2013. VEGA-QSAR: AI inside a platform for predictive toxicology. CEUR Workshop Proceedings 21–28.

Benner, B.A., Wise, S.A., Currie, L.A., Klouda, G.A., Klinedinst, D.B., Zweidinger, R.B., Stevens, R.K., Lewis, C.W., 1995. Distinguishing the contributions of residential wood combustion and mobile source emissions using relative concentrations of dimethylphenanthrene isomers. Environ. Sci. Technol. 29, 2382–2389.

bin Abas, M.R., Simoneit, B.R.T., Elias, V., Cabral, J.A., Cardoso, J.N., 1995. Composition of higher molecular weight organic matter in smoke aerosol from biomass combustion in Amazonia. Chemosphere 30, 995–1015.

Brack, W., Schirmer, K., Erdinger, L., Hollert, H., 2005. Effect-directed analysis of mutagens and ethoxyresorufin-o-deethylase inducers in aquatic sediments. Environ. Toxicol. Chem. 24, 2445–2458.

Bzdusek, P.A., Christensen, E.R., Li, A., Zou, Q., 2004. Source apportionment of sediment PAHs in Lake Calumet, Chicago: application of factor analysis with nonnegative constraints. Environ. Sci. Technol. 38, 97–103.

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. 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. Canadian Council of Ministers of the Environment, Winnipeg.

Cha, J., Hong, S., Kim, J., Lee, J., Yoon, S.J., Lee, S., Moon, H.B., Shin, K.H., Hur, J., Giesy, J.P., Khim, J.S., 2019. Major AhR-active chemicals in sediments of Lake Sihwa, South Korea: application of effect-directed analysis combined with full-scan screening analysis. Environ. Int. 133, 105199.

Choi, H.G., Moon, H.B., Choi, M., Yu, J., 2011. Monitoring of organic contaminants in sediments from the Korean coast: spatial distribution and temporal trends (2001–2007). Mar. Pollut. Bull. 62, 1352–1361.

Christophoridis, C., Dedepsidis, D., Fytianos, K., 2009. Occurrence and distribution of selected heavy metals in the surface sediments of Thermaikos Gulf, N. Greece. Assessment using pollution indicators. J. Hazard. Mater. 168, 1082–1091.

Crilley, L.R., Lucarelli, F., Bloss, W.J., Harrison, R.M., Beddows, D.C., Calzolai, G., Nava, S., Valli, G., Bernardoni, V., Vecchi, R., 2017. Source apportionment of fine and coarse particles at a roadside and urban background site in London during the 2012 summer ClearfLo campaign. Environ. Pollut. 220, 766–778.

Dassenakis, M., Andrianos, H., Depiazi, G., Konstantas, A., Karabela, M., Sakellari, A., Scoullos, M., 2003. The use of various methods for the study of metal pollution in marine sediments, the case of Euvoikos Gulf, Greece. Appl. Geochem. 18, 781–794.

Gibson, T.L., Smart, V.B., Smith, L.L., 1978. Non-enzymic activation of polycyclic aromatic hydrocarbons as mutagens. Mutat. Res-Fund. Mol. M. 49, 153–161.

Grung, M., Naes, K., Fogelberg, O., Nilsen, A.J., Brack, W., Lubcke-von Varel, U., Thomas,

K.V., 2011. Effects-directed analysis of sediments from polluted marine sites in Norway. J. Toxicol. Environ. Health A 74, 439–454.

Han, G.M., Hong, S.H., Shim, W.J., Ra, K.T., Kim, K.T., Ha, S.Y., Jang, M., Kim, G.B., 2016. Assessment of persistent organic and heavy metal contamination in Busan Coast: application of sediment quality index. Ocean Polar Res. 38, 171–184.

Hawliczek, A., Nota, B., Cenijn, P., Kamstra, J., Pieterse, B., Winter, R., Winkens, K., Hollert, H., Segner, H., Legler, J., 2012. Developmental toxicity and endocrine disrupting potency of 4-azapyrene, benzo[b]fluorene and retene in the zebrafish *Danio rerio*. Reprod. Toxicol. 213–223.

Hong, S.H., Han, G.M., Yim, U.H., Lim, D., Ha, S.Y., Kim, N.S., Shim, W.J., 2014. Integrative assessment of sediment quality in terms of chemical contamination in Jinhae Bay, South Korea. Ocean Sci. J. 49, 265–278.

Hong, S., Lee, J., Lee, C., Yoon, S.J., Jeon, S., Kwon, B.O., Lee, J.H., Giesy, J.P., Khim, J.S., 2016. Are styrene oligomers in coastal sediments of an industrial area aryl hydrocarbon-receptor agonists? Environ. Pollut. 213, 913–921.

Hong, S., Lee, Y., Yoon, S.J., Lee, J., Kang, S., Won, E.J., Hur, J., Khim, J.S., Shin, K.H., 2019. Carbon and nitrogen stable isotope signatures linked to anthropogenic toxic substances pollution in a highly industrialized area of South Korea. Mar. Pollut. Bull. 144, 152–159.

Isobe, T., Nishiyama, H., Nakashima, A., Takada, H., 2001. Distribution and behavior of nonylphenol, octylphenol, and nonylphenol monoethoxylate in Tokyo metropolitan area: their association with aquatic particles and sedimentary distributions. Environ. Sci. Technol. 35, 1041–1049.

Katsoyiannis, A., Sweetman, A.J., Jones, K.C., 2011. PAH molecular diagnostic ratios applied to atmospheric sources: a critical evaluation using two decades of source inventory and air concentration data from the UK. Environ. Sci. Technol. 45, 8897–8906.

Khalili, N.R., Scheff, P.A., Holsen, T.M., 1995. PAH source fingerprints for coke ovens, diesel, and gasoline engines, highway tunnels, and wood combustion emissions. Atmos. Environ. 29, 533–542.

Khim, J.S., Hong, S., 2014. Assessment of trace pollutants in Korean coastal sediments using the triad approach: a review. Sci. Total Environ. 470-471, 1450–1462.

Khim, J.S., Kannan, K., Villeneuve, D.L., Koh, C.H., Giesy, J.P., 1999. Characterization and distribution of trace organic contaminants in sediment from Masan Bay, Korea. 1. Instrumental analysis. Environ. Sci. Technol. 33, 4199–4205.

Khim, J.S., Lee, K.T., Kannan, K., Villeneuve, D.L., Giesy, J.P., Koh, C.H., 2001. Trace organic contaminants in sediment and water from Ulsan Bay and its vicinity, Korea. Arch. Environ. Con. Tox. 40, 141–150.

Kim, G.B., Maruya, K.A., Lee, R.F., Lee, J.H., Koh, C.H., Tanabe, S., 1999. Distribution and sources of polycyclic aromatic hydrocarbons in sediments from Kyeonggi Bay, Korea. Mar. Pollut. Bull. 38, 7–15.

Kim, D., Kim, J.H., Kim, M.S., Ra, K., Shin, K.H., 2018. Assessing environmental changes in Lake Shihwa, South Korea, based on distributions and stable carbon isotopic compositions of n-alkanes. Environ. Pollut. 240, 105–115.

Kim, J., Hong, S., Cha, J., Lee, J., Kim, T., Lee, S., Moon, H.B., Shin, K.H., Hur, J., Lee, J.S., Giesy, J.P., Khim, J.S., 2019. Newly identified AhR-active compounds in the sediments of an industrial area using effect-directed analysis. Environ. Sci. Technol. 53, 10043–10052.

Kim, S., Hong, S., Lee, J., Kim, T., Yoon, S.J., Lee, J., Choi, K., Kwon, B.-O., Giesy, J.P., Khim, J.S., 2020. Long-term trends of persistent toxic substances and potential toxicities in sediments along the west coast of South Korea. Mar. Pollut. Bull. 151, 110821.

Koh, C.H., Khim, J.S., Villeneuve, D.L., Kannan, K., Giesy, J.P., 2002. Analysis of trace organic contaminants in sediment, pore water, and water samples from Onsan Bay, Korea: instrumental analysis and in vitro gene expression assay. Environ. Toxicol. Chem. 21, 1796–1803.

Koh, C.H., Khim, J.S., Villeneuve, D.L., Kannan, K., Giesy, J.P., 2006. Characterization of trace organic contaminants in marine sediment from Yeongil Bay, Korea: 1. Instrumental analyses. Environ. Pollut. 142, 39–47.

Kwon, B.G., Moon, K.R., 2019. Physicochemical properties of styrene oligomers in the environment. Sci. Total Environ. 683, 216–220.

Kwon, B.G., Saido, K., Koizumi, K., Sato, H., Ogawa, N., Chung, S.Y., Kusui, T., Kodera, Y., Kogure, K., 2014. Regional distribution of styrene analogues generated from polystyrene degradation along the coastlines of the North-East Pacific Ocean and Hawaii. Environ. Pollut. 188, 45–49.

LaVoie, E.J., Tulley-Freiler, L., Bedenko, V., Hoffmann, D., 1983. Mutagenicity of substituted phenanthrenes in Salmonella typhimurium. Mutat. Res. 116, 91–102.

Lee, J., Hong, S., Kwon, B.O., Cha, S.A., Jeong, H.D., Chang, W.K., Ryu, J., Giesy, J.P., Khim, J.S., 2018. Integrated assessment of persistent toxic substances in sediments from Masan Bay, South Korea: comparison between 1998 and 2014. Environ. Pollut. 238, 317–325.

Lee, J., Kwon, B.-O., Kim, B., Noh, J., Hwang, K., Ryu, J., Park, J., Hong, S., Khim, J.S., 2019. Natural and anthropogenic signatures on sedimentary organic matters across

varying intertidal habitats in the Korean waters. Environ. Int. 133, 105166.

Li, A., Jang, J., Scheff, P.A., 2003. Application of EPA CMB8.2 model for source apportionment of sediment PAHs in Lake Calumet, Chicago. Environ. Sci. Technol. 37, 2958–2965.

Lin, T., Hu, L., Guo, Z., Qin, Y., Yang, Z., Zhang, G., Zheng, M., 2011. Sources of polycyclic aromatic hydrocarbons to sediments of the Bohai and Yellow Seas in East Asia. J. Geophys. Res.-Atmos. 116.

Lorgeoux, C., Moilleron, R., Gasperi, J., Ayrault, S., Bonté, P., Lefèvre, I., Tassin, B., 2016. Temporal trends of persistent organic pollutants in dated sediment cores: chemical fingerprinting of the anthropogenic impacts in the Seine River basin, Paris. Sci. Total Environ. 541, 1355–1363.

Marzo, M., Kulkarni, S., Manganaro, A., Roncaglioni, A., Wu, S., Barton-Maclaren, T.S., Lester, C., Benfenati, E., 2016. Integrating in silico models to enhance predictivity for developmental toxicity. Toxicology 370, 127–137.

Moon, H.B., Choi, H.G., Kim, S.S., Lee, P.Y., 2001. Level and origin of polycyclic aromatic hydrocarbons (PAHs) in sediments from Ulsan Bay, Korea. Environ. Sci. Bull., Korean Environ. Sci. Soc. 10, 113–119.

Ohyama, K.I., Nagai, F., Tsuchiya, Y., 2001. Certain styrene oligomers have proliferative activity on MCF-7 human breast tumor cells and binding affinity for human estrogen receptor. Environ. Health Persp. 109, 699–703.

Olson, D.A., McDow, S.R., 2009. Near roadway concentrations of organic source markers. Atmos. Environ. 43, 2862–2867.

Onodera, S., Igarashi, K., Fukuda, A., Ouchi, J., Suzuki, S., 1994. Mutagenic potentials of anthracene and phenanthrene compounds during water disinfection with chlorine. Jpn. J. Tox. Env. Health. 40, 233–243.

Peters, K.E., Sweeney, R.E., Kaplan, I.R., 1978. Correlation of carbon and nitrogen stable isotope ratios in sedimentary organic matter 1. Limnol. Oceanogr. 23, 598–604.

Pizzo, F., Lombardo, A., Manganaro, A., Benfenati, E., 2013. In silico models for predicting ready biodegradability under REACH: a comparative study. Sci. Total Environ. 463-464, 161–168.

Routledge, E.J., Sumpter, J.P., 1997. Structural features of alkylphenolic chemicals associated with estrogenic activity. J. Biol. Chem. 272, 3280–3288.

Smith, D.J.T., Harrison, R.M., 1996. Concentrations, trends and vehicle source profile of polynuclear aromatic hydrocarbons in the U.K. atmosphere. Atmos. Environ. 30, 2513–2525.

Tian, Z., Kim, S.K., Hyun, J.H., 2020. Environmental distribution of styrene oligomers (SOs) coupled with their source characteristics: tracing the origin of SOs in the environment. J. Hazard. Mater. 398, 122968.

Tobiszewski, M., Namieśnik, J., 2012. PAH diagnostic ratios for the identification of pollution emission sources. Environ. Pollut. 162, 110–119.

Tucker, J., Sheats, N., Giblin, A.E., Hopkinson, C.S., Montoya, J.P., 1999. Using stable isotopes to trace sewage-derived material through Boston Harbor and Massachusetts Bay. Mar. Environ. Res. 48, 353–375.

Van den Berg, M., Birnbaum, L.S., Denison, M., De Vito, M., Farland, W., Feeley, M., Fiedler, H., Hakansson, H., Hanberg, A., Haws, L., Rose, M., Safe, S., Schrenk, D., Tohyama, C., Tritscher, A., Tuomisto, J., Tysklind, M., Walker, N., Peterson, R.E., 2006. The 2005 World Health Organization reevaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds. Toxicol. Sci. 93, 223–241.

Villemin, D., Cherqaoui, D., Mesbah, A., 1994. Predicting carcinogenicity of polycyclic aromatic hydrocarbons from back-propagation neural Network. J. Chem. Inf. Comp. Sci. 34, 1288–1293.

Witt, G., 1995. Polycyclic aromatic hydrocarbons in water and sediment of the Baltic Sea. Mar. Pollut. Bull. 31, 237–248.

Wu, W.Z., Wang, J.X., Zhao, G.F., You, L., 2002. The emission soot of biomass fuels combustion as a source of endocrine disrupters. J. Environ. Sci. Heal. A 37, 579–600.

Yang, Z., Shen, Z., Gao, F., Tang, Z., Niu, J., 2009. Occurrence and possible sources of polychlorinated biphenyls in surface sediments from the Wuhan reach of the Yangtze River, China. Chemosphere 74, 1522–1530.

Yim, U.H., Hong, S.H., Shim, W.J., Oh, J.R., Chang, M., 2005. Spatio-temporal distribution and characteristics of PAHs in sediments from Masan Bay, Korea. Mar. Pollut. Bull. 50, 319–326.

Yim, U.H., Hong, S.H., Shim, W.J., 2007. Distribution and characteristics of PAHs in sediments from the marine environment of Korea. Chemosphere 68, 85–92.

Yoon, S.J., Hong, S., Kwon, B.O., Ryu, J., Lee, C.H., Nam, J., Khim, J.S., 2017. Distributions of persistent organic contaminants in sediments and their potential impact on macrobenthic faunal community of the Geum River Estuary and Saemangeum Coast, Korea. Chemosphere 173, 216–226.

Yoon, S.J., Hong, S., Kim, S., Lee, J., Kim, T., Kim, B., Kwon, B.-O., Zhou, Y., Shi, B., Liu, P., Hu, W., Huang, B., Wang, T., Khim, J.S., 2020. Large-scale monitoring and ecological risk assessment of persistent toxic substances in riverine, estuarine, and coastal sediments of the Yellow and Bohai seas. Environ. Int. 137, 105517.

<Supplementary Materials>

Baseline

Current contamination status of traditional and emerging persistent toxic substances in the sediments of Ulsan Bay, South Korea

Yoonyoung An, Seongjin Hong[*], Seo Joon Yoon, Jihyun Cha, Kyung-Hoon Shin,

Jong Seong Khim

Supplementary Tables

Supplementary Figures

_____

[*]**Corresponding author.**

Department of Ocean Environmental Sciences, Chungnam National University, Daejeon 34134,

Republic of Korea. Tel.: +82 42 821 6436. *E-mail address*: hongseongjin@cnu.ac.kr (S. Hong).

Supplementary Tables

Table S1. GC/MSD conditions for analyzing polycyclic aromatic hydrocarbons, styrene oligomers, and alkylphenols in sediment samples from Ulsan Bay, Korea.

Instrument	Agilent 7890B GC / 5977B MSD	
Column	DB-5ms (30 m × 250 μm × 0.25 μm)	
Gas flow	1 mL / min He	
Injection mode	splitless	
Injection volume	1 μL	
Oven temperature program	PAHs	60 °C (hold 2 min) →
		6 °C / min to 300 °C (hold 13 min)
	SOs	60 °C (hold 2 min) →
		6 °C / min to 300 °C (hold 3 min)
	APs	60 °C (hold 5 min) →
		10 °C / min to 100 °C →
		20 °C / min to 300 °C (hold 6 min)

Table S2. Target compounds, abbreviations, and target ions in the instrumental analysis, and method detection limits and recoveries of surrogate standards.

Target compounds	Abbreviation	Target ions		Method detection limit (ng g^{-1} dw)
		Quantification ion	Confirmation ion	
Polycyclic aromatic hydrocarbons (PAHs)				
Acenaphthylene	Acl	152	151	0.06
Acenaphthene	Ace	153	154	0.12
Fluorene	Flu	166	165	0.15
Phenanthrene	Phe	178	176	0.06
Anthracene	Ant	178	176	0.07
Fluoranthene	Fl	202	200	0.09
Pyrene	Py	202	200	0.12
Benzo[*a*]anthracene	BaA	228	226	0.06
Chrysene	Chr	228	226	0.03
Benzo[*b*]fluoranthene	BbF	252	253	0.08
Benzo[*k*]fluoranthene	BkF	252	253	0.20
Benzo[*a*]pyrene	BaP	252	253	0.09
Indeno[*1,2,3-cd*]pyrene	IcdP	276	138	0.09
Dibenz[*a,h*]anthracene	DbahA	278	276	0.07
Benzo[*g,h,i*]perylene	BghiP	276	138	0.12
Emerging PAHs (E-PAHs)				
3-Methylphenanthrene	3MP	192	191	0.06
2-Methylphenanthrene	2MP	192	191	0.17
2-Methylanthracene	2MA	192	191	0.81
9-Ethylphenanthrene	9EP	191	206	0.06
1,6-Dimethylphenanthrene	16DMP	206	191	0.23
1,2-Dimethylphenanthrene	12DMP	206	191	0.21
Benzo[*b*]naphtho[*2,3-d*]furan	BBNF	218	189	0.32
11H-Benzo[b]fluorene	11BF	216	215	0.23
Benzo[*b*]naphtho[*2,1-d*]thiophene	BBNT	234	235	0.12
Triphenylene	Trl	228	226	0.21
3-Methylchrysene	3MC	242	241	0.26
5-Methylbenzo[*a*]anthracene	5MBA	256	241	0.20
1,12-Dimethylbenzo[*c*]phenanthrene	BCP	242	241	0.34
1-Methylchrysene	1MC	242	241	0.14
Benzo[*j*]fluoranthene	BJF	252	253	0.52
Benzo[*e*]pyrene	BEP	252	250	0.28
Styrene oligomers (SOs)				
1,3-Diphenylpropane	SD1	105	196	0.19
cis-1,2-Diphenylcyclobutane	SD2	78	208	0.19
2,4-Diphenyl-1-butene	SD3	104	208	0.89
trans-1,2-Diphenylcyclobutane	SD4	78	208	0.11
2,4,6-Triphenyl-1-hexene	ST1	117	194	0.63
1e-Phenyl-4e-(1-phenylethyl)-tetralin	ST2	129	207	0.66
1a-Phenyl-4e-(1-phenylethyl)-tetralin	ST3	129	207	0.31
1a-Phenyl-4a-(1-phenylethyl)-tetralin	ST4	129	207	0.70
1e-Phenyl-4a-(1-phenylethyl)-tetralin	ST5	207	105	0.41
1,3,5-Triphenylcyclohexane	ST6	117	104	0.88
Alkylphenols (APs)				
4-*tert*-Octylphenol	t-OP	207	221	0.12
4-*tert*-Octylphenol monoethoxylate	t-OP1EO	251	265	0.61
4-*tert*-Octylphenol diethoxylate	t-OP2EO	295	309	0.08
Nonylphenols	NPs	207	221	3.7

Nonylphenol monoethoxylates	NP1EOs	251	265	0.45
Nonylphenol diethoxylates	NP2EOs	295	309	1.5
Internal standard				
2-Fluorobiphenyl	IS	172	171	
Surrogate standards		Quantification ion	Confirmation ion	**Surrogate recovery (%, mean ± SD)**
Acenaphthene-d10	Ace-d10	164	162	72 ± 12
Phenanthrene-d10	Phe-d10	188	189	76 ± 9
Chrysene-d12	Chr-d12	240	236	88 ± 11
Perylene-d12	Pery-d12	264	270	90 ± 11
Bisphenol A-d16	BPA-d16	368	386	75 ± 17

Table S3. Sampling locations and sediment properties, including total organic carbon, total nitrogen, and stable isotope ratios in Ulsan Bay, Korea.

Stations		Latitude	Longitude	TOC (%)	TN (%)	C/N ratio[a]	$\delta^{13}C_{OC}$ (‰)	$\delta^{15}N_{TN}$ (‰)
Rivers	R1	35°32'42.62"N	129°21'59.94"E	2.84	0.21	13.80	−26.1	3.88
	R2	35°28'0.70"N	129°20'50.32"E	2.74	0.18	15.50	−25.7	2.43
Inland	C1	35°31'26.13"N	129°22'23.50"E	4.82	0.23	20.80	−25.9	0.95
creeks	C2	35°25'33.01"N	129°21'37.20"E	6.19	0.38	16.40	−22.0	−1.91
Bay	U1	35°31'28.45"N	129°22'55.36"E	2.52	0.20	12.90	−25.2	4.17
sites	U2	35°30'35.50"N	129°23'31.67"E	1.62	0.18	9.24	−25.4	4.38
	U3	35°28'15.81"N	129°24'9.12"E	1.81	0.18	10.31	−23.7	4.83
	U4	35°27'39.35"N	129°24'20.18"E	1.78	0.28	6.43	−21.8	4.51
	U5	35°23'19.80"N	129°20'56.35"E	1.99	0.26	7.50	−21.6	5.44

[a] C/N ratio: This value was calculated based on the molar concentration.

Table S4. Concentrations of traditional polycyclic aromatic hydrocarbons, styrene oligomers, and alkylphenols in sediments from Ulsan Bay, Korea.

Target compounds	Rivers		Inland creeks		Bay sites				
	R1	R2	C1	C2	U1	U2	U3	U4	U5
Traditional PAHs									
Acl	<DL[a]	<DL	58	41	0.14	0.12	0.13	0.1	0.13
Ace	<DL	0.71	7.8	< DL	0.57	0.71	0.34	0.29	0.32
Flu	1.1	1.2	85	13	1.7	1.3	1.1	0.82	0.99
Phe	5.6	11	680	99	5.6	5.8	3.7	2.9	3.3
Ant	1.0	1.4	120	3.0	1.1	0.75	0.51	0.57	0.69
Fl	8.2	15	520	86	11	13	6.8	4.8	5.9
Py	9.4	19	500	100	11	12	6.1	3.8	4.6
BaA	3.2	6.0	290	59	4.6	5.2	2.4	1.9	2.0
Chr	4.9	11	340	37	6.1	5.8	3.1	2.5	2.7
BbF	5.5	86	360	8.6	9.0	11	6.5	5.9	7.1
BkF	<DL	88	70	5.0	3.9	5.2	2.8	2.6	2.6
BaP	3.3	6.3	260	75	4.2	5.1	2.2	1.9	1.8
IcdP	5.2	10	210	42	4.0	5.1	3.3	3.0	2.6
DbahA	0.83	2.6	74	22	1.5	1.4	0.75	0.7	0.51
BghiP	8.4	14	380	100	7.2	6.5	4.1	3.5	2.2
ΣPAHs	60	280	4000	740	71	78	44	35	37
SOs									
SD1	1.2	<DL	2.7	6.9	0.75	0.73	0.67	0.71	0.55
SD2	< DL	1.0	<DL	11	0.85	0.79	0.81	0.76	5.9
SD3	13	64	47	2900	25	37	20	67	19
SD4	0.95	5.9	2.9	72	0.52	0.49	0.47	0.46	3.6
ST1	4.3	7.2	7.6	20	5.1	4.6	3.9	3.2	6.9
ST2	1.6	8.4	3.6	11	< DL	< DL	<DL	<DL	4.4
ST3	3.2	10	5.9	11	1.7	0.61	1.0	0.87	7.5
ST4	3.1	4.5	1.7	1.8	< DL	< DL	1.9	3.7	3.2
ST5	8.0	36	29	720	5.0	10	5.5	1.4	5.4
ST6	< DL	3.3	< DL	5.5	1.2	2.2	<DL	<DL	<DL
ΣSOs	35	140	100	3800	40	57	34	78	57
APs									
t-OP	2.3	12	6.9	86	2.3	0.41	0.28	0.13	0.18

t-OP1EO	3.1	38	5.1	17	3.2	1.5	2.2	0.88	1.3
t-OP2EO	3.2	3.7	2.1	5.1	3	1.7	2.3	1	1.4
NPs	210	87	190	200	50	29	16	7	9.4
NP1EOs	41	110	120	98	34	16	19	16	20
NP2EOs	11	13	41	25	13	7.3	7.9	5.3	5.2
ΣAPs	270	264	365	433	105	57	48	30	38

[a] < DL: below detection limits.

Table S5. Comparisons of concentrations of various persistent toxic substances in sediments reported in previous studies and those obtained from the current study.

Regions	Type	Sampling Year	Number of stations	Target compounds	Concentrations (ng g^{-1} dw) Min–Max	Mean	References
PAHs							
Gyunggi Bay	Harbor	1995	19	23 PAHs	12–1400	260	Kim et al., 1999
	River		16	23 PAHs	29–230	83	
	Open sea		31	23 PAHs	3.1–170	51	
Masan coast	Inner part of bay	1997	10	24 PAHs	207–2670	1050±786	Yim et al., 2005
	Outer part of bay		10	24 PAHs		428±85.2	
Masan Bay	Bay	1998	28	16 PAHs	41.5–1100	353±252	Khim et al., 1999
Onsan Bay	River and creek	1999	9	16 PAHs	<10.0–573	118±173	Koh et al., 2002
	Bay		13	16 PAHs	<DL[a]–38.7	19.1±13.5	
Yeongil Bay	Inner part of bay	2000	4	16 PAHs	28.5–1870	737	Koh et al., 2006
	Outer part of bay		22	16 PAHs	<10.0–662	162	
Ulsan coast	Bay	2000	22	16 PAHs	14–7108	1052±1638	Moon et al., 2001
Jinhae Bay	Bay	2010	80	22 PAHs	12.4–2430	105	Hong et al., 2014
Busan coast	River and harbor	2013	37	16 PAHs	3.88–5346	390	Han et al., 2016
Sihwa lake	Lake	2013	10	22 PAHs	195–2420	1023±710	Hong et al., 2019
Masan Bay	Bay	2014	9	16 PAHs	58–1900	91	Lee et al., 2018
Saemangeum coast	Estuary and bay	2014	58	24 PAHs	2.9–158	39	Yoon et al., 2017
Sihwa lake	Inland creek	2015	6	16 PAHs	210–1900	226	Lee et al., 2017
Ulsan Bay	River and creek	2017	4	15 PAHs	61–1274	510±490	This study
	Bay		5	15 PAHs	35–78	53±18	
SOs							
Sihwa lake	Lake	2013	10	10 SOs	148–1730	689±568	Hong et al., 2019
Masan Bay	Bay	2014	9	10 SOs	73–350	130	Lee et al., 2018
Saemangeum coast	Estuary and bay	2014	58	10 SOs	0.3–261	14	Yoon et al., 2017
Sihwa lake	Lake	2015	6	10 SOs	10.1–62.6	34.2	Lee et al., 2017
Ulsan Bay	River and creek	2017	4	10 SOs	35–3759	1000±	This study
	Bay		5	10 SOs	34–78	53±15	
APs							
Masan Bay	Bay	1998	28	NP	113–3890	510±710	Khim et al., 1999
				OP	3.97–179	18.1±32.1	

Onsan Bay	River and creek	1999	9	NP	<1.00–860	123±263	Koh et al., 2002
	Bay		13	NP	<DL–3.8	1.57±1.05	
	River and creek		9	OP	<1.00–11.01	2.66±3.27	
	Bay		13	OP	<DL–4.33	1.18±0.95	
Yeongil Bay	Inner part of bay	2000	4	NP	29.9–1430	348	Koh et al., 2006
	Outer part of bay		22	NP	<1.00–63.5	25.3	
	Inner part of bay		4	OP	2.46–24.3	7.62	
	Outer part of bay		22	OP	<1.00–11.3	3.13	
Jinhae Bay	Bay	2010	80	NP	<DL–469	31.6	Hong et al., 2014
Sihwa lake	Lake	2013	10	6 APs	148–1730	689±568	Hong et al., 2019
Masan Bay	Bay	2014	9	6 APs	18–72	39	Lee et al., 2018
Saemangeum coast	Estuary and bay	2014	58	6 APs	0.6–46	9.5	Yoon et al., 2017
Ulsan Bay	River and creek	2017	4	6 APs	264–433	330±70	This study
	Bay		5	6 APs	30–105	55±26	

[a] <DL: below detection limits.

Table S6. Distributions and potential sources of emerging polycyclic aromatic hydrocarbons in sediments from Ulsan Bay, Korea.

Target compounds	Abb.[a]	Reported sources (References)	Rivers		Inland creeks		Bay sites				
			R1	R2	C1	C2	U1	U2	U3	U4	U5
Emerging PAHs											
3-Methylphenanthrene	3MP	Biomass combustion (Wu et al., 2002)	2.1	4.1	87	7.0	2.5	0.95	0.70	0.60	0.66
2-Methylphenanthrene	2MP	Biomass combustion (bin Abas et al., 1995)	3.4	6.3	58	13	4.1	1.4	1.5	1.1	1.3
2-Methylanthracene	2MA	Combustion (Yunker et al., 2012)	1.1	<DL	150	<DL	6.2	1.4	0.64	<DL	<DL
9-Ethylphenanthrene	9EP	Wood combustion (Benner et al., 1995)	<DL[c]	0.72	100	<DL	<DL	<DL	<DL	<DL	<DL
1,6-Dimethylphenanthrene	16DMP	Mobile source (Benner et al., 1995)	3.4	2.4	100	240	5.4	3.5	3.5	3.7	4.0
Benzo[*b*]naphtho[*2,3-d*]furan	BBNF	Lignite combustion (Stefanova et al., 2002)	2.1	3.1	150	2.3	8.5	6.0	4.3	4.3	4.3
11H-benzo[*b*]fluorene	11BF	Biomass combustion (Wu et al., 2002)	4.7	2.1	110	1.8	40	27	14	11	13
Benzo[*b*]naphtho[*2,1-d*]thiophene	BBNT	Diesel engine (Smith and Harrison, 1996)	2.1	1.0	110	70	5.7	2.3	0.75	0.63	0.52
3-Methylchrysene	3MC	Diesel exhaust (Olson and Mcdow, 2009)	2.1	1.9	4.4	51	6.3	4.9	2.9	2.5	2.4
5-Methylbenzo[*a*]anthracene	5MBA	na[b]	0.83	<DL	15	4.4	1.2	1.0	0.44	0.37	0.37
1-Methylchrysene	1MC	Combustion (Yunker et al., 2012)	<DL	<DL	6.8	16	1.3	0.83	0.38	0.39	0.32
Benzo[*e*]pyrene	BEP	Mobile source (Khalili et al., 1995)	8.1	4.2	240	79	24	25	14	12	11

[a] Abb.: abbreviations.
[b] na: not available
[c] <DL: below detection limits.
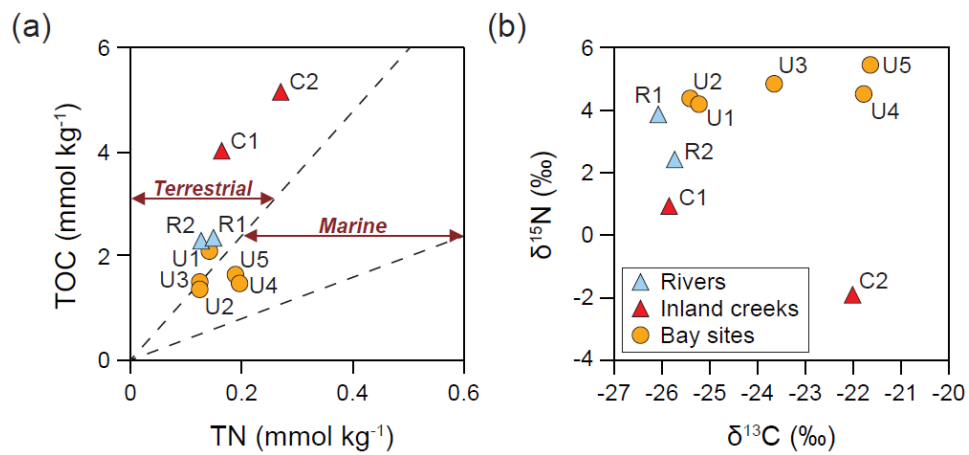
Supplementary Figures

Fig. S1. Source identification of organic matter in surface sediments using (a) C/N ratio and (b) carbon and nitrogen stable isotope ratios.

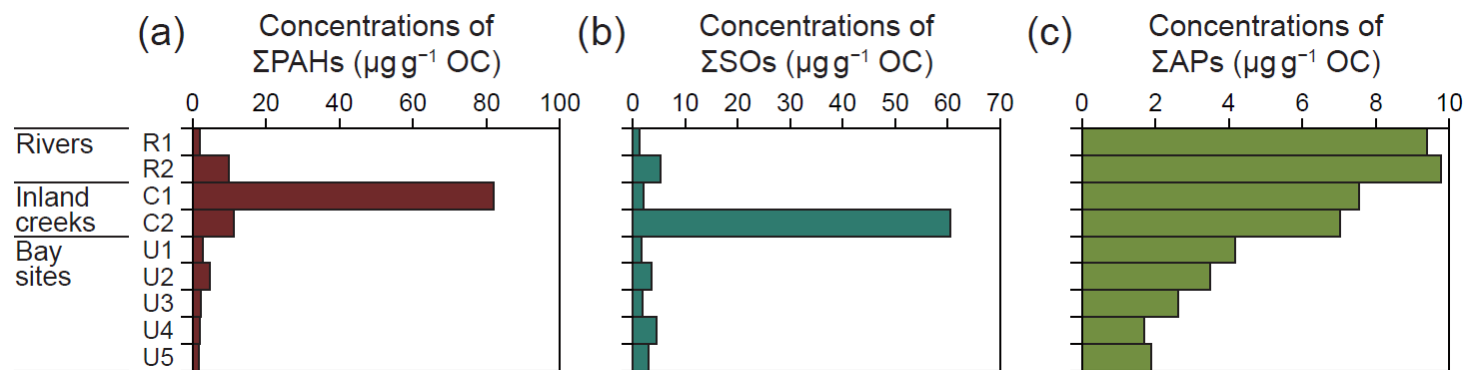**Fig. S2.** Organic carbon normalized concentrations of PTSs, including (a) PAHs, (b) SOs, and (c) APs in sediments from Ulsan Bay, Korea.
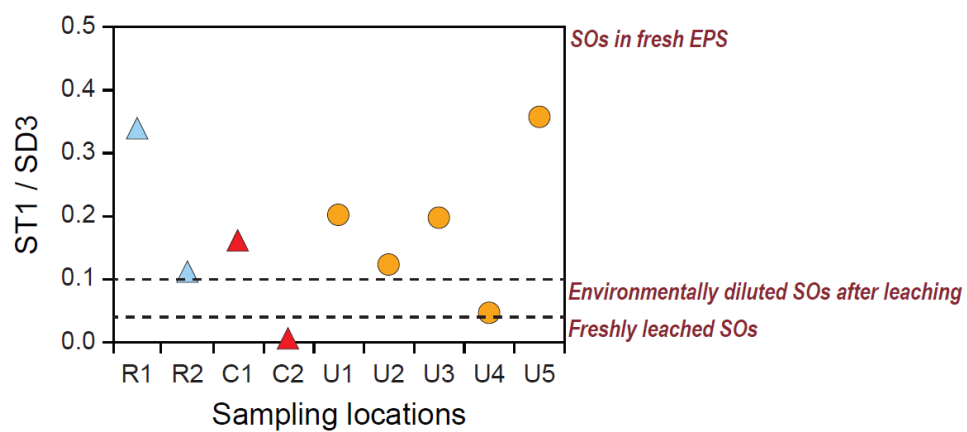
Fig. S3. Source identification of styrene oligomers using the ratio of 2,4,6-triphenyl-1-hexene (ST1) to 2,4-diphenyl-1-butene (SD3) suggested by Tian et al. (2020).

References

Benner, B.A., Wise, S.A., Currie, L.A., Klouda, G.A., Klinedinst, D.B., Zweidinger, R.B., Stevens, R.K., Lewis, C.W., 1995. Distinguishing the contributions of residential wood combustion and mobile source emissions using relative concentrations of dimethylphenanthrene isomers. Environ. Sci. Technol. 29, 2382-2389.

bin Abas, M.R., Simoneit, B.R.T., Elias, V., Cabral, J.A., Cardoso, J.N., 1995. Composition of higher molecular weight organic matter in smoke aerosol from biomass combustion in Amazonia. Chemosphere 30, 995-1015.

Han, G.M., Hong, S.H., Shim, W.J., Ra, K.T., Kim, K.T., Ha, S.Y., Jang, M., Kim, G.B., 2016. Assessment of Persistent Organic and Heavy Metal Contamination in Busan Coast: Application of Sediment Quality Index. Ocean Polar Res. 38, 171-184.

Hong, S., Lee, Y., Yoon, S.J., Lee, J., Kang, S., Won, E.-J., Hur, J., Khim, J.S., Shin, K.-H., 2019. Carbon and nitrogen stable isotope signatures linked to anthropogenic toxic substances pollution in a highly industrialized area of South Korea. Mar. Pollut. Bull. 144, 152-159.

Hong, S.H., Han, G.M., Yim, U.H., Lim, D.-i., Ha, S.Y., Kim, N.S., Shim, W.J., 2014. Integrative assessment of sediment quality in terms of chemical contamination in Jinhae Bay, South Korea. Ocean Sci. J. 49, 265-278.

Khalili, N.R., Scheff, P.A., Holsen, T.M., 1995. PAH source fingerprints for coke ovens, diesel and, gasoline engines, highway tunnels, and wood combustion emissions. Atmos. Environ. 29, 533-542.

Khim, J.S., Kannan, K., Villeneuve, D.L., Koh, C.H., Giesy, J.P., 1999. Characterization and Distribution of Trace Organic Contaminants in Sediment from Masan Bay, Korea. 1. Instrumental Analysis. Environ. Sci. Technol. 33, 4199-4205.

Kim, G.B., Maruya, K.A., Lee, R.F., Lee, J.-H., Koh, C.-H., Tanabe, S., 1999. Distribution and sources of polycyclic aromatic hydrocarbons in sediments from Kyeonggi Bay, Korea. Mar. Pollut. Bull. 38, 7-15.

Koh, C.H., Khim, J.S., Villeneuve, D.L., Kannan, K., Giesy, J.P., 2002. Analysis of trace organic contaminants in sediment, pore water, and water samples from Onsan Bay, Korea: Instrumental analysis and in vitro gene expression assay. Environ. Toxicol. Chem. 21, 1796-1803.

Koh, C.H., Khim, J.S., Villeneuve, D.L., Kannan, K., Giesy, J.P., 2006. Characterization of trace organic contaminants in marine sediment from Yeongil Bay, Korea: 1. Instrumental analyses. Environ. Pollut. 142, 39-47.

Lee, J., Hong, S., Kwon, B.O., Cha, S.A., Jeong, H.D., Chang, W.K., Ryu, J., Giesy, J.P., Khim, J.S., 2018. Integrated assessment of persistent toxic substances in sediments from Masan Bay, South Korea: Comparison between 1998 and 2014. Environ. Pollut. 238, 317-325.

Lee, J., Hong, S., Yoon, S.J., Kwon, B.-O., Ryu, J., Giesy, J.P., Allam, A.A., Al-khedhairy, A.A., Khim, J.S., 2017. Long-term changes in distributions of dioxin-like and estrogenic compounds in sediments of Lake Sihwa, Korea: Revisited mass balance. Chemosphere 181, 767-777.

Moon, H.B., Choi, H.G., Kim, S.S., Lee, P.Y., 2001. Level and Origin of Polycyclic Aromatic Hydrocarbons (PAHs) in sediments from Ulsan Bay, Environ. Sci. Bull., Korean Environ. Sci. Soc. 10, 113-119.

Olson, D.A., McDow, S.R., 2009. Near roadway concentrations of organic source markers. Atmos. Environ. 43, 2862-2867.

Smith, D.J.T., Harrison, R.M., 1996. Concentrations, trends and vehicle source profile of polynuclear aromatic hydrocarbons in the U.K. atmosphere. Atmos. Environ. 30, 2513-2525.

Stefanova, M., Marinov, S.P., Mastral, A.M., Callén, M.S., Garcí, T., 2002. Emission of oxygen, sulphur and nitrogen containing heterocyclic polyaromatic compounds from lignite combustion. Fuel Process. Technol. 77-78, 89-94.

Tian, Z., Kim, S.K., Hyun, J.H., 2020. Environmental distribution of styrene oligomers (SOs) coupled with their source characteristics: Tracing the origin of SOs in the environment. J. Hazard. Mater. 398, 122968.

Wu, W.Z., Wang, J.X., Zhao, G.F., You, L., 2002. The emission soot of biomass fuels combustion as a source of endocrine disrupters. J. Environ. Sci. Heal. A 37, 579-600.

Yim, U.H., Hong, S.H., Shim, W.J., Oh, J.R., Chang, M., 2005. Spatio-temporal distribution and characteristics of PAHs in sediments from Masan Bay, Korea. Mar. Pollut. Bull. 50, 319-326.

Yoon, S.J., Hong, S., Kwon, B.O., Ryu, J., Lee, C.H., Nam, J., Khim, J.S., 2017. Distributions of persistent organic contaminants in sediments and their potential impact on macrobenthic faunal community of the Geum River Estuary and Saemangeum Coast, Korea. Chemosphere 173, 216-226.

Yunker, M.B., Perreault, A., Lowe, C.J., 2012. Source apportionment of elevated PAH concentrations in sediments near deep marine outfalls in Esquimalt and Victoria, BC, Canada: Is coal from an 1891 shipwreck the source?. Org. Geochem. 46, 12-37.