

## DISTRIBUTIONS OF PCDD/Fs, PCBs, AND PBDES IN MARINE SEDIMENTS ALONG THE SOUTHERN COASTAL AREAS, KOREA

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### Abstract

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs) were investigated in seven surface sediment samples collected from southern coastal sea areas of Korea. Total concentration in surface sediments ranged from 17.35 to 174.8  $\mu\text{g g}^{-1}$  dry weight for PCDD/Fs, from 82.16 to 1121  $\mu\text{g g}^{-1}$  dry weight for PBDEs and from 360.5 to 931.3  $\mu\text{g g}^{-1}$  dry weight for PCBs. Among the compounds analysed, greater variation was found in total PCDD/F and total PBDE concentration.

### Introduction

Sediments are investigated to elucidate the fate of contaminants as sediments are the major sink of contaminants in global monitoring scale. Especially, hydrophobic compounds with high octanol-water partition coefficients ( $\log K_{ow}$  of approximately 4–8) have more probability to accumulate and persist in sediments. Persistent organic pollutants (POPs) like Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs) are compounds with long range transport potential, high accumulation rate according to their hydrophobicity, potential to cause adverse effect on both health and environment and persistency in environment for long time<sup>1</sup>. PCDD/Fs and PCBs are produced as byproducts of incineration and manufacturing processes<sup>2</sup>. Though Polybrominated diphenyl ethers (PBDEs) that are used as brominated flame retardants (BFR) is not yet classified as POPs, some group have reported the POPs like behaviour and effects of PBDEs. Many studies have reported the contamination level of classical polyaromatic compounds in sediments. However there is no study illustrating the comparison of concentration levels between different compounds and associated source of contamination in sediment.

Our research goal is to assess the contamination level, distribution and proportion of PCDD/Fs, PCBs and PBDEs in surface sediments of the southern shoreline of Korea and to track the dominant pollutant source affecting the study sites.

### Materials and Methods

#### *Sediment collection*

Marine sediments were collected from seven areas along the southern coast of Korea. These areas, which has number of industrial complexes, huge harbor, steel complex and metropolis, were found to be contaminated by several pollutants<sup>3,4</sup>. Sediment samples collection sites were grouped into three groups according to the environment. Group A is the area near the steel making complexes and is affected by their effluent. Group C is the area near the macro city. Group B lies between Group A and C and is an area without any industries and large stream line entering the South Sea. Sediments were collected with the core sampler that used gravitational force to allow unrestricted flow of water to pass through its tube during a drop. Sediments were stored below -20 °C until experiment. Surface sediments (~ 10 cm depth) were analyzed in this study.

#### *Sample preparation and analysis*

We followed the analytical procedure and method published elsewhere<sup>5,6</sup>. For PCDD/Fs, samples were spiked with <sup>13</sup>C internal standards, extracted with toluene, cleaned with sulfuric acid and silica column and fractionated in alumina column. For PBDE and PCB, samples were spiked with both PCB and PBDE <sup>13</sup>C internal standards, extracted with dichloromethane and cleaned with sulfuric acid and silica column. High resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) was used for the analysis of these contaminants. All data was obtained in the selected ion monitoring mode (SIM) at resolution 10,000. A DB5-MS (60m × 0.25 mm i.d. × 0.25  $\mu\text{m}$ ) and DB5-HT (30m × 0.25 mm i.d. × 0.25  $\mu\text{m}$ ) was used for analysis of

PCDD/Fs and PCBs, and PBDEs, respectively. In case of PCDD/F and PCB, congeners that have the World Health Organization-toxicity equivalent (WHO-TEQ) values were analysed. In case of PBDE, tri to hepta-BDEs were monitored out of which eleven congeners were selected for analysis.

### Results and Discussion

In Group A, mean concentrations of PBDEs and PCDD/Fs were 694.9 pg/g and 137.5 pg/g, respectively (Figure 1). These levels were up to 4~5 times higher than in Group B and C. Meanwhile, Group C had the highest PCB level (769.2 pg/g) which was less than 2 times as high as PCB levels in Group A and B. The level of contamination might be affected by the nature of the surrounding environments of each group. Group A, the area with apparent PCDD/F sources were contaminated with high levels of PCDD/Fs. However, our data falls within the relatively low level range in comparison to previous reports<sup>3,4,5</sup>. The differences in POPs level between the samples were also not significant. Thus it can be said that investigated sites might be affected by diverse urban and industrial sources without any accidental inputs of contaminants from the terrestrial system.

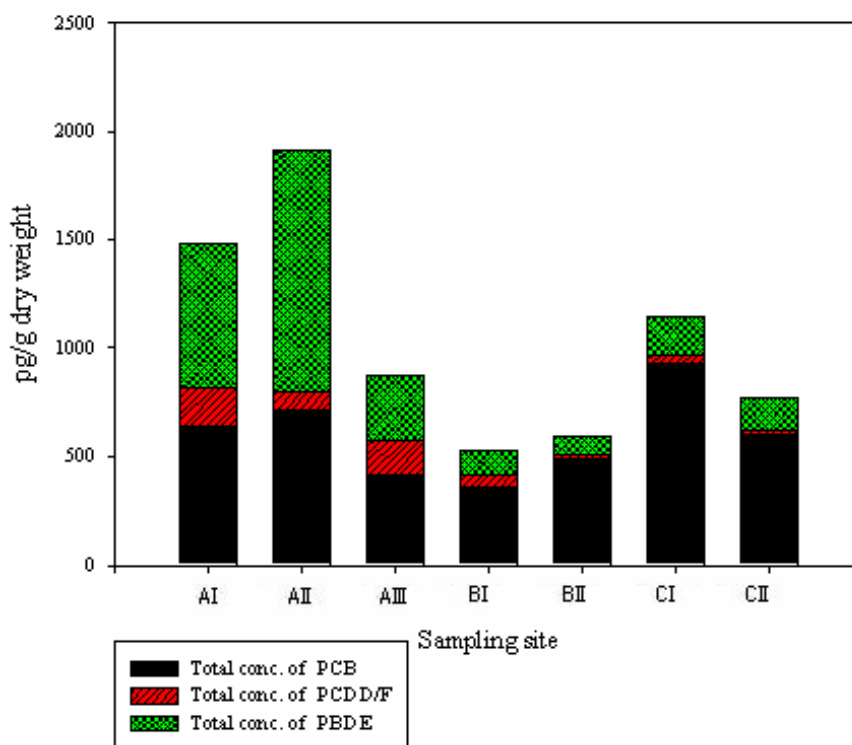


Figure 1. Total concentrations of PCBs, PCDD/Fs and PBDEs in sediments collected at different coastal sites.

Figure 2 shows the distributions of each compound in all the sediment samples. PCB-114 (48%) and PCB-118 (28%) were the dominant isomers in case of PCB. For PCDD/Fs, OCDD was the predominant in all the samples (47~62%). Samples of Group A, which were considered to be affected by steel companies, had slightly increased proportions of low chlorinated-CDFs. The predominant PBDE isomers in sediments were BDE-47 and BDE-99. As explained above, we could not find apparent characteristics of POPs distribution among groups. However, principal component analysis (PCA) revealed that specific point source might affect the sediments. To see the regional characteristics of sediments, normalized distributions of PCBs, PCDD/Fs and PBDEs were used. For PCBs and PBDEs, PCA did not show any categorization, but PCDD/Fs could be categorized despite the insignificant statistical difference. Different emission sources of these contaminants might be the reason; PCBs and PBDEs are the contaminants related with urban source, meanwhile combustion process is main source of PCDD/Fs.

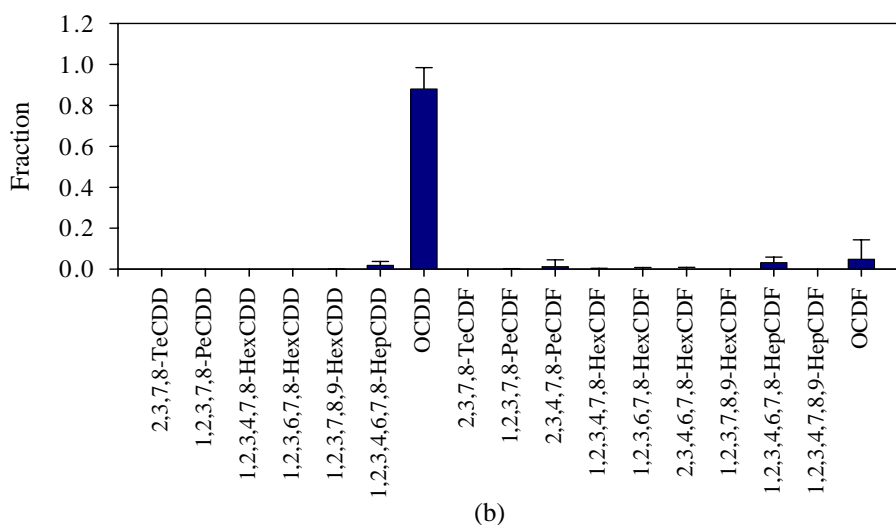
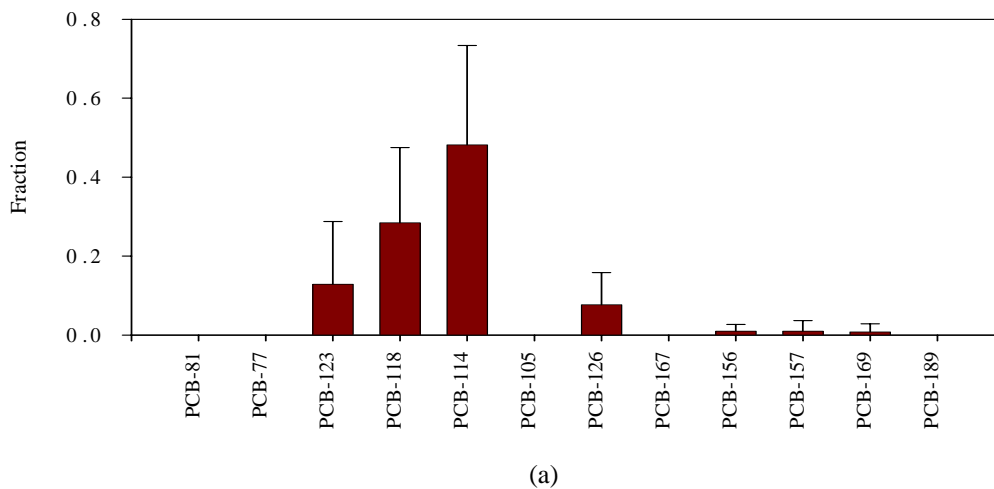
From this study, we could see the spatial distributions of conventional and new emerging POPs. Although the difference in POPs level among sites was not big, inland sources were observed to affect the level of contamination of water body. In addition, we could confirm that inconsistent distributions in each area might be the consequence of their different production and release mechanisms.

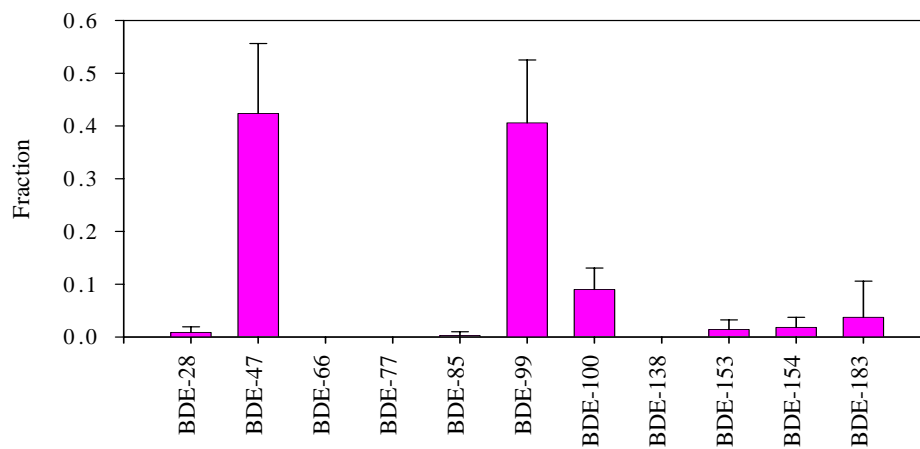
**Acknowledgements**

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(c)

Figure 2. The distributions of PCBs, PCDD/Fs, and PBDEs in all sediment samples; (a) PCBs (b) PCDD/Fs (c) PBDEs.