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Characterization of trace organic contaminants in marine sediment from Yeongil Bay, Korea: 1. Instrumental analyses

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Among various sediment contaminant classes measured, nonylphenol and PAHs are responsible for the variability among sampling sites, suggesting the existence of multiple sources in Yeongil Bay sediment.

Abstract

Concentrations of polychlorinated biphenyls (PCBs), organochlorine (OC) pesticides (HCB, HCHs, CHLs, and DDTs), polycyclic aromatic hydrocarbons (PAHs), alkylphenols (APs), and bisphenol A (BPA) were measured in 26 marine sediments collected from Yeongil Bay, Korea, in order to characterize their spatial distribution and sources. PCBs (2.85–26.5 ng/g, dry wt.) were detected mainly in the inner bay locations Mean OC pesticide ranged from 1.16 ng/g dry wt. for HCH to 0.05 ng/g dry wt. for HCB). PAH concentrations ranged from <10.0 to 1870 (mean: 309) ng/g dry wt., and were predominated 3- and 4-ring congeners. Concentrations of APs, such as nonylphenol, octylphenol, butylphenol (means 89.1, 4.61, 11.0 ng/g dry wt., respectively), were greater at locations proximal to municipal wastewater discharges. Concentrations of PCBs and PAHs were great near shipyards and industrial complexes. Vertical profiles of PAHs and APs indicated that they have been associated with sediments since the 1950s.

Keywords: Polychlorinated biphenyls (PCBs); Organochlorine pesticides; Polycyclic aromatic hydrocarbons (PAHs); Alkylphenols; Principal components analysis

1. Introduction

Yeongil Bay, located on the east coast of Korea, is considered to be one of Korea's most industrialized regions and is contaminated by persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and polycyclic aromatic hydrocarbons (PAHs). Approximately 0.3 million tons of industrial and municipal wastewater from Pohang City and several industrial complexes (ICs) including Posco IC and other steel ICs are discharged daily through the Hyeongsan River or directly into the bay. Further, agricultural and dairy farms located upstream of the Hyeongsan River generate large amounts of wastes which are eventually discharged into the river. A recent study showed great contamination by PCBs, PCDDs, PCDFs, and PAHs with maximum concentrations of 170, 1.2, 0.63 and 7700 ng/g dry wt., respectively, in river sediment collected at several locations near Posco IC

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(Koh et al., 2004). PCB and PAH concentrations in Hyeongsan River sediments were 4–7 and 2–3 fold, respectively, greater than the sediment quality guidelines (SQGs) such as effects range-low (ERL) or threshold effect concentration (TEC), respectively (MacDonald et al., 2000; Swartz, 1999).

Alkylphenols (APs), such as nonylphenol (NP) and octylphenol (OP), are degradation products of alkylphenol ethoxylates, which are widely used as surfactants (Nimrod and Benson, 1996). Because of their widespread usage in cleaning products and industrial processing aids, these compounds enter aquatic environments via industrial and municipal wastewater. Both NP and OP were found in Hyeongsan River sediments at concentrations as great as 6800 and 99 ng/g dry wt., respectively (Koh et al., 2004). Since more than 70% of the rainfall in this region occurs in the summer, large amounts of contaminants such as APs can be delivered downstream along with the river-flow and farther into the bay. Several studies have examined PCBs, PCDD, PCDFs, organochlorine (OC) pesticides, PAHs, APs, and bisphenol A (BPA) in coastal sediment from Korea and found that PAHs and APs are the predominant and ubiquitous contaminants, particularly, near more industrialized and urbanized areas (Khim et al., 1999a,b, 2001; Koh et al., 2002, 2004).

Certain PAHs such as benzo[*a*]anthracene and dibenz[*a,h*]-anthracene can act via the aryl hydrocarbon receptor (AhR) and estrogen receptor (ER)-mediated pathways in vitro (Villeneuve et al., 2002). An earlier study found, in the Hyeongsan River, elevated concentrations of PAHs and APs (Koh et al., 2004). However, there was still lack of data and knowledge on the current and historical records of these contaminants in coastal marine regions, particularly in Yeongil Bay including the Hyeongsan River. Vertical profiles of trace organic contaminants in dated sediment cores can provide information on historical trends of contaminant inputs (Yamashita et al., 2000). In addition to PAHs and APs, historical inputs of many restricted or banned chemicals such as PCBs and OC pesticides including hexachlorobenzene (HCB), hexachlorocyclohexane isomers (HCHs), chlordanes (CHLs), DDT and its derivatives (DDTs) can be determined from their vertical profiles in sediment beds (Hong et al., 2003). The results of sediment core analysis will be useful to evaluate the current and past efforts of legislative actions on the inputs of these chemicals.

Concerns about POPs and/or endocrine disrupting chemicals (EDCs) in Korean estuarine and coastal environments have been increasing since the late 1990s. This has resulted in a rapid growth in both scientific information and political actions related to the management of POPs and EDCs in Korea. The present study provides information on contaminant levels in an industrialized coastal area where no baseline data were available. This study was conducted to determine concentrations of PCBs, OC pesticides (HCB, HCHs, CHLs, and DDTs), PAHs, APs such as NP, OP, and butylphenol (BP), and BPA in sediment collected from Yeongil Bay. In addition, vertical profiles of concentrations of target compounds in a sediment core from an inner bay location were presented to understand historical input of each class of compounds into the bay. The results of an in vitro bioassay, determining dioxin-like and estrogenic potencies of Yeongil Bay sediments, are presented in the companion article (Koh et al., 2006).

2. Materials and methods

2.1. Sampling

Sediment samples were collected in March 2000 from 26 locations in Yeongil Bay (Fig. 1). Sampling was designed to determine potential sources of trace organic contaminants along several transects at 1–2-km intervals between inner locations near commercial harbors, shipping yards, and Posco IC (locations #1, 2, 19, 20, and 21) and the outer bay area. A global positioning system (GPS) was employed to identify the precise location of each site. Surface sediment (0–5 cm) was sub-sampled from triplicate grab samples (25 × 40× 30 cm) and mixed thoroughly after removing any pebbles and twigs. Sediment samples were transported to laboratory in pre-cleaned amber glass bottles on dry ice. Samples were then freeze-dried. Ground samples were stored in pre-cleaned high density polyethylene (HDPE) bottles at −20 °C until extraction. Subsamples of ca. 10 g sediments were used for the analysis of total organic carbon (TOC) content and grain size.

A sediment core was collected from Pohang Harbor near Posco IC, using a Haps corer (31.5 cm long and 13.6 cm i.d.; KC-Denmark, Silkeborg, Denmark). The core was sectioned immediately aboard the ship at 2-cm intervals up to 10 cm depth using a sediment ejector and clean stainless steel slicer. Each section was freeze-dried and stored in a pre-cleaned HDPE bottles at −20 °C until extraction. Based on the vertical profiles of ^{210}Pb, the sedimentation rate was estimated to be approximately 0.21 ± 0.05 cm/yr.

2.2. Sample preparation

Detailed descriptions of sample extraction and fractionation procedures have been presented elsewhere (Khim et al., 1999b, 2001; Kannan et al., 2003). Briefly, 40 g of sediment samples were Soxhlet extracted for 20 h using 400 ml of dichloromethane (DCM; Burdick and Jackson, Muskegon, MI, USA) and concentrated using a rotary evaporator and treated with activated copper granules to remove sulfur from the raw extracts (REs). The REs were concentrated to ca. 2 ml and were passed through 10 g of activated Florisil (60–100 mesh size; Sigma, St. Louis, MO, USA) packed in a glass column (10 mm i.d.) for fractionation. The first fraction (F1) eluted with 100 ml of hexane (Burdick and Jackson) contained PCBs, HCB and *p,p′*-DDE. Remaining OC pesticides and PAHs were eluted, in the second fraction (F2), using 100 ml 20% DCM in hexane. NP, OP, BP and BPA were eluted in the third fraction (F3) with 100 ml 50% DCM in methanol (Burdick and Jackson). Procedural blanks (PBs) were analyzed with every set of six samples to check for interference or contamination arising from solvents and/or glassware. Two field blanks (FBs) obtained during the field survey, when the sediment samples were collected, were analyzed as the cross-check for field derived contamination. Three Florisil fractions (FEs) were used for instrumental analysis and all of the REs, FEs, PBs and FBs were screened in triplicate by H4IIE-luc and MVLN cell bioassays to determine dioxin-like and estrogenic potencies in vitro, the results of which are discussed elsewhere (Koh et al., 2006).

2.3. Instrumental analysis

PCBs and OC pesticides were quantified using a gas chromatograph (Perkin–Elmer series 600) equipped with a ^{63}Ni electron capture detector (GC-ECD). An equivalent mixture of 98 individual PCB congeners (AccuStandard) with known composition and content and OC pesticide mixture (CLP-023R, CLP-024R, AccuStandard) were used as external standards for quantification. Sixteen priority PAHs were quantified using a Hewlett–Packard 5890 series II gas chromatograph equipped with a 5972 series mass spectrometer detector (GC-MSD). Reverse-phase high-performance liquid chromatography (HPLC) with fluorescence detection was used to quantify NP, OP, BP and BPA. The detection limits for PCBs, OC pesticides, PAHs, APs, and BPA were 1.0, 0.01, 10, 1.0, and 1.0 ng/g dry wt., respectively. Recoveries of target compounds through the analytical procedures were between 90% and 105%,

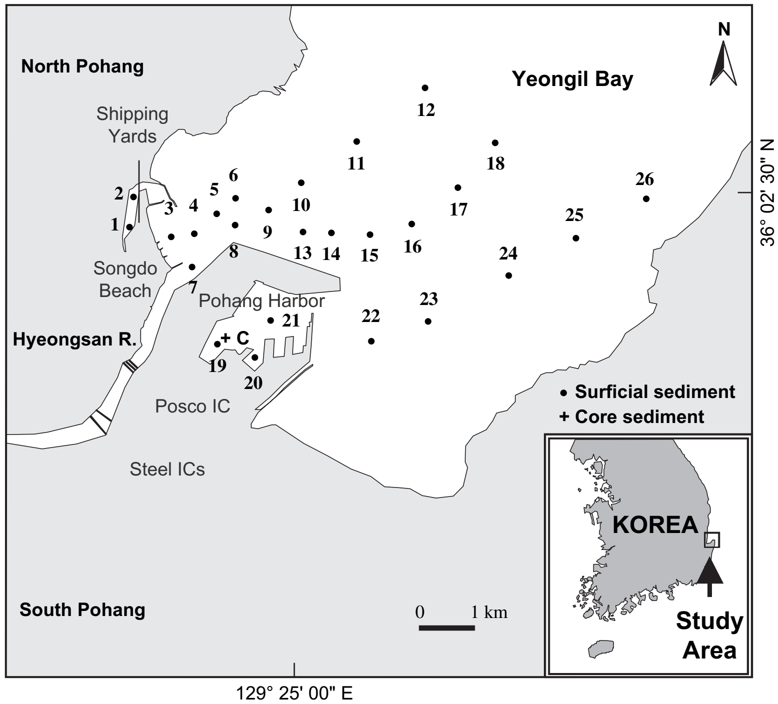

Fig. 1. Map of Yeongil Bay study area in Korea. Surficial sediment samples were collected at locations #1–26 and a sediment core (+) was obtained from the inner Pohang Harbor.

and all of the PBs and FBs did not contain detectable concentrations of target compounds.

3. Results and discussion

3.1. TOC and sediment properties

TOC content in surficial sediment from 26 locations in Yeongil Bay varied greatly, from 0.02% to 3.12% (Table 1). The greatest TOC contents of over 2% were found at innermost locations #1, 2, and 19, while the low TOC contents were associated with sediment from outer bay locations, which were dominated by coarse sand. Sediments from middle transect, at locations #13–18, consisted predominantly of silt and clay (mean: 82%) (Table 1). Increases in the proportions of silt and clay from inner to outer bay locations of the middle transect suggest movement of sediment from coastal to open bay area. There were no increase or decrease in mud content (sum of silt and clay) along the left or right transects, however. Sediment collected near Songdo beach, such as locations #3, 4, and 7, with a gradual bottom slope, contained sandy sediments. These locations were relatively close to lower reaches of the Hyeongsan River; thus sediment texture resembled that of the river sediment with a grain size ranging from 0.90 to 1.3 φ, i.e., a great proportion of gravel and sand (mean: 97%) (Koh et al., 2004). In general, TOC content was significantly correlated with mud content ($r = 0.60$, $p < 0.01$) and sediment grain size ($r = 0.61$, $p < 0.01$) (Table 2). Significant relationships between TOC content and target organic compounds such as total PCBs ($r = 0.55$, $p < 0.01$), OC pesticides ($r = 0.62$, $p < 0.01$), PAHs ($r = 0.40$, $p < 0.05$), and APs ($r = 0.62$, $p < 0.01$) suggest a strong binding affinity and equilibration of trace organic residues to TOC (Table 2).

3.2. PCBs

PCBs were detectable in sediment from 5 of 26 locations at concentrations ranging from 3.41 to 26.5 (mean: 10.7) ng/g dry wt. (Table 1). Non-, mono-, and di-*ortho* PCBs were found at concentrations ranging from 0.22 to 3.74 ng/g dry wt., contributing 2–20% of the total PCBs concentrations. The maximum concentration of total PCBs was found at the innermost location #1, which is situated in the middle of Pohang City and several large shipyards (Fig. 1). All the locations that contained PCBs were near commercial harbor, shipyard, and Posco IC; thus, the likely source of PCBs in this area is industrial wastewater originating from over 200 factories (Fig. 2) or from shipping activities. Analysis of dated sediment core revealed recent inputs of PCBs, as the top of 2 cm of the core contained detectable concentrations of PCBs (4.15 ng/g dry wt.) (Table 3). High concentrations of PCBs in sediment collected near a sewage treatment plant located near Posco IC and other steel ICs (up to 170 ng/g dry wt.) and in the downstream of the Hyeongsan River (3.1–8.8 ng/g dry wt.) indicate continuing inputs of PCBs from Pohang City to coastal areas (Koh et al., 2004). However, PCBs were not detected in the lower reaches of the Hyeongsan River such as location #7, although detectable levels were found in the upstream locations. A gradient of decreasing PCB concentrations in sediment from upstream (170 ng/g dry wt.) to downstream (3.1 ng/g dry wt.) suggests a point source in the upstream. However, PCB residues from

Table 1
Concentrations (ng/g dry wt.) of polychlorinated biphenyls (PCBs), organochlorine pesticides (HCB, HCHs, CHLs, DDTs), polycyclic aromatic hydrocarbons (PAHs), alkylphenols (NP, OP, BP), and bisphenol A (BPA) in sediment from Yeongil Bay, Korea

Location	PCBs	HCB	HCHs	CHLs	DDTs	PAHs	NP	OP	BP	BPA	TOC	Mud	Remark
1	26.5	<0.01	5.32	0.25	8.26	452	1430	24.3	48.1	191	3.1	96	Pohang downtown, ship yards
2	3.53	<0.01	3.89	0.08	1.37	114	180	4.49	15.7	<1.00	2.2	48	Pohang downtown, ship yards
3	<1.00	<0.01	1.29	<0.01	0.05	<10.0	<1.00	<1.00	<1.00	<1.00	0.6	51	Songdo beach
4	<1.00	0.02	0.35	0.03	<0.01	<10.0	52.2	<1.00	<1.00	<1.00	0.1	2.1	
5	<1.00	<0.01	0.78	<0.01	0.13	<10.0	12.2	<1.00	<1.00	<1.00	0.6	66	
6	<1.00	<0.01	0.87	0.03	0.05	14.0	3.37	<1.00	<1.00	<1.00	0.1	7.6	
7	<1.00	0.02	<0.01	<0.01	<0.01	<10.0	19.0	<1.00	2.63	<1.00	0.0	0.0	Mouth of Hyeongsan River
8	<1.00	0.01	2.92	0.11	0.05	374	37.4	1.12	<1.00	<1.00	0.1	3.9	
9	<1.00	<0.01	0.23	<0.01	0.28	14.7	19.8	<1.00	<1.00	<1.00	0.5	20	
10	<1.00	<0.01	1.60	<0.01	0.04	21.1	27.7	<1.00	<1.00	<1.00	0.4	28	
11	<1.00	0.02	0.44	<0.01	<0.01	<10.0	8.02	2.07	<1.00	<1.00	0.2	15	
12	<1.00	0.02	2.06	0.03	0.03	<10.0	23.9	<1.00	<1.00	<1.00	0.1	0.0	Farthest location in left transect
13	<1.00	<0.01	0.82	<0.01	0.05	<10.0	12.1	<1.00	<1.00	<1.00	0.7	59	
14	<1.00	0.11	1.55	<0.01	0.14	41.0	18.3	<1.00	<1.00	<1.00	0.9	65	
15	<1.00	0.07	0.18	<0.01	0.10	31.0	15.3	1.93	3.58	<1.00	0.7	83	
16	<1.00	<0.01	<0.01	<0.01	0.20	33.2	27.2	1.72	2.43	<1.00	1.0	95	
17	<1.00	0.12	1.73	0.05	0.75	568	47.3	<1.00	3.98	<1.00	1.3	94	
18	<1.00	0.10	0.02	0.15	0.38	39.5	63.5	1.41	<1.00	<1.00	1.5	97	Farthest location in central transect
19	2.85	0.03	1.13	<0.01	0.52	1220	29.9	4.27	18.7	<1.00	2.8	46	Pohang Harbor, near ICs
20	17.1	<0.01	0.18	0.53	0.33	1870	49.8	2.58	10.4	<1.00	1.0	22	Pohang Harbor, near ICs
21	<1.00	0.04	0.08	<0.01	0.02	28.5	50.3	2.46	9.81	<1.00	1.9	50	Pohang Harbor, near ICs
22	<1.00	0.03	0.11	0.49	0.05	55.6	20.4	11.3	3.11	<1.00	0.4	18	
23	3.41	0.05	0.46	0.06	0.26	662	45.9	3.78	<1.00	<1.00	0.9	57	
24	<1.00	0.02	0.36	<0.01	0.03	28.8	8.14	<1.00	<1.00	<1.00	0.4	34	
25	<1.00	0.04	1.28	0.18	0.28	224	19.2	1.71	<1.00	<1.00	0.7	51	
26	<1.00	<0.01	0.12	0.08	0.07	78.3	7.18	1.44	2.20	<1.00	0.7	49	Farthest location in right transect
Mean													
Inner mean	12.5	0.04	2.12	0.28	2.10	737	348	7.62	20.6	191	2.2	52	Inner locations
Outer mean	3.41	0.05	0.95	0.13	0.17	162	25.3	3.13	3.15	<1.00	0.6	42	Outer locations
Total	10.7	0.05	1.16	0.16	0.58	309	89.1	4.61	11.0	–	0.9	44	All locations

PCBs, sum of 98 individual congeners; HCB, hexachlorobenzene; HCHs, α- + β- + γ-hexachlorocyclohexanes; CHLs, α- + γ-chlordanes; DDTs, *p,p′*-DDE + *p,p′*-DDD + *p,p′*-DDT; PAHs, sum of 16 priority components; NP, nonylphenol; OP, octylphenol; BP, butylphenol; BPA, bisphenol A; TOC, total organic carbon content (%); Mud, mud content (%), sum of silt and clay; Mean, average for each class of compounds among detected. Inner mean indicates average for locations inside of the harbors (1, 2, 19, 20, and 21). Outer mean indicates average for all locations except for inner locations.

Table 2
Relationships (r)[a] between sediment characteristics (TOC, Mud, and grain size) and concentrations of target organic compounds in sediment from Yeongil Bay, Korea

	Mud	Mz	PCBs	OC pesticides	PAHs	APs
TOC	0.60**	0.61**	0.55**	0.62**	0.40*	0.62**
Mud		0.72**	0.22	0.30	0.03	0.34*
Mz			0.37*	0.43*	0.20	0.43*
PCBs				0.78**	0.55**	0.85**
OC pesticides					0.16	0.94**
PAHs						0.13

TOC, total organic carbon content (%); Mud, mud content (%), sum of silt and clay; Mz, sediment mean grain size (φ); PCBs, sum of 98 individual congeners; OC pesticides, HCB + HCHs + CHLs + DDTs; PAHs, sum of 16 priority components; APs, nonylphenol (NP) + octylphenol (OP) + butylphenol (BP).
[a] Statistically significant at $*p < 0.05$ or $**p < 0.01$.

the Hyeongsan River did not appear to have reached the marine sediment at location #7. Alternatively, relatively rapid and continual mixing by tidal currents at location #7 may have diluted PCB residues at that location below detectable levels.

The relative contributions of individual chlorobiphenyl (CB) isomers and congeners to total PCBs varied among locations. Sediment collected at locations #1 and 20 contained great proportions of penta-, hexa-, and hepta-CBs (67% to total PCBs), whereas that in other locations #2, 19, and 23, greater proportions of di-, tri-, and tetra-CBs (52% to total PCBs) were found. The predominant proportion of lower chlorinated congeners in sediment from locations #2, 19, and 23 was consistent with the previous reports, where tri- and tetra-CBs were the prevalent homologues accounting for approximately 50% of the total PCBs in Hyeongsan River sediments (Koh et al., 2004). A great proportion of higher chlorinated CBs at locations #1 and 20 can be explained by their locality associated with shipping activities. Overall, tetra- to hepta-CBs collectively accounted for 74% of the total PCB concentrations in Yeongil Bay (Fig. 3) and this pattern was similar to those observed in marine sediment from other Korean coastal areas (Khim et al., 1999b, 2001; Koh et al., 2002; Oh et al., 2003).

3.3. OC pesticides

Concentrations of OC pesticides detected in Yeongil Bay sediment were relatively small. Generally, HCB and CHLs were detected in sediment from about half of the locations surveyed. Concentrations of HCB and CHLs ranged from below the limit of detection to 0.12 and 0.53 ng/g dry wt., respectively (Table 1). DDTs and HCHs were detected at nearly all the locations and concentrations were as great as 8.26 and 5.32 ng/g dry wt., respectively. However, the contamination by DDTs (mean: 0.58 ng/g dry wt.) in sediment was lower than that detected in sediment from other Korean coastal areas (Koh et al., 2002, Hong et al., 2003). Overall, p,p'-DDD and p,p'-DDE contributed about 91% of the total DDTs concentrations, which indicated the transformation of p,p'-DDT to p,p'-DDD and p,p'-DDE under aerobic/anaerobic conditions.

HCHs were among the predominant OC pesticides detected in Yeongil Bay sediment, accounting for 63% of the total OC pesticides. Concentrations of HCHs at offshore locations such as location #12 were as great as 2.06 ng/g dry wt. Among

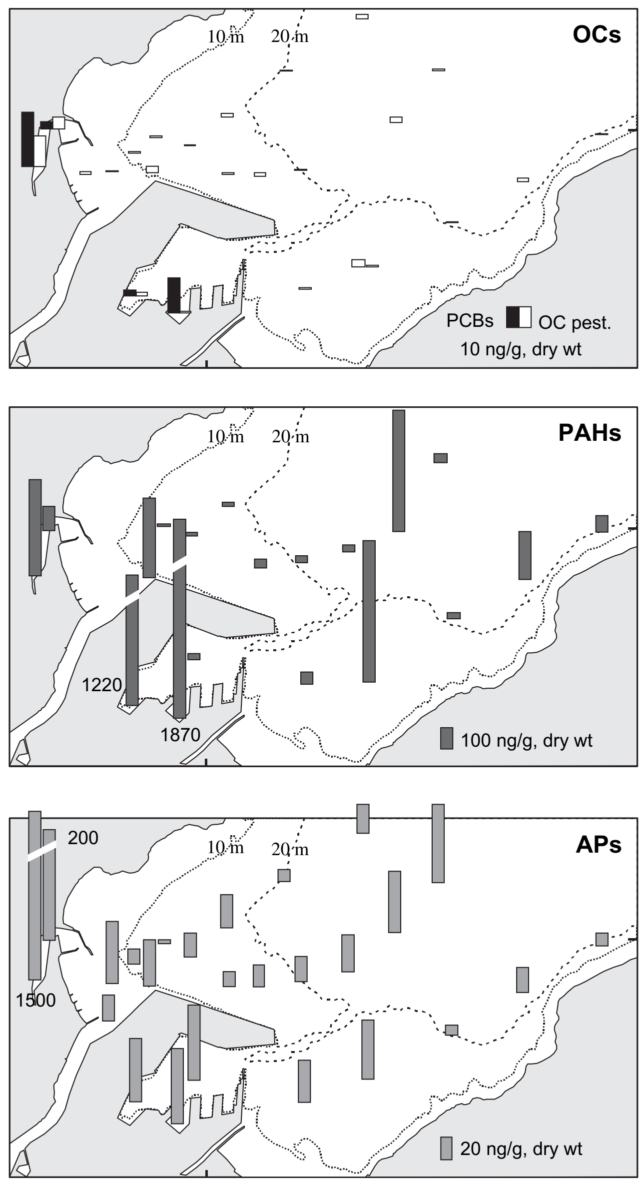

Fig. 2. Spatial distribution of OCs (PCBs and OC pesticides), polycyclic aromatic hydrocarbons (PAHs), and alkylphenols (APs) in sediment from Yeongil Bay, Korea. Concentrations are given on a ng/g dry wt. basis and unit concentrations for OCs, PAHs, and APs are 10, 100, and 20 ng/g dry wt., respectively.

Table 3
Concentration (ng/g dry wt.) profiles of target organic compounds in sediment core (0–10 cm depth) from Yeongil Bay, Korea

Compound	0–2 cm (2000–1991)[a]	2–4 cm (1990–1981)	4–6 cm (1980–1971)	6–8 cm (1970–1961)	8–10 cm (1960–1951)
PCBs	4.15	<1.00	<1.00	<1.00	<1.00
HCB	0.05	0.06	<0.01	0.09	0.04
HCHs	1.12	0.02	0.02	0.06	0.41
CHLs	<0.01	<0.01	<0.01	<0.01	0.05
DDTs	0.49	1.05	0.06	0.17	0.39
PAHs	327	63.3	143	71.0	75.4
NP	29.1	12.3	38.6	20.4	20.2
OP	1.41	1.22	<1.00	<1.00	<1.00
BP	3.96	<1.00	<1.00	<1.00	<1.00
BPA	<1.00	<1.00	<1.00	<1.00	<1.00

PCBs, sum of 98 individual congeners; HCB, hexachlorobenzene; HCHs, α- + β- + γ-hexachlorocyclohexanes; CHLs, α- + γ-chlordanes; DDTs, *p,p′*-DDE + *p,p′*-DDD + *p,p′*-DDT; PAHs, sum of 16 priority components; NP, nonylphenol; OP, octylphenol; BP, butylphenol; BPA, bisphenol A.
[a] Time interval represented is given for corresponding depth layer based on the sedimentation rate of 0.21 cm/yr at sampling location (C, see Fig. 1).

HCH isomers analyzed, γ-HCH (lindane) contributed 66% of the total HCH concentrations in sediment, which indicated the use of lindane rather than technical mixtures of HCHs. Farming activities in the upper region of the bay are considered the likely source of the HCHs found in Yeongil Bay sediments (Koh et al., 2004). An earlier study also reported HCH residues in upstream river sediment of the Hyeongsan River at concentration as great as 46.8 ng/g dry wt. (Koh et al., 2004). Although the use of OC pesticides including HCHs was banned in Korea in 1979, the sediment core results suggest an increase in HCH concentrations since the 1970s (Table 3). This suggests continuing release of HCHs into the bay from farming areas. However, the lowest proportion of β-HCH isomer (accounting for less than 10% of the total HCHs) indicates a decline in the usage of technical HCHs in this area. There are no historical data regarding OC pesticides in Yeongil Bay, thus the data presented here establish a baseline for future monitoring and management of these compounds in this area.

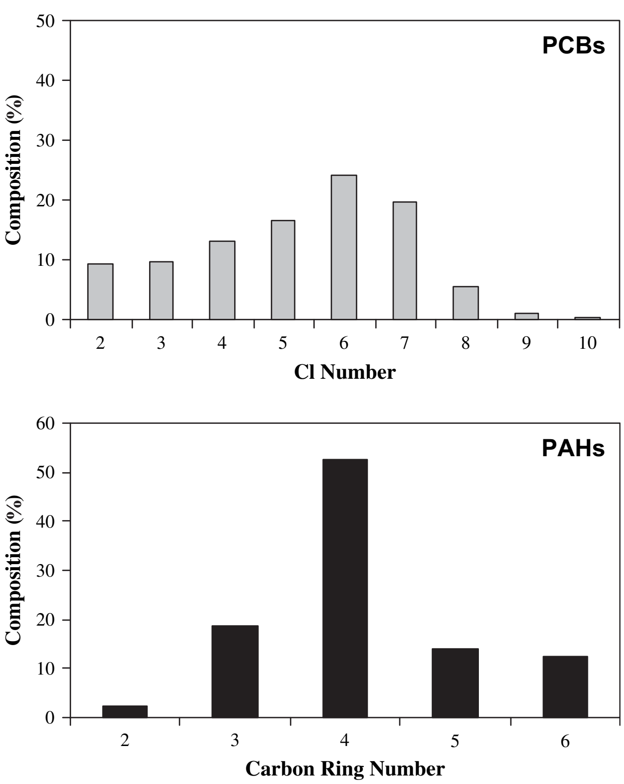

Fig. 3. Mean composition (%) of individual chlorobiphenyl (CB) congeners to total PCBs (up) and PAH ring number (weight %) to total PAHs (down) in sediment from Yeongil Bay, Korea.

3.4. PAHs

PAHs were detected in sediment from 19 locations and their concentrations varied greatly, ranging from 14 to 1870 (mean: 309) ng/g dry wt. (Table 1). Inner bay sediments generally contained greater concentrations of PAHs, particularly those from locations #19 and 20 adjacent to Posco IC (Fig. 2). Moderately great concentrations of PAHs were found in outer bay sediments at locations #23 and 27, and concentrations less than 100 ng/g dry wt., were found in outer bay locations. Elevated concentrations of PAHs in inner bay sediment suggest localized inputs of PAHs from the inland area or directly from shipping activities in Pohang Harbor. Earlier studies have reported concentrations of total PAHs in marine and riverine sediments from Ulsan and Onsan bays, located on the east coast of Korea, to range from <10.0 to 3100 (mean: 292, $n = 51$) ng/g dry wt. (Khim et al., 2001; Koh et al., 2002). Total PAHs concentrations found in Yeongil Bay sediments were within the range of PAH concentrations found in other Korean coastal areas.

Four-ring aromatic hydrocarbons, such as fluoranthene, pyrene, benzo[*a*]anthracene, and chrysene, were predominant among the 16 PAHs analyzed. The 4-ring PAHs accounted for over 50% of the total PAH concentrations in Yeongil Bay sediments (Fig. 3). Molecular ratios of fluoranthene to pyrene (Fluo/Py) and indeno[1,2,3-*cd*]pyrene to benzo[*ghi*]-perylene (IP/BP) in most sediment samples were greater than 1.0, which indicated the sources of PAHs to the Yeongil Bay were mainly pyrolytic instead of petroleum-related (Baumard et al., 1998). Only one location, #19, near Posco IC appears to have experienced contamination by petroleum inputs rather than pyrolytic sources, as the ratios of Fluo/Py and IP/BP were 0.9 and 0.2, respectively. This implies that the inner bay area receives PAH input from petrogenic sources originating from Posco IC and/or shipping activities within the harbor.

The ongoing input of petrogenic PAHs in the inner bay locations (Fig. 1) was clear from the sediment core PAHs profile (Fig. 4). The top 2 cm of the sediment represented recent 10 years of deposition based on the sedimentation rate of 0.21 cm/yr. This top 2-cm layer contained the greatest PAH concentration (327 ng/g dry wt.), which was 2.3–5.2 fold greater than those in deeper layers (Table 3). The vertical profile of PAHs was characterized by the relatively uniform concentrations from the 2 (≅year 1990) to 10 cm (≅year 1951) (Table 3, Fig. 5). This historical profile corresponds to a rapid increase in industrial activities in the Yeongil Bay area since the 1990s. Furthermore, the domestic use of petroleum and coal reached approximately 0.2 million barrels/yr and 5000 ton/yr, respectively, in Pohang City in 2000. The vertical profiles of selected PAHs and their ratios such as Fluo/Py (0.25–0.42) and IP/BP (0.74–0.85) in the sediment core confirm the petrogenic sources of PAHs in the inner locations of the bay. A relatively uniform composition of low (23 ± 3%) and high molecular weight PAHs (77 ± 3%) to total PAH concentrations in sediment core suggests that PAHs sources did not vary considerably over time (Fig. 5).

Concentrations of total PAHs in sediments from Yeongil Bay did not exceed the suggested SQGs such as ERL (402 μg/g OC) and TEC (290 μg/g OC) at any location (Long et al., 1995; Swartz, 1999). However, the maximum concentrations of several PAHs such as, acenaphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, and pyrene detected in marine sediment exceeded the ERL set for individual PAHs by 1.1–5.5 fold (Long et al., 1995; Swartz, 1999). This is similar to that observed in a previous report on PAHs in Hyeongsan River system, where concentrations of acenaphthene and fluorene exceeded the ERL guidelines (Long et al., 1995).

3.5. PAH sources

Relative abundances or ratios of selected, marker PAHs are useful in the identification of generic sources of PAH contamination in the environment. However, such ratios are often difficult to use when multiple sources of both petrogenic and pyrolytic inputs are present. In order to understand the more specific information on the sources of PAHs in Yeongil Bay, profiles of individual PAHs in sediments collected from 26 locations were analyzed by principal component analysis (PCA) (Fig. 6). The sediment PAH data were plotted against various source profiles of PAHs reported in the literature (Dickhut et al., 2000). The source profiles compared in this study include, wood burning, power plant, coke oven, diesel, gasoline, traffic tunnel and residential. The first two principal components (PCs) accounted for 85% (PC1 = 68% and PC2 = 17%) of the variation in the profiles of PAH concentrations.

The loadings of PCs of individual PAHs were plotted against PAH concentration profiles of various sources mentioned above. PC1 was significantly correlated with wood burning and diesel followed by power plant, residential and gasoline sources. PC2 was strongly correlated with PAH profiles from coke oven. However, it should be noted that volatilization or transformation of PAHs in sediment may change the source profiles significantly. For instance, low molecular weight PAHs such as naphthalene, acenaphthene and acenaphthylene are predominant in diesel fuel (Mi et al., 2000), but because of their high volatility their composition may have been reduced in sediments. The plot of PCs could cluster the locations into three groups (Fig. 6). All the locations, clustered as Group 3 contained small proportion of naphthalene (Fig. 6). The apparent grouping of the locations #4, 5, and 12 and #10, 15, and 21 was due to high proportions of naphthalene to total PAHs, (i.e., 77% and 18%, respectively). Geographically, these locations were in the midst of other sampling locations. However, the characteristic profile of PAHs in these locations suggests specific sources of exposure

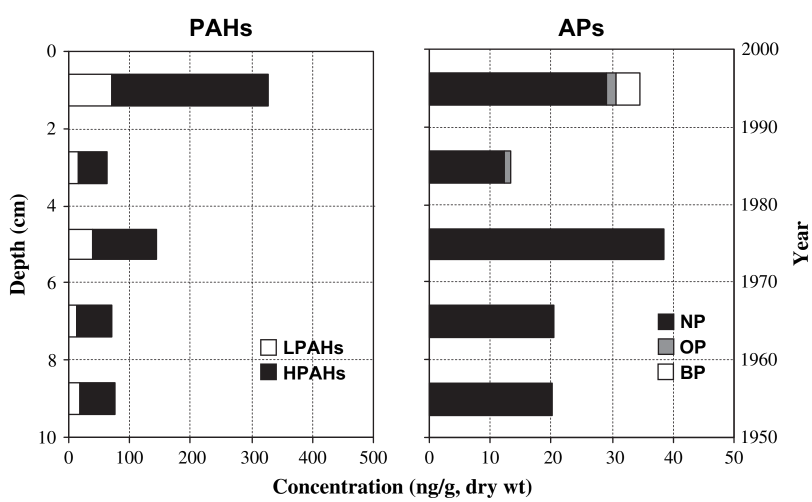

Fig. 4. Vertical profiles of PAHs (LPAHs, low molecular PAHs; HPAHs, high molecular PAHs) and alkylphenols (NP, nonylphenol; OP, octylphenol; BP, butylphenol) in sediment core (0–10 cm) from Yeongil Bay, Korea. Time interval (right *Y* axis: Year) represented is given for corresponding depth, based on a sedimentation rate of 0.21 cm/yr at sampling location.

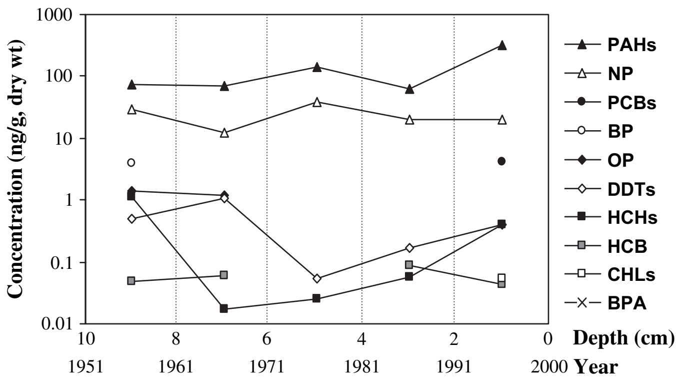

Fig. 5. Historical records of concentrations of trace organic contaminants analyzed in this study. Data are depicted in the order of residual quantity, such as PAHs > NP > PCBs > BP > OP > DDTs > HCB > HCHs > CHLs > BPA concentrations (ng/g dry wt.).

or other biogeochemical features that resulted in specific exposures. Overall, the PCA results indicated that sediment profiles were derived from multiple PAH sources in Yeongil Bay area.

3.6. Alkylphenols and bisphenol A

NP was the predominant compound, next to PAHs, in sediment samples at both inner and outer bay locations (Table 1, Fig. 2). Yeongil Bay receives both municipal and industrial wastewater of over 0.3 million ton/day from Pohang City and nearby industrial sources via the Hyeongsan River and its tributaries. The greatest concentration of NP found in sediment was 1430 (mean: 89.1) ng/g dry wt. Since the capacity of daily sewage treatment in Pohang City was limited to less than 0.1 million ton/day, the remaining 0.2 million ton of sewage may be discharged directly into the Hyeongsan River, daily. The lack of adequate sewage treatment facilities and unpermitted discharges are responsible for relatively great concentrations of NP in the coastal area of Korea.

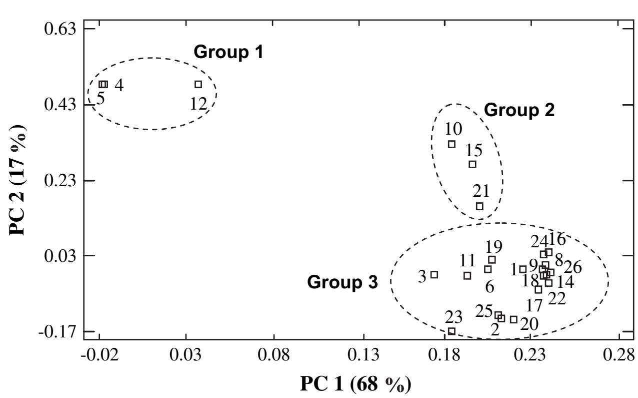

Fig. 6. Result of principal component analysis of 16 individual PAHs associated with marine sediments from Yeongil Bay, Korea. Three groups were characterized by the proportion of the naphthalene to total PAHs concentration by > 50, 20–50, and <20% for Groups 1, 2, and 3, respectively. Principal components 1 and 2 accounted for 68% and 17% of the variation in the profiles of PAH concentrations, respectively.

Concentrations of OP and BP were 1–2 orders of magnitude less than those of NP, which suggests a lesser usage of their corresponding ethoxylates than NPEs. However, relatively great concentrations of these contaminants in the inner bay sediment indicate that these compounds have been released from the inland regions including Pohang City. Rapid degradation and less binding affinity to sediment, relative to NP, may also explain lower concentrations of OP and BP in the outer bay sediments. Vertical profiles of NP, OP, and BP concentrations found in a sediment core explained the historical input of APs (Table 3, Fig. 5).

BPA was not detected in the sediment core (Table 3). Only one surficial sediment collected at location #1, which is situated in the innermost part of Yeongil Bay, contained detectable concentration of BPA (191 ng/g dry wt.). The likely sources of BPA in marine sediment are industrial wastewater. Polycarbonate plastics and synthetic resins are potential sources of BPA released from industrial activities. Since BPA was not detected in the sediment core, occurrence of BPA in sediment from the inner Yeongil Bay location indicate relatively recent and fresh input of this contaminant from Pohang City. Overall, concentrations of APs and BPA found in Yeongil Bay sediment were within the range of these contaminants found in coastal sediment from other locations in Korea (Koh et al., 2002).

3.7. Spatial variations

Spatial variations in the concentrations of various contaminants measured in sediments from the 26 locations were examined by PCA. PCA allows the exploration of similarities or differences between locations based on complex compositional data. The PCA analysis was performed with all the data shown in Table 1. The first two components accounted for 82% (PC1 = 60% and PC2 = 22%) of the between-location variation in the original data set (Fig. 7). The proximity of individual locations to each other in Fig. 7 reflects their compositional (contaminants and physical features measured in Table 1) similarity. There was no apparent grouping of the locations on the basis of contaminant compositions.

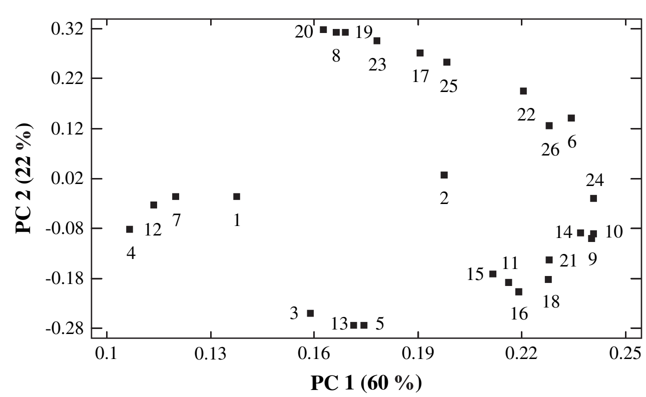

Fig. 7. Result of principal component analysis of target contaminants and physical features (TOC and mud content) measured in sediments collected from the 26 locations in Yeongil Bay, Korea. Principal components 1 and 2 accounted for 60% and 22%, respectively, of the between-location variation.

Similar results were obtained when the dataset was subjected to cluster analysis.

Among various sediment contaminant classes and physical properties measured, mud content, NP and PAH concentrations were responsible for the variability among sampling sites. This suggests the existence of multiple sources of NP and PAHs among the locations analyzed. As shown in Table 2, the lack of relationship between PAHs and AP reiterates that their sources are independent. On the other hand, concentrations of OC pesticides and PCBs were relatively uniform, suggesting a general source in this region. The influence of PAHs, NP, and mud content on multivariate similarities or differences between locations is indicated by the component loading for each variable. PC1 loadings were significantly correlated with the logarithm of mud content values. Component weights of PC2 were significantly correlated with the logarithm of total PAH concentrations in sediments. PC3, which accounted for 18% of the variability, was correlated with the logarithm of NP concentrations in sediments. Overall, the PCA results suggested that mud content, NP, and PAH concentrations were the major variables responsible for differences in profiles among sampling locations.

4. Conclusions

Varying concentrations of target organic contaminants were detected in coastal marine sediments collected from Yeongil Bay, Korea and their abundance was in the order of PAHs, APs, PCBs, and OC pesticides. PAHs and APs were predominant and have been associated with sediment in this area since the 1950s. In contrast, residuals of PCBs and OC pesticides in sediment were rather low and relatively uniform, except for hot spots (shipping yards), indicating their general sources in this region. In general, spatial distributions of target organic contaminants measured in this study suggested that their sources were multiple and independent of each other. Although PCA results indicated that there was no apparent grouping of the locations on the basis of contaminant compositions, there were some localized zones (Pohang harbor and shipping yards) with relatively greater sediment residuals. The mean concentrations of PAHs and PCBs in Yeongil Bay sediments was less than the suggested sediment quality guidelines, but their concentrations in some locations were close to or above the guidelines. Considering heavy and continuing industrial activities in Yeongil Bay area, a monitoring effort should be continued to trace the sources and historical inputs of POPs and xenoestrogens into the bay.

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References

Baumard, P., Budzinski, H., Garrigues, P., 1998. Polycyclic aromatic hydrocatbons in sediments and mussels of the western Mediterranean Sea. Environ. Toxicol. Chem. 17, 765–776.

Dickhut, R.M., Canuel, E.A., Gustafson, K.E., Liu, K., Arzayus, K.M., Walker, S.E., Edgecombe, G., Gaylor, M.O., MacDonald, E.H., 2000. Automotive sources of carcinogenic polycyclic aromatic hydrocarbons associated with particulate matter in the Chesapeake Bay region. Environ. Sci. Technol. 34, 4635–4640.

Hong, S.H., Yim, U.H., Shim, W.J., Oh, J.R., Lee, I.S., 2003. Horizontal and vertical distribution of PCBs and chlorinated pesticides in sediments from Masan Bay, Korea. Mar. Pollut. Bull. 46, 244–253.

Kannan, K., Kober, J.L., Khim, J.S., Szymczyk, K., Falandysz, J., Giesy, J.P., 2003. Polychlorinated biphenyls, polycyclic aromatic hydrocarbons and alkylphenols in sediments from the Odra River and its tributaries. Poland. Toxicol. Environ. Chem. 85, 51–60.

Khim, J.S., Villeneuve, D.L., Kannan, K., Lee, K.T., Snyder, S.A., Koh, C.H., Giesy, J.P., 1999a. Alkylphenols, polycyclic aromatic hydrocarbons (PAHs), and organochlorines in sediment from Lake Shihwa, Korea: Instrumental and bioanalytical characterization. Environ. Toxicol. Chem. 8, 2424–2432.

Khim, J.S., Kannan, K., Villeneuve, D.L., Koh, C.H., Giesy, J.P., 1999b. 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. Contam. Toxicol. 40, 141–150.

Koh, C.H., Khim, J.S., Villeneuve, D.L., Kannan, K., Giesy, J.P., 2002. Analysis of trace organic contaminants in environmental samples from Onsan Bay, Korea. Environ. Toxicol. Chem. 21, 1796–1803.

Koh, C.H., Khim, J.S., Kannan, K., Villeneuve, D.L., Senthilkumar, K., Giesy, J.P., 2004. Polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs) and 2,3,7,8-TCDD equivalents (TEQs) in sediments from Hyeongsan River, Korea. Environ. Pollut. 132, 489–501.

Koh, C.H., Khim, J.S., Kannan, K., Villeneuve, D.L., Giesy, J.P., 2006. Characterization of trace organic contaminants in marine sediment from Yeongil Bay, Korea: 2. Dioxin-like and estrogenic activities. Environ. Pollut. 142, 39–48.

Long, E.R., MacDonald, D.D., Smith, S.L., Calder, F.D., 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environ. Manage. 19, 81–97.

MacDonald, D.D., Dipinto, L.M., Christopher, J.F., Ingersoll, C.G., Long, E.R., Swartz, R., 2000. Development and evaluation of consensus-based sediment effect concentrations for polychlorinated biphenyls. Environ. Toxicol. Chem. 19, 1403–1413.

Mi, H.H., Lee, W.J., Chen, C.B., Yang, H.H., Wu, S.J., 2000. Effect of fuel aromatic content on PAH emission from a heavy-duty diesel engine. Chemosphere 41, 1783–1790.

Oh, J.R., Ikonomou, M.G., Fernandez, M.P., Hong, S.H., 2003. PCB and PCDD/F totals, TEQs, and congener patterns in Korean coastal marine environment, 1987, 1988, 1990, and 1996–1999. Arch. Environ. Contam. Toxicol. 44, 224–236.

Swartz, R., 1999. Consensus sediment quality guidelines for polycyclic aromatic hydrocarbon mixtures. Environ. Toxicol. Chem. 18, 780–787.

Villeneuve, D.L., Khim, J.S., Kannan, K., Giesy, J.P., 2002. Relative potencies of individual polycyclic aromatic hydrocarbons to induce dioxin-like and estrogenic responses in three cell lines. Environ. Toxicol. 17, 128–137.

Yamashita, N., Kannan, K., Imagawa, T., Villeneuve, D.L., Hashimoto, S., Miyazaki, A., Giesy, J.P., 2000. Vertical profile of polychlorinated dibenzo-*p*-dioxins, dibenzofurans, naphthalenes, biphenyls, polycyclic aromatic hydrocarbons in a sediment core from Tokyo Bay. Japan. Environ. Sci. Technol. 34, 3560–3567.