

Hydroxylated Polychlorinated Biphenyls (OH-PCBs) in the Aquatic Environment : Levels and Congener Profiles in Sediments from Osaka, Japan

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Abstract

In this study, levels and congener profiles of hydroxylated polychlorinated biphenyls (OH-PCBs) was investigated in the aquatic environment. OH-PCBs were determined in sediment samples from the rivers and estuaries of Osaka City, Japan. OH-PCBs extracted from samples were derivatized with dimethyl sulfate, and the methoxylated PCBs (MeO-PCBs) were quantified using a gas chromatograph/high-resolution mass spectrometer (GC/HRMS). A large number of OH-PCB congeners were detected in all the sediment samples. Mean OH-PCB concentration was 24ng/g-dry wt. (0.90-150ng/g-dry wt.), and ratios of OH-PCBs to PCBs ranged from 1.4-13%. Some unknown OH-PCB isomers were detected in sediment samples. It was speculated that most of these isomers substitute the OH-group on *meta*- or *para*-position, because they showed a distinctive fragment ion, $[M-COCH_3]^+$. OH-PCBs in sediments might be formed biologically or chemically by the oxidation process of PCBs in the environment.

Introduction

Hydroxylated polychlorinated biphenyls (OH-PCBs) are well known as metabolites of polychlorinated biphenyls (PCBs) in animals. Studies on OH-PCBs in the blood of human and wildlife are available, and it has been noted that OH-PCBs congeners with OH-group on *meta*-position and chlorine substitution on neighboring positions might cause thyroid dysfunction in human¹.

Also in the abiotic environment, it is possible that OH-PCBs can be generated by the chemical reaction between PCBs and OH radicals in the atmosphere². However, investigations on OH-PCBs in abiotic samples are limited. Darling et al.³ reported for the first time that OH-PCBs existed in precipitation and surface water samples collected from southern Ontario in Canada. In addition, they demonstrated that mono- and di-chlorinated OH-PCB congeners were mainly detected in the water sample near a sewage treatment plant (STP)³. As an expanded investigation, Ueno et al.⁴ reported that total concentrations of OH-PCBs in surface water samples ranged from 0.87 to 130pg/L, and higher levels were found near STPs, indicating release of OH-PCBs from STPs. However, their study showed similar OH-PCB congener profiles between rain and most of surface water samples, implying that atmospheric deposition of these metabolites might be another possible source to surface water. It has been also reported that OH-PCBs could be formed in the sediment through aerobic biodegradation⁵. If OH-PCBs are persistent in the aquatic environment, these metabolites may have adverse effects on wildlife and human.

In Japan, adequate treatment of wastes containing PCBs has begun in accordance with "Law Concerning Special Measures Against PCB Waste". Therefore, the possibility of OH-PCBs being unintentionally formed during the treatment process is of

concern. In this study, we investigated residue levels and congeners of OH-PCBs in sediments collected from an urban city in Japan. There are theoretically 837 OH-PCB congeners, but in the current study individually resolved peaks in sediment samples were identified using 83 synthesized standards (tri- to penta-chlorinated congeners)⁶ and 72 commercial standards.

Materials and Methods

Sediment samples ($n=18$) were collected from the rivers and estuaries of Osaka City, Japan. $^{13}\text{C}_{12}$ -labeled OH-PCBs were spiked into 5-20g of wet sample as internal standards, and OH-PCBs were extracted twice with 30mL of acetonitrile. The liquid phase was collected by centrifugation, and then was washed twice with 20mL of *n*-hexane. After 250mL of 5%NaCl/water was added to the acetonitrile phase, OH-PCBs were extracted twice with 50mL of *n*-hexane. The extract was concentrated to 1mL and passed through a florisil cartridge column (Sep-Pak Florisil, Waters, MA). The first fraction eluted with 6mL of 0.5% diethylether/*n*-hexane was discarded in order to remove interfering compounds such methoxylated PCBs (MeO-PCBs), which exist naturally in sediments. The second fraction containing OH-PCBs was eluted with 6mL of 50% acetone/methanol. This fraction was evaporated, and then OH-PCBs were derivatized to MeO-PCBs by reaction with 0.5mL of dimethyl sulfate and 4mL of 3N KOH/ethanol. The derivatized solution was heated at 70°C for an hour under alkali condition. 4mL of 5% NaCl/water was added, and then MeO-PCBs were extracted twice with 2mL of *n*-hexane. The extract solution was concentrated to 1mL, and passed through a florisil cartridge column for clean-up. After the column was washed with 2mL of *n*-hexane, MeO-PCBs were eluted with 6mL of 5% diethylether/*n*-hexane. This fraction was concentrated to 0.1mL for measurement of OH-PCBs (MeO-PCBs).

PCBs in dried sediment samples were extracted with toluene using a Soxhlet. After $^{13}\text{C}_{12}$ -labeled PCBs were spiked, the extract was cleaned up using 1N KOH/ethanol, concentrated sulfuric acid, and a silica gel cartridge column (Sep-Pak Silica, Waters, MA). The clean-up solution was concentrated to 0.1mL for measurement of PCBs.

Identification and quantification of OH-PCBs (MeO-PCBs) and PCBs were performed using a gas chromatograph (6890GC, Agilent, CA) / high-resolution mass spectrometer (Autospec-Ultima, Micromass, UK). HT-8PCB column (60m x 0.25mm id, Kanto Chemical, Japan) was used for GC. The MS was operated under selective ion monitoring (SIM) mode with resolving power of more than 10,000. Quantifications of MeO-PCBs were conducted using the most intensive molecule ion and its isotope ion. Two fragment ions ($[\text{M}-\text{CH}_3\text{Cl}]^+$ and $[\text{M}-\text{COCH}_3]^+$) were also monitored for confirmation. These fragment ions are useful to surmise substituting position of OH group; *ortho*-MeO-PCBs have $[\text{M}-\text{CH}_3\text{Cl}]^+$, and *meta*-MeO-PCBs and *para*-MeO-PCBs have $[\text{M}-\text{COCH}_3]^+$ as a distinctive fragment ion, respectively.

OH-PCBs were identified by available standards. Commercial OH-PCBs (MeO-PCBs) standards were purchased from Wellington Laboratories, Inc. (Canada) and AccuStandard, Inc. (CT). Some OH-PCB congeners were synthesized by the coupling of chlorinated aniline and chlorinated phenol⁶.

Results and Discussion

OH-PCB congeners were detected in all sediment samples. The peaks that matched the GC retention times and the isotopic ratio of molecule ion to standard solution were quantified as identified OH-PCBs, but some unidentified peaks that didn't match the retention time were found (Figure 1). These unknown peaks matched the theoretical isotopic ratio of molecule ion in OH-PCB, and hence they were also quantified as OH-PCBs. For each congener, the numbers of isomers detected in the sediment

sample, which showed the highest concentration of OH-PCBs, were 8 of OH-monoCB, 7 of OH-diCB, 26 of OH-triCB, 28 of OH-tetraCB, 23 of OH-pentaCB, 10 of OH-hexaCB, 6 of OH-heptaCB and 2 of OH-octaCB. It was speculated that the most

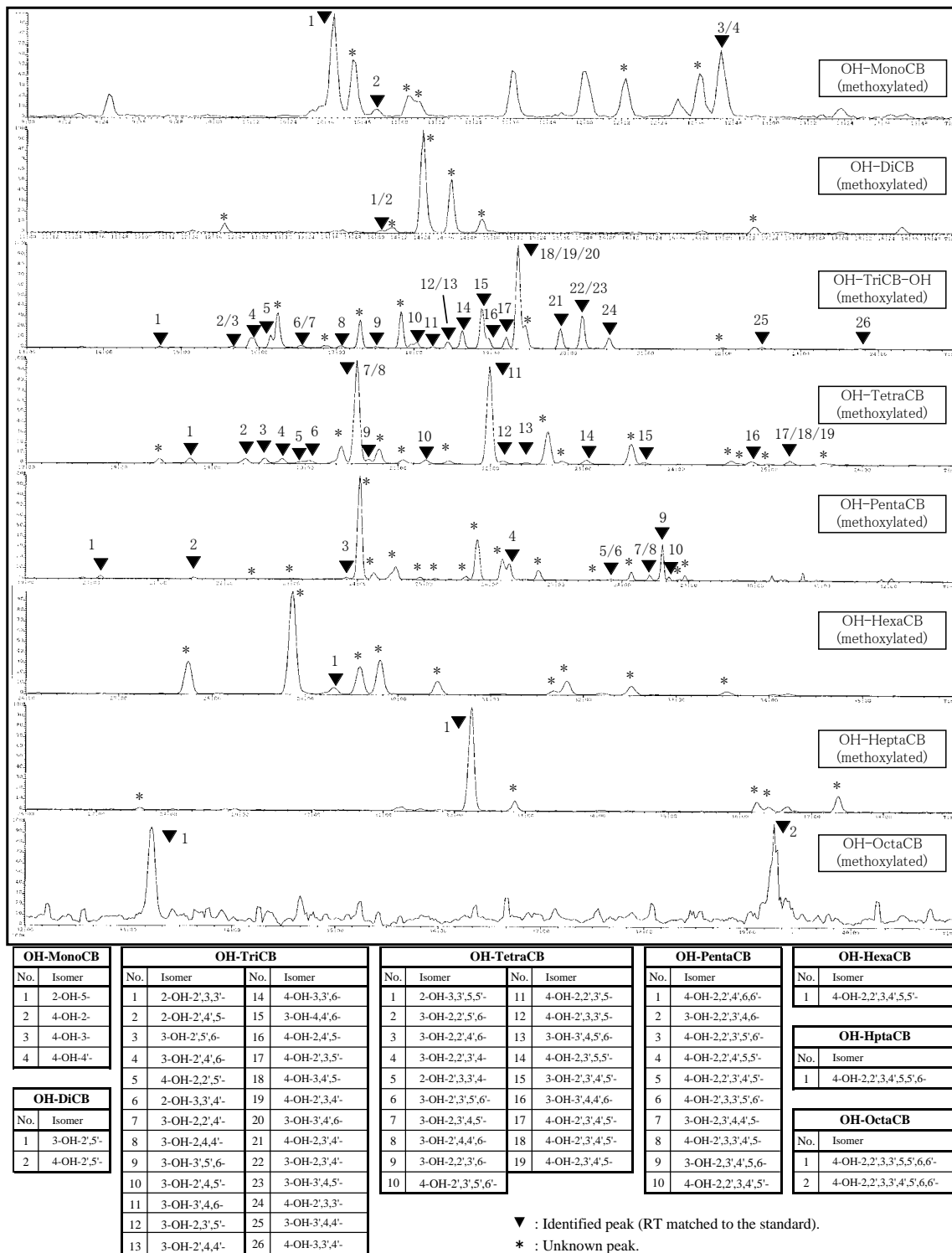


Figure 1. Mass chromatograms of OH-PCBs (MeO-PCBs) in the sediment sample, which showed the highest concentration, and list of identified isomers.

of these isomers substitute the OH-group on *meta*- or *para*-position, because they showed a distinctive fragment ion, $[M-\text{COCH}_3]^+$ (Figure 2).

Mean concentration of total OH-PCBs detected in sediment samples was 24ng/g-dry wt. (range: 0.90-150ng/g-dry wt.), and OH-PCB/PCB ratios ranged from 1.4-13% (Table 1). Relatively higher levels of tri- to hexa-chlorinated OH-PCBs were

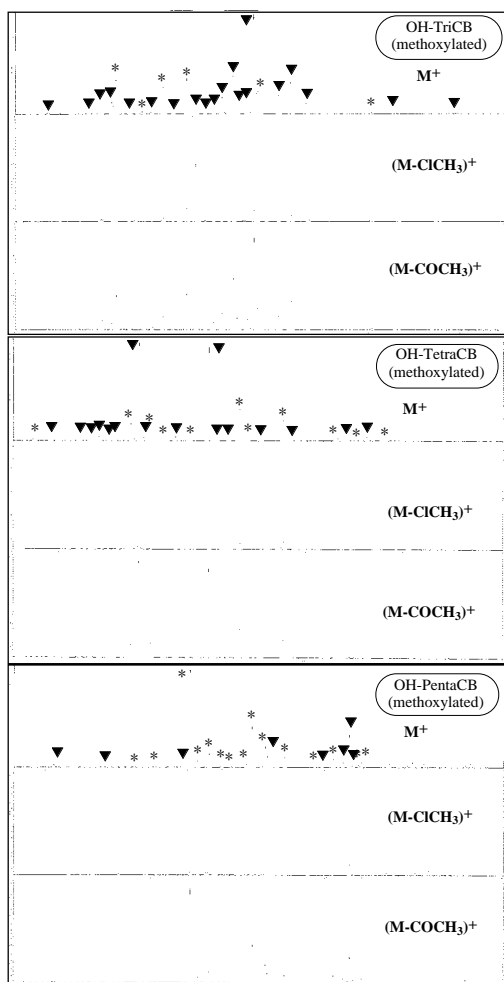


Figure 2. Typical fragment ion chromatograms of OH-PCBs (MeO-PCBs) in the sediment sample.

observed in sediment samples. The OH-PCB/PCB ratios for each congener class were 3.8-82% of mono-, 1.1-38% of di-, 1.8-16% of tri-, 0.66-15% of tetra-, 1.3-22% of penta-, 0.37-9.6% of hexa-, 0.62-7.0% of hepta-, and below 0.2% of octa-chlorinated class. Mono-chlorinated OH-PCB/PCB ratio was the highest in almost all the samples, and OH-PCB/PCB ratio tended to decrease with higher chlorinated class.

OH-PCBs in sediments might be derived by chemical reaction between PCBs and OH-radicals² and/or biological degradation of PCBs by bacteria⁵. It is unlikely that OH-radical reacts with PCBs in sediments, because sunlight doesn't easily reach the bottom of the water. Therefore, it is also speculated that OH-PCBs in sediments come from atmospheric deposition⁴. To elucidate sources and behavior of OH-PCBs in the aquatic environment, further investigations are needed.

Table 1. Concentrations of OH-PCBs and OH-PCBs/PCBs ratios in sediment samples from the rivers and estuaries of Osaka City, Japan.

	Concentrations (ng/g-dry)			OH-PCB/PCB ratios (%)		
	mean	median	range	mean	median	range
OH-MonoCB	0.24	0.16	(0.017 - 0.71)	38	38	(3.8 - 82)
OH-DiCB	1.6	0.74	(0.044 - 6.9)	9.9	5.2	(1.1 - 38)
OH-TriCB	7.2	1.4	(0.36 - 41)	6.2	5.4	(1.8 - 16)
OH-TetraCB	8.1	1.4	(0.19 - 53)	5.3	4.6	(0.66 - 15)
OH-PentaCB	5.2	1.8	(0.21 - 36)	6.5	4.3	(1.3 - 22)
OH-HexaCB	1.5	0.33	(0.016 - 14)	3.4	3.3	(0.37 - 9.6)
OH-HeptaCB	0.41	0.14	(0.024 - 3.5)	2.3	2.0	(0.62 - 7.0)
OH-OctaCB	0.091	-	(- - -)	0.19	-	(- - -)
Total	24	6.0	(0.90 - 150)	5.2	4.2	(1.4 - 13)

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