

Trace Organic Contaminants in Sediment and Water from Ulsan Bay and Its Vicinity, Korea

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Abstract. Sediment and water samples collected from 32 locations in Ulsan Bay and adjacent inland areas were analyzed for polycyclic aromatic hydrocarbons (PAHs), nonylphenol (NP), octylphenol (OP), bisphenol A (BPA), organochlorine (OC) pesticides (HCB, HCHs, CHLs, and DDTs), and polychlorinated biphenyls (PCBs) to characterize their spatial distribution and contamination status. PAHs were detected in nearly all sediment and water extracts from Ulsan Bay and its inland locations. The sedimentary PAH concentrations ranged from 17 to 3,100 ng/g on a dry weight basis (DW), which were predominated by two- and three-ring aromatic hydrocarbons in river and/or stream, and four- to six-ring compounds in Ulsan Bay sediment. Concentrations of PAHs in pore water samples were generally two or three orders magnitude less than those of corresponding sediment samples. Maximum concentrations of NP, OP, and BPA in sediments were 1,040, 120, and 54 ng/g DW, respectively. Concentrations of OP and BPA were, on average, 5- to 13-fold less than those of NP. PCB concentrations in sediment ranged from 1.4 to 77 ng/g DW, which were predominated by lower chlorinated congeners such as di-through pentachlorinated biphenyls. Among different OC pesticides analyzed, concentrations of DDTs were the greatest, ranging from 0.02 to 41.9 ng/g DW. NP concentrations were greater at inner locations proximal to municipal wastewater discharges into rivers and/or streams, whereas the concentrations of PCBs and PAHs were great near the sites of high industrial activities. Sediment-pore water partitioning coefficients correlated with those of reported K_{oc} or K_{ow} values for selected PAHs in Ulsan Bay, but these varied by an order of magnitude for stream and/or river sediments.

The highly industrialized region of Ulsan Bay, located on the east coast of Korea, is considered to be one of the most contaminated areas in Korea. Approximately 600,000 tons of industrial and domestic wastewater, mainly from Ulsan City,

are discharged daily through several rivers and/or streams into the Bay. The Ulsan petrochemical industrial complex alone discharges up to 200,000 ton/day of effluent to Ulsan Bay, via the Woihwang and Taehwa Rivers (Kang *et al.* 1999). The Ulsan Bay has also the largest industrial port in Korea. Industrialization in this area has long been associated with social and environmental health problems (Kang *et al.* 1999). Despite the potential for direct and accidental discharges of organic contaminants into the bay, little is known regarding organic contaminants in aquatic ecosystems in this region. In this study concentrations, distribution, and biological potency of organic contaminants were examined in sediment and water from the Ulsan Bay and its vicinity. Target compounds were polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorine (OC) pesticides, and several suspect xenoestrogens, such as nonylphenol (NP), octylphenol (OP), and bisphenol A (BPA).

PAHs are a group of common environmental contaminants. They originate from anthropogenic sources, such as waste incineration, coal gasification, and accidental oil spills, as well as natural processes, like fossil fuel and wood combustion (Neff 1979). Because of their hydrophobicity, low water solubility, and vapor pressures, PAHs tend to accumulate in sediment and other organic phases. Occurrence of PAHs in the environment is of concern due to their carcinogenic properties and ability to exert toxic effects through aryl hydrocarbon receptor (AhR)-mediated mechanism, similar to those of dioxins (Mastrangelo *et al.* 1996; Sanderson *et al.* 1996). Most surveys of PAH contamination in coastal and estuarine sediments have been in North America and some European countries, and little information is available in Asian countries. PCBs and OC pesticides, such as hexachlorobenzene (HCB), hexachlorocyclohexane isomers (HCHs), chlordanes (CHLs), DDT and its derivatives (DDTs), have been detected in sediments and waters for over the last 30 years. Despite a ban on the use of PCBs and DDTs in many countries (including Korea) during the early 1970s, these compounds are ubiquitous and persistent in various environmental media and biota. These chemicals have been suspected to cause a variety of adverse effects, including hormone-dependent cancers, compromised reproductive fitness, and abnormal reproductive system development in wildlife and humans (Tyler *et al.* 1998; Giesy and Kannan 1998; Zacharewski 1998). Thus, they remain a cause for concern.

Alkylphenols (APs), such as NP and OP, are degradation products of alkylphenol ethoxylates (APEs), which are widely used as surfactants (Nimrod and Benson 1996). APEs have been used in a wide variety of industrial and household products and released into the environment since the 1940s (White *et al.* 1994). BPA is released through its use in polycarbonate manufactures and has been reported to be present in various environmental matrices (Staples *et al.* 1998; Khim *et al.* 1999b; Masunaga *et al.* 2000). These compounds have been reported to elicit estrogenic responses in aquatic organisms (Tyler *et al.* 1998; Nimrod and Benson 1996). Because of their common usage in cleaning products and as industrial processing aids, APs, APEs, and BPA enter aquatic environments via industrial and municipal wastewater effluents. Relative to reports on the presence of APs in industrial and municipal wastewater and sewage sludge, few studies have reported their occurrence in sediment and pore water. The high production volumes, moderate persistence in sediments, and documented toxicity (including estrogenic effects) to aquatic organisms have resulted in concern over the risk posed by this class of chemicals.

Due to the complex nature of contaminants in environmental matrices, several schemes have been developed to isolate and identify contaminants and their toxic potentials. A bioassay-directed fractionation procedure has been used to separate lake and marine sediment samples into less complex fraction, which were tested for both dioxin-like activity and estrogenic activity using *in vitro* bioassay techniques (Khim *et al.* 1999a, 1999c). The fractionation scheme may vary depending on the characteristics of target contaminants and sample matrix examined. In this study, sediment, pore water (PW), and water samples (dissolved fraction, DF; particulate matter, PM) collected from Ulsan Bay were analyzed using instrumental analyses and *in vitro* bioassays to quantify target contaminants and evaluate dioxin-like and estrogenic potencies, respectively, in both raw extract and fractionated extracts. This article presents the results of instrumental analysis on the occurrence and distribution of PAHs, NP, OP, BPA, PCBs, and OC pesticides (HCB, HCHs, CHLs, and DDTs). The results of *in vitro* bioassays and mass balance analyses are presented elsewhere (Khim *et al.* 2001).

Materials and Methods

Study Area

Ulsan Bay and its inland drainage basin are located on the east coast of Korea (Figure 1). The area encompasses Ulsan Bay (U1–16), and the Taehwa River (T0–4), Yeocheon Stream (Y0–5), and Jangsaengpo (J0–4). The area adjacent to Ulsan Bay is one of the most highly industrialized regions in Korea and encompasses the most active industrial port, which contributes to about 20% of the total import and/or export activities in Korea. The Ulsan petrochemical industrial complex, made up of over 100 plants, discharges up to 200,000 t of effluent per day to Ulsan Bay via Taehwa and Woihang Rivers. Ulsan City of 1,055 km² area surrounding the bay is highly populated (over 1 million people) and developed during the past two decades due to the rapid industrialization and urbanization. Approximately, 280,000 t and 300,000 t of domestic and industrial waste, respectively, is discharged daily into the coastal region from Ulsan City and industrial complexes.

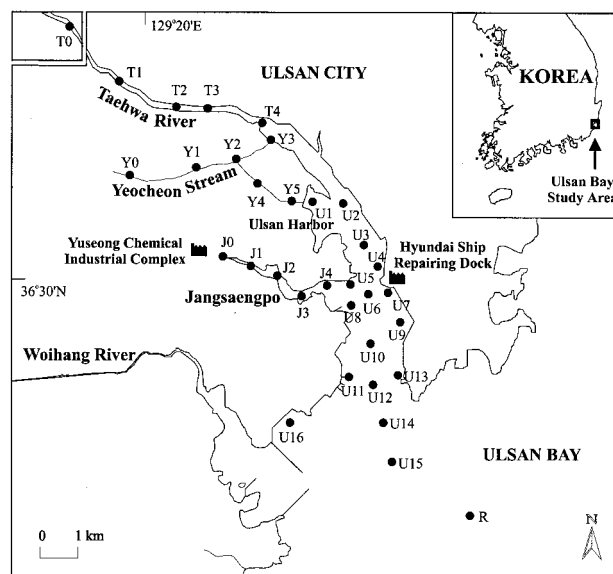


Fig. 1. Map of the study area. Samples were collected from 32 locations from Taehwa River (T locations), Yeocheon Stream (Y locations), Jangsaengpo (J locations), and Ulsan Bay (U locations and R; reference site) in May 1999

Sample Collection

Sediment and water samples were collected at 32 locations in the Ulsan Bay and its inland areas, Korea, in 1999 (Figure 1). A global positioning system (GPS) was employed to identify the precise location of each site. Marine sediment samples were collected using a Van Veen grab sampler (25 × 40 × 30 cm). After collection, pebbles and twigs were removed, then samples were freeze-dried and ground with a mortar and pestle. Samples were stored in pre-cleaned amber glass bottles at -20°C until extraction. Total organic carbon (TOC) was analyzed using a CHN analyzer. PW samples (about 1 L) were obtained using a pressurized (squeezing) method (Carr and Chapman 1995) and extracted immediately using the method described below. Water samples were collected in clean 4-L glass bottles. PM and DF were separated using glass fiber filters (GF/F) and membrane filter (final pore size: 0.45 μm). PM was freeze-dried and stored in pre-cleaned aluminum foil at -20°C until extraction. DF samples were extracted by the following methods.

Sample Preparation for Chemical Analyses

PCBs, PAHs, OC pesticides, APs, and BPA were analyzed following methods described elsewhere (Khim *et al.* 1999a, 1999b). Sediment and PM samples were Soxhlet extracted for 20 h using dichloromethane (DCM; Burdick & Jackson, Muskegon, MI). Extracts were then treated with acid-activated copper granules to remove sulfur. PW and DF samples were extracted using an Empore disk (3M Corporation, St. Paul, MN) filtration method (Snyder *et al.* 1999). Aliquots of extracts were concentrated to approximately 5 ml by rotary evaporation (39°C), and then to 1 ml under a gentle stream of nitrogen.

Extracts were purified and fractionated by passage through 10 g of activated florisil (60–100 mesh size; Sigma, St. Louis, MO) packed in a glass column (10 mm ID). The first fraction (F1) eluted with 100 ml of hexane (Burdick & Jackson) contained PCBs, HCB, and *p,p'*-DDE. Remaining OC pesticides and PAHs were eluted in the second fraction

Table 1. Total organic carbon (TOC) content, water content, grain size composition, and mean grain size (Mz) of sediment samples from Ulsan Bay and its inland areas, Korea

| Region | Sampling Location | TOC Content (%) | Water Content (%) | Grain Size Composition | | | | Mz (ϕ) |
|-----------------|-------------------|-----------------|-------------------|------------------------|----------|----------|----------|---------------|
| | | | | Gravel (%) | Sand (%) | Silt (%) | Clay (%) | |
| Taehwa River | T0 | NA ^a | 20.1 | NA | NA | NA | NA | NA |
| | T1 | 0.41 | 40.0 | 0.32 | 94.5 | 1.45 | 0.73 | 2.13 |
| | T2 | 0.21 | 26.8 | 0.74 | 98.2 | 0.65 | 0.38 | 1.80 |
| | T3 | 0.10 | 25.8 | 0.29 | 98.9 | 0.48 | 0.30 | 1.59 |
| | T4 | 1.25 | 38.5 | 6.31 | 69.4 | 23.10 | 1.20 | 2.26 |
| Yeocheon Stream | Y0 | 1.64 | 42.7 | 4.95 | 74.4 | 13.8 | 6.86 | 3.52 |
| | Y1 | 6.92 | 43.7 | 0.00 | 43.9 | 43.8 | 12.3 | 4.89 |
| | Y2 | 4.94 | 31.3 | 12.4 | 59.6 | 21.7 | 6.30 | 2.88 |
| | Y3 | 1.46 | 50.1 | 0.78 | 48.5 | 38.9 | 11.9 | 4.68 |
| | Y4 | 6.37 | 35.5 | 1.02 | 40.4 | 41.8 | 16.8 | 5.15 |
| Jangsaengpo | Y5 | 4.00 | 48.0 | 3.45 | 47.0 | 37.1 | 12.4 | 4.59 |
| | J0 | 0.65 | 36.0 | 13.4 | 73.8 | 9.20 | 3.62 | 1.97 |
| | J1 | 2.58 | 39.1 | 14.8 | 71.2 | 10.7 | 3.31 | 2.08 |
| | J2 | 2.38 | 55.1 | 0.12 | 1.75 | 87.0 | 11.1 | 5.95 |
| | J3 | 1.96 | 42.2 | 2.04 | 2.91 | 67.6 | 27.5 | 6.65 |
| Ulsan Bay | J4 | 1.59 | 48.5 | 3.97 | 14.3 | 60.7 | 21.0 | 5.84 |
| | U1 | 2.97 | 49.5 | 0.31 | 26.0 | 65.9 | 7.74 | 5.21 |
| | U2 | 1.53 | 45.8 | 0.96 | 61.7 | 29.3 | 7.97 | 3.83 |
| | U3 | 1.30 | 44.3 | 0.00 | 65.1 | 21.5 | 13.4 | 4.17 |
| | U4 | 0.76 | 48.2 | 1.27 | 47.9 | 38.7 | 13.2 | 4.33 |
| | U5 | 1.33 | 48.0 | 1.65 | 3.71 | 69.1 | 25.6 | 6.64 |
| | U6 | 1.32 | 46.1 | 0.00 | 18.3 | 60.6 | 7.74 | 6.13 |
| | U7 | 1.49 | 42.9 | 9.44 | 50.8 | 29.4 | 10.4 | 3.50 |
| | U8 | 1.69 | 53.3 | 0.00 | 10.7 | 67.4 | 21.9 | 6.34 |
| | U9 | 1.30 | 55.0 | 0.00 | 15.3 | 58.9 | 25.8 | 6.33 |
| | U10 | 1.30 | 51.1 | 0.00 | 2.19 | 65.4 | 32.5 | 7.11 |
| | U11 | 1.18 | 52.3 | 0.00 | 4.73 | 67.0 | 28.3 | 6.84 |
| | U12 | 1.16 | 51.4 | 0.00 | 20.0 | 54.3 | 25.7 | 6.10 |
| | U13 | 1.32 | 52.7 | 0.00 | 11.2 | 65.8 | 23.0 | 6.30 |
| | U14 | 1.31 | 48.4 | 0.00 | 1.73 | 69.4 | 28.9 | 6.88 |
| | U15 | 1.39 | 49.0 | 3.20 | 35.9 | 51.1 | 9.78 | 4.86 |
| U16 | NA | 19.8 | 62.0 | 37.8 | 0.06 | 0.10 | -1.34 | |
| Reference | R ^b | 1.44 | 55.6 | 0.34 | 32.7 | 46.8 | 20.1 | 5.38 |

^a NA: not analyzed

^b R: reference site, see study map for the location

(F2) using 100 ml of 20% DCM in hexane. NP, OP, and BPA were eluted in the third fraction (F3) with 100 ml of 50% DCM in methanol (Burdick & Jackson). Florisil separation was confirmed using a spike recovery test ($n = 3$) and standard reference material (SRM), 1974a sediment, obtained from the National Institute of Standards and Technology (Gaithersburg, MD). Recoveries of target analytes through all the analytical steps were between 90% and 105%. Subsamples of F1 and F2 were treated with concentrated H₂SO₄ to provide additional clean-up, which improved the detection limits for PCBs and OC pesticides. Further details regarding the fractionation procedure are presented elsewhere (Khim *et al.* 1999a, 1999c).

Instrumental Analysis

PAHs were quantified using a Hewlett Packard 5890 series II gas chromatograph equipped with a 5972 series mass spectrometer detector. A fused silica capillary column (30 m \times 0.25 mm ID) coated with DB-17 [(50% phenyl)-methyl polysiloxane; J&W Scientific, Folsom, CA] at 0.25 μ m film thickness was used. Details of instrumental parameters are provided elsewhere (Khim *et al.* 1999a, 1999b). The PAH standard (AccuStandard, New Haven, CT) consisted of 16 priority pollutant PAHs

identified by the U.S. Environmental Protection Agency (Method 8310). The mass spectrometer was operated under selected ion monitoring (SIM) mode using the molecular ions selective for individual PAHs (Khim *et al.* 1999b). The detection limits of PAHs for sediment and water samples were 10 ng/g DW and 10 ng/L, respectively.

PCBs and OC pesticides were quantified using a gas chromatograph (Perkin Elmer series 600) equipped with ⁶³Ni electron capture detector. A fused silica capillary column coated with DB-5MS [(5%-phenyl)-methylpolysiloxane, 30 m \times 0.25 mm ID; J&W Scientific] having a film thickness of 0.25 μ m was used. Helium and nitrogen were used as carrier and make-up gas, respectively. A solution containing 98 individual PCB congeners with known composition and content was used as a standard and concentrations of 98 individually resolved peaks were summed to obtain total PCB concentrations (Khim *et al.* 2000). PCB congeners have been referred by Ballschmitter and Zell numbers. OC pesticides were quantified from individually resolved peak areas based on the peak areas of standards. Detection limits of sedimentary OC pesticides and PCBs were 0.01 and 1.0 ng/g DW, respectively, and those for waterborne OC pesticides and PCBs were 0.1 and 10 ng/L, respectively.

Reverse phase high-performance liquid chromatography (HPLC) with fluorescence detection was used to quantify NP, OP, and BPA (Khim *et al.* 1999c). Samples and standards were injected (10 μ l) by a Perkin Elmer

Table 2. Concentrations of polycyclic aromatic hydrocarbons in sediment, pore water, sea water (DF: dissolved fraction, PM: particulate matter) samples from Ulsan Bay and its inland area

| Sampling Location | Sediment (ng/g DW) | Pore Water (μg/L) | Water-DF (μg/L) | Water-PM (μg/L) |
|-------------------|--------------------|-------------------|-----------------|-----------------|
| T0 | NA ^a | NA | 0.08 | 0.08 |
| T1 | < 10.0 | 0.28 | 0.03 | 0.52 |
| T2 | < 10.0 | 0.70 | 0.04 | 0.05 |
| T3 | < 10.0 | 0.19 | 0.03 | 0.05 |
| T4 | NA | 0.54 | 0.12 | 0.08 |
| Y0 | < 10.0 | 0.34 | 0.22 | 0.08 |
| Y1 | 54.4 | 0.28 | NA | NA |
| Y2 | 86.8 | 0.29 | 0.07 | 0.38 |
| Y3 | < 10.0 | 0.74 | 0.19 | 0.09 |
| Y4 | 1,370 | 0.23 | 0.12 | 0.23 |
| Y5 | 951 | 0.51 | 0.10 | 0.21 |
| J0 | 53.8 | 0.18 | 0.33 | 0.09 |
| J1 | 601 | 0.68 | 0.07 | 0.64 |
| J2 | 97.7 | 0.18 | 0.04 | 0.04 |
| J3 | 184 | NA | NA | NA |
| J4 | 214 | NA | NA | NA |
| U1 | 174 | 0.18 | < 0.01 | < 0.01 |
| U2 | 20.8 | NA | 0.02 | 0.04 |
| U3 | 29.2 | NA | NA | NA |
| U4 | 93.8 | NA | NA | NA |
| U5 | 79.7 | 0.02 | < 0.01 | < 0.01 |
| U6 | 870 | NA | NA | NA |
| U7 | 1,310 | 0.02 | < 0.01 | 0.92 |
| U8 | 83.9 | NA | NA | NA |
| U9 | 445 | NA | NA | NA |
| U10 | 33.0 | NA | NA | NA |
| U11 | 54.7 | NA | NA | NA |
| U12 | 40.0 | NA | NA | NA |
| U13 | 112 | NA | NA | NA |
| U14 | 17.0 | NA | NA | NA |
| U15 | 57.5 | NA | NA | NA |
| U16 | 3,100 | NA | 0.11 | 0.03 |
| R ^b | 39.0 | 0.06 | 0.06 | 0.03 |

^a NA: not analyzed. ^b R: reference site, see study map for the location

Series 200 autosampler (Perkin Elmer, Norwalk, CT) onto an analytical column, Prodigy[®] ODS (3), 250 × 4.6 mm column (Phenomenex, Torrance, CA), which was connected to a guard column (Prodigy ODS (3), 30 × 4.6 mm) and eluted with a flow of acetonitrile (ACN; Burdick & Jackson) and water at a gradient from 50% ACN in water to 98% ACN in water delivered by Perkin Elmer Series 200 pump for 20 min. Detection was accomplished using a Hewlett Packard 1046A fluorescence detector (Hewlett-Packard, Wilmington, DE) with an excitation wavelength of 229 nm and an emission wavelength of 310 nm. NP, OP, and BPA detection limits for the analytical method were 1 ng/g DW. Sample extracts were injected into a gas chromatograph equipped with a mass selective detector (GC-MS) for the confirmation of the identity of NP, OP, and BPA by SIM mode (Khim *et al.* 1999c).

Results

Sediment Characteristics

Marine sediments from outer bay locations consisted predominantly of silt and clay (mean: 73%), indicating that their

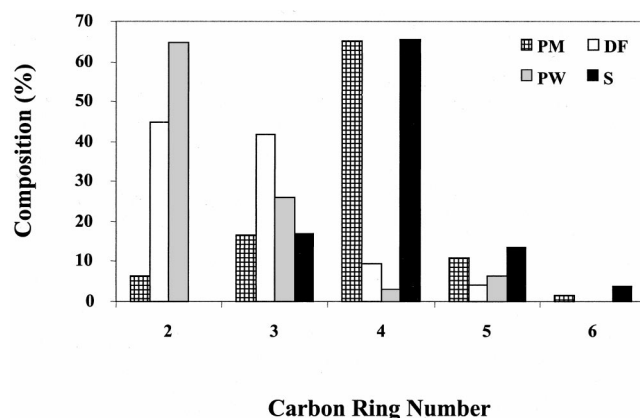


Fig. 2. Mean composition of PAH ring number (weight %) to total PAH concentrations in sediment (S), pore water (PW), and water (PM: particulate matter, DF: dissolved fraction) samples from Ulsan Bay and its inland areas, Korea

texture ranges from sandy mud to mud (Table 1). The river and/or stream sediment samples composed primarily of gravel and sand (> 90%) in upstream locations and sand and silt (> 80%) in downstream locations. TOC concentrations varied from 0.10 to 6.92% (Table 1). TOC concentrations of Taehwa River sediments except at location T4 were generally one order of magnitude less than those observed for other locations (mean ± SD: 0.24 ± 0.16%). Relatively great TOC concentrations were found in Yeocheon Stream sediment (mean ± SD: 4.22 ± 2.31%). All marine sediments except U1 contained TOC less than 2% (mean ± SD: 1.42 ± 0.47%). TOC contents of river and/or stream sediments were poorly correlated with mud content ($r^2 = 0.15$), whereas TOC content of marine sediment samples was consistent throughout the bay. No significant relationships were observed between TOC content and total OC concentrations. The correlation between TOC content and total PAHs was poor. However, there was a significant correlation between TOC content and AP concentrations in sediment ($r^2 = 0.47$, $p < 0.05$).

Contaminant Concentrations and Distributions

PAHs were detected in nearly all sediment extracts from Ulsan Bay and inland rivers and/or streams. (Table 2). PAH concentrations ranged from 17 to 3,100 (mean 405) ng/g DW. The greatest concentration of total PAHs was found at location U16. None of the Taehwa River sediment samples contained detectable concentrations of PAHs. Sediments from Yeocheon and Jangsaengpo stream contained PAH concentrations as great as 1,370 and 601 ng/g DW, respectively. There was a concentration gradient of PAHs in river and/or stream sediment samples, which decreased from upstream to downstream. Concentrations of PAHs in Ulsan Bay were localized. PAH concentrations at locations U6, U7, and U9 near Hyundai Ship Repairing Dock were the highest of up to 1,310 ng/g DW. Sediment from other locations in the bay contained PAH concentrations less than 100 ng/g DW. PAHs were predominated by two- and three-ring aromatic hydrocarbons in Yeocheon and

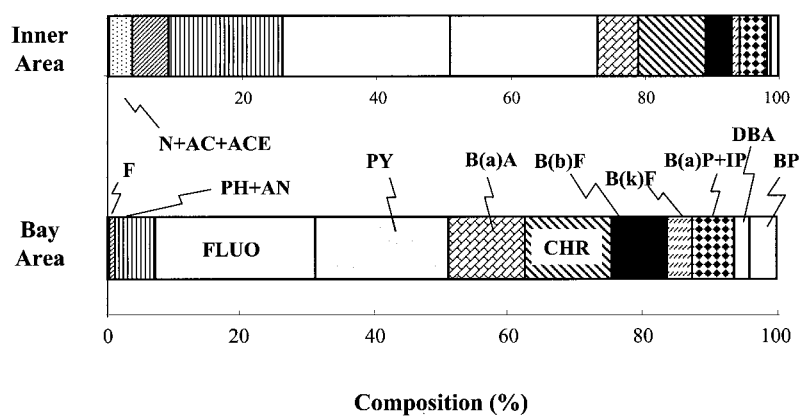


Fig. 3. Mean composition of individual PAHs to total PAH concentrations in sediment from Ulsan Bay and its inland areas, Korea. N—naphthalene, AC—acenaphthene, ACE—acenaphthylene, F—fluorene, PH—phenanthrene, AN—anthracene, FLUO—fluoranthene, PY—pyrene, B(a)A—benzo(a)anthracene, CHR—chrysene, B(b)F—benzo(b)fluoranthene, B(k)F—benzo(k)fluoranthene, B(a)P—benzo(a)pyrene, IP—indeno(1,2,3-*cd*)pyrene, DBA—dibenz(*a,h*)anthracene, BP—benzo(*g,h,i*)perylene

Jangsaengpo streams and four- to six-ring aromatic hydrocarbons in Ulsan Bay sediment samples (Table 2; Figures 2 and 3). Concentrations of PAHs in PW samples were generally two or three orders magnitude less than those of corresponding sediment samples. In general, PAH concentrations in water column were less than 0.5 and 1.0 ng/L for DF and PM samples, respectively. PW and DF samples contained low molecular weight PAHs (two- and three-ring PAHs), which contributed more than 80% to the total PAHs, whereas PM and sediment samples were predominated by four-ring aromatic hydrocarbons, such as fluoranthene (Fluo), pyrene (Py), benzo(a)anthracene (B(a)A), and chrysene (CHR).

APs and BPA were next in abundance to PAHs in Ulsan Bay sediment samples (Table 3). Mean concentrations of NP, OP, and BPA were 97.9, 17.7, and 10.9 ng/g DW, respectively. NP was detectable in sediment from nearly all locations, and OP and BPA were detected at only about 30% of the locations (Table 2). Maximum concentrations of NP, OP, and BPA in sediments were 1,040, 120, and 53.5 ng/g DW, respectively, and were found in river and/or stream sediments. Concentrations of OP and BPA were, on average, 5- to 13-fold less than those of NP. Concentrations of APs and BPA in off-shore locations were less than 20 ng/g DW. AP concentrations in Yecheon Stream sediments showed distinct concentration gradient from upstream to downstream sites.

PCBs were detectable in 26 of 30 locations at concentrations ranging from 1.44 to 76.7 (mean: 17.6) ng/g DW (Table 4). The maximum concentration of 76.7 ng/g DW was detected in Ulsan Bay location U7, which had the second greatest total PAH concentration of 1,310 ng/g DW. Total PCB concentrations in sediment were generally one or two orders magnitude less than those of PAHs and NP. PCB concentrations greater than 20 ng/g DW were found at locations Y5, J1, U7, and U9 situated along Jangsaengpo and the middle part of Ulsan Bay (Table 3, Figure 1). The contribution of individual chlorobiphenyl (CB) isomers and congeners to the total PCB concentration varied among locations. Sediment collected from Ulsan Bay contained higher proportions of di- through penta-CBs, contributing 70% of the total PCB concentrations (Figure 4). Concentrations of PCBs in corresponding PW samples measured at 16 locations ranged from 0.08 to 0.66 $\mu\text{g/L}$. In general, PCB concentrations of PW samples were one or two orders of magnitude less than those of corresponding sediment samples (Table 4). Pore water PCB concentrations were correlated

significantly ($r^2 = 0.67$, $p < 0.05$) with concentrations in the bulk sediment. Concentrations of PCBs in DF and PM were 420 and 180 times less than those in sediment, respectively. There was a significant relationship between dissolved and particulate PCB concentrations ($r^2 = 0.74$, $p < 0.05$).

Among a number of OC pesticides that were screened for, DDT concentrations in sediment samples were the greatest, ranging from 0.02 to 42 ng/g DW (Table 5). Three Ulsan Bay locations, U7, U8, and U10, contained high DDT concentrations of 21.1, 41.9, and 12.6 ng/g DW, respectively. Concentrations of other OC pesticides, namely HCB, HCHs, and CHLs were, on average, less than 1 ng/g DW in sediment samples, however. The maximum concentrations of HCB, HCHs, and CHLs were all detected in Yecheon Stream locations, which were 3.23, 4.55, and 3.96, respectively. Concentrations of OC pesticides in PW, DF, and PM samples were generally less than 100 ng/L.

Discussion

Correlations with Sediment Characteristics

Poor relationships among concentrations of PAHs, APs, and OCs suggest that their sources are independent of each other. Because of the low affinities of lipophilic organic contaminants to sand, concentrations are to be normalized to sediment grain size or organic carbon (Jeffery and Baker 1999). In general, there were no relationships between the mean grain size and three classes of organic contaminants analyzed. This suggests that proximity to sources may be the most important determining factor for the dominance of these contaminants. Ulsan Bay area is a complex, dynamic system having variety of potential sources of environmental contaminants. An earlier study also reported a poor relationship between sediment grain size and total PAHs or PCBs in sediment from Baltimore Harbor, a heavily industrialized and urbanized area in the United States (Jeffery and Baker 1999). This suggests that contamination in Ulsan Bay area seems to be localized. Petrochemical and industrial complexes for PAHs and municipal sewage for APs are the potential sources.

Table 3. Concentrations of nonylphenol (NP), octylphenyl (OP), and bisphenol A (BPA) in sediment from Ulsan Bay and its inland area

| Sampling Location | NP | | OP | | BPA | |
|-------------------|------------|-------------------------|------------|------------|------------|------------|
| | (ng/g sed) | (ng/g TOC) ^a | (ng/g sed) | (ng/g TOC) | (ng/g sed) | (ng/g TOC) |
| T0 | 2.58 | NA ^b | < 1.00 | NA | < 1.00 | NA |
| T1 | 11.3 | 2,730 | 1.25 | 303 | 17.6 | 4,250 |
| T2 | 12.4 | 5,920 | 4.25 | 2,020 | 1.60 | 763 |
| T3 | < 1.00 | — | 2.94 | 2,970 | < 1.00 | — |
| Y0 | < 1.00 | — | < 1.00 | — | < 1.00 | — |
| Y1 | 1,040 | 15,000 | 120 | 1,730 | < 1.00 | — |
| Y2 | 335 | 6,790 | 56.3 | 1,140 | < 1.00 | — |
| Y3 | 2.83 | 194 | 2.19 | 150 | < 1.00 | — |
| Y4 | 57.3 | 899 | 1.49 | 23.3 | < 1.00 | — |
| Y5 | 248 | 6,200 | 11.0 | 275 | < 1.00 | — |
| J0 | 1.49 | 230 | < 1.00 | — | < 1.00 | — |
| J1 | 666 | 25,800 | 8.78 | 340 | 53.5 | 2,080 |
| J2 | 12.2 | 513 | < 1.00 | — | < 1.00 | — |
| J3 | 7.25 | 370 | < 1.00 | — | 1.09 | 55.9 |
| J4 | 2.98 | 187 | < 1.00 | — | 2.33 | 146 |
| U1 | 19.9 | 668 | < 1.00 | — | 1.23 | 41.4 |
| U2 | 2.07 | 135 | < 1.00 | — | < 1.00 | — |
| U3 | 1.05 | 81.0 | < 1.00 | — | < 1.00 | — |
| U4 | 1.18 | 156 | < 1.00 | — | < 1.00 | — |
| U5 | 1.82 | 137 | < 1.00 | — | < 1.00 | — |
| U6 | 1.95 | 148 | 2.91 | 221 | 10.4 | 794 |
| U7 | 6.37 | 427 | 1.22 | 82.2 | 13.1 | 880 |
| U8 | 3.76 | 223 | < 1.00 | — | 1.42 | 84.5 |
| U9 | 2.45 | 188 | 1.17 | 89.4 | 6.76 | 518 |
| U10 | NA | — | NA | — | NA | — |
| U11 | 1.05 | 89.3 | < 1.00 | — | < 1.00 | — |
| U12 | < 1.00 | — | < 1.00 | — | < 1.00 | — |
| U13 | 2.04 | 154 | < 1.00 | — | < 1.00 | — |
| U14 | < 1.00 | — | < 1.00 | — | < 1.00 | — |
| U15 | < 1.00 | — | < 1.00 | — | < 1.00 | — |
| U16 | 3.75 | NA | < 1.00 | NA | < 1.00 | NA |
| R ^c | 1.48 | 102 | < 1.00 | — | < 1.00 | — |

^a (ng/g TOC): TOC normalized concentrations did not calculate in the case of the concentrations less than detection limits

^b NA: not analyzed

^c R: reference site, see study map for the location (Figure 1)

Spatial Distribution and Sources

PAHs were the predominant and fairly widespread contaminants in the Ulsan Bay (Table 2). Relatively great concentrations of PAHs were found in sediment collected from the lower reaches of Yecheon Stream (Y4, Y5) and in the middle part of the Ulsan Bay (U6, U7, and U9). Ulsan Harbor and Hyundai Ship Repairing Dock are situated near these locations and may be the potential sources of PAHs (Figure 1). Some molecular ratios of specific PAH compounds were calculated to evaluate the characteristics of PAHs arising from different sources (Baumard *et al.* 1998). The ratios of fluoranthene to pyrene concentrations (Fluo/Py) were less than 1.0 in Y4, Y5, U6, U7, and U9 locations, which suggests that petroleum hydrocarbons are the sources of PAHs in these locations. Further ratios of indeno(1,2,3-cd)pyrene to benzo(ghi)perylene concentrations (IP/BP) were less than 1.0 from the same locations. This further implies that the sources of PAHs in Ulsan Bay are mainly petrogenic.

The spatial distributions of AP concentrations were different from those observed for PAHs. PAHs were fairly widespread, but APs were detected mainly in river and/or stream sediments

close to municipal sewage disposal areas (Table 3, Figure 1). Ulsan Bay receives 280,000 t of municipal waste water daily from Ulsan City via the discharge from several rivers and/or streams, which are major sources of these compounds. Spatial distribution of NP and OP concentrations in sediment from Yecheon and Jangsaengpo Streams revealed a gradual decrease in concentrations with distance from source. NP concentrations decreased dramatically with distance in Ulsan Bay sampling locations except U1, concentrations were less than 10 ng/g DW. Distribution of BPA was similar to those of PAHs except at the T1 location. Similar to that for PAHs, relatively high concentrations of BPA were detected in U6, U7, and U9 near the Hyundai Ship Repairing Dock (Table 3, Figure 1). The likely sources of BPA in sediment were leachates from polycarbonate and plastic materials (Khim *et al.* 1999b).

PCBs and OC pesticides were detectable in nearly all samples of sediment and water. PCB concentrations were greater in sediment and water samples collected near industrial areas than those from nonindustrial locations. Relatively greater concentrations of PCBs were measured in sediments from locations J1, U6, U7, and U9 suggesting possible inputs of PCBs along the midwestern part of the bay. In general, di-through hepta-

Table 4. Concentrations of polychlorinated biphenyls in sediment, pore water, sea water (DF: dissolved fraction, PM: particulate matter) samples from Ulsan Bay and its inland area

| Sampling Location | Sediment (ng/g DW) | Pore Water ($\mu\text{g/L}$) | Water-DF ($\mu\text{g/L}$) | Water-PM ($\mu\text{g/L}$) |
|-------------------|--------------------|--------------------------------|------------------------------|------------------------------|
| T0 | < 1.00 | NA | 0.06 | 0.03 |
| T1 | NA ^a | 0.37 | 0.07 | 0.07 |
| T2 | < 1.00 | 0.33 | 0.09 | 0.03 |
| T3 | < 1.00 | 0.27 | 0.07 | 0.05 |
| T4 | NA | 0.30 | 0.12 | 0.15 |
| Y0 | 1.44 | 0.22 | NA | 0.08 |
| Y1 | 11.9 | 0.38 | 0.13 | 0.17 |
| Y2 | 14.2 | 0.26 | NA | NA |
| Y3 | 5.99 | 0.26 | 0.14 | 0.14 |
| Y4 | 21.7 | 0.22 | 0.28 | 0.14 |
| Y5 | NA | 0.31 | 0.27 | 0.23 |
| J0 | 8.66 | 0.16 | 0.12 | 0.12 |
| J1 | 52.2 | 0.66 | 0.31 | 0.30 |
| J2 | 11.6 | 0.14 | 0.10 | 0.08 |
| J3 | 17.9 | NA | NA | NA |
| J4 | 12.1 | NA | NA | NA |
| U1 | 18.7 | 0.12 | NA | NA |
| U2 | 12.9 | NA | 0.03 | 0.08 |
| U3 | 15.8 | NA | NA | NA |
| U4 | 15.5 | NA | NA | NA |
| U5 | 18.9 | < 0.01 | NA | NA |
| U6 | 19.4 | NA | NA | NA |
| U7 | 76.7 | < 0.01 | NA | NA |
| U8 | 15.2 | NA | NA | NA |
| U9 | 25.1 | NA | NA | NA |
| U10 | 15.9 | NA | NA | NA |
| U11 | 5.52 | NA | NA | NA |
| U12 | 11.3 | NA | NA | NA |
| U13 | 5.52 | NA | NA | NA |
| U14 | 11.5 | NA | NA | NA |
| U15 | 13.2 | NA | NA | NA |
| U16 | < 1.00 | NA | 0.08 | 0.08 |
| R ^b | < 1.00 | 0.07 | 0.01 | 0.13 |

^a NA: not analyzed

^b R: reference site, see study map for the location (Figure 1)

CB congeners were predominant throughout the different type of samples analyzed (Figure 4). This is consistent with the previous studies, which reported the presence of lower chlorinated PCB congeners in sediment and mussel collected from Masan and Ulsan Bays in Korea (Khim *et al.* 1999b, 2000).

Comparison to Other Studies

This study is the most comprehensive evaluation of sedimentary and waterborne organic contaminants in the Ulsan Bay area. PCB concentrations in sediment samples collected from the Ulsan Bay in 1997 ranged from 0.27 to 121 (mean = 18.9) ng/g DW (Jeong *et al.* 1999), which is similar to those found in this study (mean = 17.6; Table 3). Several studies have examined the occurrence and distribution of PCBs, PAHs, and APs in sediment from Kyeonggi Bay, Lake Shihwa, and Masan Bay in Korea (Kim *et al.* 1999; Khim *et al.* 1999a, 1999b). PAH concentrations in sediment from Kyeonggi Bay, Lake Shihwa, and Masan Bay were 9.1–1,400, 16.8–30.8, 36.6–1,100 ng/g

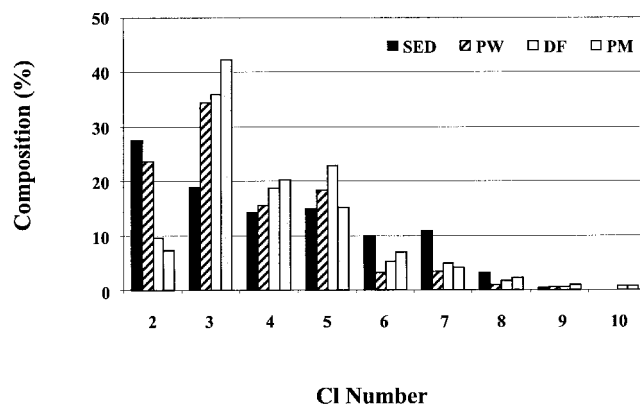


Fig. 4. Mean homolog composition (%) of PCBs in sediment (S), pore water (PW), and water (PM: particulate matter, DF: dissolved fraction) samples from Ulsan Bay and its inland areas, Korea

DW respectively (Kim *et al.* 1999; Khim *et al.* 1999a, 1999b). Ulsan Bay PAH concentrations were generally greater than those from other industrialized areas in Korea. This is not surprising considering the shipping activities in Ulsan Bay. However, AP concentrations in sediments of Ulsan Bay were, on average, five to six times less than those for Lake Shihwa and Masan Bay in Korea (Khim *et al.* 1999a, 1999b). This can be explained by the greater populations in cities located near Lake Shihwa (Incheon and Seoul) and Masan Bay (Masan and Changwon) than those around Ulsan Bay. There is no historical data regarding PAHs, NP, OP, and BPA concentrations in and around Ulsan Bay. The concentrations of PCBs, PAHs, and APs detected in this study seem reasonable relative to those reported in earlier studies in Korean bays and harbors, given the regulatory, historical, and geographical context. The data presented here establishes the baseline for future monitoring of these compounds in Ulsan Bay areas.

Potential for Biological/Ecological Effects

Sediment quality guidelines (SQGs) are indices that are used to predict potential toxicological and biological effects and/or to compare the degree of contamination in sediments. Several SQGs, such as screening level concentration, lowest apparent effects threshold, toxic effect threshold, effect range low (ERL), etc., have been suggested for PAHs and PCBs based on a variety of laboratory, field, and mathematical models. However, the validity of each guideline is under debate (Swartz 1999; MacDonald *et al.* 2000). Consensus SQGs for organic compounds including 13 individual PAHs, total PAHs, *p,p'*-DDE, total DDTs, and total PCBs were suggested recently to provide a unifying synthesis of existing SQGs (Swartz 1999; MacDonald *et al.* 2000). Three consensus-based on sediment effect concentrations for total PAHs, including threshold (TEC), median (MEC), and extreme effects concentrations (EEC) were 290, 1,800, and 10,000 $\mu\text{g/g}$ OC, respectively (Swartz 1999). TEC, MEC, and EEC for total PCBs were 0.035, 0.34, and 1.6 mg/kg DW, respectively (MacDonald *et al.* 2000).

None of the locations exceeded the ERLs for PAHs. There

Table 5. Concentrations of organochlorine pesticides (HCB, HCHs, CHLs, DDTs) in sediment from Ulsan Bay and its inland area

| Sampling Location | HCB (ng/g) | HCHs (mg/g) | CHLs (ng/g) | DDTs (ng/g) | Total OC Pesticides ² (ng/g) |
|-------------------|-----------------|-------------|-------------|-------------|---|
| T0 | < 0.01 | 0.04 | < 0.01 | 0.02 | 0.06 |
| T1 | NA ^b | 0.05 | < 0.01 | < 0.01 | 0.05 |
| T2 | < 0.01 | 0.08 | < 0.01 | 0.02 | 0.10 |
| T3 | < 0.01 | 0.03 | < 0.01 | 0.02 | 0.05 |
| Y0 | 0.04 | 0.19 | 3.96 | 0.12 | 4.32 |
| Y1 | 0.11 | 0.03 | 0.16 | 0.30 | 0.60 |
| Y2 | 0.11 | 0.02 | 0.20 | 0.29 | 0.62 |
| Y3 | 0.02 | 0.03 | < 0.01 | 0.03 | 0.08 |
| Y4 | 3.23 | 4.55 | 0.07 | 1.16 | 9.01 |
| Y5 | NA | 1.34 | 0.33 | 0.88 | 2.55 |
| J0 | < 0.01 | 0.03 | < 0.01 | 0.90 | 0.93 |
| J1 | 1.56 | 0.30 | < 0.01 | 0.80 | 2.66 |
| J2 | < 0.01 | 0.05 | < 0.01 | 0.03 | 0.08 |
| J3 | < 0.01 | 0.35 | < 0.01 | 0.58 | 0.93 |
| J4 | < 0.01 | 0.24 | < 0.01 | 0.58 | 0.82 |
| U1 | 0.39 | 4.12 | 0.10 | 1.99 | 6.60 |
| U2 | < 0.01 | 0.05 | < 0.01 | 3.94 | 4.00 |
| U3 | 0.03 | 0.11 | < 0.01 | 0.14 | 0.28 |
| U4 | < 0.01 | 2.41 | 0.24 | 1.65 | 4.30 |
| U5 | 0.13 | 0.03 | < 0.01 | 2.78 | 2.94 |
| U6 | 0.48 | 0.46 | 0.10 | 1.00 | 2.04 |
| U7 | < 0.01 | 2.26 | 0.16 | 21.1 | 23.5 |
| U8 | 0.17 | 0.50 | 0.79 | 41.9 | 43.4 |
| U9 | < 0.01 | 0.15 | 1.08 | 3.22 | 4.45 |
| U10 | 0.11 | 0.13 | 0.13 | 12.6 | 12.9 |
| U11 | 0.10 | 0.29 | < 0.01 | 0.54 | 0.93 |
| U12 | 0.09 | 0.31 | 0.04 | 0.45 | 0.91 |
| U13 | < 0.01 | 0.17 | 0.05 | 0.33 | 0.54 |
| U14 | 0.02 | 0.03 | 0.08 | 2.39 | 2.52 |
| U15 | 0.03 | 0.03 | < 0.01 | 0.21 | 0.26 |
| U16 | < 0.01 | 0.03 | < 0.01 | 0.71 | 0.74 |
| R ^c | < 0.01 | 0.74 | < 0.01 | 0.37 | 1.11 |

^a Total OC pesticide concentrations are sum of HCB, HCH, CHL, and DDT concentrations

^b NA: not analyzed

^c R: reference site, see study map for the location (Figure 1)

was no TOC data available for U16, which contained the greatest concentrations of PAHs. Assuming a TOC content of 1%, concentrations of four high molecular weight PAHs (Fluo, Py, B(a)A, and CHR) exceeded the ERL values (Long *et al.* 1995). When TEC reported for total PAHs was compared, only one location (U16) exceeded the limit of 290 $\mu\text{g/g}$ OC. None of the total PCB concentrations at all the locations exceeded ERL value of 22.7 $\mu\text{g/g}$ OC. Comparing the TEC guideline of 35 ng/g DW for total PCBs, two locations, J1 and U7, exceeded the consensus SQGs, however. Generally, the concentrations of total PAHs and PCBs were less than the suggested SQGs, although their concentrations in some locations were close to or above the SQGs for toxic effects in benthic organisms.

Partitioning and Fate of PAHs

Among the organic compounds analyzed in this study, PAHs were dominant and ubiquitous contaminants in various environmental media, such as sediment, pore water, and surface water samples from Ulsan Bay. Therefore it was possible to examine the relationship between sediment and pore water

concentrations of PAHs. Several partitioning models have been developed by various researchers to understand the equilibrium partitioning and kinetic geochemistry of compounds in the environment. (Gschwend and Wu 1985; McGroddy *et al.* 1996). Previous studies of the distribution and partitioning of PAHs between pore water and sediments of Boston Harbor and San Francisco Bay have revealed that the measured pore water concentrations were lower than those predicted by equilibrium partitioning models (McGroddy and Farrington 1995; Maruya *et al.* 1996). To evaluate a partitioning behavior and fate of PAHs in Ulsan Bay system, *in situ* sediment-pore water partition coefficient (K_{oc}') was derived as

$$K_{oc}' = K_p' / f_{oc} \quad (\text{Eq. 1})$$

$$K_p' = C_s / C_{aq} \quad (\text{Eq. 2})$$

where C_s is the solid-phase concentration, C_{aq} is the aqueous-phase concentration, and f_{oc} is the sediment fractions of organic carbon (McGroddy and Farrington 1995; Maruya *et al.* 1996).

Values of K_{oc}' for PAHs that were detectable in PW samples in Ulsan Bay were generally in the same order of magnitude as

Table 6. *In situ* sediment–pore water partition coefficient (log K_{oc}') for selected PAHs in sediment from Ulsan Bay and its inland area

| PAH ^a | log K_{ow} ^b | log K_{oc} ^c | log K_{oc}' | | |
|------------------|---------------------------|---------------------------|---------------|-------------|-----------|
| | | | Yeocheon S. | Jangsaengpo | Ulsan Bay |
| N | 3.36 | | 2.17 | 2.69 | 3.58 |
| ACE | 3.90 | | 4.14 | 4.47 | |
| F | 4.20 | 4.79 | 4.32 | 4.14 | 4.04 |
| PH | 4.57 | 4.12 | 5.35 | 5.03 | 4.70 |
| PY | 5.18 | 4.80 | 5.24 | 5.37 | 4.63 |

^a N: naphthalene, ACE: acenaphthylene, F: fluorene, PH: phenanthrene, PY: pyrene

^b Values from Chiou *et al.* (1998)

^c Values from McGroddy and Farrington (1995)

literature values of octanol–water partition coefficient (K_{ow}) or sediment–pore water partition coefficient (K_{oc}). The K_{oc}' values for naphthalene in sediment or stream were less than those in Ulsan Bay, whereas these values were greater for pyrene and phenanthrene and one order magnitude greater than K_{ow} or K_{oc} in river and/or stream sites (Table 6). This indicates that only a fraction of measured sediment PAH concentrations was available to partition rapidly into aqueous samples, suggesting a rate-limited desorption of PAHs from the organic fraction of sediment. Mean log K_{oc}' was linearly correlated with log K_{ow} (> 0.77) within each sampling locations (Yeocheon Stream, Jangsaengpo, and Ulsan Bay). Naphthalene (two-carbon ring PAH), with high solubility in water, tends to partition into aqueous phase (pore water) relatively rapidly. In general, there was a good agreement of equilibrium partitioning hypothesis between sediment and pore water phases from Ulsan Bay, but in rivers and streams the measured K_{oc}' values varied by an order of magnitude depending on the PAH compounds.

Summary

The relative abundance of organic contaminants measured in the Ulsan Bay was in the order of PAHs $>$ NP $>$ OP $>$ PCBs $>$ OC pesticides $>$ BPA. Spatial distributions of target organic contaminants analyzed in this study suggested that their sources were independent of each other. However, there were some localized zones (Ulsan Harbor and ship-building areas) of relatively greater concentrations of PAHs and APs. Generally there were poor relationships between sediment characteristics, such as TOC content and mean grain size, to concentrations of target organic compounds examined. Waterborne concentrations of each class of compounds were generally two orders of magnitude less than the sedimentary concentrations. Total PAH and PCB concentrations are less than the suggested SQGs in nearly all the locations.

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