# DISTRIBUTION AND PROFILES OF POLYBROMINATED DIPHENYL ETHERS (PBDES), HEXABROMOCYCLODODECANES (HBCDS) AND NON-PBDE BROMINATED FLAME RETARDANTS IN SEDIMENT FROM ULSAN AND ONSAN BAY IN KOREA

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## Introduction

Polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDs) are widely used brominated flame retardants (BFRs). These flame retardants (FRs) are used as additives with manufacturing products and migrate out of the products and into environments[1]. Due to growing environmental and human health concerns, the penta- and octa-BDE mixtures were banned in Europe and United States (US)[2]. The physicochemical properties of HBCDs are similar to those of PBDEs[1]. Furthermore, the penta- and octa-BDE commercial formulations and HBCDs have been listed as persistent organic pollutants (POPs) in 2009 and 2013, respectively under the Stockholm Convention[3]. The reduction in the use of PBDEs and HBCDs caused the introduction of non-PBDE flame retardants (NBFRs) in place of the banned formulations[4]. Following worldwide regulations on PBDEs and HBCDs, non-PBDE brominated flame retardants (NBFRs) have been replacements in recent years.

Ulsan Bay located on the east coast of Korea, is a one of the most highly industrialized regions in Korea and contains many commercial harbors[5]. Approximately 600,000 tons of industrial and domestic wastewater, mainly from Ulsan and Onsan cities, is discharged through several streams (Gosa stream) and rivers (Woihwang River, Taehwa River) into the bay. Many Industrial complexes in Ulsan/Onsan produce petrochemical products, machinery, non-ferrous metals, automobiles, and ships. This industries discharge high amounts of organic pollutants into the Bay. Ulsan Bay designated as a specially managed region since 2000. The Korean Ministry of Environment has been managed water quality such as COD, TN in water of Ulsan/Onsan Bay. Two national industrial complexes exist in this area (Ulsan-Mipo National Industrial Complex and Onsan National Industrial complex), and these complex occupied 32% of total national production. In this study is to determine the concentrations and chemical profiles of PBDEs, HBCDs, and NBFRs, to investigate contamination status and potential sources of these chemicals in Ulsan/Onsan Bay, Korea. Futher, temporal variation of PBDEs between 2003 and 2014 were determined whether or not regulation, such as total pollution load management system (TPLMS), Water quality criteria such as COD and TN.

## Materials and methods

*Sample collection*

The collection of surface sediment ($n$=42) was performed from the inner to the outer parts of Ulsan/Onsan Bay; Taehwa River (T1-7), Ulsan Bay (U1-18), Gosa Stream (G1-5), Woihwang River (W1-4), and Onsan Bay (O1-8) using a van-veen grab on November 2014. The collected sediment samples were freeze-dried and stored at −20ºC until analysis.

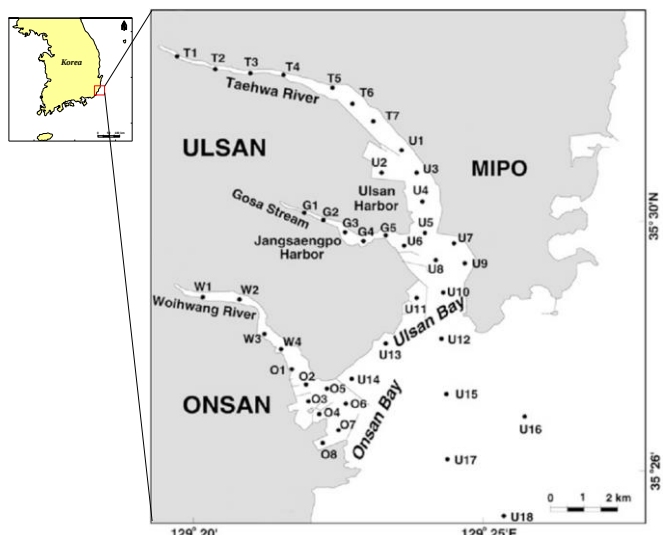


Figure 1. Sampling stations of Ulsan and Onsan Bay, Korea

*Sample and Instrumental analysis*

Freeze-dried sediment samples were initially extracted using 300 mL of 75% dichloromethane (DCM) in $n$-hexane using a Soxhlet apparatus. The surrogate standards were spiked with 100 ng mixture of CBs 103, 198 and 209 before Soxhlet extraction. The extracts were concentrated to 1 mL then extracs were divided into two parts for the analysis of PBDEs, and NBFRs and HBDEs. For PBDEs and NBFRs analysis, 10 ng BDE 77 and 50 ng $^{13}$C-BDE 209 were spiked into the extracts and the extracts were pre-cleaned by passage through a multilayer silica gel column (300 mm length × 20 mm i.d.) with 150 mL of 15% DCM in $n$-hexane. For HBCD analysis, 10 ng $^{13}$C-$\alpha$-, $\beta$-,

and $\gamma$-HBCD were spiked into the extracts and the extracts were pre-cleaned by passage through a multilayer silica gel column with 100 mL of 50% DCM in *n*-hexane. All eluates were concentrated to 100 µL for instrumental analysis. Identification and quantification of 22 PBDE congeners and 10 NBFR compounds were accomplished with a gas chromatograph coupled to mass spectrometer (GC/MSD; Agilent 7890/5975C), under the electron capture negative chemical ionization (ECNI) mode with selected ion monitoring (SIM) mode. HBCDs were analyzed by a high-performance liquid chromatography tandem mass spectrometer (LC-MS/MS; Agilent 1260/AB SCIEX). A eclipse plus $C_{18}$ column (2.1 mm i.d. × 150 mm length × 3.5 µm particle size) were used for the separation of the HBCDs. The mobile phases were 25% MeOH in $H_2O$ and 30% MeOH in acetonitrile with 400 µL/min flow rate.

**Results and discussion**

*Occurrences and spatial distributions*

The concentrations of PBDEs, HBCDs, and NBFRs in sediment from Ulsan/Onsan Bay collected in 2014 ranged from <LOQ to 63.5 ng/g dry weight (dw) (mean: 9.61 ng/g dw) for PBDEs, 0.52 to 1586 ng/g dw (157 ng/g dw) for HBCDs, and <LOQ to 149 ng/g dw (28.9 ng/g dw) for NBFRs, in respectively. The overall concentrations of HBCDs were an one or two orders of magnitude higher than PBDEs and NBFRs in sediments. The BDE 209 concentration in this study was lower than other countries. While the concentration of HBCDs was the highest compared to previously reported worldwide studies, indicating the high usage amount of HBCDs in industrial purpose on flame retardants from Korea. The concentration of DBDPE was similar or slightly higher than other countries, suggesting the usage demand of NBFRs as one of alternative of PBDEs in Korea.

Almost of the PBDEs, HBCDs and NBFRs in sediment from Ulsan/Onsan Bay were concentrated in inner locations such as the Gosa Stream and Woihwang River, and the concentrations decreased with the distance from inner bay to outer bay. It is implies the presence of contamination source located in inside of bay such as industrial complexes and domestic harbors, indicating certain point source exist in Gosa Stream and Woihwang River. In particular, the highest concentrations of PBDEs, HBCDs, and NBFRs showed in close to petrochemical plants, suggesting that discharge from petrochemical plants could be contribute to PBDEs, HBCDs, and NBFRs contamination.

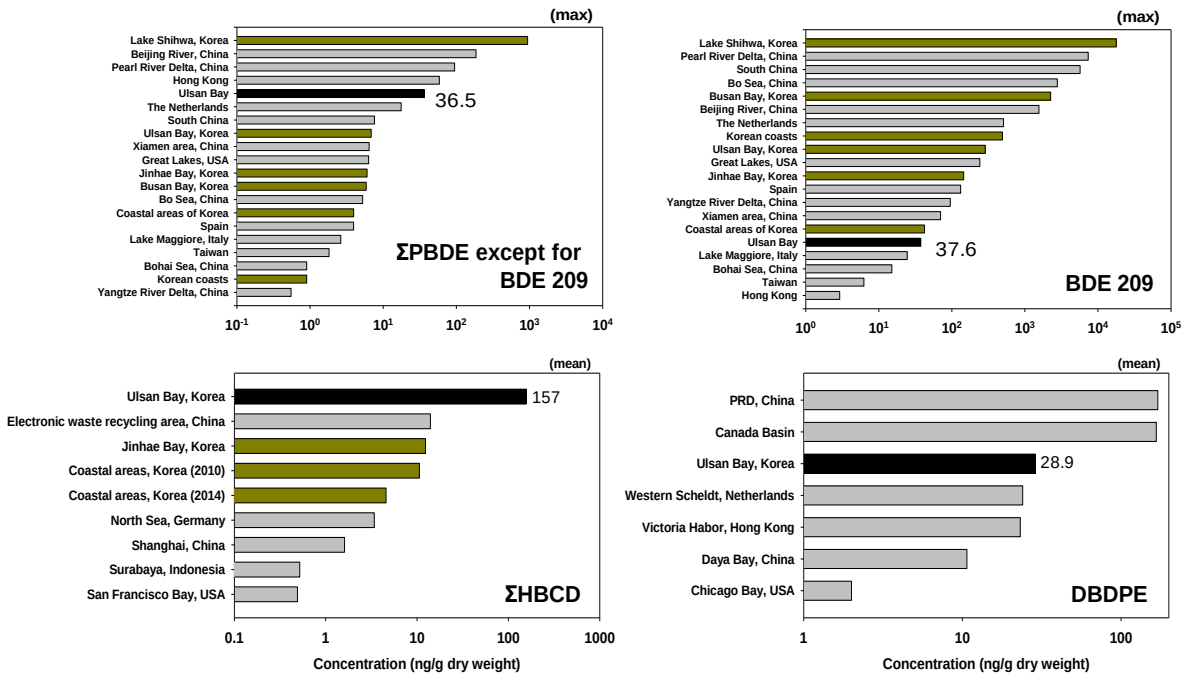


Figure 2. Global comparison of ∑PBDE (except for BDE 209), BDE 209, ∑HBCD, and DBDPE in sediment studies

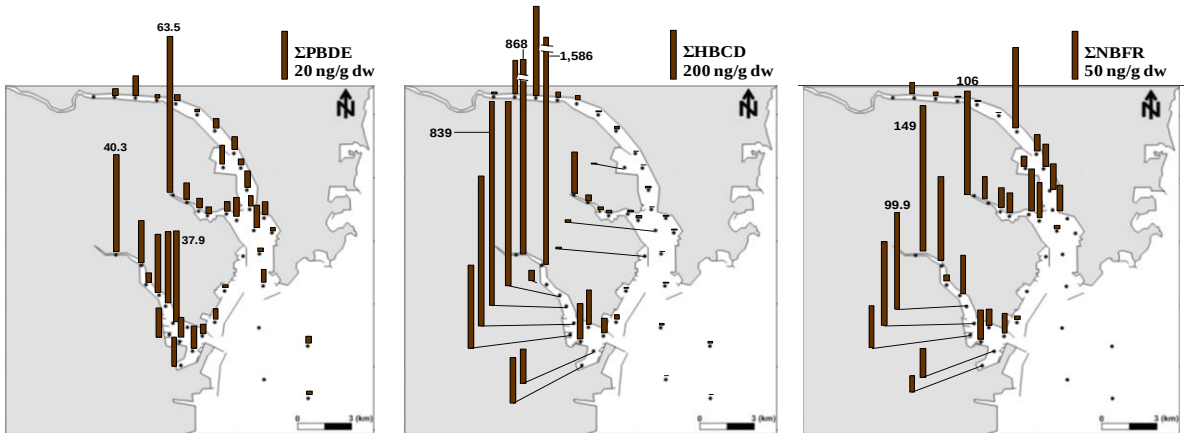


Figure 2. Spatial distributions of PBDEs, HBCDs, and NBFRs in sediment from Ulsan/Onsan Bay

*Chemical distribution profiles*

The relative contributions of PBDEs, HBCDs and NBFRs sediments from Ulsan/Onsan Bay are summarized in Figure 3. In overall, the major congeners/compounds were BDE 209 (mean: 54.2% to ∑PBDE), *γ*-HBCD (73.6% to ∑HBCD) , and BTBPE and DBDPE (44.8% and 30.6% to ∑NBFR). The major contributor of PBDEs and NBFRs was different in Ulsan Bay and Onsan Bay areas. BDE 209 was dominant (70% to ∑PBDE) in surrounding of Ulsan Bay stations (Taehwa River, Ulsan Bay and Gosa Stream), whereas BDE 47 was dominant (54% to ∑PBDE) in Onsan Bay stations (Onsan Bay and Woihwang River). For NBFRs, DBDPE was dominant in Gosa stream, in while BTBPE was dominant Ulsan Bay, Onsan Bay and Woihwang Bay. This result is indicating that the usage pattern of PBDEs and NBFRs are different by characteristics of industrial complexes located in Ulsan and Onsan Bay. While, higher levels of *γ*-HBCD were observed across all stations of this study area, consistent result with previous studies[6,7]. This result could be reflects the commercial HBCD consist mainly *γ*-HBCD[6].

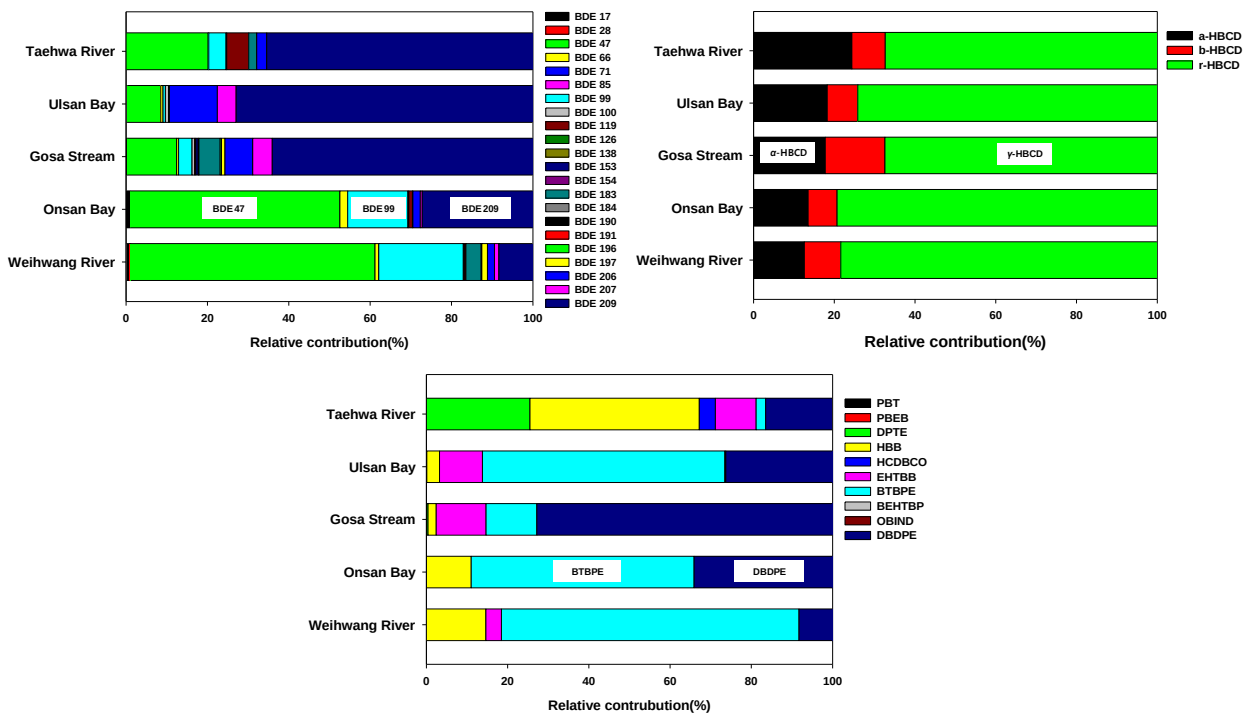


Figure 3. Congener/Compound profiles of PBDEs, HBCDs, and NBFRs in sediment from Ulsan /Onsan Bay

*Temporal variation*

Ulsan/Onsan Bay collected in 2003 (Figure 5). In caparison with 2003, the levels of total PBDEs were highly decreased in all of stations in 2014 sediments. The mean concentrations of PBDEs between 2003 and 2014 significantly declined from 58.3 ng/g dw to 8.88 ng/g dw ($p < 0.05$), a reduction rate of approximately 85%. This reduction seems to be the reflection of recent ban on the use and production of PBDE technical mixtures in Korea and many countries[5]. Although NBFRs did not measured in 2003 from Ulsan Bay, the concentration of NBFRs are higher than PBDE concentration in sediment from 2014, implying that the PBDEs have been replaced to certain compounds of NBFRs in industrial area. Our results indicate that the global regulation on chemical usage pattern could be associated with the reduction of PBDEs levels in Ulsan Bay and Onsan Bay. This result could be related to several legislative actions on water quality such as COD, TN in Ulsan/Onsan Bay.

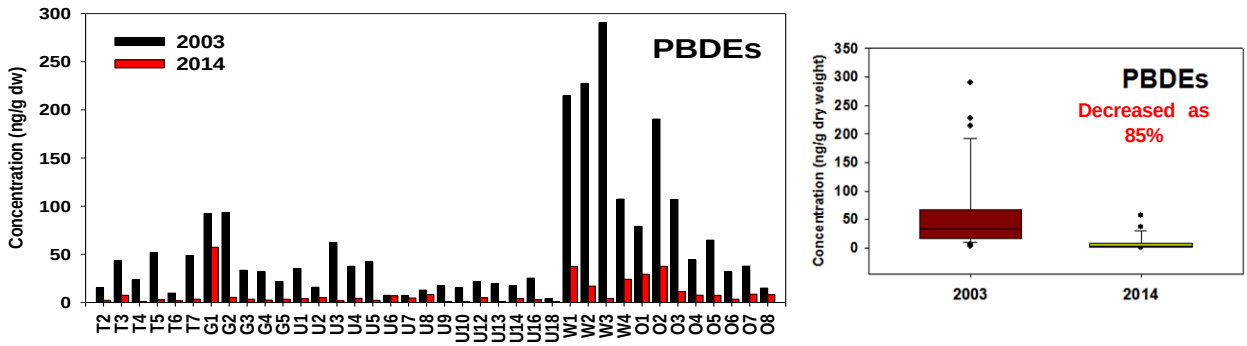


Figure 4. Comparison of the average concentrations of ΣPBDE in sediment from Ulsan/Onsan Bay between 2003 and 2014 (38 sites).

**Acknowledgements**
This study was funded by a Grant from the Ministry of Oceans and Fisheries (MOF), Korea

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