



Baseline

Long-term trends of persistent toxic substances and potential toxicities in sediments along the west coast of South Korea



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ABSTRACT

For decades, in response to industrialization and urbanization, environmental qualities of estuarine and coastal areas of the west coast of Korea have been deteriorating. Long-term changes in concentrations of persistent toxic substances (PTSs) in sediments, including PAHs, styrene oligomers, nonylphenols, and metals and their potential toxicities via AhR- and ER-mediated potencies, and bioluminescent bacterial inhibition, were investigated. Long-term monitoring in five estuarine and coastal areas (2010–2018; 10 sites) showed that concentrations of PAHs and nonylphenols in sediments have declined while concentrations of some metals, Cd, Cr, and Hg have increased. Similarly, AhR-mediated potencies in sediments have declined, but inhibitions of bioluminescent bacteria have increased. Concentrations of sedimentary PAHs and AhR-mediated potencies were significantly ($p < 0.01$) and positively correlated. Sources of PAHs from combustion have been gradually declining while inputs from vehicle exhaust by-products have been increasing. Overall, this study brought our attention a balanced regulation in chemical-specific manner.

Coastal sediments can be final sinks of hazardous substances that originate from terrestrial environments (Khim and Hong, 2014). Organic and inorganic substances originate in various locations, including from industries that produce industrial and domestic products. Toxic substances are introduced into coastal environments via point and non-point sources, such as from surface runoff, outflow from estuaries, and atmospheric deposition. Physicochemical properties of hazardous substances determine their distributions and fate (Klopffer et al., 1982; Turner and Rawling, 2001). Contamination of coastal sediments reflects the inflow of persistent toxic substances (PTSs) from surrounding land, and sediments accumulate PTSs from polluted water over the long-term (Khim and Hong, 2014; Hong et al., 2019). PTSs accumulating in coastal sediments can adversely affect benthic organisms and can be released directly back into the water column or during resuspension or even through trophic transfer from benthic to pelagic organisms (Christophoridis et al., 2009; Dassenakis et al., 2003). Thus, studies quantifying distributions of PTSs in coastal sediments are crucial for evaluating influences of anthropogenic activities on marine ecosystems and environmental health status (Chapman and Anderson, 2005).

However, due to the thousands of organic and inorganic toxic substances in polluted sediments, without knowledge of what one is looking for, it is often difficult to identify major toxicants residing in sediments (Brack, 2003).

Although assessing sediments by chemical analyses has its limitations, biological assessments (bioassays) can compensate for such limitations (Burton et al., 2002). Instrumental analyses of pollutants in sediments can identify the concentrations of target chemicals, but the disadvantage of this approach is that one is usually unable to determine the integrated biological potencies including interactions among individual compounds (Hong et al., 2016). Chemicals which are not measured when present at concentrations less than limits of detection, or concentrations less than sediment quality guidelines, can act independently or interact with agonists or antagonists to affect the biological potencies of the mixture of pollutants present in marine environments (Cha et al., 2019; Kim et al., 2019a). In order to protect coastal ecosystems, it is essential to identify and reduce the export of priority pollutants (chemicals of most concern) to coastal environments. The following criteria might be useful when selecting priority

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pollutants for environmental management: (1) pollutants exceeding established sediment quality guidelines (Choueri et al., 2009); (2) bioaccumulative and/or biomagnifiable pollutants (Brown and Wania, 2008); (3) pollutants known to be particularly significant in contributing to effects (Khim et al., 2018); and (4) pollutants that are increasing over time in marine environments (West et al., 2017). It is challenging to select the chemicals of concern based only on short-term monitoring, thus long-term monitoring is needed. However, long-term monitoring is infrequently performed due to time and cost constraints.

Over the last several decades, the west coast of South Korea has become more urbanized and industrialized and although these rapid changes have generated economic wealth, the changes have also contributed to localized contamination of marine environments with PTSs, such as polycyclic aromatic hydrocarbons (PAHs), styrene oligomers (SOs), nonylphenols (NPs), and metals and metalloids (Khim et al., 1999; Hong et al., 2012; Jeon et al., 2017). From the 1970s to the early 1990s, construction of sea dikes (or estuary dams) and landfill projects have been executed to expand useable land, reduce flood damage, and provide freshwater for industrial and agricultural uses (Yim et al., 2018). As a result, most major rivers and estuaries along the west coast of South Korea have been disconnected from the open sea, which prevents or reduces flushing of contaminated water to the sea.

Water quality in both freshwater and seawater is regularly monitored in South Korea at a national scale, but sediment quality is less frequently monitored, particularly for PTSs and potential toxicities in sediments of coastal waters. However, the water quality of seawater in coastal environments does not always appear in connection with the quality of freshwater in rivers and lakes (Fig. S1 of the Supplementary Materials). For example, monitoring of the inner parts of Lake Asan and Geum River has shown them to have generally poor water quality based on chemical oxygen demand (COD), one freshwater water quality index (Water Environment Information System (WEIS), 2019). In contrast, the water quality index (WQI), an ecologically-based water quality indicator for coastal waters in South Korea, has been generally acceptable for the Asan Bay (Marine Environment Information System (MEIS), 2019) on the seaward (downstream) side of the sea dike. The inside of the estuary dams or sea dikes is composed of freshwater except for Lake Sihwa. In the case of Lake Sihwa, in 2000, due to poor water quality, desalination of the inner lake of Lake Sihwa was abandoned (Lee et al., 2014). After initiating operations of tidal power plants, water and sediment qualities have improved significantly in certain areas (Hong et al., 2019).

In this study, spatial and temporal distributions and sources of PTSs (15 PAHs, 10 SOs, 3 NPs, and 7 metals and 1 metalloid) and potential toxicities (via AhR- and ER-mediated potencies and bioluminescent bacteria inhibition) in sediments along the west coast of South Korea were determined from 2010 to 2018. Based on data from long-term monitoring, priority toxic substances were determined in sediments at locations along the Yellow Sea (on the west coast of South Korea). The results of our study can be used as baseline data for future coastal pollution management and reduction policies.

Samples of surface sediments on both sides of five estuary dams or sea dikes ($n = 10$ stations) were collected, during the same period (May) annually from 2010 to 2018 along the west coast of Korea (Fig. 1). Sediments from behind dams or dikes were identified with a "1", whereas samples from the estuary side were identified with a "2". After collecting samples, they were transported immediately to the laboratory and stored them at $-20\text{ }^{\circ}\text{C}$ until further analysis. Detailed descriptions of sample preparation for PTSs and in vitro cell bioassays (H4IIE-*luc* and MVLN) have been published previously (Khim et al., 1999; Hong et al., 2016; Yoon et al., 2017).

In brief, twenty grams of freeze-dried sediment samples were extracted for 16 h on a Soxhlet extractor with 350 mL dichloromethane (DCM) (Burdick & Jackson, Muskegon, MI). Elemental sulfur was removed by adding activated copper powder (Sigma-Aldrich, Saint Louis, MO). The extracts were concentrated to 2 mL and separated into two

aliquots for use in the instrumental analysis and in vitro bioassays. For the chemical analysis, 1 mL of the aliquot was passed through an 8 g activated silica gel column (70–230 mesh, Sigma-Aldrich) for fractionation. Fractions were collected by elutions with 50 mL of 20% DCM in hexane (F1: aromatics) and 50 mL of 60% DCM in acetone (F2: polar). Before the instrumental analysis, elutriates were concentrated to 1 mL with a rotary evaporator, followed by a gentle stream of nitrogen gas. For the in vitro bioassay, the aliquot was exchanged to produce dimethyl sulfoxide (DMSO, Sigma-Aldrich).

Concentrations of PAHs, SOs, and NPs in extracts of sediments were quantified by use of an Agilent 7890B gas chromatography equipped with a 5977B mass-selective detector (GC-MSD) (Agilent Technologies, Santa Clara, CA). Details of instrumental settings for PTSs analysis are provided in Table S1. A total of 28 PTSs, including 15 PAHs [acenaphthylene (Acl), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fl), pyrene (Py), benz[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[1,2,3-*c,d*]pyrene (IcdP), dibenz[*a,h*]anthracene (DahA), 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 (isomer mix) (ST6)], and 3 NPs [(nonylphenol (NP), nonylphenol monoethoxylates (NP1EO), and nonylphenol diethoxylates (NP2EO)] were quantified. Method detection limits were $0.16\text{--}0.56\text{ ng g}^{-1}$ dry mass (dm) for PAHs, $0.23\text{--}4.20\text{ ng g}^{-1}$ dm for SOs, and $0.45\text{--}0.70\text{ ng g}^{-1}$ dm for NPs. Concentrations of the 15 PAHs and 3 NPs in sediments from 2010 to 2014 were partially reported in the previous study (Jeon et al., 2017).

Metals and one metalloid (As) were analyzed, with some modifications, following Korean standard methods for sampling metals in the marine environment (Ministry of Oceans and Fisheries (MOF), 2013; Woo et al., 2019). For the analysis of metals, 0.2 g of freeze-dried sediments were digested with 3 mL of HNO_3 and 1 mL of HClO_4 for 4 h in a Teflon beaker. After evaporating samples to near dryness, 3 mL of HF and 1 mL of HClO_4 were added, then heated at $140\text{ }^{\circ}\text{C}$ for 6 h. After cooling to room temperature, samples were evaporated again and diluted with 1% HNO_3 to 10 mL. For quantifying As in samples, 0.2 g of samples were digested with 10 mL of 10% HNO_3 for 24 h and then centrifuged at $2000 \times g$ at $25\text{ }^{\circ}\text{C}$ for 10 min. In testing for Hg, 0.5 g of samples were digested with 50 mL of 10% HCl for 24 h and then centrifuged at $2000 \times g$ at $25\text{ }^{\circ}\text{C}$ for 10 min. Each supernatant was collected for instrumental analysis. Metals (Cd, Cr, Cu, Ni, Pb, and Zn) and metalloid (As) were quantified by use of the ICP-MS (ELAN 6100 System, PerkinElmer, Waltham, MA) and ICP-OES (Optima7300DV, PerkinElmer). Mercury was quantified by use of a flow injector mercury analyzer (FIMS100, PerkinElmer).

H4IIE-*luc* bioassay was performed to measure aryl hydrocarbon receptor (AhR)-mediated potencies and MVLN bioassay was used to measure estrogen receptor (ER)-mediated potencies in the sediment organic extracts according to the previously published method (Khim et al., 1999). Bioassay responses were expressed as mean relative luminescence units (RLU) and converted to percentages of the maximum response of 50 nM benzo[*a*]pyrene (BaP) (%BaP_{max}) and 1235 nM 17 β -estradiol (E2) (%E2_{max}). Trypsinized H4IIE-*luc* cells were diluted to concentrations of approximately $7 \times 10^4\text{ cell mL}^{-1}$ and MVLN cells to $1.25 \times 10^5\text{ cell mL}^{-1}$ and then seeded them into the 96-well plates with 250 μL of medium per well. After incubating for 24 h, cells were exposed to sediment extracts dosed at 0.25 μL (0.1% dose) with each cell's duration of exposure (4 h for H4IIE-*luc* and 72 h for MVLN). After exposure, luminescence of luciferase was measured using a Victor X3 multilabel plate reader (Perkin-Elmer). Statistical significances were defined as three times the standard deviation of the mean of solvent controls (sensu Horii et al., 2009). AhR- and ER-mediated potencies in

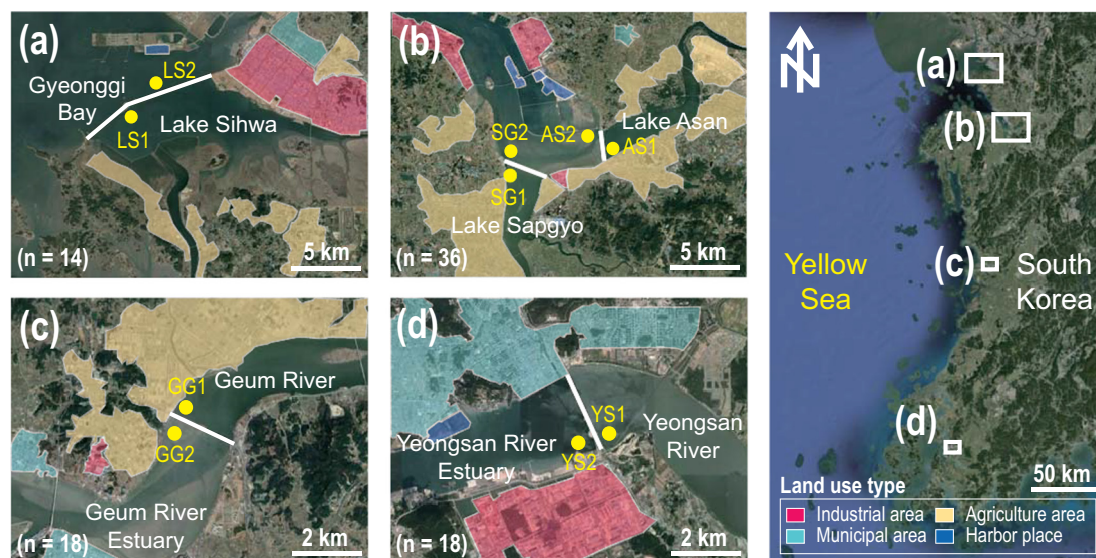


Fig. 1. Sampling locations for long-term sediment monitoring (2010–2018) on the west coast of South Korea. Panels: (a) Lake Sihwa, (b) Lake Sapgyo and Lake Asan, (c) Geum River Estuary, and (d) Yeongsan River Estuary.

sediments from 2010 to 2014 were partially reported previously (Jeon et al., 2017).

The N-Tox bioassay is based on the inhibition of bioluminescence of the marine bacterium *Vibrio fischeri* following exposure to toxicants (Bulich, 1986; Jacobs et al., 1993). Two grams of samples were placed in a 50-mL Teflon centrifuge tube. Samples were extracted with 20 mL filtered seawater by horizontal shaking at 200 rpm for 1 h. After centrifuging for 3 min at 2000 rpm, supernatant was filtered through a 1.0- μ m membrane filter for further analysis. One milliliter of reconstituted solution of VF100® (NeoEnBiz Inc.) was added to the lyophilized *V. fischeri* to reactivate the bacterium. A bacterial solution consisted of 1 mL of bacterial reagent with 50 mL of diluent (at 4 °C) (Lee et al., 2008). We prepared serially-diluted test water with sediment extracts in a 96-well plate (200 μ L to each well). Then 25 μ L of bacterial solution was added to each well. *V. fischeri* bioluminescence was measured with an N-Tox model 200 luminescent bacteria toxicity instrument (NeoEnBiz Inc., Bucheon, Korea).

After inorganic carbon was removed by treatment with HCl, total organic carbon (TOC) in sediment was measured by use of an elemental analyzer (EA, Elementar, Hanau, Hesse). Total nitrogen (TN) was measured without removing inorganics. Due to heterogeneity of the coastal environments, sediment characteristics can vary slightly from year to year, even if the same sites are monitored each year. TOC and TN of sediments collected from 2010, 2014, and 2018 were measured and compared (Table S2). Results showed some variabilities in TOC and TN, but they did not show a large difference along the years. Accordingly, in this study, we assumed that the effect of influx of toxic substances is more effective than that from the differences in sediment properties in terms of spatiotemporal heterogeneity of samples.

Relationships between PTSs contamination and potential toxicities in coastal sediments and emissions and transportation of hazardous substances from the land were estimated. For the period 2010–2016 in South Korea, data on the amount of discharged toxic wastewater flowing into rivers (Sapgyo, Geum, and Yeongsan) was obtained from the Ministry of Environment of Korea (MOE, 2019). Toxic wastewater refers to wastewater containing metals and organic pollutants (e.g., Cu, Pb, Hg, As, Cr, Cd, organophosphorus, cyanide, tetrachloroethylene, trichloroethylene, phenol, polychlorinated biphenyls, selenium, benzene, tetrachloromethane, dichloromethane, 1,1-dichloroethylene, 1,2-dichloroethane, chloroform, dioxins, diethylhexyl phthalate, vinyl chloride, acrylonitrile, bromoform, acrylamide, naphthalene, formaldehyde, epichlorohydrin, and pentachlorophenol), which are

treated within the workplace and eventually discharged to adjacent rivers. Data on detection, emission, and consumption of hazardous substances was obtained from the Pollutant Release and Transfer Registry (PRTR, 2019). PRTR data provides information regarding point-source emissions of metals, carcinogens, and toxic substances.

Temporal trends, either increase, decrease, or no change of PTSs and potential toxicity in sediments along the west coast of South Korea were assessed by use of the linear correlations between concentrations (or toxicities) and sampling years. Non-linear increasing or decreasing of PTS concentrations and potential toxicities in sediments by sampling year were also assessed. Statistical differences were determined between two groups, such as inner (upstream) and outer (downstream/seaward) sides of sea dikes (or estuary dams) with the Student's *t*-test. The positive matrix factorization (PMF) model was applied to identify the source(s) of PAHs in sediments. Detail descriptions of this approach have been reported in previous studies (Larsen and Baker, 2003; Lin et al., 2011; Jang et al., 2013). The PMF model is widely used in various applications and is the most advanced method for identification of sources of environmental pollutants based on concentrations and composition data sets (Christensen et al., 2019; Li et al., 2019; Norris et al., 2014). We applied the PMF model to address the long-term changes in sources of sedimentary PAHs contamination in the Korean coastal waters. The number of factors (viz., sources) was extracted and sources are estimated by types of individual compounds contributing to the given factors. We identified three sources of coal combustion, biomass combustion, and vehicle exhaust and estimated the corresponding source contribution to the given factor. Finally, we demonstrated the temporal pattern and variations of PAHs sources in a long-term aspect to address historical PAHs contamination in the Korean coastal sediments. In addition, to test the relationship between bioluminescence inhibition and concentrations of various PTSs in sediments, a Pearson correlation analysis was performed. Statistical analyses were performed by use of SPSS 23.0 software (SPSS Inc., Chicago, IL). All statistical significances were defined as $p < 0.05$.

In spatial and temporal distributions of PTSs and toxic potencies in sediments along the west coast of Korea from 2010 to 2018, concentrations of organic pollutants in sediments, such as PAHs, SOs, and NPs, were site- and compound-specific (Fig. 2 and Table 1). For example, were greater at Sites SG2, GG1, and GG2, whereas concentrations of SOs were greater at Site LS2. In addition, concentrations of NPs were greatest at Sites LS2, GG1, and GG2, whereas concentrations of metals and the metalloid As in sediments were greatest at Sites AS1,

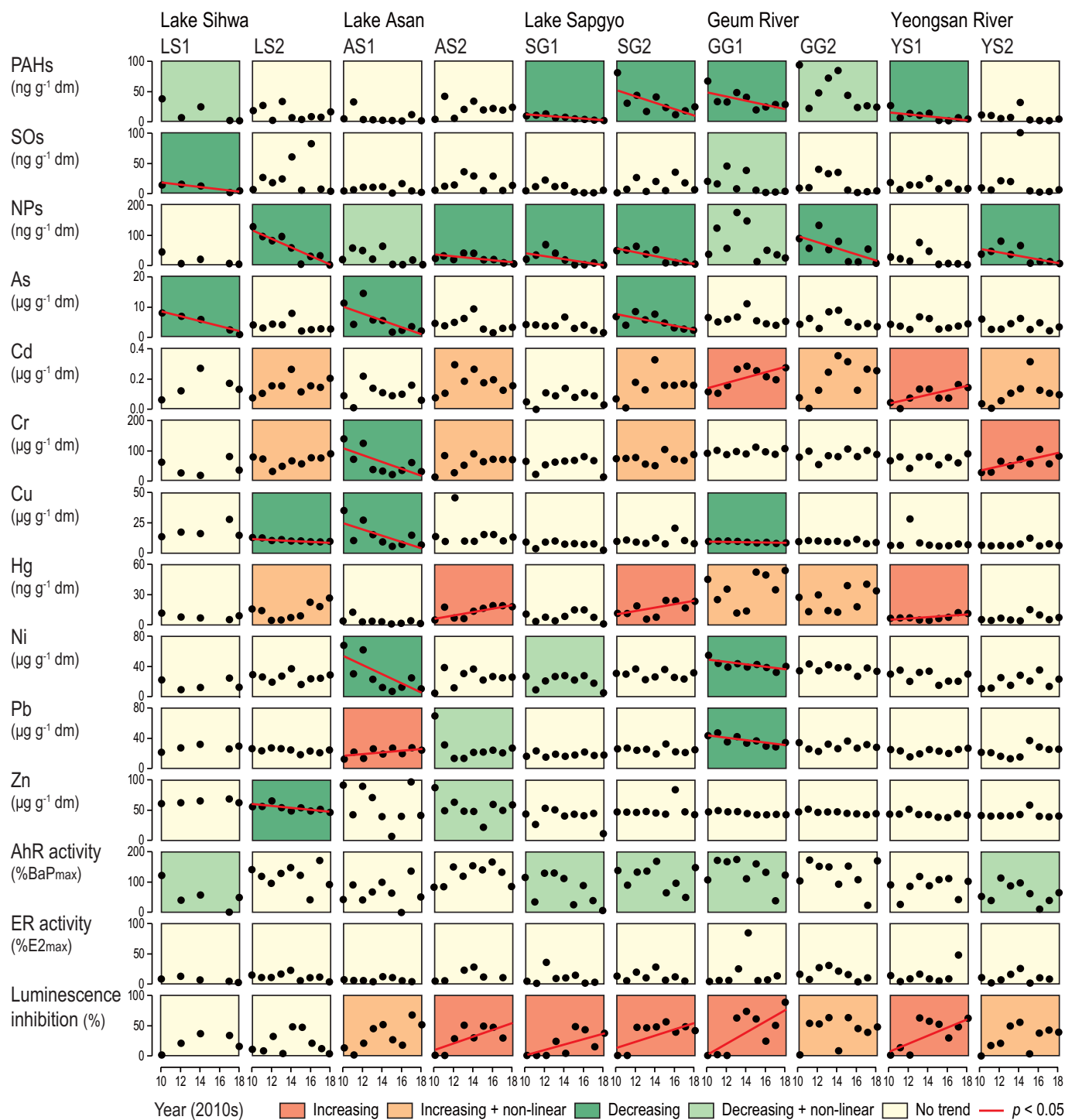


Fig. 2. Spatial and temporal distributions of persistent toxic substances (PTs) and potential toxicities in sediments along the west coast of South Korea from 2010 to 2018. PTs include organic pollutants, metals, and the metalloid As. Potential toxicities include AhR- and ER-mediated potencies and bioluminescence inhibition.

GG1–2, and LS1–2. AhR-mediated potencies were significant at all sites in study areas, whereas ER-mediated potencies were relatively small. In addition, bioluminescence inhibition was greater in sediments from Lake Sapgyo and the Geum and Yeongsan Rivers. None of the target organic and inorganic substances in sediments exceeded existing interim sediment quality guidelines (ISQG) established by the Canadian Council of Ministers of the Environment (CCME) (CCME, 2002). Concentrations below guidelines suggest that sediment quality along the west coast of Korea is acceptable. In fact, concentrations of PTs in sediments along the west coast of Korea were lower than those analyzed

in other polluted coastal regions of South Korea (Khim and Hong, 2014).

This study was designed to compare the inner (i.e., landward) and outer (i.e., seaward) regions of structures constructed to prevent seawater from flowing up estuaries (e.g., via estuary dams or sea dikes), except that the structure at Lake Sihwa, which was a tidal power plant (constructed in 2011) that allowed tides to pass through. In contrast, upstream sides of the other dikes hold freshwater. Various PTs in coastal sediments are assumed to originate from the land. Thus, it was expected that relatively greater concentrations of PTs would be found

Table 1

Concentrations of persistent toxic substances and potential toxicities in sediments on the west coast of South Korea from 2010 to 2018 [min–max (mean)].

Target analytes	Sampling year									
	2010	2011	2012	2013	2014	2015	2016	2017	2018	
	(n = 10)	(n = 9)	(n = 10)	(n = 10)	(n = 10)	(n = 10)	(n = 10)	(n = 10)	(n = 10)	
Persistent toxic substances										
ΣPAHs (ng g ⁻¹ dm)	3.2–94 (35)	2.0–42 (23)	1.2–47 (16)	2.4–72 (23)	1.7–84 (28)	nd–43 (12)	nd–23 (10)	nd–27 (11)	nd–30 (12)	
ΣSOs (ng g ⁻¹ dm)	nd–19 (7.9)	4.0–24 (10)	10–44 (21)	2.2–34 (16)	11–99 (33)	nd–64 (3.2)	nd–80 (19)	nd–17 (3.9)	nd–12 (4.4)	
ΣNPs (ng g ⁻¹ dm)	17–130 (44)	19–120 (54)	3.5–130 (54)	18–170 (61)	17–140 (56)	nd–6.2 (2.9)	nd–44 (12)	3.0–60 (17)	nd–18 (2.2)	
As (μg g ⁻¹ dm)	3.9–11 (5.8)	2.5–5.9 (3.9)	2.5–14 (5.5)	3.5–8.1 (5.6)	5.3–11 (7.4)	1.4–5.2 (3.1)	1.4–4.7 (3.0)	2.0–4.3 (2.9)	0.8–5.0 (2.9)	
Cd (μg g ⁻¹ dm)	nd–0.11 (0.06)	nd–0.1 (0.03)	nd–0.29 (0.14)	0.1–0.3 (0.15)	0.1–0.4 (0.22)	0.1–0.3 (0.17)	0.1–0.2 (0.13)	0.1–0.3 (0.15)	nd–0.3 (0.15)	
Cr (μg g ⁻¹ dm)	7.8–140 (68)	21–100 (68)	22–120 (57)	35–97 (61)	16–89 (63)	18–110 (69)	32–104 (75)	56–98 (71)	13–110 (67)	
Cu (μg g ⁻¹ dm)	6.3–35 (13)	3.5–13 (8.5)	6.5–46 (17)	6.2–15 (9.7)	6.6–16 (9.7)	5.2–15 (9.0)	6.1–20 (10)	7.5–28 (11)	2.3–14 (8.4)	
Hg (ng g ⁻¹ dm)	4.0–45 (14)	3.5–25 (12)	3.1–36 (13)	3.7–14 (6.5)	3.2–14 (8.0)	1.0–53 (20)	1.6–49 (18)	4.2–41 (16)	1.1–54 (19)	
Ni (μg g ⁻¹ dm)	3.9–68 (31)	8.8–45 (30)	9.0–62 (28)	16–45 (29)	12–40 (29)	6.7–44 (24)	12–40 (26)	14–38 (24)	4.8–43 (24)	
Pb (μg g ⁻¹ dm)	12–70 (29)	21–47 (27)	13–35 (21)	13–42 (24)	15–33 (23)	18–37 (28)	19–29 (24)	17–31 (24)	17–34 (26)	
Zn (μg g ⁻¹ dm)	41–92 (57)	27–56 (45)	40–90 (27)	40–71 (50)	40–65 (47)	6.7–58 (39)	38–85 (49)	39–97 (53)	12–62 (43)	
Potential toxicity										
AhR activity (%BaP _{max})	44–140 (99)	25–170 (92)	42–170 (110)	69–170 (120)	61–170 (110)	22–160 (99)	ns–170 (83)	26–170 (74)	2.8–170 (89)	
ER activity (%E2 _{max})	1.4–13 (7.4)	ns–7.2 (2.9)	ns–36 (11)	ns–27 (14)	4.3–82 (23)	ns–14 (6.1)	ns–9.8 (4.4)	ns–45 (9.4)	na	
Luminescence inhibition (%)	ns–12 (2.1)	ns–53 (9.9)	ns–52 (22)	ns–63 (44)	3.5–73 (41)	3.5–63 (44)	11–47 (32)	8.5–67 (38)	ns–89 (38)	

nd: not detected (below detection limit); ns: not significant; na: not analyzed.

in sediments in upstream sites (landward side) of dikes. However, there were no significant differences between concentrations of PTSs in sediments on opposite sides of the dikes and that potential toxicities were also similar (except for PAHs and AhR-mediated potencies) (Fig. S2). AhR-mediated potency, which is associated with PAHs and dioxin-like chemicals, was greater on the downstream side of dikes. This observation can be explained by the fact that industrial complexes and large cities have proliferated along the coastline (on the downstream sides of sea dikes or estuary dams) and are likely the source of PAHs in sediments. It was also suspected that atmospheric depositions of PTSs are important (Lin et al., 2011). Furthermore, PTSs appear to accumulate in coastal sediments due to the relatively greater particle adsorption affinity in saltwater (Fernandes et al., 1997; Turner and Rawling, 2001).

From 2010 to 2018, temporal distributions of PAHs and NPs slightly declined from year to year, whereas concentrations of SOs remained constant (Table 1 and Fig. 2). Concentrations of low molecular PAHs, such as Flu, Phe, Ant, Fl, and Py, styrene trimers (STs), and NPs in sediments also declined from 2010 to 2018 (Fig. S3). In previous studies, ratios of styrene dimers (SDs) to STs and NPs to NPEOs (NP1EOs + NP2EOs) were used to approximate the inflow of recent pollutants (i.e., fresh sources) (Li et al., 2008; Hong et al., 2016). Using this approach, it was observed that fresh inputs of SOs and NPs gradually declined over the 2010–2018 period (Fig. S4). Likewise, concentrations of the metalloid, As, decreased significantly over the same period, but other metals did not show any consistent changes in concentrations. Changes in concentrations of metals differed over time by element (e.g., some declined, some increased) and by region. Concentrations of metals Cu, Ni, Pb, and Zn and the metalloid As in sediments along the west coast of South Korea decreased slightly over time, but Cd, Cr, and Hg increased in sediments from 2010 to 2018. Regarding potential toxicities in sediments, AhR-mediated potency declined over time, ER-mediated potency showed no trend over time, and bioluminescence increased from 2010 to 2018.

Temporal changes in concentrations of PAHs and NPs in sediments appear to be related to the enactment of environmental management policies (MOE, 2014; Kim et al., 2019b). Decreases in concentrations of organic pollutants in sediments can be explained by the effectiveness of environmental regulations on the discharge of persistent organic pollutants (MOE, 2014). The South Korean government has regulated dioxin emissions from waste incinerators since 1999 (Kim et al., 2019b).

As a result, influxes of unwanted by-products, particularly dioxins and PAHs, from combustion sources to the environment have been reduced (Boonyatumanond et al., 2006; Park et al., 2009; Yim et al., 2007). Thus, decreases in concentrations of PAHs in sediments from 2010 to 2018, and the decrease in AhR-mediated potencies observed in this study could be attributed to the environmental regulation of air pollution (Fig. S5). The decrease in concentrations of NPs was also due to enforcement of usage regulations for hazardous substances in South Korea. The South Korean government banned use of NPs in household cleaners in 2002, in all domestic applications in 2007, in paint and ink used for industrial applications in 2010, and for all industrial applications in 2016 (Choi et al., 2011; Jeon et al., 2017). Thus, because emissions have been reduced, concentrations have decreased in coastal sediments. Meanwhile, SOs have been recently reported being environmentally hazardous (Kwon et al., 2015; Hong et al., 2016; Yoon et al., 2017). Because, until now, the precursor to SOs, polystyrene plastic, was not regulated, there has been no noticeable reduction of SOs in coastal sediments along the west coast of South Korea.

Concentrations of metals and As in sediments did not show significant relationships with emissions. For example, concentrations of Cd and Hg in sediments increased gradually over time even while emissions were declining (Fig. 2 and Fig. S5). This observation suggests that inflows from non-point sources were becoming more important than inflows from relatively more controllable point sources (Tsapakis et al., 2003; Lin et al., 2011). To strengthen environmental regulations for emissions of hazardous substances, point sources for metals could be better controlled by constructing more sewage treatment plants, improving maintenance of sewage pipes to reduce leakage, and conducting more frequent ecotoxicological testing of discharged water. However, non-point sources, including unmanaged stormwater inflows, can be difficult to control and appear to have increased exports of pollutants to aquatic systems (Loganathan et al., 1997). Thus, future environmental management policies should focus on better managing of non-point source pollution. Stormwater is mainly introduced to coastal environments through pipes emptying into inland creeks located near industrial complexes, which have been identified as major point sources of PTSs (Hong et al., 2019). On the west coast of South Korea, contamination of sediments by PTSs does not exceed sediment quality guidelines, but some substances (e.g., Cd, Cr, and Hg) have begun to show gradual increases in concentrations over time. Therefore, the export of such substances should be better controlled, especially at non-

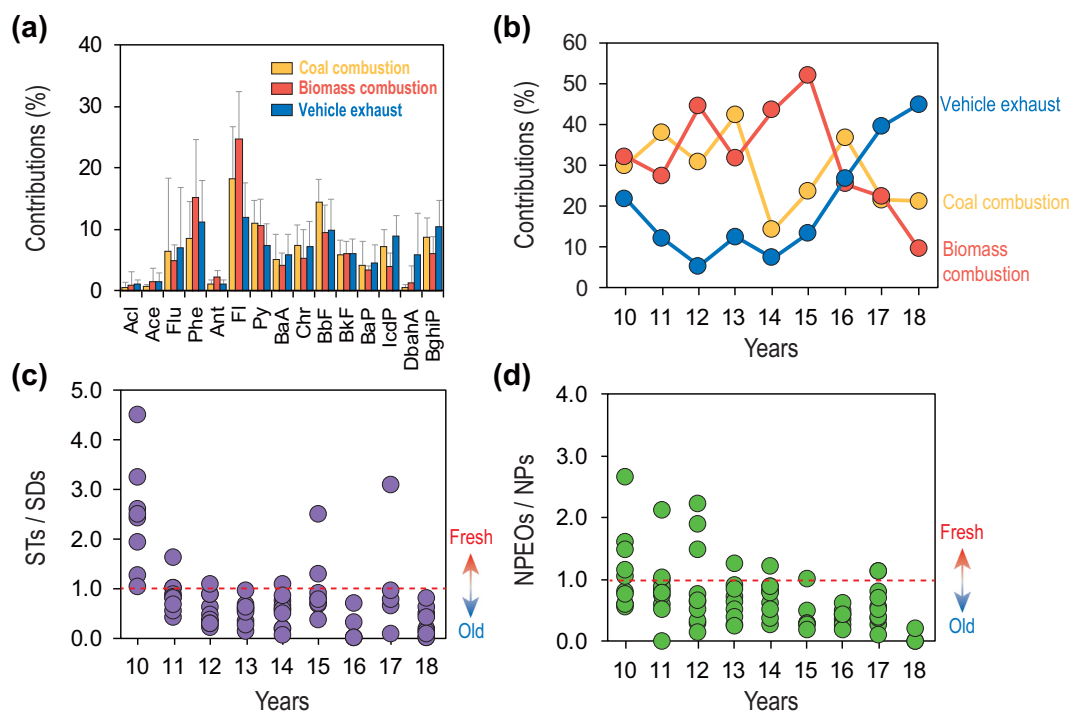


Fig. 3. Data from sediments along the west coast of South Korea from 2010 to 2018. Panels: (a) results of positive matrix factorization (PMF) model for identifying PAHs sources, including by-products of coal combustion, biomass combustion, and vehicle exhaust, (b) temporal trends showing the contribution of each source of PAHs in sediments, (c) temporal trends of STs/SDs ratios, and (d) temporal trends of NPEOs/NPs ratios.

point sources.

Concentrations of PAHs in sediments have gradually decreased over the period 2010–2018. Using the PMF model, sources of PAHs were identified by analyzing compositions of individual compounds. In doing so, three potential sources were identified: coal combustion, biomass combustion, and by-products from vehicle exhaust (Lin et al., 2011; Jang et al., 2013; Zheng et al., 2017) (Fig. 3a). Based on relative contributions of sources of PAHs, relative contributions of PAHs in sediments along the west coast of Korea over time were identified (Fig. 3b). These results indicate that contributions of biomass combustion by-products to PAHs in sediments have been gradually declining since 2015; however, the relative contribution of vehicle exhaust by-products has been increasing. In general, concentrations of PAHs have declined, mainly due to decreases in influxes of combustion by-products, such as PAHs. Meanwhile, based on ratios of STs/SDs and NPEOs/NPs to estimate influxes of recent pollutant sources (Li et al., 2008; Hong et al., 2016), it was found that both groups of compounds, SOs and NPs, are gradually decreasing, which indicates that inputs of fresh sources are also decreasing (Fig. 3b and c). This seems to be due to lesser export of SOs and NPs as an outcome of effective usage regulations and more sewage treatment facilities. Concentrations of SOs in sediments did not show a significant decreasing trend from 2010 to 2018. However, STs/SDs ratios showed that concentrations of STs decreased, indicating that the inflow of fresh sources of SOs decreased gradually. Continuous monitoring is needed in the future.

Overall, concentrations of toxic organic substances in sediments along the west coast of South Korea appear to be gradually decreasing. However, emerging organic contaminants, untargeted in this study, such as perfluoroalkyl acids (PFAAs), organophosphate flame retardants (OPFRs), and cyclic and linear siloxanes have recently been reported from sediments and so data are not yet available on their potential sources or masses of release (Hong et al., 2015; Lee et al., 2018a, 2018b; Shen et al., 2018). Thus, there is a need to design monitoring programs for emerging contaminants in coastal sediments.

AhR-mediated potencies measured in sediments during this study

were related to PAHs, whereas ER-mediated potencies were related to NPs contamination, and bioluminescence was related to contamination by metals (Khim and Hong, 2014; Hong et al., 2016; Jeon et al., 2017). A significant, positive correlation was observed between concentrations of PAHs and AhR-mediated potencies in sediments ($p < 0.01$) (Fig. 4a). Likewise, ER-mediated potency was significantly correlated with concentrations of NPs ($p < 0.01$) (Fig. 4b). However, results of previous studies have shown that PAHs and NPs do not fully account for total induced AhR- and ER-mediated potencies in sediments, respectively (Hong et al., 2016; Jeon et al., 2017; Kim et al., 2019a). Thus, further research on unknown AhR and ER agonists in monitoring samples is needed. The correlation between Cd concentration and bioluminescent inhibition showed that the most significant positive correlation among the metals we examined (Fig. 4c and Table S3). *V. fischeri* bioluminescence has been widely used as a sensitive tool for monitoring soil and sediment toxicities, especially because results can be obtained quickly and at low cost (An et al., 2012; Parvez et al., 2006; Serafim et al., 2013). Because Cd might interact with other chemicals, this interaction puts organisms in aquatic environments at risk from their integrated effects (Wang et al., 2009). For example, concentrations of cadmium and bioluminescence toxicity have been increasing recently in time-series analyses of sediments, thus the effects of those interactions with other chemicals require monitoring (Fig. 2).

The metals Cd, Cr, and Hg, concentrations of which have increased recently, and their inhibition of bioluminescence, have not been shown to be significantly related to the emission amounts of these metals (Fig. S5). For example, emissions of Cd and Hg have been declining while concentrations in sediments have been gradually increasing, whereas emissions of Ni and Zn have been increasing while concentrations in sediments have been gradually declining. Our study examined the correlation between emissions from toxic wastewater and concentrations of Cd, Cr, and Hg in sediments and bioluminescent inhibitions (MOE, 2019) (Fig. 5). A significant, positive correlation was observed between amounts of wastewater discharged to the rivers and concentrations of Cd, Cr, and Hg in sediments carried by the rivers. Thus, it

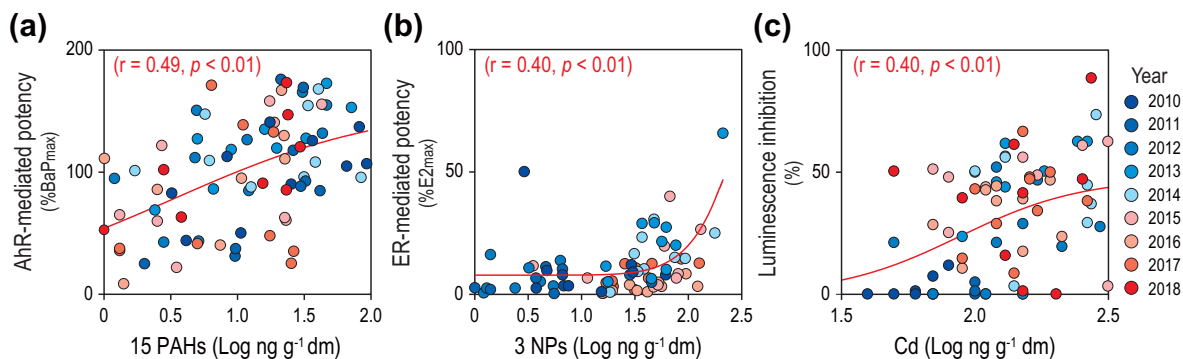


Fig. 4. Relationships between chemical analysis and bioassays for sediments collected from the west coast of South Korea from 2010 to 2018. Panels: (a) log concentrations of 15 PAHs vs. AhR-mediated potencies, (b) log concentrations of 3 NPs vs. ER-mediated potencies, and (c) log concentrations of Cd vs. luminescence inhibition.

is proposed that inflows of wastewater into rivers are a likely source of metals to sediments. Based on this long-term monitoring data of PTSs and potential toxicities in the sediments, it can be concluded that sediments in west coast of Korea are gradually accumulating emerging organic substances and metals (Cd, Cr, and Hg). Therefore, toxic effects of emerging organic substances and metals need to be studied further in sediments along the west coast of South Korea.

Sediments accumulate hazardous substances originated from land generated by human activities. Highly PTSs accumulating in sediments over a long time may adversely impact benthic and nektonic organisms. Because environmental policies to control PTSs usage have been effective, we suspect that concentrations of PTSs in coastal sediments should decline over time. Thus, assessing the contamination status of PTSs and potential toxicities in sediments cannot only be employed to indicate potential biological impacts, but they can also be used to indicate contamination from surrounding areas. Sediments from cores can sometimes be used to assess pollution input over time, but sediments of coastal waters are difficult to accurately date due to irregular sedimentation rates and bioturbation (Valette-Silver, 1993). Thus, long-term monitoring of surface sediments is very important, even though the costs and level of effort can be high. In addition, assessment of

potential toxicities in sediments can partially compensate for limitations of targeted chemical analyses in cases where not all toxic substances can be analyzed. In the future, continuous coastal sediment monitoring, such as applied in this study, is expected to improve the assessment of terrestrial hazardous substances being input into marine environments and thus help improve marine ecosystem health.

Author statement

- Seonju Kim: Conceptualization, Formal analysis, Investigation, Visualization, Writing - Original Draft
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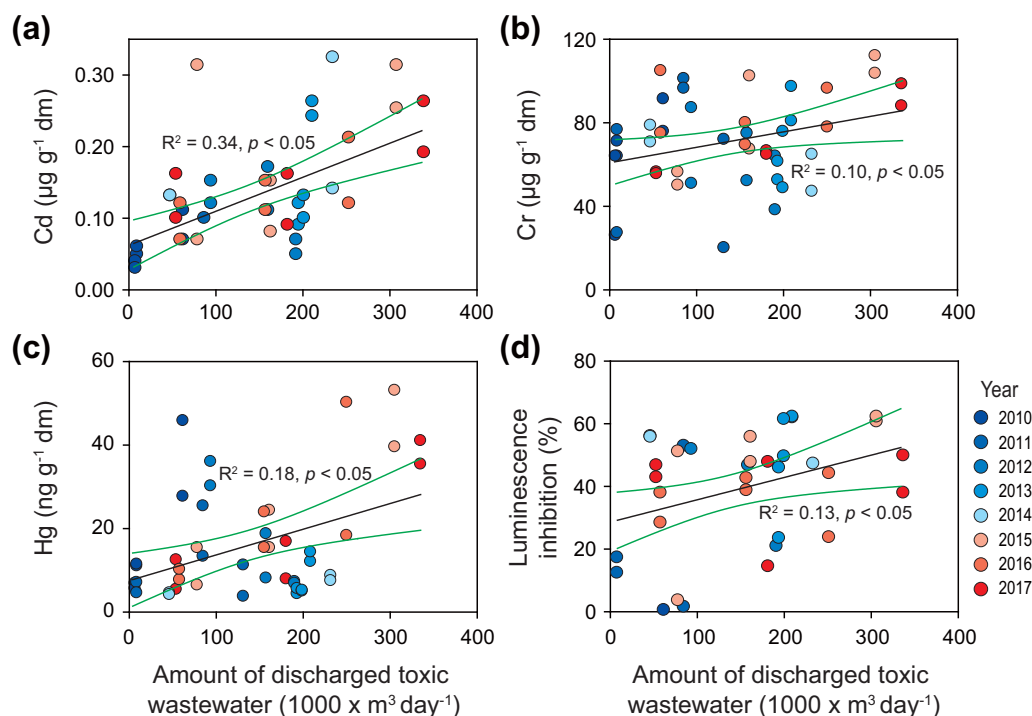


Fig. 5. Relationships between concentrations of metals in sediments and amount of discharged toxic wastewater flowing into rivers along the west coast of South Korea from 2010 to 2017 (MOE, 2019). Panels: (a) Cd, (b) Cr, (c) Hg, and (d) bioluminescence inhibition. Sampling stations correspond to rivers feeding them: SG (Lake Sapgyo), AS (Lake Asan), GG (Geum River), and YS (Yeongsan River).

Project administration, Funding acquisition, 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.

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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.2019.110821>.

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Long-term trends of persistent toxic substances and potential toxicities in sediments along the west coast of South Korea

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Supplementary Tables

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Supplementary Figures

Fig. S1. History of the study area along the west coast of South Korea. (a) Lake Sihwa, (b) Lake Sapgyo & Lake Asan, (c) Geum River Estuary, and (d) Yeongsan River Estuary. All estuarine areas were separated from the sea by an artificial sea dike or estuary dam. Temporal distributions of water quality in upstream freshwater portions (chemical oxygen demand, COD) and downstream saltwater portions (water quality index, WQI).	S5
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Supplementary Tables

Table S1. GC-MSD instrumental conditions for determining 15 PAHs, 10 SOs, and 3 NPs.

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	1.0 mL/min (He)	
Injection mode	Splitless	
MS temperature	180 °C	
Detector temperature	230 °C	
Oven temperature	60 °C hold 2 min Increase 6 °C/min to 300 °C 300 °C hold 13 min	60 °C hold 5 min Increase 10 °C/min to 100 °C Increase 20 °C/min to 300 °C 300 °C hold 6 min
Injection volume	2 μL	1 μL
Target compounds	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), Perylene (Pery), Indeno[1,2,3-cd]pyrene (IcdP), Dibenz[a,h]anthracene (DbahA), Benzo[g,h,i]perylene (BghiP), 1,3-Diphenylpropane (SD1), cis-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)	Nonylphenol (NP), Nonylphenol monoethoxylate (NP1EO), and Nonylphenol diethoxylate (NP2EO)

Table S2. Total organic carbons (TOC, %) and total nitrogen (TN, %) in sediments collected from Lake Sihwa, Lake Asan, Lake Sapgyo, Geum River Estuary and Yeongsan River Estuary in 2010, 2014, and 2018.

Regions	Sites	TOC (%)			TN (%)		
		2010	2014	2018	2010	2014	2018
Lake Sihwa	LS1	0.66	0.14	0.13	0.13	0.06	0.02
	LS2	0.50	0.69	0.80	0.10	0.11	0.11
Lake Asan	AS1	0.12	0.83	0.02	0.06	0.02	0.03
	AS2	0.06	0.79	0.66	0.02	0.15	0.11
Lake Sapgyo	SG1	0.27	0.33	0.05	0.05	0.08	<0.02
	SG2	0.67	0.82	1.00	0.13	0.17	0.15
Geum River	GG1	1.24	0.87	1.31	0.17	0.12	0.08
	GG2	0.90	1.52	1.60	0.14	0.28	0.10
Yeongsan River	YS1	0.57	0.68	1.14	0.10	0.15	0.05
	YS2	0.25	0.48	0.98	0.05	0.10	0.05

Table S3. Pearson correlation test results showing relationships between the metals concentrations and bioluminescent inhibition in sediments from sites along the west coast of South Korea.

		Heavy metals							Bioassay	
		Cr	Cu	Pb	Ni	Cd	As	Hg	Zn	Luminescence inhibition
Heavy metals	Cr									
	Cu	-0.02								
	Pb	0.36**	0.12							
	Ni	0.86**	0.11	0.35**						
	Cd	0.31**	0.33**	0.30**	0.35**					
	As	0.32**	0.19	0.15	0.54**	0.28**				
	Hg	0.62**	0.09	0.44**	0.54**	0.38**	-0.00			
	Zn	-0.06	0.90**	0.11	0.06	0.26*	0.16	0.03		
Bioassay	Luminescence inhibition	0.18	-0.16	0.08	0.15	0.42**	0.11	0.04	-0.21*	

* Significant correlation at the level of 0.05; ** Significant correlation at the level of 0.01.

Supplementary Figures

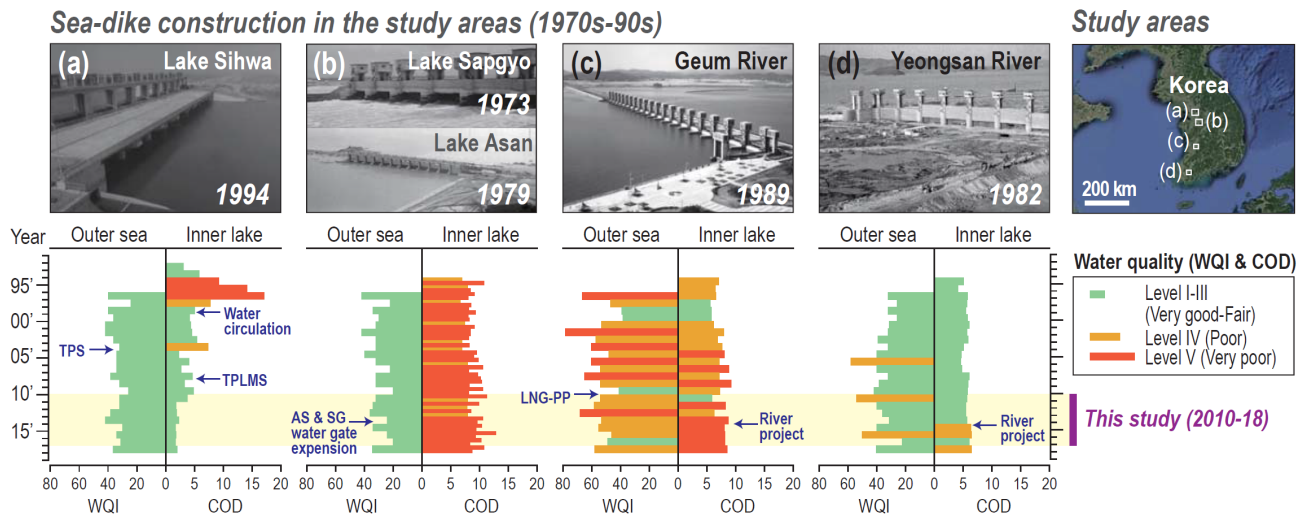


Fig. S1. History of the study area along the west coast of South Korea. (a) Lake Sihwa, (b) Lake Sapgyo & Lake Asan, (c) Geum River Estuary, and (d) Yeongsan River Estuary. All estuarine areas were separated from the sea by an artificial sea dike or estuary dam. Temporal distributions of water quality in upstream freshwater portions (chemical oxygen demand, COD) and downstream saltwater portions (water quality index, WQI). Water quality data were referred from MEIS (2019) and WEIS (2019).

Marine Environment Information System (MEIS), 2019. Water Quality Index (WQI) by Year, Ministry of Oceans and Fisheries and Korea Marine Environment Management Corporation. Available on line at <<http://www.meis.go.kr>>.

Water Environment Information System (WEIS), 2019. Water quality monitoring network (rivers and lakes), Ministry of Environment. Available online at <<http://water.nier.go.kr>>.

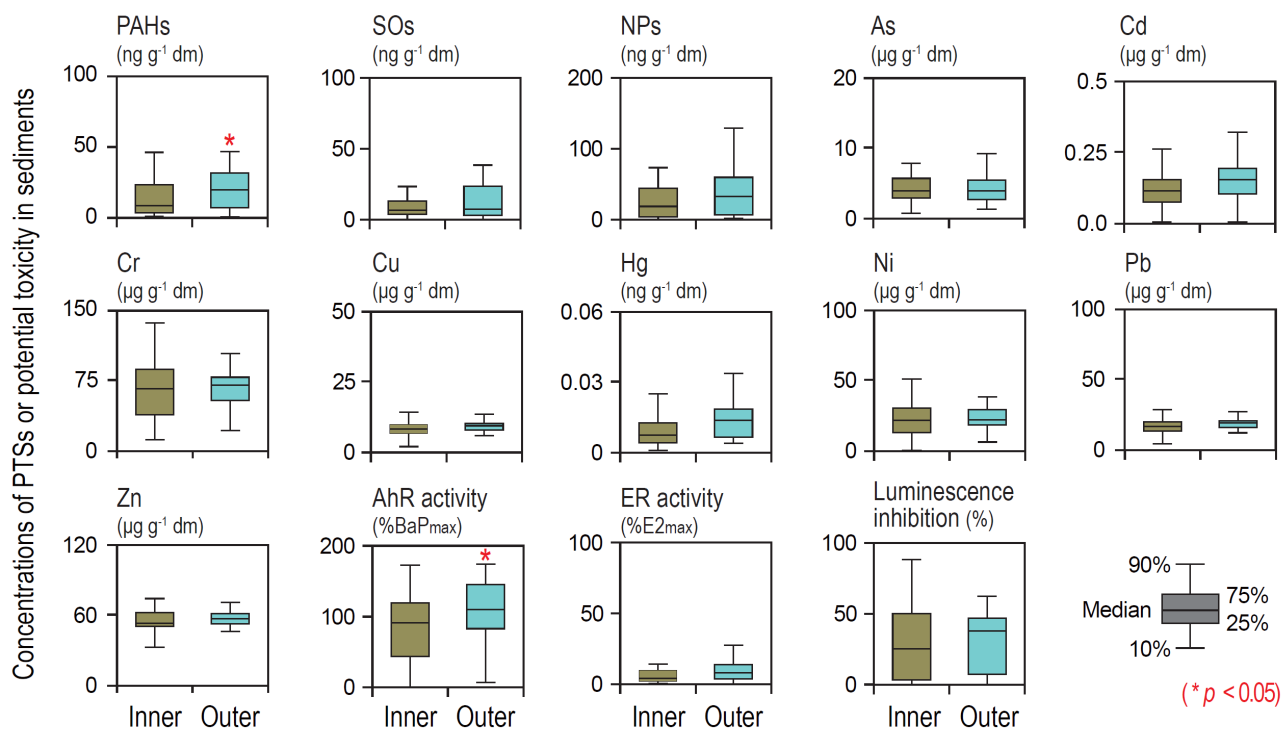


Fig. S2. Box plots for comparisons of persistent toxic substances and potential toxicities in sediments for locations upstream and downstream of sea dikes and estuary dams for sites along the west coast of South Korea.

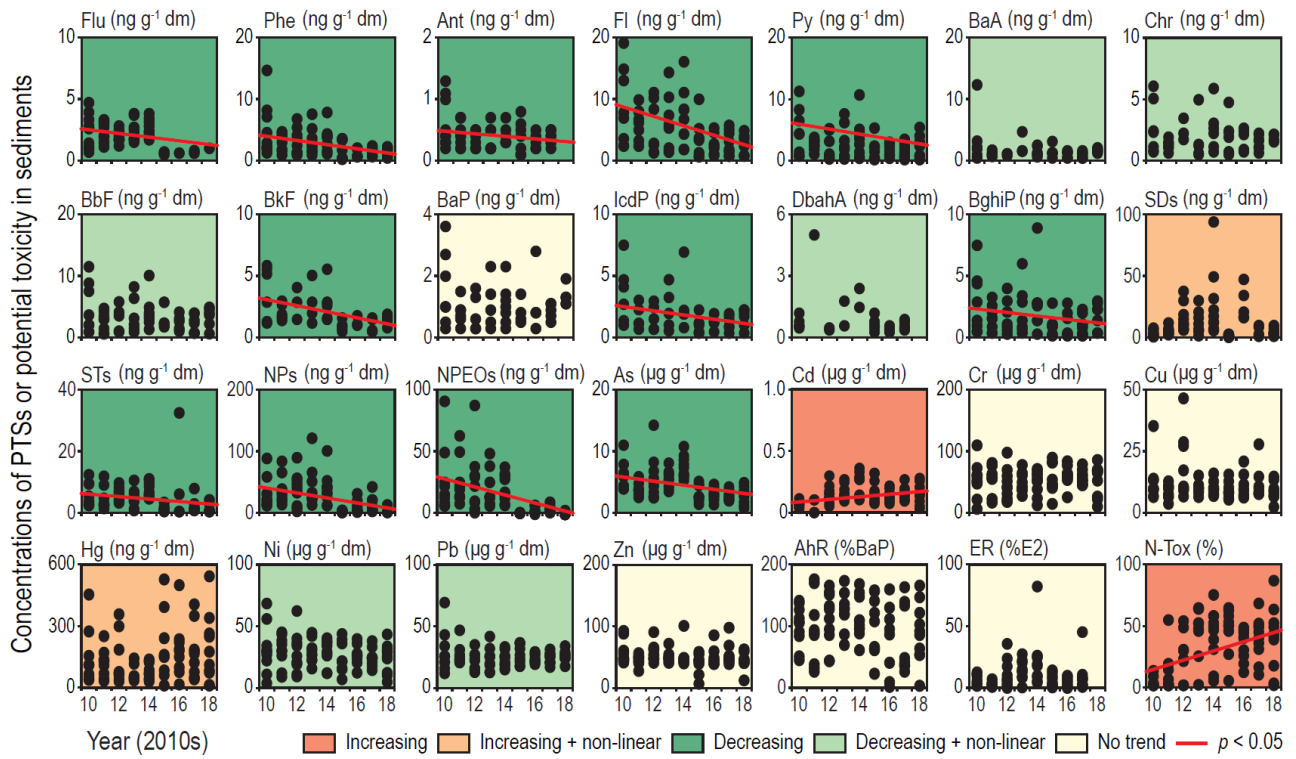


Fig. S3. Temporal distributions of individual PAHs, SOs, NPs, heavy metals, and potential toxicities in sediments collected from sites along the west coast of South Korea from 2010 to 2018.

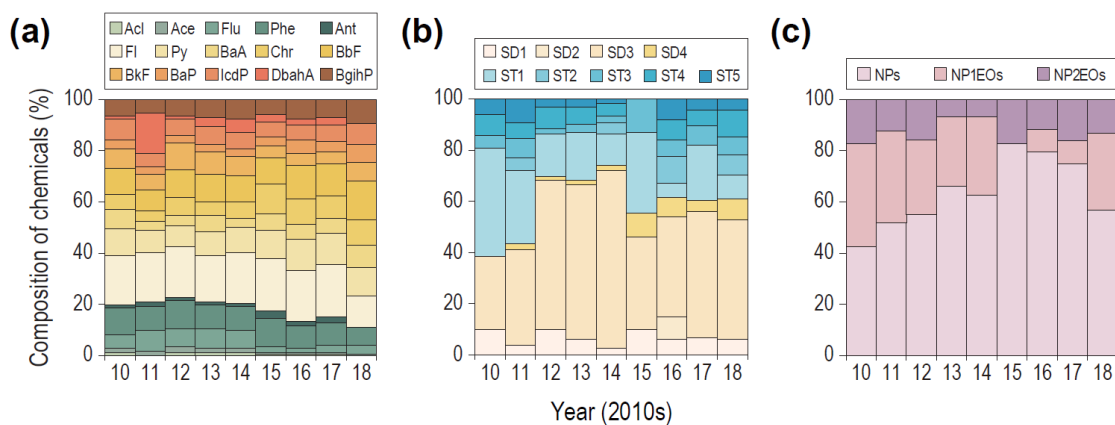


Fig. S4. Relative compositions of PAHs, SOs, and NPs in sediments collected from sites along the west coast of South Korea from 2010 to 2018.

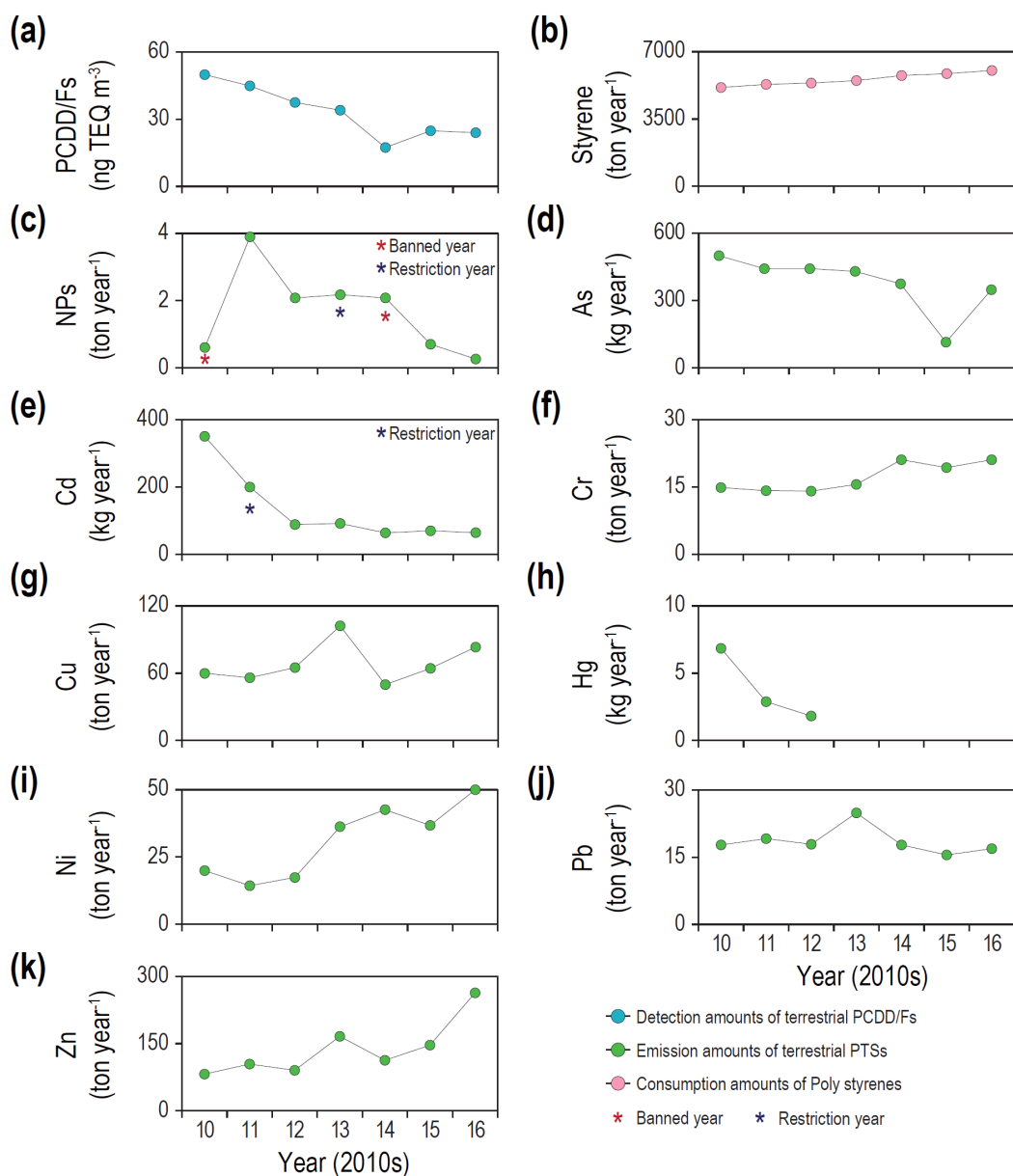


Fig. S5. Detection, emission, or consumption of persistent toxic substances in South Korea from 2010 to 2016 (Data were obtained from Pollutant Release and Transfer Register Information System; available online at <<http://icis.me.go.kr/prtr/>>).