

CONTAMINATION STATUS AND POTENTIAL SOURCES OF CHLORINATED AND BROMINATED DIOXINS IN COASTAL AREAS OF SETO INLAND SEA, JAPAN

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Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) are unintentionally generated by waste incineration¹, and/or byproducts during the manufacturing processes of some organochlorines such as pentachlorophenol (PCP), chloronitrofen (CNP) and polychlorinated biphenyls (PCBs)^{2,3}. In many countries, residue levels of PCDD/Fs in various environmental media and biota have already decreased during the last few decades^{4,5,6}, due to the implementation of highly efficient incinerators and strict regulations on the production and usage of hazardous organochlorines. On the other hand, contamination by polybrominated dibenzo-*p*-dioxins (PBDDs) and dibenzofurans (PBDFs) have apparently spread all over the world with augmented global demand for brominated flame retardants (BFRs), especially polybrominated diphenyl ethers (PBDEs)⁷. In Japan, as large amount of technical PBDE mixtures have been used as additive BFRs until recent years, PBDD/Fs have become a matter of concern due to their spreading contamination in the environment and adverse effects to humans and wildlife.

Additionally, it was also shown that some specific PBDD isomers bio-synthesized by marine organisms such as algae, sponge and cyanobacteria were detected in fish and shellfish living in the Baltic sea^{8,9,10}. Therefore, it is assumed that anthropogenic PBDD/Fs and also naturally-derived PBDDs coexist in coastal environment, but their distribution, temporal trend and potential sources remain to be elucidated. Considering this background, our group investigated the spatio-temporal profiles and potential sources of PBDD/Fs in marine sediment cores collected from Tokyo Bay, Japan¹¹. In this earlier study, we found widespread contamination by anthropogenic- and naturally-derived PBDD/Fs in the entire area of the bay. Furthermore, it was clearly found that PBDF levels have apparently increased after the 1950s with augmented use of technical PBDEs, indicating that recent contamination by PBDD/Fs in Tokyo Bay was mostly dominated by anthropogenic sources of PBDFs. However, there is still little information on the contamination by PBDD/Fs in the coastal areas of Japan and their ecological effects to marine ecosystem.

The purpose of this study is to clarify the contamination status of anthropogenic- and naturally-derived dioxins in marine sediment and mussel samples collected from Seto Inland Sea which is the largest semi-closed coastal sea in Japan (Figure 1).

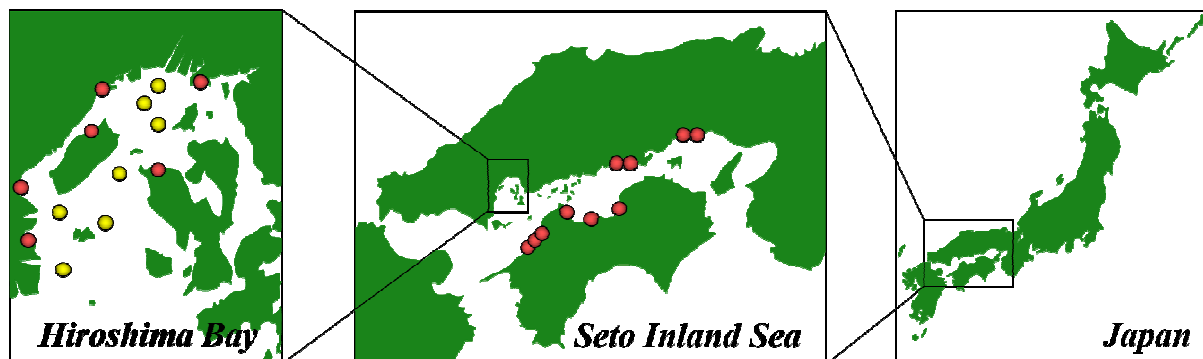


Figure 1. Sampling locations of sediments and mussels. Yellow circle: sediments; Red circle: mussels.

Materials and methods

Samples

Marine sediments were collected in June 2012 from the Hiroshima Bay which is in Northwest Seto Inland Sea (Figure 1). Blue mussels (*Mytilus edulis*) and Green mussels (*Perna viridis*) were also collected from the Hiroshima Bay and various locations covering the whole area of the Seto Inland Sea during June–November 2012 (Figure 1). Shucked mussel tissues from each location were pooled. Sediment and mussel samples were stored at -25 °C in the Environmental Specimen Bank (*es*-BANK) of Ehime University until chemical analysis.

Chemical Analysis

Chemical analysis of PCDD/Fs and PBDD/Fs were carried out following the procedures described in a previous study with slight modification¹¹. Briefly, freeze-dried samples were extracted with a High Speed Solvent Extractor (SE-100, Mitsubishi Chemical Analytechs, Japan). The extract was treated with sulfuric acid, passed through a multilayer silica gel column and then subjected to an activated carbon-dispersed silica gel reversible column (Kanto Chemical Co. Inc., Japan) clean-up. PCDD/Fs and PBDD/Fs were determined by GC-HRMS (JMS-700D, JEOL, Japan).

Results and discussion

Marine Sediments

PCDD/Fs and PBDD/Fs were detected in all the sediment samples analyzed in this study. Total levels of PCDDs (1410–1890 pg/g dw) were generally one order of magnitude higher than those of PCDFs (90–140 pg/g dw) and O₈CDD was the dominant isomer contributing 64–75% of the total PCDD/Fs. The isomer pattern of sediments were similar to that of PCP formulations containing high concentrations of PCDD/Fs (ie, H₇CDD/Fs and O₈CDD/Fs)². Approximately 170,000 tons of PCP was used as herbicide in Japan and as a result a large amount of PCDD/Fs had been emitted into the environment during the past several decades². Furthermore, CNP formulations had also been used until 1990s as alternatives to PCPs², and their impurities such as 1,3,6,8-, 1,3,7,9-T₄CDD and 1,2,3,6,8-P₅CDD were also detected in all locations of the bay. This suggests that the dominant emission sources of PCDD/Fs in Hiroshima Bay were agrochemical formulations.

Total levels of PBDD/Fs (60–111 pg/g dw) were broadly one order of magnitude lower than that of PCDD/Fs (1520–2007 pg/g dw). The prominent PBDD/F congeners were D₂BDDs and T₃BDDs which, apart from anthropogenic sources, are also bio-synthesized marine organisms^{7,8,9}, and account for 73–98% of the total PBDD/Fs except in the urban coastal area (33%). In this area, 1,2,3,4,6,7,8-heptaBDF was found as the major isomer (34% of PBDD/Fs), which has been already reported as an impurity of technical DecaBDE¹², and/or unintentional product of flame-resistant resins treated with BFRs¹³. Therefore, it is clear that anthropogenic PBDD/Fs and also naturally-derived PBDDs exist in the Hiroshima Bay.

To understand the contamination patterns of PCDD/Fs and PBDD/Fs, we compared the results of the present study from Hiroshima Bay with those from Tokyo Bay reported previously¹¹. Although total PCDD/F levels were significantly lower in Hiroshima Bay than in the Tokyo Bay (Figure 2), the isomer profiles were similar. In contrast, contamination profiles of PBDD/Fs were clearly different between Hiroshima Bay and Tokyo Bay (Figure 2). Remarkably, naturally-derived PBDD levels in the Hiroshima Bay were approximately 5–10 times higher than in the Tokyo Bay, suggesting that marine fish and shellfish living in the Hiroshima Bay may have continually been exposed to high levels of

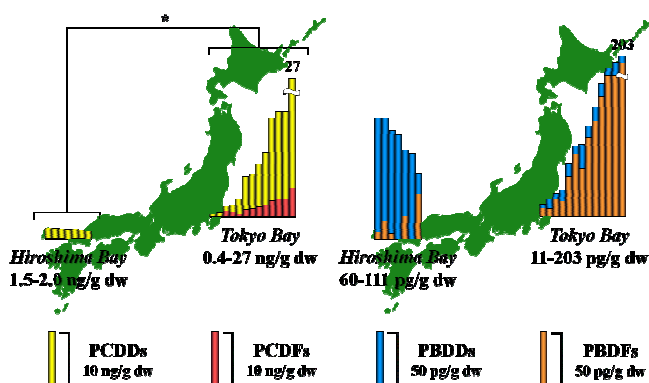


Figure 2. Geographical distribution of PCDD/Fs and PBDD/Fs in the surface marine sediments collected from coastal areas of Japan. Asterisks indicate significant differences between locations (**p* < 0.05, Mann-Whitney U-test).

natural PBDDs.

Mussel Monitoring

Based on the above results, we also conducted the *Mussel Monitoring* to elucidate the contamination status and potential sources of anthropogenic- and naturally-derived dioxins in Seto Inland Sea. PCDD/Fs (1.1-35 ng/g lw) and PBDD/Fs (2.9-68 ng/g lw) were detected in all of the mussel samples analyzed in this study (Figure 3). Total PCDD/F levels were significantly higher in the east side of sea compared to the west side and 1,3,6,8-/1,3,7,9-T₄CDD derived from CNP were the two predominant isomers. Actually, the total shipping volume of pesticides including CNP as active ingredient were larger in east side. These results indicate that the residue profile of PCDD/Fs reflect the contamination by CNP used as herbicide in the past.

In contrast, the horizontal distribution pattern of PBDDs were obviously different from that of PCDD/Fs and PBDFs (Figure 3). Additionally, significantly higher levels of PBDDs were found in mussels from locations with lower industrial activity than in areas with higher industrial activity. Therefore, it was assumed that the natural origins of PBDDs are ubiquitous and occurs highly in the western Seto Inland Sea.

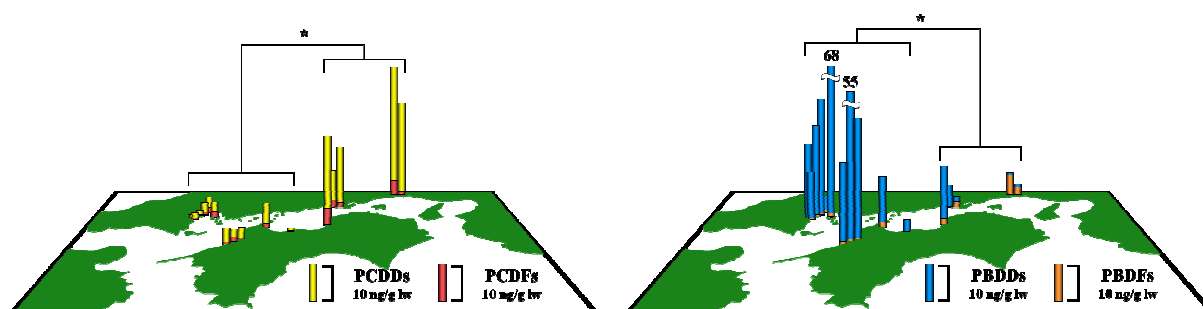


Figure 3. Horizontal distribution of PCDD/Fs and PBDD/Fs in the mussels collected from the Seto Inland Sea, Japan. Asterisks indicate significant differences between locations (* $p < 0.05$, Mann-Whitney U-test).

There is the possibility that naturally-derived dioxins levels might change as a result of the destruction in marine ecosystem caused by human activity such as coastal development, global warming and eutrophication. Therefore, it is necessary to conduct continuous monitoring and risk assessment of anthropogenic- and also naturally-derived dioxins for human and wildlife.

Acknowledgements

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