PBDEs & PCBs CONTAMINATION IN MASAN BAY, KOREA

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Abstract
Congener specific determination of Polybrominated diphenyls ethers (PBDEs) and Polychlorinated biphenyls (PCBs) in 21 surface sediment samples and a sediment core with 24 cross sections was carried out in Masan Bay, Korea. Among the 40 PBDE congeners targeted only 29 were detectable. The congener profile revealed the domination of BDE 209 followed by BDEs-99, -47,-153,-183 in that order in surface sediments. BDE-209 was dominant in core sample as well. On an average, sum of PCBs were three times higher than sum of PBDEs in surface sediment. However, sediment core sections reveal that this trend will soon change as PCB levels decrease over years while PBDE levels are in the increase. Distribution and correlation patterns of PBDEs and PCBs concentration in surface sediments reveal different sources for these contaminants. Shipping and other industrial activities are principal sources for PCBs while domestic & industrial waste discharge in Masan Bay is the source for PBDEs. The average concentration ranges for PBDEs and PCBs in surface sediments are 5.80, 14.81 ng/g dry weight (dw), which is not alarming at this moment.

Introduction
PBDEs become compounds of great concern recently as Korean economy depends heavily on industries such as computers, home appliances, textiles and automobiles which use brominated flame retardants in the manufacture. Masan Bay has been the focus of many previous studies on pollution monitoring[1-4], as it has been designated as a 'special management coastal area' since 1983. Some of these pollutants, including xenoestrogens, are introduced into the coastal waters from rivers or streams via discharges of industrial waste, municipal sewage, and urban and agricultural runoff. Masan Bay is semi-enclosed embayment with its mouth opened to Korean Strait (Fig.1) and there are strong semi-diurnal tidal currents along the deep channel at the bay mouth, while very weak currents (2-3 cm/s) are observed in the inner bay with long residence time (10–12 h) where most pollutants are loaded. In summer time, red tide events frequently occur, which lead to anoxic condition of bottom sediment[5]. Heavily populated (2682 people per km^2) Masan, Changwon and Chinhae cities surround Masan Bay and several industrial complexes (approximately, 1300 industrial complexes) comprised of petrochemical, heavy metal, electrical, and plastic industries discharge significant amounts of organic pollutants into the bay. This discharge (0.5 x 105 ton/day) enter the bay either after a secondary treatment or directly without it.

Materials and Methods
Surface sediment samples were collected from 21 stations using a van Veen grab sampler (Fig. 1) in February 2004. Approximately 2 cm of the top sediments were taken by a stainless steel spoon and stored in pre-combusted amber glass jar. The collected samples were immediately frozen and transferred to the laboratory for analysis. The sediment samples were prepared for organic contaminant analysis in accordance with previously reported method[3] that includes, silica gel and alumina column chromatography, size-exclusion high pressure liquid chromatography (HPLC) for clean-up and chemical separation. PBDE congeners were analyzed following the method of Zhu and Hites[6] using an Agilent 6890 series gas chromatograph coupled to an Agilent 5975 mass spectrometer with helium as the carrier gas. The 1-μL injections were made in the pulse splitless mode, with a purge time of 2.0 min. The injection port was held at 285 °C. For the determination of all PBDEs

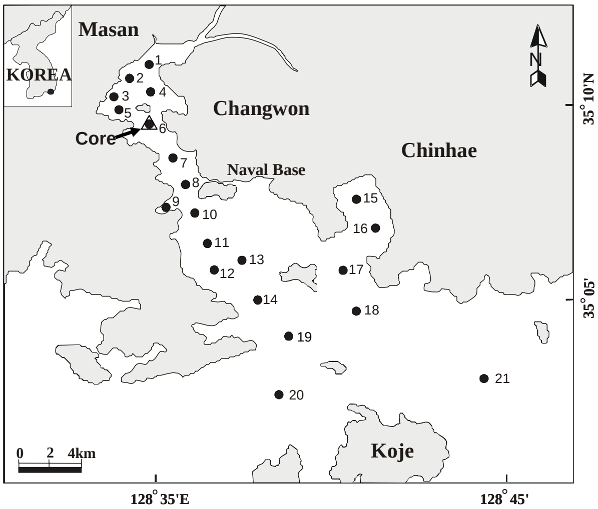

Figure 1. Sampling locations of surface sediments (Sts. 1 - 21) and a core sample collected from Masan Bay.

except for BDE-209, the GC column was a 60 m x 250 μm (i.d.) fused-silica capillary tube coated with DB-5-MS (0.25-μm film thickness; J&W Scientific, Folsom, CA). The GC oven temperature program was as follows: isothermal at 110 °C for 1.90 min, 15 °C/min to 180 °C, 1.85 °C/min to 300 °C, and held at 300 °C for 45 min. The GC-to-MS transfer line was held at 280 °C. The mass spectrometer was operated in electron capture negative ionization mode (ECNI) using methane as the reagent gas, and the ion source temperature was 150 °C. Selected ion monitoring of the two bromide ions at m/z 79 and 81 was used to detect the PBDEs. The response factors for all compounds were determined using quantitation standards with known amounts of all the target compounds, internal standards, and recovery standards. The internal standard PCB198 was used as a retention time reference, and BDE-139 was used as the internal standard to quantitate all the PBDE congeners. PCB-189 was used as a recovery standard which eluted in the middle of the retention range of all the congeners; thus, it provides satisfactory response factors for all congeners investigated. ECNI was also used for the determination of BDE-209. It was analyzed on a shorter DB-5-MS column (15-m x 250-μm i.d.; 0.25- μm film thickness; J&W Scientific) with the following temperature program: 110 °C for 1 min, 15 °C/min to 300 °C, and held at 300 °C for 17 min. Selected ion monitoring of the two bromide ions at m/z 487 and 484 was selected to detect BDE-209. [$^{13}C_{12}$]-BDE- 209 was used as the internal standard to quantitate it. Analyses of reference materials were incorporated into the analysis of samples and used to monitor the overall accuracy of the methods. The material used was WMF-01 from Wellington laboratories which contains certified reference values for BDE congeners 28, 47, 99, 100, 153 and 154.

Results and Discussion

Sum of detected PBDEs in surface sediment samples ranged from 1.24 to 20 ng/g dw. Their levels in all the 21 sampling sites are presented in Fig.2.

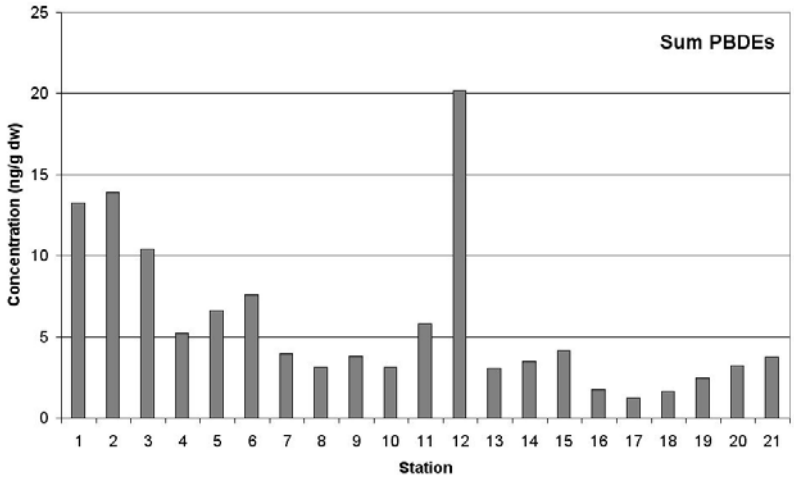

Figure 2. Sum of PBDEs (ng/g dw) in surface sediments of Masan Bay

As the samples were collected from inner to outer bay, PBDE levels indicate a concentration gradient from inner to outer bay with one single exception, namely, St.# 12. The inner bay receives waters from creeks that carry both domestic and industrial contamination, it provides space for harbors and ship building industries that form the source of PBDEs contamination. However, St.#12 receives water from a local Sewage Treatment Plant which apparently is not efficient enough to filter residues of flame retardants and other contaminants. In fact, our recent results with PCDDs and PCDFs in surface sediment from the same samples indicate that this zone is a principal source of contamination to Masan Bay[7]. The distribution pattern of PCBs on the other hand (Fig. 3) is quite

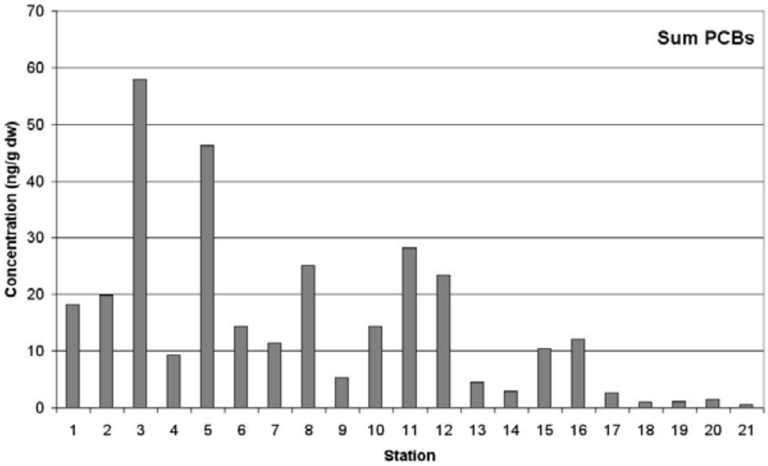

Figure 3. Sum of PCBs (ng/g dw) in surface sediments of Masan Bay

different. The correlation coefficient of sum of PCBs concentrations versus sum of PBDEs, which is 0.24 indicates that their point sources are different. Apparently industrial activities in the inner bay contributed more to PCB contamination than sewage outlet. In general, a nationwide survey for PCB contamination in Korea revealed very low contamination status[8] compared to USA and Europe. The composition of PBDEs in surface sediment showed an enhanced BDE-209 level pointing to the use of Deca formulation in Korea unlike other countries that use Penta formulation more. BDE-209 covers >80% of the composition leaving behind BDEs -99, -47, -153, -183 in that order. Lower brominated BDEs such as -07, -12 have contributed in little ways as well.

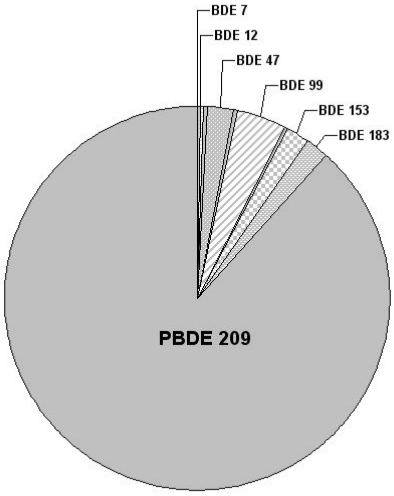

Figure 4. A pie chart of average composition of PBDEs in 21 surface samples analyzed in Masan Bay.

A sediment core sample was taken in the inner bay area to understand the time trend of these chemicals. The core was divided into 24 sections and analyzed for PBDEs and PCBs. It revealed clearly that PCB usuage in the past was prominent as seen in most industrialized nations with definite declining trend in recent times. On the other hand, PBDEs usage is found to be recent with an increasing trend. This is fully understandable as PCBs have been banned in Korea but PBDEs are still in use. Korea consumes nearly 10% of global flame retardant market[9].

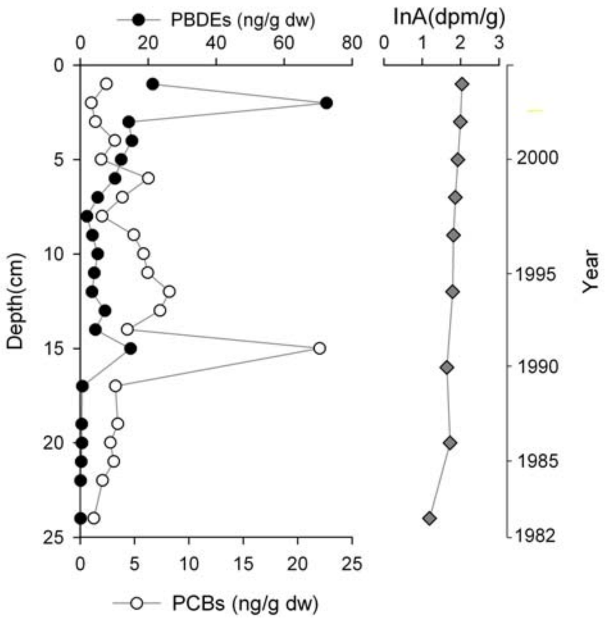

Figure 5. Vertical profile of PBDEs and PCBs and Pb210 estimated sediment age, as revealed from a sediment core in Masan Bay.

Thus analysis of PCBs and PBDEs in Masan Bay revealed that PCB levels are currently higher (about 3 times) than PBDEs but this trend will soon be reversed as seen from the sediment core.

Acknowledgements

This work was supported by KORDI (PE 979-04) and Korea Research Foundation grant funded by the Korean Government (MOEHRD) (KRF-2006-210-C00008).

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