INVESTIGATION OF HYDROXYLATED POLYCHLORINATED BIPHENYLS (OH-PCBs) IN THE AIR AND THE SEDIMENTS AROUND THE PAPER RECYCLING PLANT

Suzuki M[1,2], Takemine S[1], Tsurukawa M[1], Matsumura C[1], Nakano T[1] and Imaishi H[3]
[1]Hyogo Prefectural Institute of Environmental Sciences, Yukihira-cho 3-1-27, Suma-ku, Kobe, Hyogo 654-0037, Japan; [2]Graduate School of Agricultural Science, Kobe University, Rokkodaicho 1-1, Nada, Kobe, Hyogo 657-8501, Japan; [3]Functional Analysis of Environmental Genes Research Center for Environmental Genomics, Kobe University, Rokkodaicho 1-1, Nada, Kobe, Hyogo 657-8501, Japan

Abstract

Hydroxylated polychlorinated biphenyls (OH-PCBs) were detected in the variety of sediments, environmental waters and living beings. Recently it was reported that OH-PCBs were reacted in paper recycling plant without PCBs. In this study, the concentration of OH-PCBs in the air was investigated for the first time. And the environmental pollution of OH-PCBs in wastewater from the paper recycling plant was investigated. The concentration of OH-PCBs was detected 1.1pg/m^3 - 2.1pg/m^3 in the air samples and OH-MonoCBs and OH-DiCBs were the major homologues. The loads of OH-MonoCBs and OH-DiCBs by wastewater from paper recycling plant did not influence seriously the sediments in Ibo River, Japan. It was speculated that the pollution of OH-PCBs was affected by metabolite of PCBs in the river because the homologue distributions of OH-PCBs were similar to PCBs'.

Introduction

Hydroxylated polychlorinated biphenyls (OH-PCBs) are considered as one of the endocrine disturbing chemicals because OH-PCBs have negative impacts on the some thyroid and female hormones[1]. OH-PCBs are produced by metabolism and OH radical reaction[2] of PCBs. And recently, it was reported that OH-PCBs were produced by chlorination of other chemicals at chlorine breaching in paper recycling plant and contaminated wastewater there[3]. The concentrations of OH-PCBs in the environmental waters, the sediments[4] and living things[5] have been investigated and OH-PCBs have been detected from every medium. In Canada, OH-PCBs were also detected from the rain and snow[6]. It is necessary for revealing the environmental pollution of OH-PCBs to investigate them in more media.
In this study, the concentration of OH-PCBs in the air was investigated for the first time. And the environmental pollution of OH-PCBs caused by wastewater from the paper recycling plant was investigated by analyzing the concentration of OH-PCBs in the sediments around the paper recycling plant.

Materials and Methods

1. Sampling

The air was sampled at the roof of our institute. The air (1000-2500m^3) was introduced into quartz micro fiber (QMF), 1st poly urethane foam (PUF), activated carbon felt (ACF) and 2nd PUF which were set to Hi-Volume air sampler (HV-1000F, SHIBATA) for a day or two (Fig.1). Those collection media have been conditioned by washing with acetone or toluene and drying in vacuum.
Sampling points for investigating the influence of wastewater from the paper recycling plant were indicated in Fig.2. The sediments (15-30g-wet) were sampled at point A (sediment A), point C (sediment C) and point D (sediment D). The water (8.2L) was sampled at point B (water B). Point A is about 9km upstream from the mouth of Ibo River. Point B is downstream of waterway from the paper recycling plant. The waterway was jointed at about 0.2km upstream from the point C. Point D is about 0.8km downstream of point C. At another urban river in Hyogo, the sediment (15g-wet) was sampled as a reference.

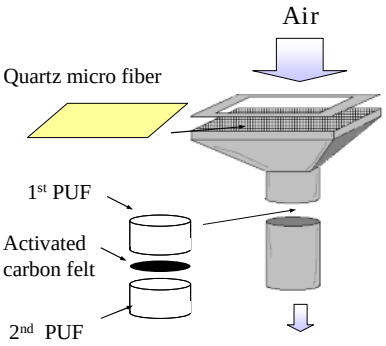

Fig.1 Diagrammatic illustration of High Volume Air Sampler (Hi-Vol).

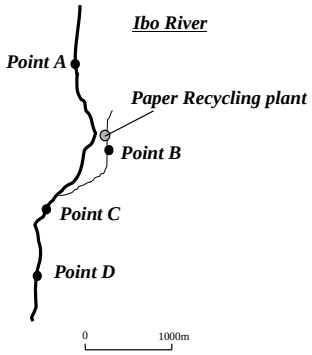

Fig.2 The map of sampling points around the paper recycling plant.

2. Analytical procedure

Analytical procedure of OH-PCBs and PCBs in the air, the water and the sediment samples is shown in Fig.3. The clean-up and derivatization were based on the method by Sakiyama et al[4]. Identification and quantification of OH-PCBs (MeO-PCBs) and PCBs were performed using a gas chromatograph (HP6890N, Agilent) / high-resolution mass spectrometer (800D, JEOL Ltd.) equipped with HT-8PCB capillary column (60m*0.25mm id, Kanto Chemical). OH-PCB congeners were identified by checking isotope ratio and using 83 synthesized standards[7] and 72 commercial standards (OH-MonoCBs ~ OH-NonaCBs).
For air samples, the recovery tests were performed by adding OH-PCBs standard mixture (OH-MonoCBs ~ OH-HeptaCBs) to QMF and sampling time was 24 hours.

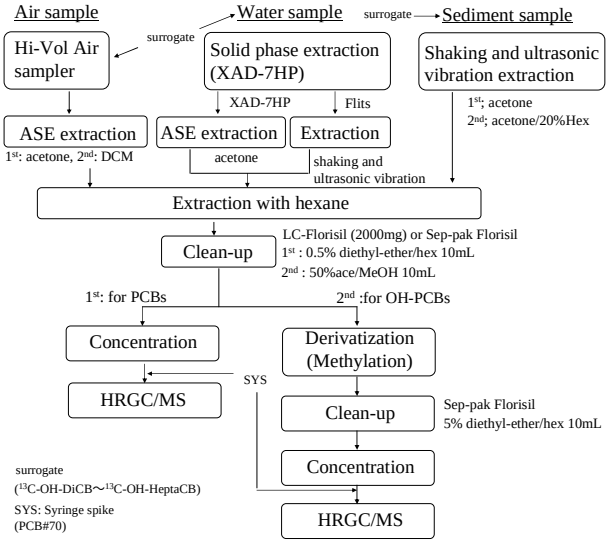

Fig.3 The analytical procedure of OH-PCBs and PCBs in the air, the water and the sediment samples.

Results and Discussion

The recovery ratios of OH-PCBs (OH-MonoCBs - OH-HeptaCBs) in each collection medium for the air sample are shown in Fig.4. Lowly chlorinated OH-PCBs tend to be collected in 1st PUF and highly ones tend to be collected in QF. It was indicated that lowly chlorinated OH-PCBs might tend to gasify comparatively. Though the recovery ratios of OH-PCBs tended to decrease as chlorine lowered, OH-PCBs were recovered over 70% except OH-MonoCBs. It was indicated that lowly chlorinated OH-PCBs might tend to evaporate or degrade in sampling or pretreatment.
In the air samples, OH-PCBs were detected 1.1pg/m^3 -2.1pg/m^3 (Table1). The concentration ratio of OH-PCBs/PCBs was approximately 1.5% in the air sampled between Apr. 9 and Apr. 10. The dominant congeners were OH-MonoCBs and OH-DiCBs in the air (Fig.5). The

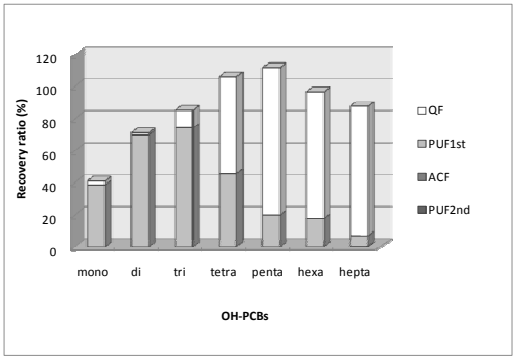

Fig.4 The recovery ratios of OH-PCBs in each collection medium in the air sample.

chromatogram of OH-MonoCBs detected in the air sampled between May 20 and May 22 is shown in Fig.6. Seven peaks were matched isotope ratio of OH-MonoCBs and peak No2, 3 and 6 in figure were matched retention times with 2-OH-CB5, 4-OH-CB2 and 4-OH-CB3 respectively. OH reaction rate of PCBs have been reported to increase as chlorine of PCBs lowers in the vapor-phase[2]. Therefore it might be considered that lowly chlorinated OH-PCBs were dominant in the air because of OH radical reaction.

The isomer ratios of 3, 3'-dichlorobiphenyl (CB11)/ Σ DiCBs in samples around the paper recycling plant are shown in Fig.7. In the paper recycling plant, CB11 was known to be produced by reaction of another chemicals contained in ink. The percentages of CB11/ Σ DiCBs in the water B, the sediment C and the sediment D were higher than sediment A and the reference sediment. CB11 was not detected in the sediment A. It was indicated that the sediment C and the sediment D were affected by the wastewater from paper recycling plant. The concentrations of each homologue of OH-PCBs and PCBs between MonoCBs and HeptaCBs in samples are shown in Fig.8. The sediment A was not described in the figure because only OH-HeptaCBs were detected at very low concentration. It was revalidated that the sediment C was affected by wastewater from paper recycling plant determinably, because the concentration of DiCBs there was highest homologue. In the water B, OH-MonoCBs, OH-DiCBs and OH-TriCBs were detected dominantly and the concentration of total OH-PCBs was 1.3ng/L. The result was similar to the one of other paper recycling plant conducted by Nanba et al[3]. The discharge of OH-PCBs could be estimated to approximately 5.6g/day by OH-PCBs concentration in water B and the discharge of wastewater from the paper recycling plant (4400m^3/day). Although OH-MonoCBs and OH-DiCBs were also detected in the sediment C that was most affected by the wastewater, their concentration ratios were not very high. In the sediment D at downstream of point C, OH-MonoCBs and OH-DiCBs were detected little. The dominant homologue was OH-TetraCBs in the sediment C and the sediment D. On the other

Table1. The concentrations of OH-PCBs and PCBs in the air.

sampling period	OH-PCBs	PCBs
Jan. 9～10, 2009	2.1	n.a.
Apr. 9～10, 2009	1.6	110
May 20～22, 2009	1.1	n.a.

(unit:pg/m^3)

*n.a.=not analyzed

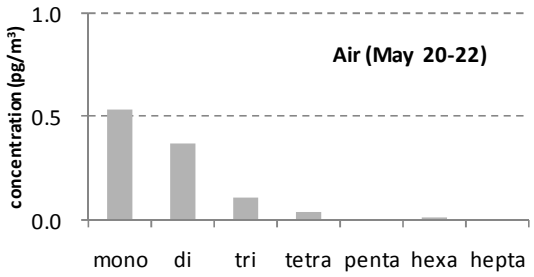

Fig.5 The concentration of each OH-PCBs homologue in the air (May 20 – 22)

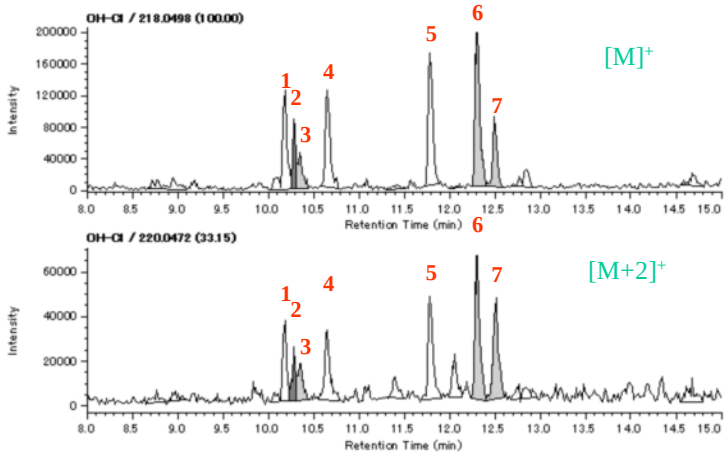

Fig.6 The chromatogram of OH-MonoCBs (methoxylated) in the air sample (May 20-22). Isotope ratios of Peak1-7 were matched with OH-MonoCBs and retention times of peak2, 3 and 6 were matched with 2-OH-CB5, 4-OH-CB2 and 4-OH-CB3 respectively.

hand, OH-TriCBs were detected dominantly in the reference sediment in another urban river. Those homologue distributions of OH-PCBs were similar to PCBs' at the same point. The concentration ratios of OH-PCBs / PCBs (MonoCB-HeptaCB) in the samples are shown in Fig. 9. OH-PCBs / PCBs ratio was 51% in the water B. However in the sediment C and the sediment D, OH-PCBs / PCBs ratios were not higher than that of reference and were similar to the value in existence (1.4% - 13%) [4].

It was found that the loads of OH-MonoCBs and OH-DiCBs by wastewater from paper recycling plant did not be affected seriously the sediments in Ibo River. However, OH-MonoCBs and OH-DiCBs were dominant in the air samples. Therefore it was considered that behaviors of OH-MonoCBs and OH-DiCBs were different from highly chlorinated OH-PCBs in the environment.

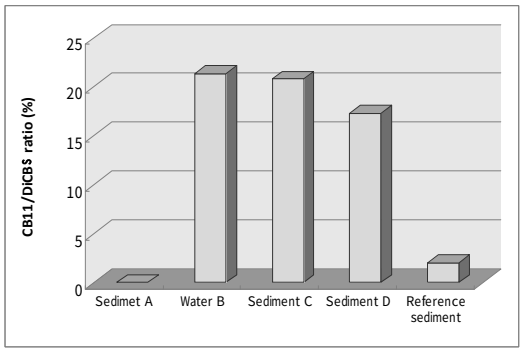

Fig.7 The isomer ratio of CB11/ΣDiCBs in the samples

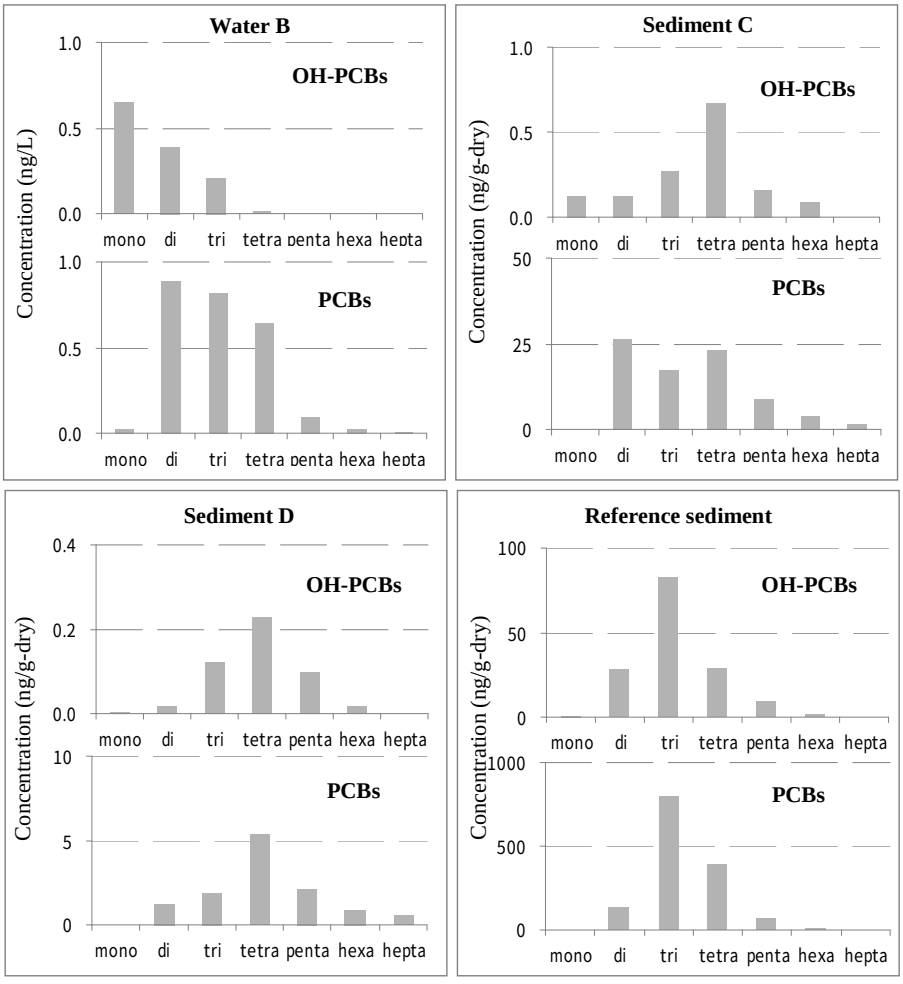

Fig.8 The concentrations of each homologue of OH-PCBs and PCBs (monoCB-heptaCB) in the sediments and the water samples

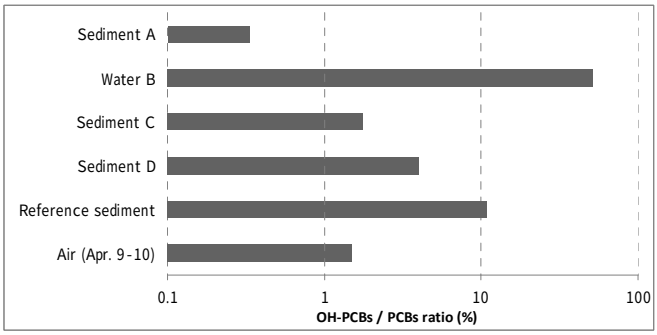

Fig.9 The concentration ratio of OH-PCBs / PCBs (MonoCB-HeptaCB) in the samples

Acknowledgements

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