

Characterization and Distribution of Trace Organic Contaminants in Sediment from Masan Bay, Korea. 1. Instrumental Analysis

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Masan Bay, located on the southeast coast of Korea, is a long and narrow inlet of a semi-closed bay that receives industrial and municipal wastewaters from the cities of Masan and Changwon. In this study, sediments collected from 28 locations on Masan Bay were analyzed for total organic carbon (TOC), nonylphenol (NP), octylphenol (OP), bisphenol A (BPA), organochlorine pesticides (HCB, HCHs, CHLs, and DDTs), individual polychlorinated biphenyl (PCB) congeners, and 16 polycyclic aromatic hydrocarbons (PAHs) to characterize their spatial distribution and contamination status. Concentrations of NP in sediment ranged from 113 to 3890 ng/g on a dry weight basis (dry wt), whereas concentrations of OP and BPA were, on average, 20–110-fold less than those of NP. PAHs were predominated by 4–6-ring compounds with concentrations in the range of 54.1–1100 ng/g dry wt. Concentrations of PCBs in sediment, which were predominated by tetra- and pentachlorobiphenyl congeners, ranged from 10.3 to 148 ng/g, dry wt. Among different OC pesticides analyzed, concentrations of DDTs were the greatest, ranging from 0.4 to 12.6 ng/g dry wt. NP concentrations were greater at coastal locations proximal to the discharges of creeks from inland areas, whereas the concentrations of PCBs and PAHs were greater near the sites of industrial and shipping activities. Concentrations of target analytes were not related to TOC. Although the mean concentrations of PCBs and PAHs in sediments were less than the suggested sediment quality guidelines (SQG), their concentrations in some locations were close to or above the SQG for toxic effects in benthic organisms.

Introduction

Nonylphenol (NP) is a degradation product of nonylphenol polyethoxylates (NPE) that are primarily used in cleaning products and as industrial processing aids (1, 2). Both NP and NPE enter aquatic environments via industrial and municipal wastewater effluents (1–6). The high production

volumes, moderate persistence in sediments, and documented toxicity including estrogenic effects to aquatic organisms have resulted in concern over the environmental risk posed by this class of chemicals (1, 7–11).

Bisphenol A (BPA) is another environmental contaminant released through its use in polycarbonate plastics, epoxy resins, and phenoxy resins, which are utilized in food storage containers and in dental sealants (12–16). BPA has log organic carbon to water partitioning coefficients (K_{oc}) between 2.5 and 3.18 (16), which suggests that sediment is a sink for BPA released into surface waters. Little information is available regarding the concentrations of BPA in sediments.

Polychlorinated biphenyls (PCBs), organochlorine (OC) pesticides such as hexachlorobenzene (HCB), HCH isomers (HCHs), chlordanes (CHLs), DDT, and its derivatives (DDTs) have been detected in sediments for over the last 30 years. Despite a 1970s ban on the use of PCBs and DDTs in many countries including Korea (17, 18), these compounds are ubiquitous and persistent in various environmental media and biota. Thus, they remain a cause for concern (18, 19). Similarly, polycyclic aromatic hydrocarbons (PAHs) are a group of environmental contaminants, many of which are known to be mutagenic and carcinogenic (20). Combustion of fossil fuels, waste incineration, and oil spills are the potential sources of PAHs in the environment (20). Because of their hydrophobicity and recalcitrance, sediment acts as a reservoir for chlorinated organics and PAHs.

Due to the complex nature of contaminants in environmental matrixes, several schemes have been developed to isolate and identify contaminants and their toxic potentials (21). A bioassay-directed fractionation procedure has been used to isolate sewage-treatment work effluents into fractions of decreasing complexity, which were tested for estrogenic activity using a yeast-based estrogen screen (22). The fractionation scheme may vary depending on the characteristics of target contaminants and sample matrix examined. In this study, marine sediment collected from Masan Bay, located at the southeast coast of Korea (Figure 1), was fractionated into three fractions. Instrumental analysis and *in vitro* bioassays were performed to quantify target contaminants and to evaluate estrogenic and dioxin-like potencies, respectively, in each fraction. This paper presents the results of instrumental analysis on the distribution of NP, OP, BPA, individual PCB congeners, OC pesticides (HCB, HCHs, CHLs, and DDTs), and PAHs in sediment. The results of *in vitro* bioassays and mass balance analyses are presented elsewhere (ref 23).

Materials and Methods

Study Area. Masan Bay, located on the southeast coast of Korea, is a long and narrow inlet of a semi-closed bay (Figure 1). Approximately, 75 mg of domestic and industrial wastewater is discharged through several streams into the bay, mainly from the cities of Masan and Changwon. These cities are heavily populated and industrialized. Several industrial complexes comprised of petrochemical, heavy metal, electrical, and plastic industries are located in this region. Primary treatment (sedimentation) is done for wastewater generated from certain industries, and the rest is discharged directly into the bay. A municipal sewage treatment plant exists 3 km west of location 28 of this study but is capable of performing only primary clarification.

Sampling Location and Sampling. Surface sediment (0–5 cm) samples were collected from 28 locations on Masan Bay in May 1998. A global positioning system was employed to identify each location precisely. All samples were collected

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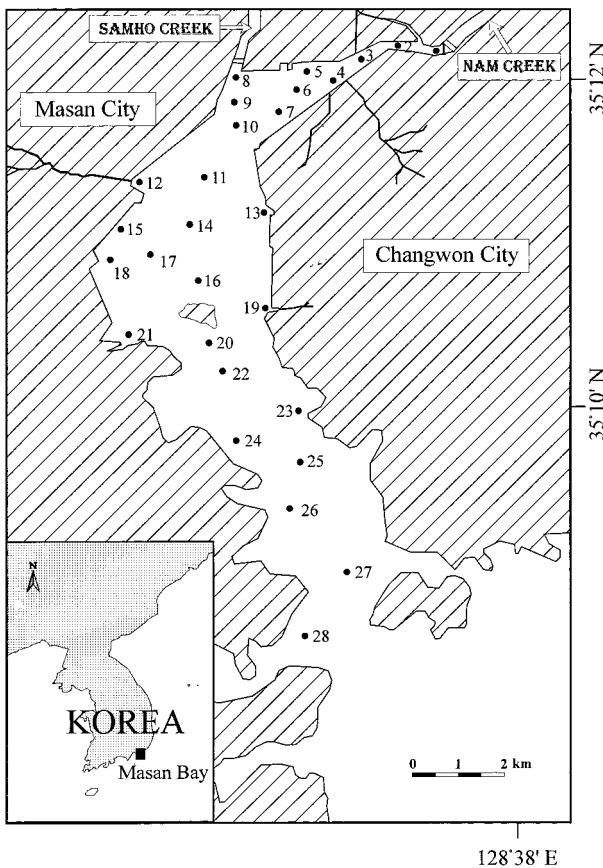


FIGURE 1. Map of the Masan Bay study area in Korea. Sediment samples were collected at locations 1–28.

using a Van Veen grab sampler ($25 \times 40 \times 30$ cm). After collection, pebbles and twigs were removed, then the samples were freeze-dried and ground with a mortar and pestle. Although freeze-drying has been used in PAH and OC analysis of sediment, it is not known whether this process would affect NP and BPA concentrations in sediment. Therefore, it should be noted that the concentrations of NP and BPA presented in this study refer to those for a freeze-dried sediment. Samples were stored in precleaned high-density polyethylene (HDPE) bottles at -20°C until extraction. Total organic carbon (TOC) was analyzed at the Soil and Plant Nutrient Laboratory at Michigan State University.

Extraction and Fractionation. NP, OP, BPA, PAHs, OC pesticides, and PCBs in sediments were extracted following the methods described elsewhere (11, 24) with some modifications. Sediment samples (~ 20 g + ~ 100 g of Na_2SO_4) were Soxhlet extracted for 20 h using 400 mL of high-purity dichloromethane (DCM). Extracts were treated with acid-activated copper granules to remove sulfur and concentrated to 1 mL.

Extracts were passed through 10 g of activated Florisil (60–100 mesh size; Sigma, St. Louis, MO) packed in a glass column (10 mm i.d.) for cleanup and fractionation. The first fraction (F1) eluted with 100 mL of high-purity hexane contained PCBs, HCB, and *p,p'*-DDE. Remaining OC pesticides and PAHs were eluted in the second fraction (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 high-purity methanol.

Instrumental Analysis. Reverse-phase high-performance liquid chromatography (HPLC) with fluorescence detection was used to quantify NP, OP, and BPA (6, 11). Details of HPLC analysis and columns are described elsewhere (11). NP, OP, and BPA detection limits for the analytical method

were 1 ng/g dry weight (dry wt). Sample extracts were injected into a gas chromatograph equipped with a mass selective detector (GC-MS) for the confirmation of NP and BPA by selected ion monitoring (SIM). Ions monitored were *m/z* 107, 135, and 121 for NP and *m/z* 213, 228, and 119 for BPA. Representative chromatograms of sediment samples and standards are shown in Figure 5 (in Supporting Information). The oven temperature program and column conditions for GC-MS are described below.

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 i.d.) coated with DB-17 [(50% phenyl)-methyl polysiloxane; J&W Scientific, Folsom, CA] at 0.25 μm film thickness was used. The PAH standard (AccuStandard, New Haven, CT) consisted of 16 priority pollutant PAHs identified by the U.S. Environmental Protection Agency (U.S. EPA) method 8310. The mass spectrometer was operated under the SIM mode. Molecular ions were monitored at the following *m/z*: 128 for naphthalene; 152 for acenaphthylene; 154 for acenaphthene; 165 and 166 for fluorene; 178 for phenanthrene and anthracene; 202 for fluoranthene and pyrene; 228 for chrysene and benz[a]anthracene; 252 for benzo[a]pyrene, benzo[k]fluoranthene, and benzo[b]fluoranthene; and 276 and 278 for indeno[1,2,3-*cd*]pyrene, benzo[ghi]perylene, and dibenz[a,h]anthracene. The detection limit for PAHs was 10 ng/g dry wt.

OC pesticides and PCBs were quantified using a gas chromatograph (Perkin-Elmer series 600) equipped with ^{63}Ni electron capture detector (GC-ECD). Concentrations of 98 individually resolved peaks were summed to obtain total PCB concentrations. PCB congeners are referred by Ballschmiter and Zell numbers. OC pesticides were quantified from individually resolved peak areas based on the peak areas of standards. Detection limits of OC pesticides and PCBs for this method were 0.01 and 1.0 ng/g dry wt, respectively.

Sediments were spiked with NP, OP, BPA, PAH, OC pesticide mixture (CLP-023R, CLP-024R, AccuStandard), and PCB standards and passed through the entire analytical procedure to determine recoveries ($n = 3$). Recoveries of individual PCB congeners and *p,p'*-DDE in F1 were $99 \pm 5\%$ and $90 \pm 5\%$ ($n = 3$), respectively. No other spiked compounds were detected in F1. Recoveries of PAHs and OC pesticides in F2 were $84 \pm 9\%$, and $105 \pm 5\%$, respectively. No other spiked compounds were detected in F2. Recoveries of NP, OP, and BPA in F3 were $73 \pm 14\%$, $65 \pm 11\%$, $60 \pm 8\%$, respectively (Table 5 in Supporting Information). No other spiked compounds were detected in F3. Reported concentrations were not adjusted for recovery. Procedural blanks were analyzed with every set of six samples to check for interference or contamination arising from solvents or glassware.

Results and Discussion

Alkylphenols and Bisphenol A. NP, OP, and BPA were detected in sediment extracts from all 28 locations in Masan Bay (Table 1). Concentrations of NP in sediment ranged from 113 to 3890 (mean: 510) ng/g dry wt. OP concentrations ranged from 3.97 to 179 (mean: 18.1) ng/g dry wt. Reported concentrations of NP and OP in sediments varied widely depending on the location. Generally, NP concentrations were greater in coastal sediments collected near the outfalls of creeks and streams draining through the inland areas. NP concentrations in Masan Bay sediments fell within the range reported for a study of 30 U.S. rivers except for those at location 9, which contained greater concentrations than those reported for U.S. sediments (2). The greatest concentration of 3890 ng/g dry wt is 5.5-fold greater than the standard deviation of the mean NP concentration and, thus, appears to qualify as an outlier. However, the highest concentration

TABLE 1. Total Organic Carbon (TOC) Content (%) and Concentrations (ng/g, Dry Wt) of Nonylphenol (NP), Octylphenol (OP), and Bisphenol A (BPA) in Sediment from Masan Bay, Korea

sampling location ^a	TOC	NP ^b	OP	BPA
1	1.22	329	12.9	10.8
2	0.75	141	3.97	14.6
3	0.93	369	6.04	10.9
4	1.28	1090	30.7	15.4
5	1.74	339	7.47	5.44
6	1.39	284	10.4	4.95
7	1.73	646	11.5	50.1
8	2.49	832	14.1	5.34
9	4.06	3890	179	50.3
10	2.26	1020	14.0	21.2
11	1.55	289	13.7	5.81
12	1.62	713	26.4	10.3
13	1.74	126	5.22	4.92
14	1.57	175	9.24	6.42
15	2.67	395	7.35	13.9
16	1.62	346	6.96	6.76
17	2.15	453	9.25	2.70
18	2.55	320	23.6	13.4
19	2.44	224	13.7	8.29
20	1.97	255	6.83	13.2
21	2.15	417	7.02	11.0
22	2.44	143	7.81	5.49
23	2.73	329	15.8	9.95
24	1.70	336	15.0	7.92
25	1.68	120	8.34	2.95
26	1.80	346	15.2	3.25
27	2.15	113	8.60	3.11
28	2.15	227	17.3	4.84

mean \pm SD 1.95 ± 0.65 510 ± 710 18.1 ± 32.1 11.5 ± 11.8

^a See Figure 1 for details. ^b NP also indicates approximately 10% nonylphenol monoethoxylate (NPE10) for all samples except location 9 in which NPE10 contributed 50% of NP concentration.

in sediment collected at location 9 can be explained by its proximity to sources. Sediment at this location has been directly exposed to inputs from Samho Creek, which drains through Masan City.

In the reverse-phase HPLC method used in this study, NP and NPE10 (nonylphenol monoethoxylate) eluted very closely. Therefore, a portion of NP measured in this may represent NPE. To separate NP from NPE, sample extracts were injected to a GC-MS. On the basis of chromatographic characteristics, it was found that the concentrations of NPE were approximately 10% to the total NP concentrations for most samples, which had concentrations greater than 500 ng/g (Figure 5 in Supporting Information).

NP and OP are both biodegradation products of their corresponding ethoxylates, which are used as nonionic surfactants (9). Masan Bay receives industrial and municipal wastewaters both directly via discharge to the bay and indirectly via discharge to Nam and Samho Creeks and several small streams, which are the major sources of these compounds. Spatial distribution of NP concentrations in sediment from Masan Bay revealed a decrease in concentration with the distance from the source (Figure 2). Generally, in open waters, NP concentrations decreased by 2–4-fold relative to those in the adjacent coastal location. NP concentrations in sediment were least at a more open area (location 27; 113 ng/g dry wt), which was 34-fold less than the greatest concentration measured in this study.

Concentrations of OP were about 1–2 orders of magnitude less than those of NP, which suggests lesser usage of octylphenol polyethoxylates than NPEs. In general, there does not appear to be any relationship between the concentrations of APs and the sediment TOC content or PCB and PAH concentrations (Table 2). This suggests that the sources of APs are independent from those of PCBs and PAHs.

BPA concentrations in sediment ranged from 2.70 to 50.3 ng/g dry wt (mean: 11.5). Similar to that for NP and OP, BPA concentrations were the highest at location 9. The likely sources of BPA in sediment were leachates from polycarbonate and plastic materials (15, 25).

PAHs. PAHs were next in abundance to APs in Masan Bay sediments. PAHs were detectable in sediments at all 28 locations (Table 3). Concentrations of PAHs ranged from 36.6 to 1100 ng/g dry wt. The greatest concentration of total PAHs was detected at location 12 (1100 ng/g; Figure 2). The measured concentrations of PAHs were comparable to those reported earlier in 1996 for Masan Bay sediment (208–2670 ng/g dry wt; 26). This is despite the fact that the earlier study had measured 24 individual PAHs in sediments while in the present study only 16 PAHs were measured. A consensus marine sediment quality guideline (SQG) for total PAHs has been suggested to be 290 μ g/g OC (27). The organic carbon-normalized concentrations of total PAHs in sediment from Masan Bay were (mean: 18 μ g/g), on average, 16 times less than the suggested threshold effect concentrations. However, the greatest concentration of PAHs measured at location 12 was only 4 times less than the threshold effect concentrations. When threshold effect concentrations reported for individual PAHs were compared (27), benzo[a]pyrene, benzo[b]fluoranthene, and benzo[k]fluoranthene concentrations in sediment collected at location 12 exceeded the limits of 9, 7, and 6 μ g/g OC, respectively.

High molecular weight PAHs with four to six rings predominated in sediment samples (Figure 3). Benzo[b]fluoranthene and benzo[k]fluoranthene were the most dominant components collectively accounting for, on average, 17% of the total PAH concentrations. Benzo[ghi]perylene was the next dominant aromatic hydrocarbon comprising approximately 15% of the total PAHs (Figure 3).

PAHs originate mainly from petrogenic and pyrolytic sources. Some molecular ratios of specific hydrocarbons have been developed to distinguish between PAHs generated from different sources (28). For instance, a ratio of fluoranthene to pyrene concentrations (Fluo/Py) greater than 1.0 is characteristic of a pyrolytic origin whereas ratios less than 1.0 are characteristic of petroleum hydrocarbons. Similarly a ratio of indeno[1,2,3-cd]pyrene to benzo[ghi]perylene (I123cdP/BghiP) greater than 1.0 suggests combustion sources, whereas I123cdP/BghiP ratios less than 1.0 imply petrogenic sources. Nevertheless, for both the ratios the limits between the two processes are not precise (28, 29). The Fluo/Py ratios for Masan Bay sediment samples varied depending on the locations with an overall mean value of 1.01. Generally the northeastern locations had Fluo/Py ratios more than 1, while the southern parts had Fluo/Py ratios less than 1. The ratios of I123cdP/BghiP were less than 1.0 for all the locations (range: 0.26–0.76). These results suggest that the sources of PAHs to Masan Bay were both petrogenic and pyrolytic. The northern locations, which are proximal to urban and industrial areas, may receive more pyrolytic inputs whereas the southern locations may be influenced by petroleum inputs.

The spatial distribution of PAH concentrations were different from those observed for APs (Figure 2). Relatively greater concentrations of PAHs were found in sediment collected along the northwestern locations of the bay (Figure 2), which suggest the presence of local sources in this region.

PCBs. PCBs were detected in all the sediment samples at concentrations ranging from 10.3 to 148 ng/g dry wt (Table 3). Few studies have reported PCB concentrations in Korean sediment. Sediment collected from Masan Bay in 1992 contained PCB concentrations ranging from 8 to 210 ng/g dry wt (30), which are similar to those reported for sediment collected in 1998 that are reported in this study. This suggests the persistence and possibly continuing inputs of PCBs in

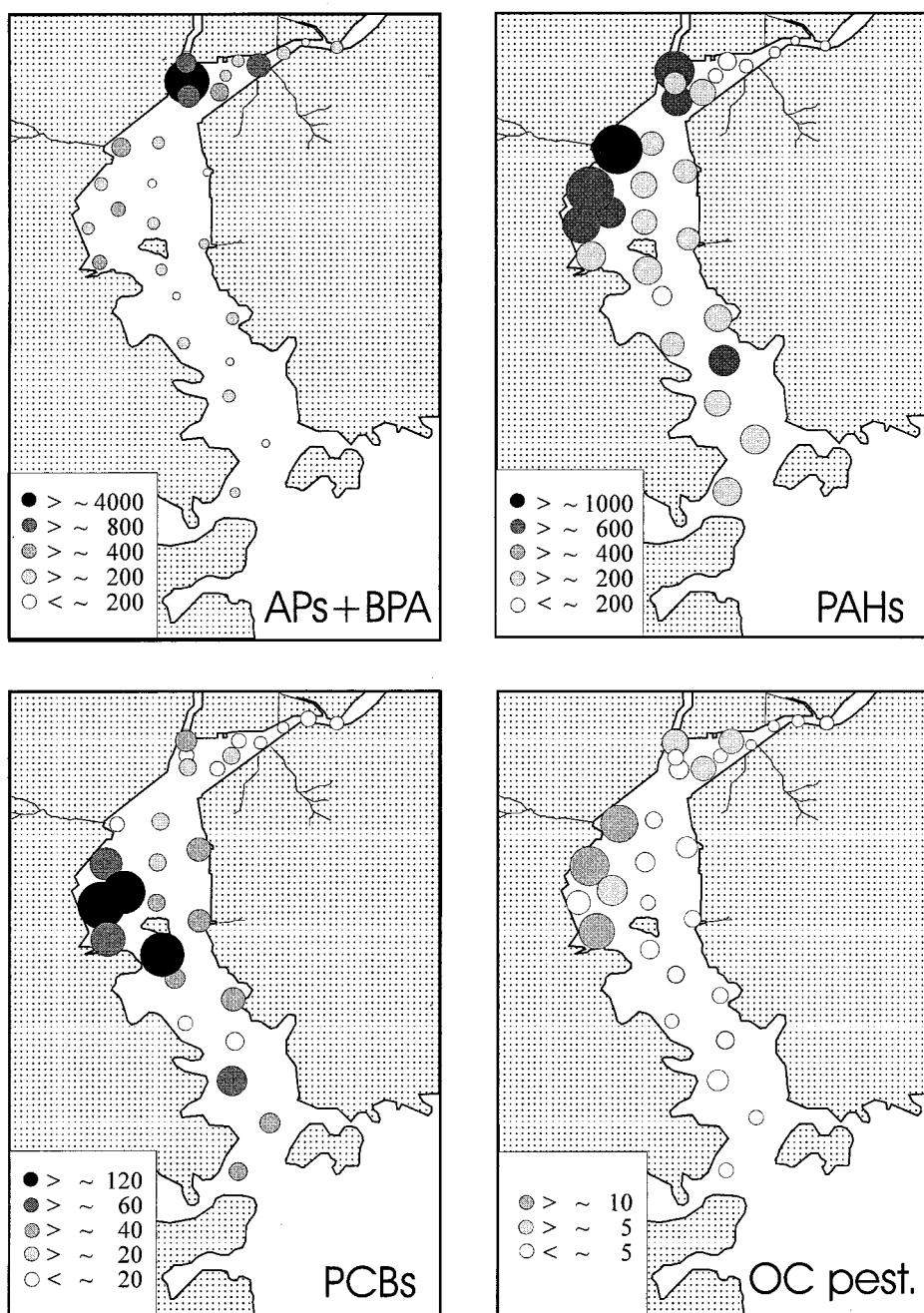


FIGURE 2. Spatial distribution of alkylphenols (APs), bisphenol A (BPA), PAHs, PCBs, and organochlorine (OC) pesticides in sediment from Masan Bay, Korea. Concentration units are in nanograms/gram, dry wt.

TABLE 2. Relationships (r) between TOC (%) and Concentrations (ng/g, Dry Wt) of Alkylphenols (APs), Polychlorinated Biphenyls (PCBs), and Polycyclic Aromatic Hydrocarbons (PAHs) in Sediment from Masan Bay, Korea

TOC	APs ^a	PCBs ^b	PAHs ^c
TOC	0.002	0.081	0.156
APs		0.024	0.069
PCBs			0.116
PAHs			

^a APs = nonylphenol + octylphenol + bisphenol A. ^b PCBs = sum of 98 individual congeners. ^c PAHs = sum of 16 priority components.

Masan Bay. Soil and sediment collected from Nakdong River Estuary in southeastern Korea contained PCB concentrations in the range of 0.3–8500 ng/g dry wt (31). PCB concentrations were greater in soils and sediment collected near industrial

areas than that from nonindustrial locations in Korea (31). The organic carbon-normalized concentrations of PCBs in sediments ranged from 365 to 6450 ng/g OC (mean: 1930 ng/g). Although the mean concentration was less than a suggested SQG based on equilibrium partitioning, which was 2900 ng/g OC (32), sediment samples collected at locations 17, 18, 20, 21, and 26 exceeded the guidelines.

Spatial distribution of PCB concentrations in sediment suggested the presence of sources along the midwestern locations of Masan Bay (Figure 2). PCB concentrations greater than 100 ng/g dry wt were found at locations 17, 18, and 20 situated along the midwestern region of the bay. Concentrations of PCBs were not related to TOC or any other target analytes measured in this study (Table 2). However, the hypothesis that the increase in PCB or PAH concentrations with an increase in organic carbon content may have been obscured by the differences in sample locations.

TABLE 3. Concentrations (ng/g, Dry Wt) of Polychlorinated Biphenyls (PCBs), Organochlorine Pesticides (HCB, HCHs, CHLs, DDTs), and Polycyclic Aromatic Hydrocarbons (PAHs) in Sediment from Masan Bay, Korea

sampling location ^a	PCBs ^b	HCB ^c	HCHs ^d	CHLs ^e	DDTs ^f	PAHs ^g
1	12.8	0.72	0.53	<0.01	0.66	54.1
2	17.2	0.91	0.11	<0.01	0.40	41.5
3	10.3	0.72	0.15	<0.01	0.42	55.9
4	11.8	0.54	0.10	<0.01	0.49	90.6
5	15.2	0.95	1.65	0.22	3.11	144
6	19.6	0.35	0.23	0.06	1.27	95.8
7	14.9	0.90	0.36	0.19	4.28	316
8	31.8	1.27	0.39	0.34	4.97	688
9	14.8	0.65	0.09	<0.01	1.77	224
10	20.3	1.87	0.18	0.12	1.61	428
11	19.6	0.46	0.15	0.07	2.18	255
12	15.6	<0.01	0.56	0.24	12.5	1100
13	38.1	0.80	0.31	0.04	3.19	266
14	20.0	0.42	0.19	0.05	3.12	308
15	67.0	1.54	0.28	0.17	12.6	984
16	20.9	0.36	0.14	0.08	1.69	275
17	119	1.23	0.29	0.22	6.71	434
18	148	0.41	0.27	0.04	4.78	589
19	35.1	0.25	0.18	0.07	2.22	330
20	127	0.25	0.23	0.04	2.99	342
21	80.2	<0.01	0.27	0.21	11.3	567
22	28.6	0.38	0.15	0.05	2.27	299
23	37.4	0.39	0.18	0.07	1.76	424
24	15.5	<0.01	0.21	0.03	1.77	233
25	21.5	0.40	0.20	0.02	2.39	391
26	60.6	0.87	0.38	0.07	3.20	276
27	28.8	0.43	0.21	0.03	1.55	359
28	21.6	0.32	0.41	0.02	1.51	347
mean \pm SD	38.4 \pm 37.2	0.62 \pm 0.45	0.30 \pm 0.29	0.09 \pm 0.09	3.45 \pm 3.38	353 \pm 252

^a See Figure 1 for details. ^b PCBs = sum of 98 individual congeners. ^c HCB = hexachlorobenzene. ^d HCHs = α - + β - + γ -hexachlorocyclohexanes. ^e CHLs = α - + γ -chlordanes. ^f DDTs = *p,p'*-DDE + *p,p'*-DDD + *p,p'*-DDT. ^g PAHs = sum of 16 priority components.

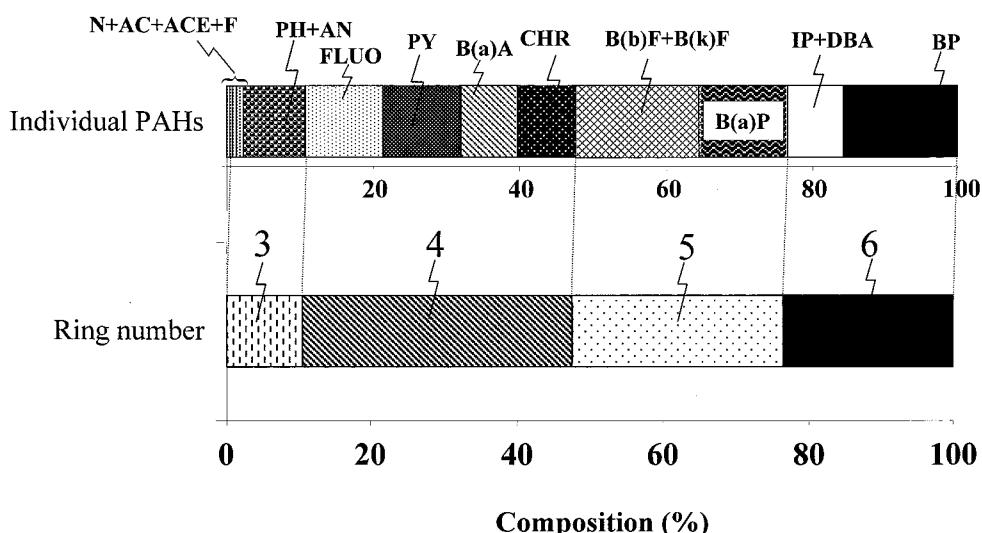


FIGURE 3. Mean composition of PAH ring number (wt %) and individual PAHs to total PAH concentrations in sediment from Masan Bay, Korea. N, naphthalene; AC, acenaphthene; ACE, acenaphthylene; F, fluorene; PH, phenanthrene; AN, anthracene; FLUO, fluoranthene; PY, pyrene; B(a)A, benz[a]anthracene; CHR, chrysene; B(b)F, benzo[b]fluoranthene; B(k)F, benzo[k]fluoranthene; IP, indeno[1,2,3-*cd*]pyrene; DBA, dibenz[a,h]anthracene; BP, benzo[ghi]perylene.

The contribution of individual chlorobiphenyl (CB) isomers and congeners to the total PCB concentrations varied among locations. Sediment collected at locations 4, 5, and 7 contained great proportions of di-, tri-, and tetra-CBs, whereas those from locations 1, 2, 8, 10, and 23 had higher proportions of penta-, hexa-, and hepta-CBs. Overall, tri-, tetra- and penta-CBs collectively accounted for 81% of total PCB concentrations (Figure 6 in Supporting Information). This pattern is different from those observed in sediments from several marine coastal locations in which penta-, hexa-

hepta-, or octa-CBs contributed to greater proportions of the total PCBs (24, 33, 34). An earlier study also reported the presence of lower chlorinated PCB congeners resembling Kanechlor 300 or Aroclor 1242 in several locations in Masan Bay (30). In general, congeners 110 (2,3,3',4',6-pentaCB) and 31+28 (2,4',5- and 2,4,4'-triCBs) were prevalent in most samples each accounting for approximately 5% of the total PCB concentrations (Figure 4). Non-*ortho*-coplanar PCB congener 77 (3,3',4,4'-tetraCB) was detected in some samples, while other non-*ortho*-substituted congeners 126 (3,3',4,4',5-

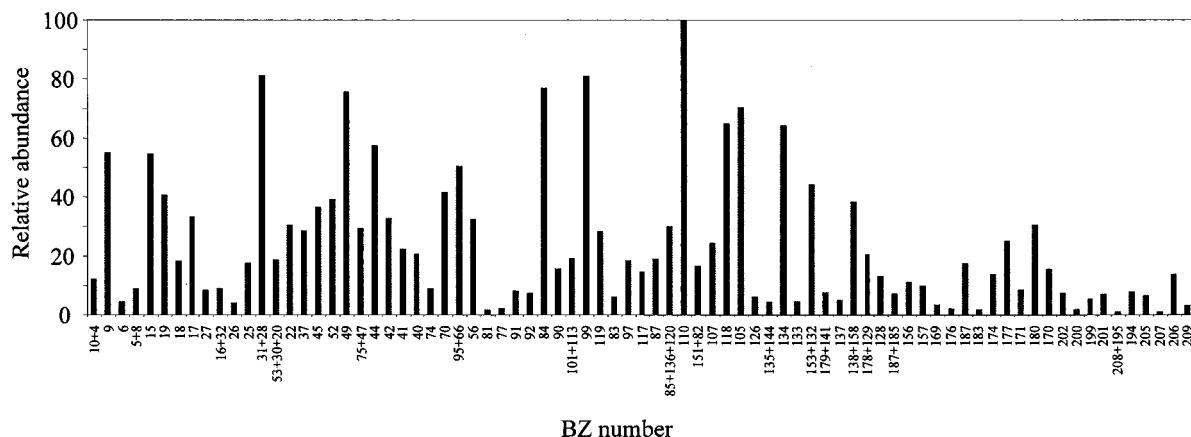


FIGURE 4. Relative composition of PCB isomers and congeners in sediment from Masan Bay, Korea. Abundances are normalized to BZ number 110, which is treated as 100. Concentration of the congener 110 represents 1.9 ng/g, dry wt.

TABLE 4. Mean Concentrations of Non- and Mono-*ortho*-PCB Congeners and Their 2,3,7,8-Tetrachlorodibenzo-*p*-Dioxin Equivalents (TEQs; pg/g, Dry Wt) in Sediment from Masan Bay, Korea

PCB congener	TEF ^a	PCB concn	TEQs concn
77	0.0001	40 (<20–60) ^b	0.004 (<0.002–0.006)
126	0.1	<20	<2
169	0.01	<20	<0.2
105	0.0001	1340 (130–7510)	0.134 (0.013–0.751)
118	0.0001	1230 (160–4610)	0.123 (0.016–0.461)
156	0.0005	210 (40–900)	0.105 (0.02–0.45)
total TEQs			0.366 (0.049–1.66)

^a Toxic equivalency factors, from ref 39. ^b Values in parentheses indicate range.

pentaCB) and 169 (3,3',4,4',5,5-hexaCB) were not detected (<20 pg/g dry wt) (Table 4). 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin equivalents (TEQs) were estimated using mammalian toxic equivalency factors (TEF) for non- and mono-*ortho*-PCB congeners (35). Concentrations of TEQs ranged from 0.049 to 1.66 pg/g dry wt (Table 4). The suggested SQG for 2,3,7,8-TCDD ranges from 0.014 to 210 pg/g dry wt (36). Thus the TEQs estimated for PCBs in sediment were at the lower end of the guideline values. PCB congeners 105 (2,3,3',4,4'-pentaCB) and 118 (2,3',4,4',5-pentaCB) were the predominant contributors to TEQs in sediment.

Organochlorine Pesticides. Concentrations of OC pesticides in Masan sediment extracts were relatively low (Table 3). Among the different OC pesticides analyzed, concentrations of DDTs were the greatest, ranging from 0.4 to 12.6 ng/g dry wt. Concentrations of other OC pesticides were less than 10 ng/g, dry wt (Table 3). In general, DDTs accounted for 77% of the total organochlorine pesticide concentrations in sediments (Figure 7 in Supporting Information). *p,p'*-DDD contributed 61% of the total DDT concentrations in sediments, which is consistent with the transformation of *p,p'*-DDT to *p,p'*-DDD under anaerobic conditions.

Low concentrations of OC pesticides in sediment can be explained by the fact that there is little farming activity around Masan Bay. Furthermore, OC pesticide use was banned in Korea in the 1970s (17). There is no historical data regarding OC pesticide concentrations in Masan Bay. The data presented here establish the baseline for future monitoring of these compounds in Masan Bay. Overall the analysis suggested that OC pesticides were not of significant concern at the time the samples were collected.

Summary

The relative abundance of organic contaminants measured in Masan Bay was in the order NP > PAHs > PCBs > OP > BPA > OC pesticides. Spatial distributions of these contaminants in Masan Bay suggested that their sources were independent of each other. The predicted water concentrations of NP and BPA in Masan Bay, based on their concentrations in sediment and *K_{oc}* values, were less than those reported to elicit toxic responses in aquatic organisms. Concentrations of PCBs and PAHs exceeded the proposed sediment quality guidelines at some locations in Masan Bay.

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Supporting Information Available

Table 5 showing the recoveries of target analytes spiked and passed through the whole analytical procedure; Figure 5 showing GC-MS selected ion monitoring chromatograms of NP, NPE, and BPA standards and a sediment sample extract from Masan Bay; Figure 6 showing mean homologue composition (%) of PCBs in sediment; and Figure 7 showing relative distribution of OC pesticides and the composition of individual isomers/congeners to their corresponding total concentrations (5 pages). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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SUPPORTING INFORMATION

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6 Supplementary Information Available

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8 A table (Table 5) showing the recoveries of target analytes spiked and passed through the whole
9 analytical procedure, figure 5 showing GC-MS-selected ion monitoring chromatograms of NP,
10 NPE and BPA standards and a sediment sample extract from Masan Bay, figure 6 showing mean
11 homolog composition (%) of PCBs in sediment, and figure 7 showing relative distribution of OC
12 pesticides and the composition of individual isomers/congeners to their corresponding total
13 concentrations will appear as supporting information.

14

15 **FIGURE 5.** Gas chromatograms of NP, NPE and BPA standards (A) and a sediment sample
16 extract (B) from Masan Bay. Samples were analyzed using GC-MS by selected ion
17 monitoring (SIM). For the ions monitored and GC conditions refer text.

18

FIGURE 6. Mean homolog composition (%) of PCBs in sediment from Masan Bay, Korea.

19

20

FIGURE 7. Relative distribution of OC pesticides in sediment and the composition (%) of
individual isomers or derivatives to their corresponding total concentrations.

21

SUPPORTING INFORMATION**TABLE 5.** Recoveries (%) of Target Analytes^a

Compound	Recovery (%)
	Mean (SD)
NP ^a	73 (14)
OP ^b	65 (11)
BPA ^c	60 (8)
PCBs ^d	99 (5)
HCHs ^e	99 (3)
CHLs ^f	110 (5)
DDTs ^g	111 (5)
PAHs ^h	84 (9)

^a NP = nonylphenol. ^b OP = octylphenol. ^c BPA = bisphenol A.

^d PCBs = polychlorinated biphenyls, average for 37 dominant congeners.

^e HCHs = α + β + γ -hexachlorocyclohexanes.

^f CHLs = α - + γ -chlordanes.

^g DDTs = *p,p'*-DDE + *p,p'*-DDD + *p,p'*-DDT.

^h PAHs = polycyclic aromatic hydrocarbons, 16 priority components.

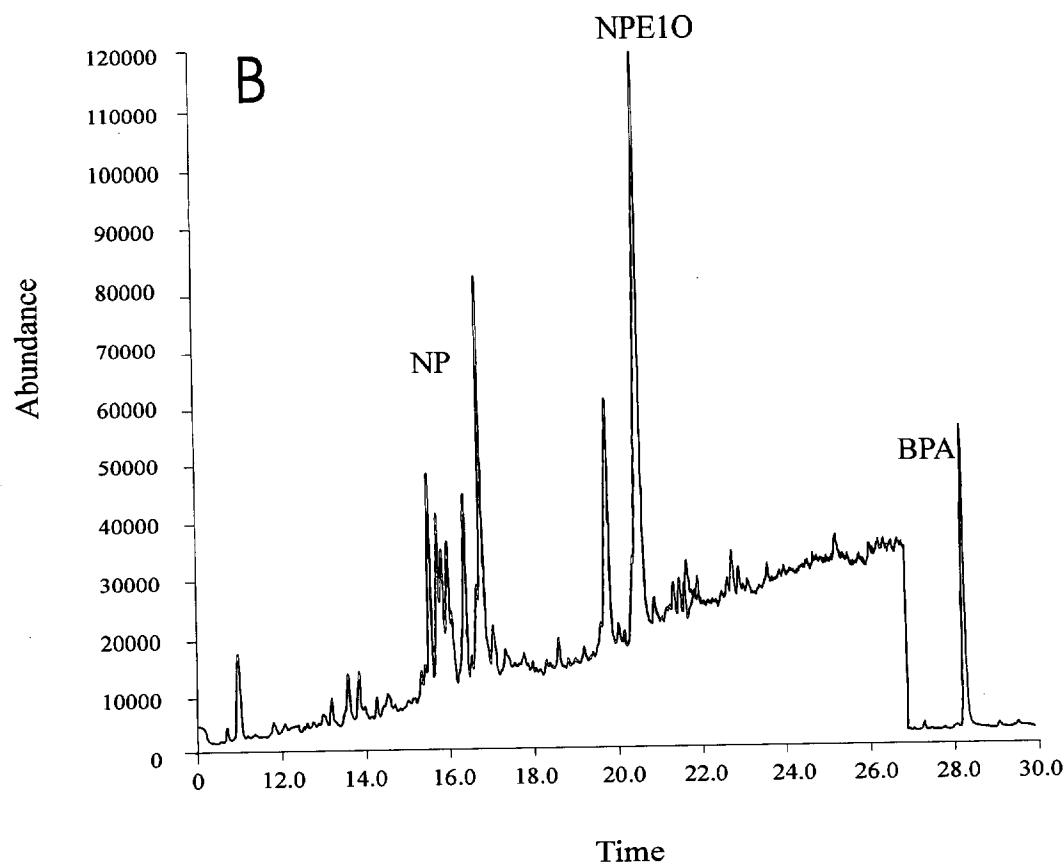
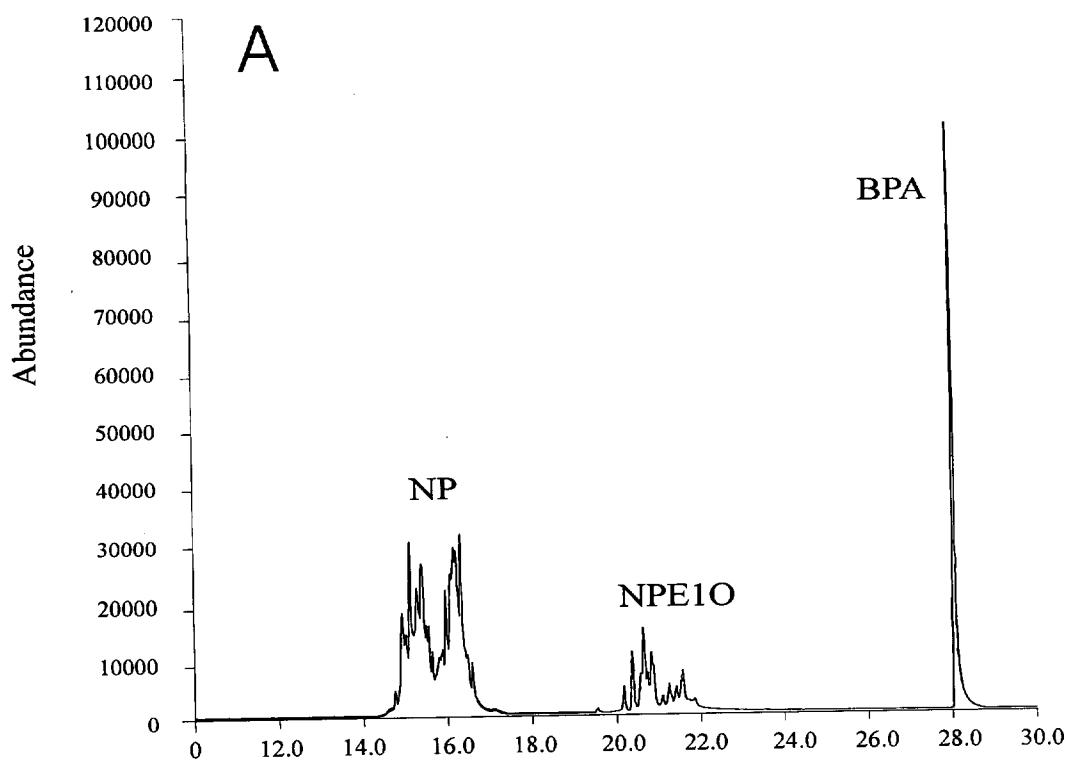


Fig. 6, supporting information
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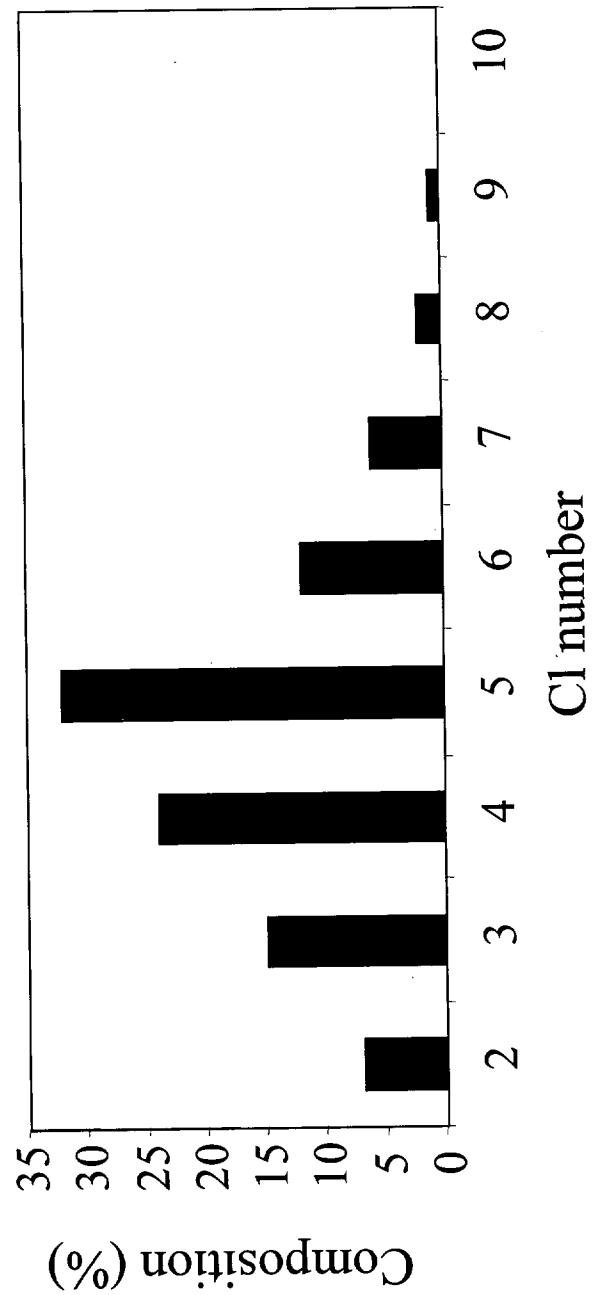


Fig. 7., supporting information
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